Reactions of Phosphonates with Organohaloboranes: New Route to Molecular Borophosphonates

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Phosphonates $RPO(OR')_2$ (R = Me, R′ = Et (**1**); R = CH_2Ph, R′ = Et (**2**); R = $CH{=}CH_2$, R′ = Et (**3**); R = $CH_2{-}CH{=}CH_2$, R′ = Me (**4**); R = CH_2N_3, R′ = Et (**5**)) react with $CyBCl_2$ (**6**; Cy = C_6H_{11}) in a 1:1 molar ratio in toluene at −30 °C to form the primary adducts $CyBCl_2{\cdot}O{=}PR(OR')_2$ (**7**−**11**). These products undergo a thermally induced bis-chlorodealkylation with the formation of mixtures of oligomers $[-O-PR(O-)-O-BCy(O-)]_n$ (**22**−**26**) having isovalent P−O−B groupings. Under electron impact mass spectral conditions, the ions $[RPO_3BCy]_4-Cy$, which may be attributed to tetramers $[RPO_3BCy]_4$ (**22′**−**26′**), are detected. Compounds **22′**−**26′** presumably possess a central cubic $M_4O_{12}P_4$ framework that is analogous to those found in alumino- and gallophosphate materials. NMR monitoring shows that $[CyBCl(\mu_2\text{-}O)_2PR(OR')]_2$ (**12**−**16**) are formed as intermediates in these reactions. These unstable dimers **12**−**16** possess a cyclic core analogous to the single-four-ring (4R) secondary building units (SBUs) found in zeolites and phosphate molecular sieves. Hydrolysis of **12**−**16** and **22**−**26** with methanol at 30 °C gave respectively $RPO(OH)(OR')$ (**17**−**21**) and $RPO(OH)_2$ (**27**−**31**). NMR monitoring reveals that the cyclic dimer $[Me_2B(\mu_2\text{-}O)_2P(CH_2Ph)(OEt)]_2$ (**35a**) is the primary adduct in the reaction of $PhCH_2PO(OEt)_2$ (**2**) with Me_2BBr (**34**). Heating or prolonged storage at room temperature leads to a mixture of **35a**, cyclic borophosphonate $Me_2BC(\mu_2\text{-}O)_2P(CH_2Ph)(OEt)$ (**35b**), and the mixed anhydride of benzylphosphonic acid and dimethylborinic acid (**35c**).

Introduction

Although Al-, Ga-, and In-containing layered phosphates and phosphonates have been studied in detail over the past few years, until two recent reports published in 1997, no organic-soluble materials with isovalent P−O−B groupings were known. Roesky and co-workers have described the synthesis of the molecular cage molecule $[t\text{-}BuPO_3BEt]_4$ from the reaction of BEt_3 and $t\text{-}BuPO(OH)_2$ in refluxing toluene/1,4-dioxane.[1] Kuchen and co-workers have reported the preparation in low yield (14%) of the cage borophosphonate $[t\text{-}BuPO_3BPh]_4$ by reaction of $PhBCl_2$ and $t\text{-}BuPO(OSiMe_3)_2$.[2] In each case corners of the cubanoid P_4B_4 framework are alternately occupied by boron and phosphorus atoms, each of which is tetrahedrally coordinated to three oxygen atoms and one carbon atom. The 12 O atoms are located approximately in the middle of the edges. These cage molecules show structures with nearly equal P−O and B−O bond lengths, making them structurally quite similar to silicate analogues.[3,4]

It has been shown recently by us that the alkyl halide elimination reaction involving haloboranes and phosphonates is a facile way for the formation of the P−O−B groupings.[5] A general synthesis of *N*-alkyl/aryl-α- and *N*-alkyl/aryl-*β*-aminophosphonic acids based on reductive alkylation of α- and *β*-azidophosphonates with organodichloroboranes has been proposed.[5]

Our experience in this field prompted us to explore the possibility of synthesizing suitable molecular borophosphonate clusters from organohaloboranes and phosphonates. The presence of reactive B−C and/or P−C bonds at the corners of such cage models in principle

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(1) Ganapati Walawalkar, M.; Murugavel, R.; Roesky, H. W.; Schmidt, H.-G. *Organometallics* **1997**, *16*, 516.
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(4) For some recent work on phosphonates and phosphates, see: (a) Byrd, H.; Clearfield, A.; Poojary, D. M.; Reis, K. P.; Thompson, M. E. *Chem. Mater.* **1996**, *8*, 2239. (b) Song, P.; Xu, J.; Zhao, Y.; Yue, Y.; Xu, Y.; Xu, R.; Hu, N.; Wie, G.; Jia, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1171. (c) Gendraud, P.; de Roy, M. E.; Besse, J. P. *Inorg. Chem.* **1996**, *35*, 6108. (d) Bonavia, G.; Haushalter, R. C.; O'Conner, C. J.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 5603. (e) Soghomonian, V.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1995**, *7*, 1648. (f) Roca, M.; Marcos, M. D.; Amoros, P.; Beltran-Porter, A.; Edwards, A. J.; Beltran-Porter, D. *Inorg. Chem.* **1996**, *35*, 5613. (g) Bellito, C.; Federici, F.; Ibrahim, S. A. *J. Chem. Soc., Chem. Commun.* **1996**, 759. (h) Ganapati Walawalkar, M.; Murugavel, R.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G. *J. Am. Chem. Soc.* **1997**, *119*, 4656.
(5) Mortier, J.; Gridnev, I. D.; Fortineau, A.-D. *Org. Lett.* **1999**, *1*, 981.

