Syntheses, Spectroscopy, Structures, and Reactivity of Neutral Cubic Group 13 Molecular Phosphonates†

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The syntheses of cubic group 13 molecular phosphonate cages of the formulas $[RPO_3MR']_4$ (R = Me, Et, *t*-Bu, Ph; MR′ = BEt, BBu-*s*, GaMe, InMe; all combinations, **1**−**16**), $[t\text{-BuPO}_3\text{AlBu-}i]_4$ (**17**), and $[\text{MePO}_3\text{AlBu-}t]_4$ (**18**) have been achieved by the facile reactions of alkyl- or arylphosphonic acids with the corresponding alkyl compounds under appropriately chosen reaction conditions. Compounds **1**−**18** have been characterized by analytical and spectroscopic techniques. In all cases, the central $M_4O_{12}P_4$ inorganic cubic framework is shielded by alkyl/aryl groups. The phosphonates bearing *tert*-butyl groups on the phosphorus are highly soluble in common organic solvents such as *n*-hexane, Et_2O, and THF. The molecular structure of representative examples $[t\text{-BuPO}_3\text{BEt}]_4$ (**3**) and $[t\text{-BuPO}_3\text{BBu-}s]_4$ (**7**) as determined by single-crystal X-ray diffraction studies reveal the presence of a central cubic $M_4O_{12}P_4$ framework that is analogous to those found in alumino- and gallophosphate materials. Most of these cubic phosphonates are air and moisture stable. In the presence of excess phenol, it is possible to react one of the M−C bonds at the corners of the cube **3** and prepare its monophenoxy derivative $[t\text{-BuPO}_3\text{-BEt}]_3[t\text{-BuPO}_3\text{B(OPh)}]$ (**19**) in very low yields. However, in spite the presence of reactive M−C bonds, these cubic phosphonates are unreactive toward alcohols, amines, carboxylic acids, H_2O, and air under ambient conditions.

Introduction

Studies on metal organophosphates and phosphonates have received considerable attention due to the interest in their structural chemistry, intercalation behavior, ion-exchange properties, and catalytic applications. Early studies on phosphates and phosphonates have focused on the incorporation of transition metals such as V, Zr, and Zn into their frameworks.[1,2] However, the discovery[3] of a new group of aluminophosphate-based molecular sieves with exceptional properties has recently shifted the focus toward the synthesis of new group 13 element based phosphates and phosphonates.[4] Most of these materials are synthesized either under hydrothermal conditions in the presence of structure-directing organic templates or by high-temperature solid-state synthesis routes.

On the other hand, in the last few years there has been an increasing realization of the importance of devising soft chemical routes or the so-called *molecular routes* for the synthesis of advanced materials.[5] This is partly due to the large success in using *sol*−*gel* methods for the preparation of a variety of glasses and related ceramic materials.[6] Since the molecular level control over the final formation of three-dimensional extended structures would provide rational routes to a new class of materials with tailored properties, we have been concentrating on the use of discrete silanetriols and a variety of organometallic derivatives as starting materials for the synthesis of metallasiloxane cages which show excellent solubility properties.[7] In particular, our recent success with the synthesis of a multitude of framework group 13 silicates[8] prompted us to extend this approach to the isoelectronic phosphate and phosphonate systems.[9,10] Continuing our studies in this area, we wish to report the synthesis and structural characterization of a series of phosphonate cage molecules of B, Al, Ga, and In. This series of compounds,

† Dedicated to Professor Anton Meller on the occasion of his 65th birthday.

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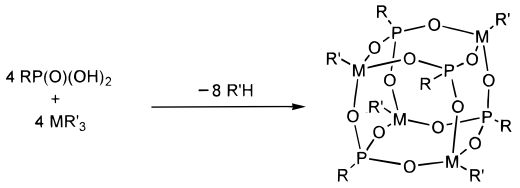
Scheme 1



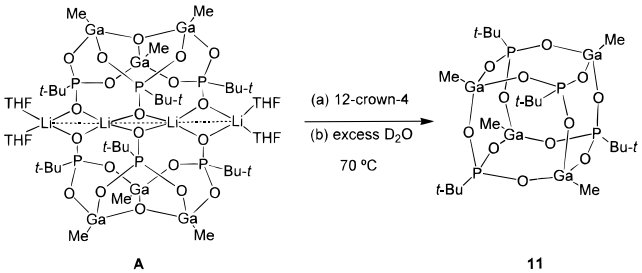
	M	R	R'		M	R	R'
1	B	Me	Et	**10**	Ga	Et	Me
2	B	Et	Et	**11**	Ga	*t*-Bu	Me
3	B	*t*-Bu	Et	**12**	Ga	Ph	M
4	B	Ph	Et	**13**	In	Me	Me
5	B	Me	*s*-Bu	**14**	In	Et	Me
6	B	Et	*s*-Bu	**15**	In	*t*-Bu	Me
7	B	*t*-Bu	*s*-Bu	**16**	In	Ph	Me
8	B	Ph	*s*-Bu	**17**	Al	*t*-Bu	*i*-Bu
9	Ga	Me	Me	**18**	Al	Me	*t*-Bu

existing in the form of three-dimensional cubic cage structures, possess a $M_4O_{12}P_4$ core that is analogous to the D4R (double-four-tetrahedral-atom-ring) secondary building units (SBUs) of $AlPO_4$ materials. A preliminary communication of this work has already appeared.[10] While this paper was in preparation, a few interesting structurally analogous soluble group 13 phosphonates were also reported by Mason (Al and Ga),[11,12] Barron (Ga),[13] and Kuchen (B)[14] and their co-workers.

Results and Discussion

Synthesis. The reaction between phosphonic acids $RP(O)(OH)_2$ (R = Me, Et, *t*-Bu, Ph) and an equimolar quantity of trialkyl derivatives of group 13 elements yield cubic phosphonates of the formula $[RPO_3MR']_4$ (**1**−**18**) in good yields (Scheme 1). In the case of Al, Ga, and In phosphonates, the reactions are very facile in THF even at room temperature (or in few cases at 65 °C), leading to good yields of the products. When the synthesis of the borophosphonates were carried out under similar conditions (*e.g.* in THF at 65 °C for 24 h), a substantial amount of unreacted phosphonic acid was also recovered from the reaction mixture. Hence, the syntheses of borophosphonates starting from BEt_3 were carried out using high-boiling solvents (a toluene/1,4-dioxane mixture, 1:1) and longer reaction periods (48 h).[15] The change of ethyl groups on boron to *sec*-butyl groups further slows the reaction rate, and hence the reactions involving $B(Bu\text{-}s)_3$ were carried out in a toluene/1,4-dioxane mixture typically for more than 55 h under reflux conditions. Under these forcing conditions, however, a slight decomposition of the reaction products was observed.

Scheme 2



During the reactivity studies of an anionic lithium gallium phosphonate cage molecule $Li_4[(MeGa)_6(\mu_3\text{-}O)_2(t\text{-}BuPO_3)_6]\cdot 4THF$ (**A**) (derived from $LiGaMe_4$ and $t\text{-}BuP(O)(OH)_2$),[16] we also discovered that it is also possible to quantitatively prepare the cubic gallophosphonate **11** by a delithiation reaction of **A** in the presence of 12-crown-4 and D_2O as shown in Scheme 2. The details of this investigation are described elsewhere.[16]

It should be emphasized that, although in principle other synthetic routes can be used for the preparation of cubic phosphonates,[17] in our hands, the alkane elimination reaction between the group 13 trialkyls and an acidic hydrogen containing compound as shown in Scheme 1 proved to be the most facile route for synthesizing the title compounds in good yields. Moreover, the workup procedure in this case is very simple and most of the products were normally isolated in an analytically pure form after washing the crude reaction product with either cold *n*-hexane or THF depending upon the solubility of the final product. In the case of borophosphonate **3**, it is possible to obtain the pure product as single-crystals in almost quantitative yield after crystallizing the crude product from *n*-hexane. With the exception of indium compounds **13**−**16**, all other phosphonates described here can be handled in air without any detectable decomposition for sufficiently long periods. When the indium phosphonates were left open in air for extended periods, a considerable amount of decomposition was observed, as evidenced by ^{31}P NMR spectroscopy.

Spectra. The new phosphonates **1**−**18** have been fully characterized by means of analytical and spectroscopic (EI MS, IR, and NMR) techniques. Single-crystal X-ray diffraction studies were carried out to establish the solid-state structures of representative examples $[t\text{-}BuPO_3BEt]_4$ (**3**) and $[t\text{-}BuPO_3\text{-}BBu\text{-}s]_4$ (**7**). Selected spectroscopic data obtained on these compounds are gathered in Table 1. The compounds that contain bulky alkyl groups either on phosphorus (e.g., *t*-Bu) or on group 13 metals (e.g., BBu-*s*, AlBu-*i*, or AlBu-*t*) yield phosphonates that are completely soluble in all common organic solvents. On the other hand, the phosphonates that contain only phenyl or methyl groups as substituents show poor solubility,

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(15) Although this observation contrasts with the instantaneous reaction between *tert*-butylphosphonic acid and aluminum/gallium alkyls at ambient temperature,[10] it is consistent with the higher reactivity of the Al−C bond compared to the B−C bond.