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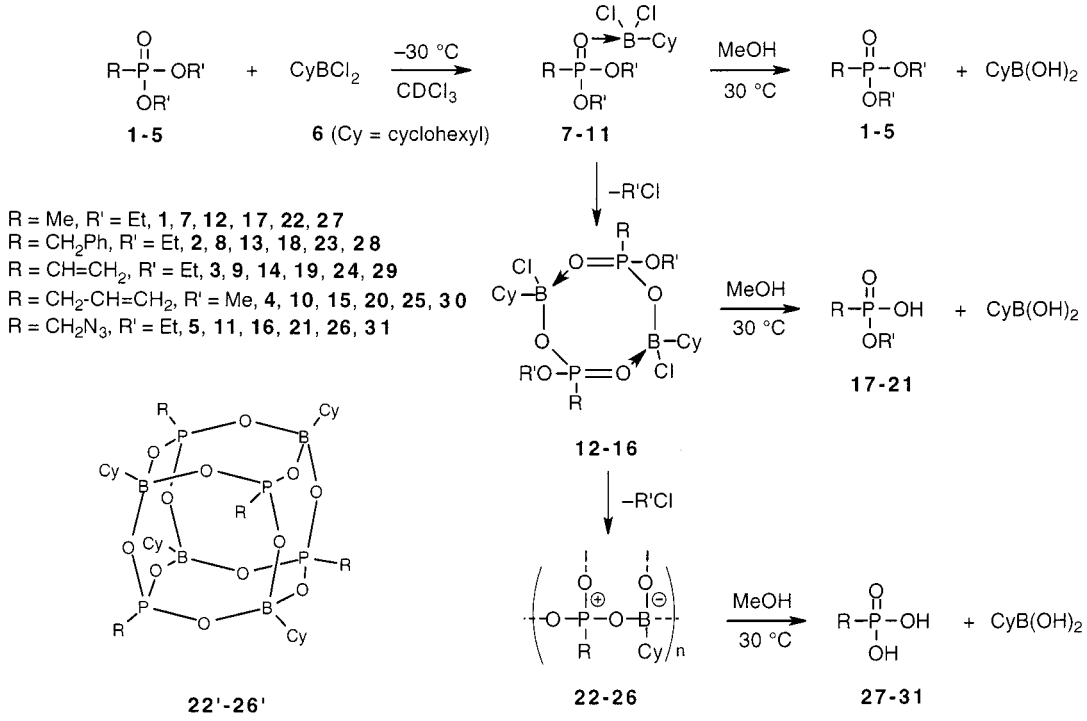
Scheme 1



offers scope for using them as useful starting materials for the preparation—through cage-fusion—of crystalline solid-state boron phosphate materials with potential catalytic and sorptive properties.[3a,6] The preliminary results of this investigation are reported in this paper.

Results and Discussion

Synthesis and Characterization of Borophosphonates 22−26. The interaction of dialkylphosphonates **1**−**5** with cyclohexyldichloroborane (**6**)[7] in a 1:1 molar ratio in toluene at −30 °C afforded the corresponding complexes **7**−**11**, which were characterized by ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra (Scheme 1). In all complexes **7**−**11** the ^{11}B chemical shifts are about 11 ppm, which corresponds to a tetracoordinated boron atom (Table 1). The values of ^{31}P chemical shifts in complexes **7**−**11** are comparatively higher than those of the corresponding phosphonates; therefore, the bond between boron and phosphorus in complexes **7**−**11** is coordinative.

Complexes **7**−**11** yielded mixtures of oligomers **22**−**26** and 2 equiv of the corresponding alkyl chloride when either heated for 12 h at 70 °C or stored for 2−3 days at room temperature. The ESM microprobe analysis showed for **22**−**26** an atomic ratio of phosphorus to oxygen near 1:3 and a remaining chlorine content of less than 0.5%. Borophosphonates **22**−**25** are insoluble in common organic solvents, whereas **26** is soluble in hydrocarbons.[8] We have managed to characterize **22**−**25** with NMR, preparing them from diluted solutions of the corresponding complexes. Clear gels first formed in such experiments could be analyzed by NMR. However, the oligomers obtained from such gels after evaporation of the solvent could not be solubilized.

All borophosphonates **22**−**26** were easily hydrolyzed either by methanol at 30 °C or by refluxing with 10% aqueous HCl, providing quantitative yields of the corresponding phosphonic acids **27**−**31** and cyclohexylboronic acid.[9,10]

Table 1. Parameters of ^{11}B and ^{31}P NMR Spectra for the Compounds 1−5, 7−11, 12−16, and 22−26

R	R′	compd	$\delta(^{11}B)^a$	$\delta(^{31}P)^b$
Me	Et	**1**		30.58
		7	11.5	37.55
		12	5.7	24.38, 24.71
		22	3	10
$PhCH_2$	Et	**2**		27.70
		8	11.3	30.05
		13	5.6	18.51, 18.68
		23	−4	9
CH_2=CH	Et	**3**		17.72
		9	11.3	18.75
		14	5.5	16.86, 16.95
		24	−4	−2
CH_2=$CHCH_2$	Me	**4**		30.15
		10	11.6	34.3
		15	8.1	21.27, 21.29
		25	0	9
N_3CH_2	Et	**5**		20.5
		11	11.7	24.53
		16	7.3	13.77, 13.83
		26	−4	0

[a] Referenced to external BF_3·Et_2O. [b] Referenced to external 10% H_3PO_4.