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(17) Other synthetic routes known for group 13 phosphonates: Mason *et al.* have used the reaction between the silyl phosphate ester $P(O)(OSiMe_3)_3$ and $t\text{-}BuAlCl_2$ to prepare the cubic aluminophosphate $[(OSiMe_3)PO_3AlBu\text{-}t]_4$; likewise, Kuchen *et al.* employed the same strategy to prepare $[t\text{-}BuPO_3BPh]_4$.

Table 1. Selected Physical, Analytical, and Spectroscopic Data for Cubic Metallophosphonates

compound	yield, %	mp, °C	C, H anal., % found	C, H anal., % calcd	IR (ν(M−O−P)),[a] cm^{-1}	EI MS,[b] *m/z*	^{31}P NMR, ppm	ref
[MePO$_3$BEt]$_4$ (**1**)	82	>310	27.4, 6.3	26.9, 6.0	1070, 1087	507 (M$^+$ − Et, 40%)	*d*	this work
[EtPO$_3$BEt]$_4$ (**2**)	85	210 dec	32.6, 6.8	32.5, 6.8	1069, 1108	563 (M$^+$ − Et, 100%)	33.3[e]	this work
[*t*-BuPO$_3$BEt]$_4$ (**3**)	>95	311	41.6, 8.2	41.0, 8.0	1080, 1097	675 (M$^+$ − Et, 100%)	7.3[f]	this work
[PhPO$_3$BEt]$_4$ (**4**)	90	>280	48.8, 5.2	49.0, 5.2	1072, 1087	755 (M$^+$ − Et, 60%)	19.3[g]	this work
[MePO$_3$BBu-*s*]$_4$ (**5**)	66	>250	36.8, 7.4	37.1, 7.5	1055, 1093	591 (M$^+$ − Bu, 80%)	31.9[e]	this work
[EtPO$_3$BBu-*s*]$_4$ (**6**)	72	>250	40.3, 8.0	41.0, 8.0	1056, 1092	647 (M$^+$ − Bu, 100%)	34.6[e]	this work
[*t*-BuPO$_3$BBu-*s*]$_4$ (**7**)	80	283	47.5, 8.9	47.1, 8.9	1033, 1097	759 (M$^+$ − Bu, 40%)	6.7[f]	this work
[PhPO$_3$BBu-*s*]$_4$ (**8**)	77	280 dec	54.0, 6.3	53.6, 6.3	1071, 1086	839 (M$^+$ − Bu, 100%)	17.7[e]	this work
[*t*-BuPO$_3$BPh]$_4$	14	300 dec	53.4, 6.2	53.6, 6.3		897 (M+H$^+$, 100%)[h]	9.3[f]	14
[MePO$_3$GaMe]$_4$ (**9**)	85	>280	14.6, 3.8	13.4, 3.4	1055, 1090	701 (M$^+$ − Me, 70%)	*d*	this work
[EtPO$_3$GaMe]$_4$ (**10**)	80	>280	19.1, 4.3	18.7, 4.2	1064, 1085	757 (M$^+$ − Me, 60%)	17.4[g]	this work
[*t*-BuPO$_3$GaMe]$_4$ (**11**)	88	>280	28.0, 5.7	27.2, 5.5	1030, 1073	869 (M$^+$ − Me, 100%)	21.0[g]	this work
[PhPO$_3$GaMe]$_4$ (**12**)	75	250 dec	35.6, 3.5	34.9, 3.3	1040, 1070	949 (M$^+$ − Me, 100%)	*d*	this work
[PhPO$_3$GaBu-*t*]$_4$	88		42.4, 5.1	42.5, 5.0		1075 (M$^+$ − Bu, 100%)	3.2[g]	12
[MePO$_3$InMe]$_4$ (**13**)	60	>280	11.0, 3.2	10.7, 2.7	1040, 1095	880 (M$^+$ − Me, 100%)	*d*	this work
[EtPO$_3$InMe]$_4$ (**14**)	62	>280	15.6, 3.9	15.1, 3.4	1034, 1123	937 (M$^+$ − Me, 100%)	*d*	this work
[*t*-BuPO$_3$InMe]$_4$ (**15**)	55	>250	23.0, 4.7	22.6, 4.5	1045, 1074	1049 (M$^+$ − Me, 70%)	31.1[g]	this work
[PhPO$_3$InMe]$_4$ (**16**)	51	>300	29.6, 3.5	29.4, 2.8	1025, 1097	1129 (M$^+$ − Me, 60%)	*d*	this work
[*t*-BuPO$_3$AlBu-*i*]$_4$ (**17**)	75				1070, 1090	824 (M$^+$ − Bu, 100%)	16.9[f]	this work
[MePO$_3$AlBu-*t*]$_4$ (**18**)	65	>280				655 (M$^+$ − Bu, 100%)	12.0[f]	this work

[a] Recorded as Nujol mulls between KBr/CsI plates. [b] Recorded at 70 eV. [c] Reference 85% H$_3$PO$_4$. [d] Poor solubility precluded ^{31}P NMR analysis. [e] In C$_6$D$_6$/THF. [f] In C$_6$D$_6$. [g] In CDCl$_3$. [h] DCI-MS spectrum.