(6) For general aspects of porous materials, see: (a) *Zeolite Microporous Solids: Synthesis, Structure and Reactivity*; Derouane, E. G., Lemos, F., Naccache, C., Ribeiro, F. R., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1992. (b) *Catalytic Science and Technology*; Yoshida, S., Takezawa, N., Ono, T., Eds.; Kodansha: Tokyo, and VCH: Weinheim, Germany, 1991; Vol. 1.

(7) **6** was prepared by the reaction of cyclohexene with dichloroborane ethyl etherate in the presence of boron trichloride: Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 2396.

(8) Gel chromatography of the soluble borophosphonate **26** showed a broad mass distribution for $n = 3-7$.

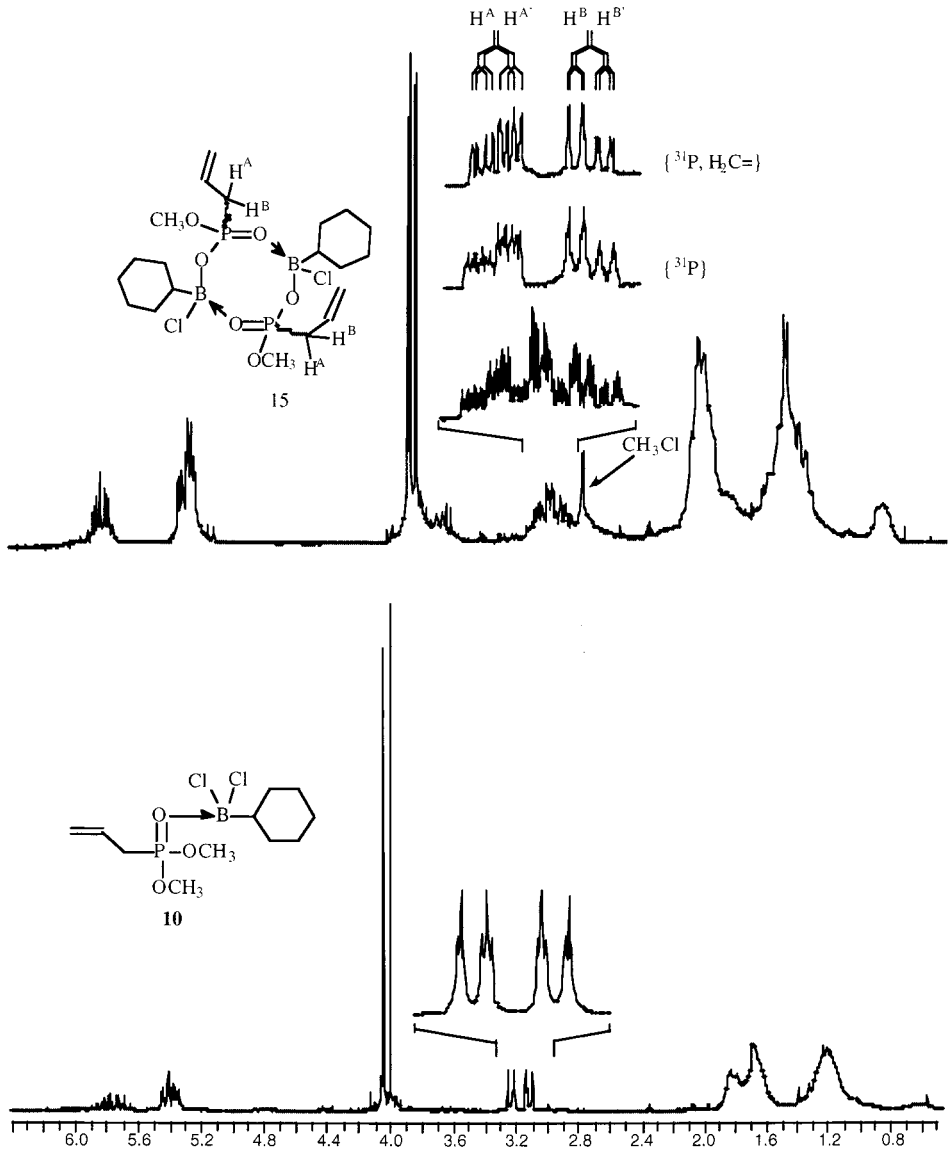


Figure 1. ^{1}H NMR spectra (300 MHz, toluene-d_8, 297 K) of complex **10** and dimer **15**. The inserts in the upper spectrum show the appearance of the signal of aliphatic CH_2 groups with decoupling from phosphorus (middle) and under the conditions of triple resonance from phosphorus and the exo methylene group of the double bond.

NMR Monitoring of the Reactions between Dialkyl Phosphonates and Cyclohexyldichloroborane (7). To gain further insight into the mechanism of these reactions and to be able to analyze their individual steps, we have in each case monitored the reaction by means of multinuclear NMR spectroscopy. Overnight storage at room temperature of a sample containing a solution of complex **7**, **8**, **10**, or **11** led to notable changes in the NMR spectra: the signals of the evolving alkyl chloride were detectable in the ^{1}H and ^{13}C NMR spectra, and new signals appeared in the ^{31}P and ^{11}B NMR spectra. However, the complex **9**, obtained from vinylphosphonate **3**, was unchanged under similar conditions. Moreover, the character of the changes observed for the complexes **7**, **8**, **10**, and **11** was also different and was dependent on the solvent and concentration of the sample.

In the case of the complex of allyl dimethylphosphonate **10**, the clean formation of **15**—whose octahedral core resembles the single-four-ring (4R) secondary building unit (SBU) found in zeolites and phosphate molecular sieves—was observed after 2 days at room temperature. The monitoring of this process by ^{1}H and ^{13}C NMR showed that the transformation is direct and quantitative: no stable intermediates were observed between **10** and **15**, and the dimer **15** does not react further before all complex **10** is consumed (Figure 1 and Figure 2a,b).

Compound **15** has been characterized by ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectroscopy and by HRMS. While the chemical shift of phosphorus is remarkably high-field-shifted in **15** compared to complex **10**, the same is valid, although to a lesser extent, for the chemical shift of boron (Table 1). The $\delta(^{31}P)$ value of 21.3 is intermediate between these in the starting phosphonate (δ 30.15) and the resulting borophosphonate **25** (δ 9).[2]

(9) The initially formed dimethyl cyclohexylborate was further hydrolyzed under these conditions.

(10) Dealkylation of phosphonate diisopropyl esters using Me_3-SiBr: (a) Salomon, C. J.; Breuer, E. *Tetrahedron Lett.* **1995**, *36*, 6759. Phosphonate ester hydrolysis catalyzed by lanthanum ions: (b) Tsubouchi, A.; Bruice, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 7399. (c) Tsubouchi, A.; Bruice, T. C. *J. Am. Chem. Soc.* **1994**, *116*, 11614.

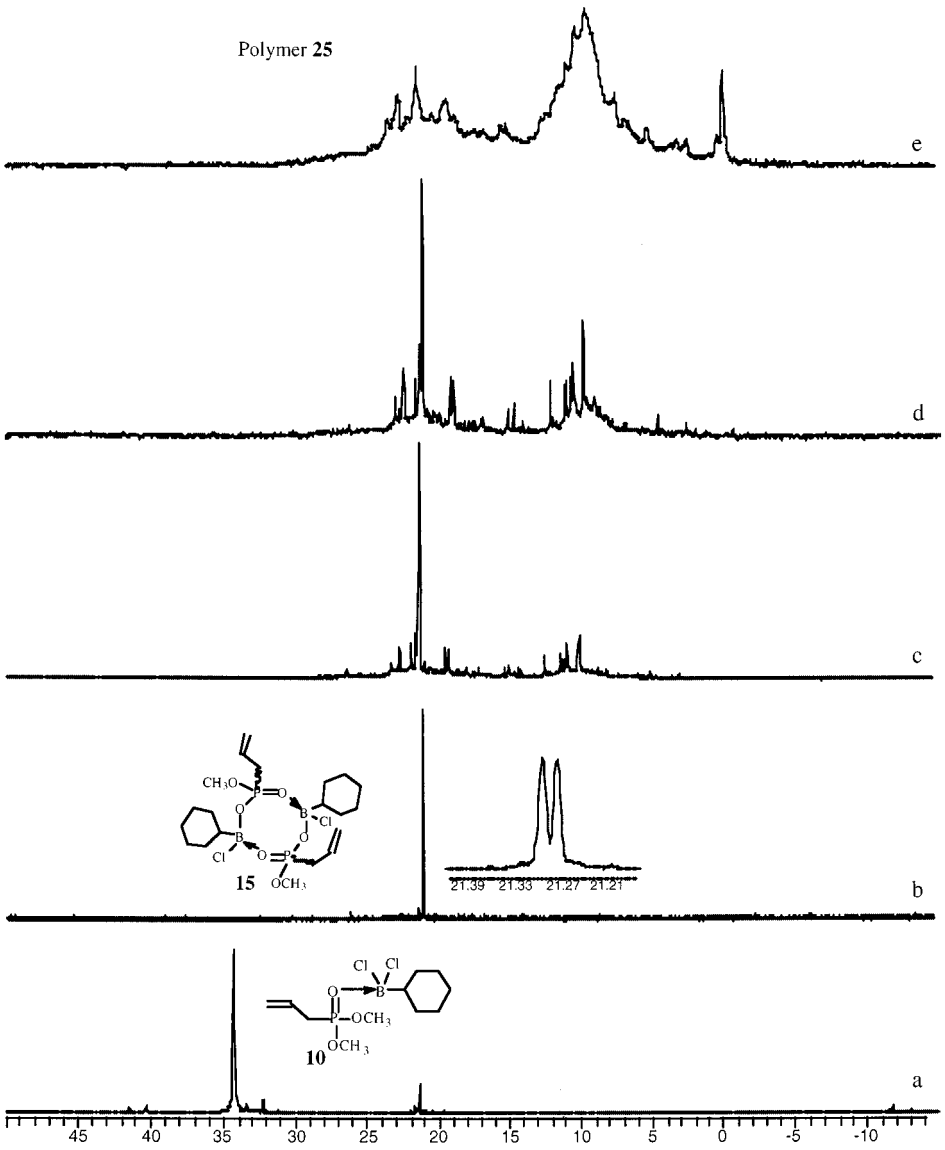


Figure 2. Evolution of the ^{31}P NMR spectrum (121 MHz, toluene-d_8, 300 K) of the sample obtained by mixing equivalent amounts of dimethyl allylphosphonate (**4**) and cyclohexyldichloroborane (**6**): (a) initial spectrum; (b) after 2 days; (c) after 4 days; (d) after 1 week; (e) after 2 weeks.