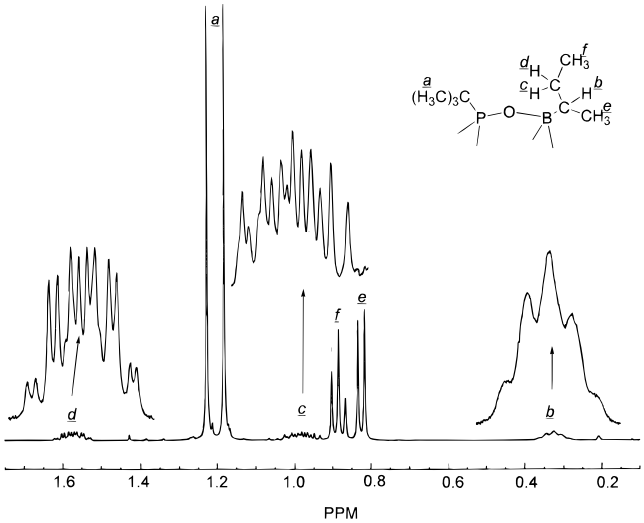
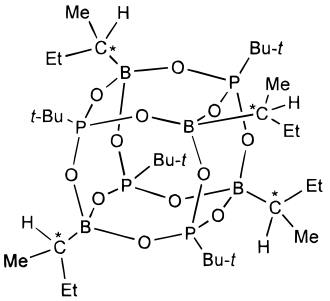


Figure 1. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of **7**.

and hence it has not been possible to obtain ^{31}P NMR chemical shifts in these cases (Table 1).

As it is evident from Table 1, all the cubic phosphonates are thermally stable and do not melt below 200 °C. In most cases, the compounds were found to either melt or decompose only above 280 °C. Further, it is of interest to note that under electron impact mass spectral conditions (70 eV), the cubic core in these molecules (**1**−**18**) remains intact. In all cases, the peak due to the M$^+$ − R′ fragment is observed as the most prominent peak (often base peak) apart from the presence of molecular ion (M$^+$) peaks in a few cases with a lower intensity. The subsequent fragmentations are due to the loss of alkyl groups from the group 13 metals. The IR spectra are devoid of any absorptions in the region 3000−3500 cm^{-1}, indicating complete reaction of all P−OH groups with MR$_3$′. Further, all the metallaphosphonates show two very strong absorptions between 1030 and 1110 cm^{-1} that are assignable to ν(P−O−M) vibrations (Table 1). These vibrations are also observed as prominent peaks in other transition metal containing phosphonates synthesized by us.

The ^{1}H NMR spectral data are consistent with the structure of the products. In all cases where spectra could be obtained, the integrated ^{1}H NMR intensities reveal that there is only one alkyl group remaining on the metal (B, Al, Ga, or In). The protons of these alkyl groups attached to the metals show, as expected, a high-field shift. The protons of the phosphorus substituents show coupling to the phosphorus centers to which they are bonded. Particularly interesting are the observed ^{1}H NMR spectra for the borophosphonates derived from B(Bu-*s*)$_3$ (Figure 1). Due to the presence of a vicinal chiral center, the geminal methylene protons in **7** are nonequivalent and appear



7

as two separate complex multiplets (0.98 and 1.57 ppm, respectively). The resonance of the methylene proton appears as broad high-field multiplet (0.33 ppm) as a result of coupling with boron and other protons of the *sec*-butyl group. The various coupling constants for this resonance are unresolved even at 400 MHz. The methyl groups of the *sec*-butyl group appear as a doublet and a triplet (0.82 and 0.88 ppm, respectively). In the case of borophosphonates, the ^{11}B NMR spectra show a single broad peak for all the four boron nuclei in the molecule.

Although it has not been possible to obtain the ^{31}P NMR shifts for all the compounds because of poor solubility, the observed ^{31}P NMR chemical shifts of these compounds show a periodic trend. In some cases, the spectra were recorded in a mixture of solvents (THF 90%/C$_6$D$_6$ 10%) for solubility reasons. In the case of indium phosphonates, it was difficult to obtain good NMR spectra because of the presence of many minor soluble impurities, and hence the compounds were repeatedly washed and crystallized with cold pentane to obtain the NMR samples. It was also not possible to obtain analytically pure samples for the indium phosphonates (Table 1).