Two isomers of **15** in a 1:1 ratio are found in the NMR spectra. Thus, in the ^{31}P NMR spectrum, two sharp signals of equal intensity are observed (Table 1 and Figure 2b). Similar splittings are found for the signal of the CH_2P group in the ^{13}C NMR spectrum. In the ^{1}H NMR spectrum of **15** the protons of the CH_2P group of each isomer give an AB system, in contrast to complex **10**, where the two protons of the CH_2P group are equivalent (Figure 1). Five isomers distinguishable by NMR are possible for the molecule of **15**. Fast dissociation−association of coordinative bonds in **15** averages the signals of the isomers, which differ in the configuration at the boron atoms.

The characteristic NMR spectra of dimeric molecules such as **15** allowed us to detect in the corresponding reaction mixtures the signals of dimers **12**−**14** and **16** (Table 1). However, in these cases the dimers were observed together with already formed oligomers **22**−**24** and **26** and some unidentified intermediates. Apparently, the possibility of observing a clear formation of a dimer, as in the case of compound **15**, is regulated by the relative rates of several competitive processes and is strongly dependent on the electronic properties of the radicals of the phosphonate and the borane, as well as on the solvent, concentration, temperature conditions, etc.

Further transformation of **15** is not selective even at room temperature (Figure 2c−e). Together with the decrease of intensity of the signal corresponding to **15**, at least 10 signals of comparable intensity appear after 4 days (Figure 2c), and after 2 weeks the most intense broad signal corresponds to oligomer **25** (Figure 2e).

Analysis of the values of the chemical shifts of boron and phosphorus for the starting phosphonates, complexes **7**−**11**, dimers **12**−**16**, and the resulting borophosphonates **22**−**26** (Table 1) shows that the process of oligomerization is characterized by a gradual shift of the signals in the ^{11}B and ^{31}P NMR spectra toward zero and even negative values, indicating that the resulting oligomers are truly borophosphonates and not mixed

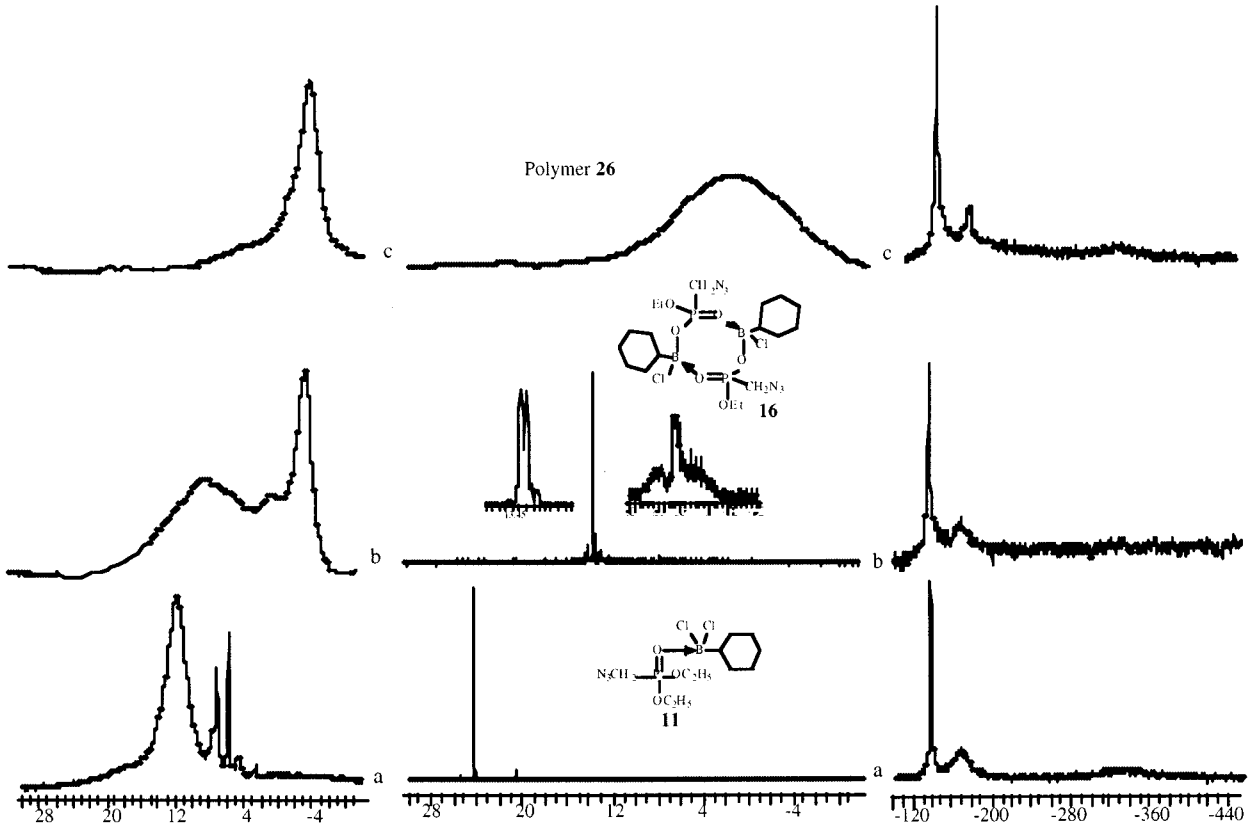
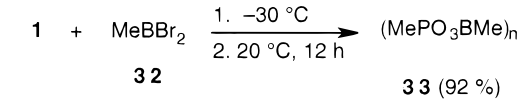


Figure 3. ^{11}B (96 MHz, $CDCl_3$, 300 K; left) ^{31}P (121 MHz, $CDCl_3$, 300 K; middle), and ^{14}N (22 MHz, $CDCl_3$, 300 K; right) NMR spectra: (a) complex **11**; (b) dimer **16** mixed with oligomer; (c) oligomer **26**.

Scheme 2



anhydrides, as had been proposed by Gerrard.[11] This is well illustrated by Figure 3, which displays the spectral changes observed during the formation of the borophosphonate **26**. It is of interest to note that the ^{14}N NMR spectrum is unchanged, attesting to the complete conservation of azido groups in the resulting oligomer, although the organic azides are known to react rapidly with dichloroboranes.[12]

The use of dibromoborane **32** in the reaction with phosphonate **1** facilitates the formation of a borophosphonate. Thus, the high yield of $[MePO_3BMe]_n$ (**33**) has been obtained after overnight storage of the reaction mixture at ambient temperature (Scheme 2).

Study of the Dynamic Behavior of the Cyclic Dimer 35a. The main difficulty in studying the properties of cyclic dimers **12**−**16** is their easy further transformation to the oligomeric borophosphonates **22**−**26**. To prepare a stable compound similar to **12**−**16**, we have treated diethyl benzylphosphonate (**2**) with dimethylbromoborane (**34**)[13] in deuteriochloroform (Scheme 3). After several minutes at room temperature 1 equiv of ethyl bromide was formed, and a mixture of cyclic borophosphonates **35a**,**b** and the mixed anhydride of benzylphosphonic acid and dimethylborinic acid (**35c**) in a 10:1:1 ratio was obtained quantitatively. Methanolysis of **35a**−**c** afforded benzylphosphonic acid monomethyl ester (**18**) and dimethylborinic acid.

The relative integral intensities in the ^1H NMR spectrum of **35** show the loss of one ethoxy group from the starting phosphonate **2**. In the high-resolution mass spectrum molecular peaks at *m*/*z* 440 (**35a**) and 220 (**35b**,**c**) with the expected isotopic distributions were found. In the ^{31}P spectrum (Figure 4) two close signals at 17.65 and 17.66 ppm correspond to two isomers of **35a**, whereas a broad resonance at 25.5 ppm originates from **35b**,**c** (Figure 4a). In ^{11}B NMR **35a**,**b** resonate at 11.2 ppm, whereas **35c** gives a signal at 32 ppm.

Storage of a sample containing the solution of **35** in deuteriochloroform at room temperature for 2 weeks resulted in a dramatic change of the relative concentrations of **35a**−**c**. The relative ratios of **35a**−**c** could be estimated now as 2:3:3, and in addition a new broad signal at approximately 22 ppm appeared. From the appearance of the spectrum shown in Figure 4b it is clear that compounds **35a**−**c** are in dynamic equilibrium with each other. To study this phenomenon more precisely, we have measured NMR spectra of **35** at various temperatures (Figure 5).

Pronounced dynamic effects were found in the ^1H, ^{13}C, and ^{31}P NMR spectra of compound **35**. Most informative are temperature-dependent ^{31}P NMR spectra at a concentration of 1 mol/L. At 60 °C compound **35** gives a single resonance at δ 25 (Figure 5f). Lowering the temperature leads first to the broadening of this signal (Figure 5e), which splits into three separate broad

(11) Gerrard, W.; Griffey, P. F. *Chem. Ind.* **1959**, 55.
(12) Suzuki, A.; Sono, S.; Itoh, M.; Brown, H. C.; Midland, M. M. *J. Am. Chem. Soc.* **1971**, *93*, 4329.
(13) Noth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *11*, 399.