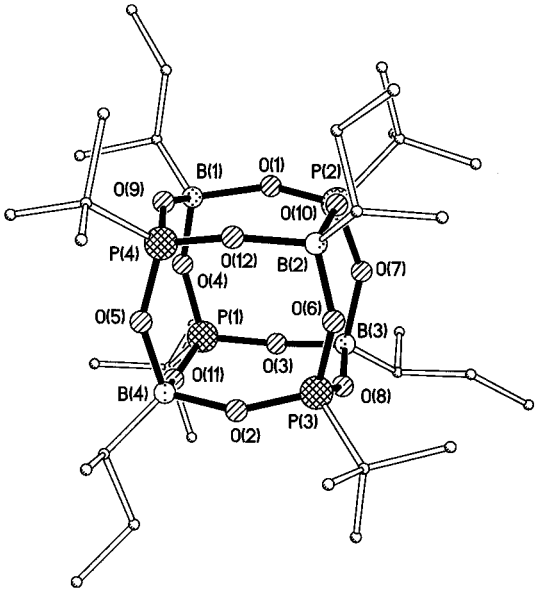


Figure 2. Molecular structure of the cubic borophosphonate **7**.

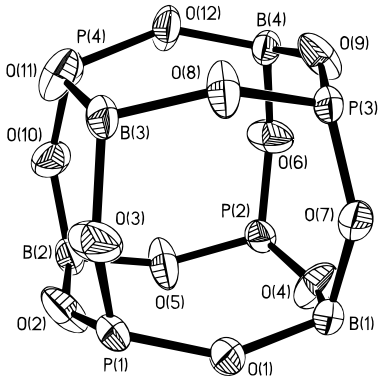


Figure 3. Shape of the core $B_4O_{12}P_4$ polyhedron in **7** also revealing the C_4-crown conformation of the faces of the cube.

The comparison of ^{31}P chemical shift data is hence made from the spectra obtained for the *tert*-butylphosphonic acid derived boron, aluminum, gallium, and indium phosphonates (compounds **3**, **17**, **11**, and **15**, respectively) whose spectral values are listed in Table 1. As can be seen from Table 1, the chemical shifts of all metal-containing phosphonates are high-field-shifted compared to that of *tert*-butylphosphonic acid (δ 42.4 ppm). The highest shift was observed in the case of borophosphonate **3** (δ 7.3 ppm, $\Delta\delta = 35.1$ ppm), while the least high-field shift was observed for the indium compound **15** (δ 31.1 ppm, $\Delta\delta =$ 11.3 ppm). In the case of [*t*-$BuPO_3BEt$]$_4$ and [*t*-$BuPO_3BBu$-*s*]$_4$, the observed chemical shifts compare well with that reported for [*t*-$BuPO_3BPh$]$_4$ (δ 9.3 ppm).[14]

Crystal Structure Descriptions for 3 and 7. In order to further ascertain the solid-state structures of these compounds, single-crystal X-ray diffraction studies were carried out on borophosphonates **3** and **7**. In a previous publication, the molecular structure of [*t*-$BuPO_3AlBu$-*i*]$_4$ (**17**) was described.[9] The cubic borophosphonate **3** crystallizes in the centrosymmetric tetragonal space group $I4_1/a$ with one-fourth of the molecule in the asymmetric part of the unit cell, while borophosphonate **7** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with one full molecule in the asymmetric unit. The final refined molecular structure of **7** is shown in Figure 2, and the central B−O−P framework is depicted in Figure 3. The details of molecular structure determination of **3** have been described in detail elsewhere in a preliminary communication.[10] In the structure of both **3** and **7**, a cube-shaped polyhedron can be defined as the central core which comprises four boron and four phosphorus atoms occupying the alternate vertices. Each of the B···P edges of the polyhedron is bridged by an oxygen atom in a μ_2-fashion, which results in the formation of six nonplanar $B_2O_4P_2$ eight-membered rings. Each of these eight-membered rings adopt a pseudo-C_4 crown conformation (Figure 3). While the two B and two P atoms are coplanar, the four oxygen atoms of the ring form another almost parallel plane just above the former plane. The periphery of the central $B_4O_{12}P_4$ polyhedron is surrounded by hydrophobic alkyl groups (*tert*-butyl and ethyl or *sec*-butyl), explaining the high solubility of **3** and **7** in common organic solvents.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **7**