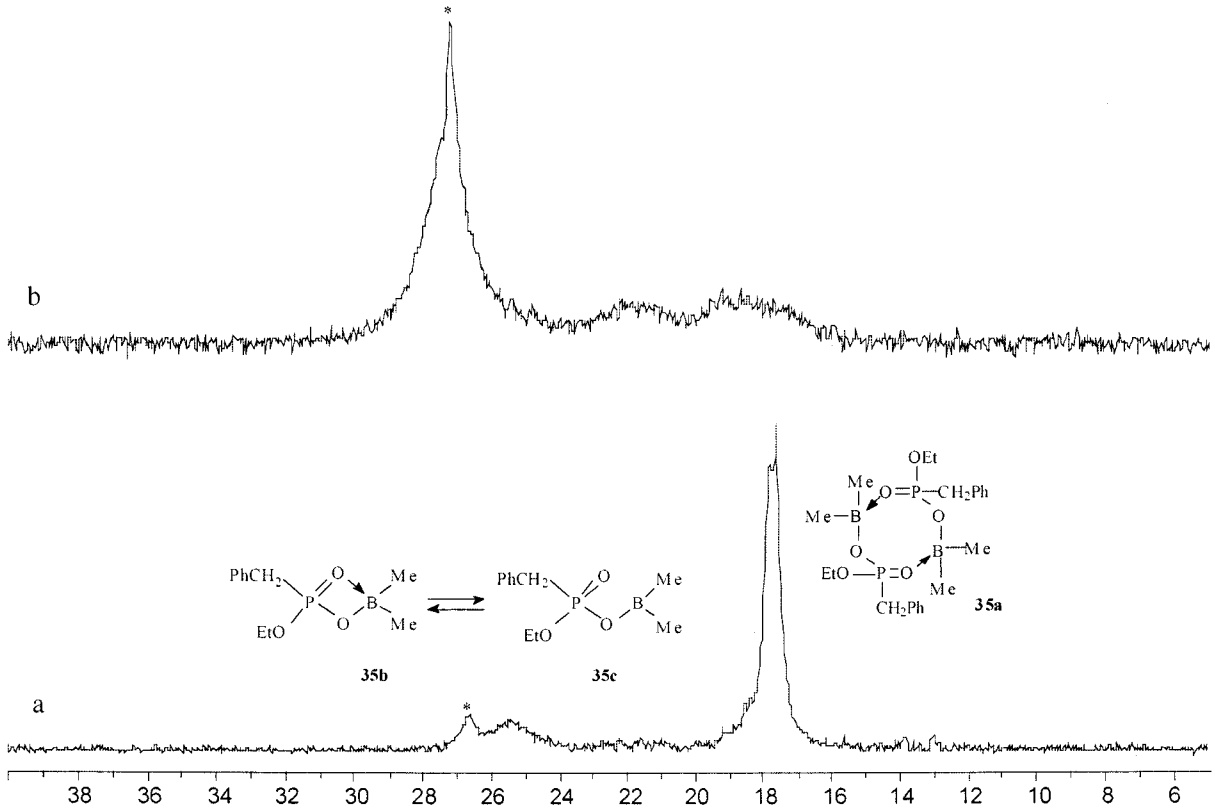
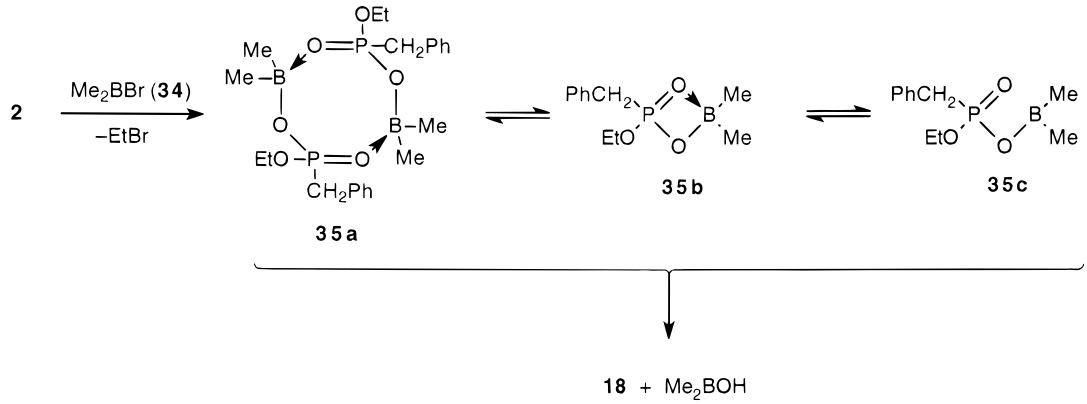


Figure 4. Evolution of the ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 300 K) of compound **35**: (a) immediately after preparation; (b) after 2 weeks. Asterisks indicate an impurity of the starting phosphonate **2**.

Scheme 3



resonances at room temperature at δ values of approximately 18, 22, and 28 ppm, corresponding to **35a**–**c**, respectively (Figure 5d). Further lowering of the temperature affects these three signals differently.

The high-field signal of **35a** at −20 °C is transformed to two sharp signals of two isomers at 19.6 and 19.7 ppm (Figure 5c). The most intense low-field signal (δ 28 at 24 °C) gives at −20 °C a broad resonance of two collapsed signals. At −40 °C two broad signals of equal intensity are observed (Figure 5b), one of which is split into two resonances at −55 °C (Figure 5a). Additionally, the broad peak of low intensity observed in the ^{31}P NMR at room temperature at 22 ppm turns at −20 °C into 10 or 12 small peaks in the chemical shift interval 21–25 ppm. From the temperature dependence of the line shape it is clear that all compounds producing these resonances are involved in the whole equilibrium, but the elucidation of their structure is extremely complicated due to their great number and low concentration.

On the basis of this temperature dependence of the phosphorus spectrum we conclude that **35b**,**c** are in a fast equilibrium, whereas the equilibrium between **35c** and **35a** is relatively slow (Scheme 4). Two peaks for **35b** in the ^{31}P spectrum at −55 °C probably correspond to compounds with equatorial and axial orientations of the benzyl group. Larger cycles similar to **35a** are probably involved in the equilibrium at high concentrations.

Thus, the dimer **35a** is the primary product in the reaction of phosphonate **2** with dimethylbromoborane (**32**). Heating or prolonged storage at room temperature transforms **35a** into a mixture in equilibrium consisting of **35a**–**c** and other unidentified products. The equilibrium concentration of **35a** is rather low (about 5%), but