P(1)−O(3)	1.492(6)	P(1)−O(1)	1.494(5)
P(1)−O(2)	1.497(6)	P(2)−O(4)	1.490(6)
P(2)−O(6)	1.494(5)	P(2)−O(5)	1.499(5)
P(3)−O(7)	1.495(5)	P(3)−O(9)	1.500(5)
P(3)−O(8)	1.499(5)	P(4)−O(10)	1.498(5)
P(4)−O(11)	1.503(5)	P(4)−O(12)	1.506(5)
B(1)−O(1)	1.467(9)	B(1)−O(4)	1.482(11)
B(1)−O(7)	1.483(10)	B(1)−C(21)	1.591(11)
B(2)−O(10)	1.453(10)	B(2)−O(2)	1.483(10)
B(2)−O(5)	1.484(10)	B(2)−C(41)	1.577(12)
B(3)−O(11)	1.452(10)	B(3)−O(8)	1.487(9)
B(3)−O(3)	1.493(10)	B(3)−C(61)	1.574(11)
B(4)−O(6)	1.467(10)	B(4)−O(9)	1.468(9)
B(4)−O(12)	1.473(9)	B(4)−C(81)	1.582(11)
O(3)−P(1)−O(1)	110.4(4)	O(3)−P(1)−O(2)	111.6(4)
O(1)−P(1)−O(2)	113.1(4)	O(3)−P(1)−C(11)	107.0(4)
O(1)−P(1)−C(11)	107.4(3)	O(2)−P(1)−C(11)	107.0(3)
O(1)−B(1)−O(4)	109.2(6)	O(1)−B(1)−O(7)	107.4(6)
O(4)−B(1)−O(7)	107.4(6)	O(1)−B(1)−C(21)	111.5(7)
O(4)−B(1)−C(21)	110.7(7)	O(7)−B(1)−C(21)	110.6(7)
B(1)−O(1)−P(1)	147.4(5)	B(2)−O(2)−P(1)	147.5(5)
B(3)−O(3)−P(1)	146.2(5)	B(1)−O(4)−P(2)	147.1(5)
B(2)−O(5)−P(2)	146.6(5)	B(4)−O(6)−P(2)	148.5(5)
B(1)−O(7)−P(3)	146.9(5)	B(3)−O(8)−P(3)	147.4(5)
B(4)−O(9)−P(3)	148.2(5)	B(2)−O(10)−P(4)	148.9(5)
B(3)−O(11)−P(4)	148.2(5)	B(4)−O(12)−P(4)	146.6(5)

The bond parameters of **7** compare well with those observed for **3**. Selected bond lengths and angles are listed in Table 2. There are no formal P−O and P═O bonds in the molecule. In case of **7**, the observed average P−O bond length (1.50 Å) is much shorter than a formal P−O bond (1.59−1.60 Å) and considerably longer than a formal P═O bond (1.45−1.46 Å).[18] Moreover, the observed values are slightly shorter than the P−O distances found in many phosphates and phosphonates (1.506−1.543 Å).[4] The average B−O distance in the molecule is 1.47 Å. The observed B−O distances in **7** are much longer than those found in the eight-membered ring borosiloxane [*t*-Bu_2SiO_2BPh]$_2$ (average 1.35 Å)[19] and other borosiloxanes[20] but comparable to the values found in [*t*-$BuPO_3BPh$]$_4$ (average 1.46 Å).[14] The average B−O−P angle (147.5°) is comparable to the M−O−Si angles found in many of the cubic heterosiloxanes described in the literature. The B and P atoms adopt nearly ideal tetrahedral geometries with the average angles around them being 109.4 and 109.4°, respectively.

A structural comparison of the cubic borophosphonates **3** and **7** with other group 13 cubic phosphonates recently described is illustrated in Table 3. Unfortunately, the data remain incomplete without a crystal structure determination for a cubic indium-

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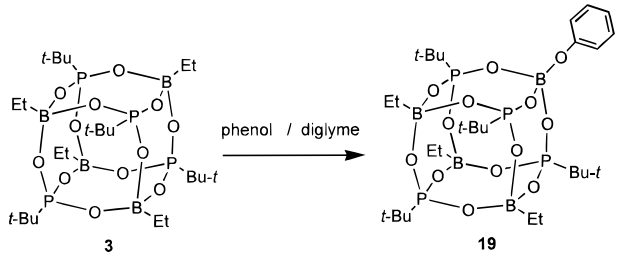
Table 3. Comparision of Molecular Structural Parameters of Cubic Group 13 Phosphonates

structural feature	$[t\text{-BuPO}_3\text{BEt}]_4$	$[t\text{-BuPO}_3\text{BBu-s}]_4$	$[t\text{-BuPO}_3\text{BPh}]_4$	$[t\text{-BuPO}_3\text{AlBu-}i]_4$	$[\text{PhPO}_3\text{GaBu-}t]_4$
space group	$I4_1/a$	$P\bar{1}$	$P2_1/c$	$I4_1/a$	$P\bar{1}$
polyhedral shape	cubic	cubic	cubic	cubic	cubic
$M_2O_4P_2$ ring conformn	C_4-crown	C_4-crown	C_4-crown	C_4-crown	C_4-crown
P−O length (av), Å	1.50	1.50	1.50	1.52	1.51
M−O length (av), Å	1.47	1.47	1.46	1.76	1.85
P···M length (av), Å	2.85	2.85	2.84	3.17	3.22
P···P length (av), Å	3.92	3.93	3.93	4.42	4.42
M···M length (av), Å	4.12	4.13	4.15	4.56	4.69
body diagonal (av), 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 (av), deg	147.8	147.5	146.8	150.5	150
ref	this work	this work	14	9	12

Scheme 3



containing phosphonate. So far, our attempts to crystallize an indium compound have been unsuccessful. As can be seen from Table 3, 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 $[\text{PhPO}_3\text{GaBu-}t]_4$ 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 (Table 3). The length of the body diagonal in the cage of Ga compounds is ca. 0.63 Å longer than the corresponding values observed in the case of borophosphonates. Another interesting structural feature that stems from the data in Table 2 is the very small change in the M···P, M···M, P···P, and body diagonal distances between the aluminum and gallium derivatives $[t\text{-BuPO}_3\text{AlBu-}i]_4$ and $[\text{PhPO}_3\text{GaBu-}t]_4$. In short, the changes observed in the size of the cubic core on going from B to Al are more pronounced than the corresponding changes observed on going from Al to Ga.

Reactivity Studies. Owing to its good isolated yield and ease of purification, compound **3** was chosen for the reactivity studies. The B−C bonds of compound **3** do not react either with alcohols or with primary or secondary amines in THF under reflux conditions. The reaction of **3** with a large excess of acetic acid under reflux conditions does not yield the expected acetate derivative. The ^{31}P NMR of the reaction mixture in this case reveals extensive decomposition of the starting material. When compound **3** was reacted with phenol under reflux in high boiling solvents, the resulting material was analyzed to be $[t\text{-BuPO}_3\text{BEt}]_3[t\text{-BuPO}_3\text{B(OPh)}]$ (**19**) (Scheme 3). However, the conversion is less than 5%, as evidenced by ^{31}P NMR spectroscopy, even after reaction periods of 72 h. The EI mass spectrum of **19** shows a peak due to $M^+ - \text{Et}$ at *m/e* 739 with the expected isotope pattern. The results of this experiment clearly demonstrate that it is possible to functionalize the cubic framework with appropriately chosen reagents (which would however require forcing conditions). In the future, it should be possible to adopt this strategy and link these cubic phosphonates to prepare supramolecular phosphonate frameworks.

Conclusion

In this paper we have demonstrated the use of commonly available starting materials as precursors for framework boron-, aluminum-, gallium-, and indium-containing phosphonates through a facile alkane elimination reaction. The structural similarities of the central M/O/P framework in these molecules to the basic structural units found in cloverite, ULM-5,[21] and gallophosphate-A[22] offer the possibility of using this class of compounds for the preparation of boron-, aluminum-, gallium-, and indium-containing phosphonate molecular sieves under mild conditions using sol−gel techniques. We also plan to investigate the use of these compounds as secondary building units in synthesizing supramolecular group 13 phosphate structures through cage fusion reactions utilizing the reactive M−C bonds located on the four vertices of the cube under forcing conditions. Moreover, owing to the well-known use of oligophosphate-based boron compounds in boron neutron capture therapy (BNCT),[23] it should also be possible to extend the chemistry described in this paper to develop new water-soluble borophosphonate superstructures and study their use in cancer therapy.

Experimental Section

General Information. All experimental manipulations were carried out under a dry, prepurified nitrogen atmosphere, using Schlenk techniques and rigorously excluding moisture and air.[24] The samples for spectral measurements were prepared in a drybox. Solvents were purified by conventional procedures and were freshly distilled prior to use.[25] All ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument. The chemical shifts are reported in ppm with reference to $SiMe_4$ (external) for ^{1}H and to 85% H_3PO_4 (external) for ^{31}P nuclei. The upfield shifts from the reference are negative. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer (only strong absorptions are reported; vide infra). Mass spectra were obtained on a Finnigan MAT system 8230 or a Varian MAT CH5 mass spectrometer. Melting points were obtained on an HWS-SG 3000 apparatus and are reported uncorrected. CHN analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Starting Materials. Methylphosphonic acid, ethylphosphonic acid, *tert*-butylphosphonic acid, and phenylphosphonic acid (Aldrich) were dried under high vacuum prior to use. Triethylboron (1 M solution in THF, Janssen), tri-*sec*-butylboron (Aldrich), diisobutylaluminum hydride (1 M solution in hexanes, Aldrich), trimethylgallium (Strem), and trimethylindium (Strem) were used as received.

Synthesis of Borophosphonates $[\text{RPO}_3\text{BEt}]_4$ (1−4) and $[\text{RPO}_3\text{BBu-}s]_4$ (5−8). All borophosphonates were prepared by similar procedures. To a solution of the respective phosphonic acid (1 mmol) in toluene (20 mL) and 1,4-dioxane (5 mL) was added slowly BR'_3 (1 mL of 1 M solution in THF, 1 mmol) via a syringe at room temperature, and the

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mixture was stirred for 2 h. No evolution of ethane gas was noted during this period. The reaction mixture was subsequently heated under reflux for 48 h (for **1**−**4**) or 55 h (for **5**−**8**), during which the evolution of ethane gas ceased. After the reaction mixture was cooled, the solvent was removed under reduced pressure at room temperature, the residue was redissolved in a THF (6 mL)/*n*-hexane (2 mL) mixture, and the solution was cooled to yield analytically pure products. In the case of the synthesis of **1**, **2**, and **4**, subsequent to the heating under reflux, the reaction mixtures were stirred for an additional 2 days.

Synthesis of Gallium Phosphonates [RPO$_3$GaMe]$_4$ (9−12). All of these phosphonates were synthesized by similar procedures. To a solution of RP(O)(OH)$_2$ (1 mmol) in THF was added slowly a solution of GaMe$_3$ (1 mmol) in THF (5 mL) via a syringe at 0 °C. The reaction mixture was allowed to warm to room temperature, during which evolution of methane gas ceased. In order to ensure the completion of the reaction, the reaction mixtures were additionally heated under reflux for 30 min, after which the volatiles were removed *in vacuo*. In the case of **11**, the crude product was purified by crystallization from a THF/*n*-hexane mixture. The other derivatives (**9**, **10**, and **12**) were purified by repeatedly washing with cold THF.

Synthesis of Indium Phosphonates [RPO$_3$InMe]$_4$ (13−16). All of these phosphonates were synthesized by similar procedures. To a solution of InMe$_3$ (1 mmol) in THF (50 mL) was added slowly a solution of RP(O)(OH)$_2$ (1 mmol) in THF (5 mL) via a syringe at 0 °C. The reaction mixture was allowed to warm to room temperature, during which evolution of methane gas ceased. In order to ensure the completion of the reaction, the reaction mixtures were additionally refluxed for 1 h, after which the volatiles were removed *in vacuo*. In the case of **15**, the crude product was purified by crystallization from a THF/*n*-hexane mixture. The other derivatives (**13**, **14**, and **16**) were purified by repeatedly washing with cold THF.

Synthesis of Aluminum Phosphonates 17 and 18. Compounds **17** and **18** were prepared from the respective phosphonic acids and Al(Bu-*i*)$_2$H (for **17**) or Al(Bu-*t*)$_3$[26] (for **18**) by a procedure similar to that described for gallium phosphonates **9**−**12**. The products were purified by cooling an *n*-hexane solution to −20 °C.

The yields, melting points, analytical data, and selected spectroscopic data for the new phosphonates **1**−**18** are presented in Table 1. Additional IR spectral data for **1**−**17** are provided in the Supporting Information.

X-ray Structure Determination. Crystals of **7** suitable for X-ray diffraction studies were grown from a dilute 3:1 toluene/*n*-heptane solution at room temperature over 72 h by slow evaporation. Intensity data were collected on a Siemens-Stoe AED2 four-circle diffractometer using an $\omega-2\theta$ scan mode. The cell parameters were determined from randomly chosen and well-centered high-angle reflections. The structure solution (direct methods) and refinement (by full-matrix least-squares calculations on F^2) were carried out using SHELXS-90[27] and SHELXL-93[28] programs. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined isotropically. Other details pertaining to data collection and structure solution and refinement are listed in Table 4.

Table 4. Crystal Data and Structure Refinement Details for **7**

empirical formula	$C_{32}H_{72}B_4O_{12}P_4$
fw	816.02
T, K	250(2)
wavelength, Å	0.710 73
crystal system	triclinic
space group	$P\bar{1}$
a, Å	10.678(2)
b, Å	10.775(2)
c, Å	21.171(4)
α, deg	77.19(3)
β, deg	80.14(3)
γ, deg	85.95(3)
V, Å^3	2338.9(8)
Z	2
D_{calcd}, g·cm^{-3}	1.159
μ, mm^{-1}	0.211
F(000)	880
crystal size, mm	1.0 × 0.4 × 0.2
θ range, deg	3.5 to 22.0
index range	$-11 \le h \le 11$, $-11 \le k \le 11$, $-18 \le l \le 22$
no. of total reflns	4934
no. of independent reflns	4345 (R_{int} = 0.081)
refinement method	full-matrix least-squares on F^2
data/restraints/params	4246/0/489
R1, R2 ($I > 2\sigma(I)$)	0.0809, 0.2323
R1, R2 (all data)	0.1032, 0.2724
S	1.060
largest diff peak and hole, e·Å^{-3}	0.976, −0.335

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Supporting Information Available: A listing of additional IR spectral data for **1**−**18** and tables of structure refinement details, positional and thermal parameters, bond distances and angles, and anisotropic thermal parameters for **7** (8 pages). Ordering information is given on any current masthead page.

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