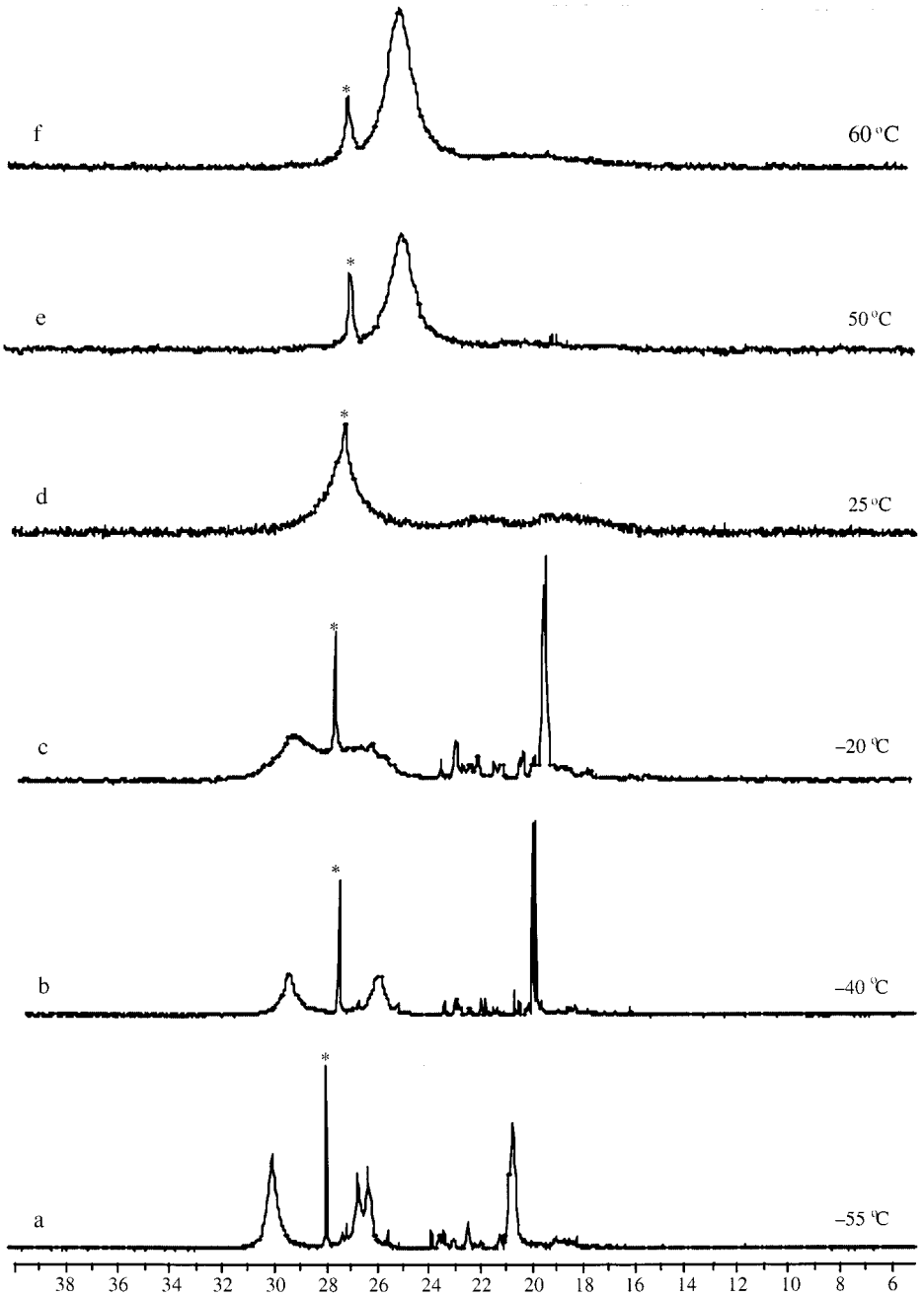


Figure 5. Temperature dependence of the ^{31}P NMR spectrum (121 MHz, $CDCl_3$, 1 mol/L) of compound **35**; for discussion see text. Asterisks indicate an impurity of the starting phosphonate **2**.

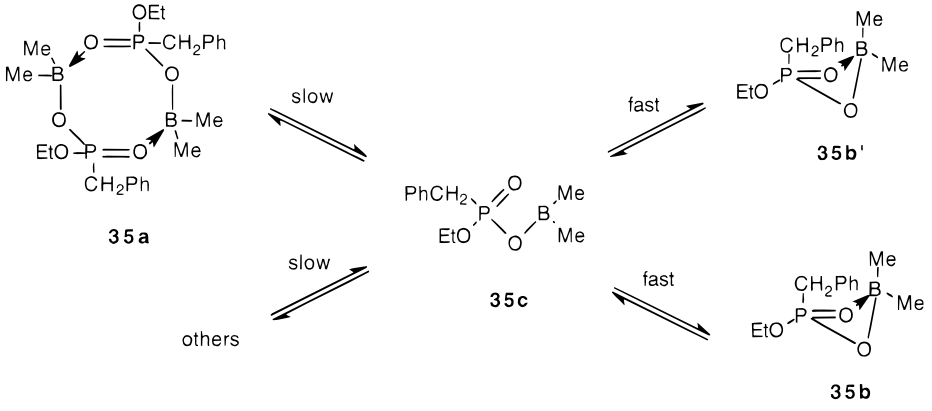
its relatively high barrier of dissociation makes possible the detection of **35a** as a primary product.

Our observations allow us to propose that dimers **12**−**16** are also primary products in the oligomerization reaction of complexes **7**−**11**. Complexes **7**−**11** do not react with an excess of **6** but react vigorously with an additional amount of the corresponding phosphonate, producing soluble oligomers. Therefore, the molecule of a phosphonate incorporated into the complex is deactivated, and the most probable result is a bimolecular push−pull mechanism, resulting directly in a dimer (Scheme 4). On the basis of the dynamic properties of the dimer **35a** we propose that similar equilibria operate also in the case of dimers **12**−**16**. Therefore, when the dimer is formed, it may isomerize to a monomer, which in turn would produce a statistical oligomer.

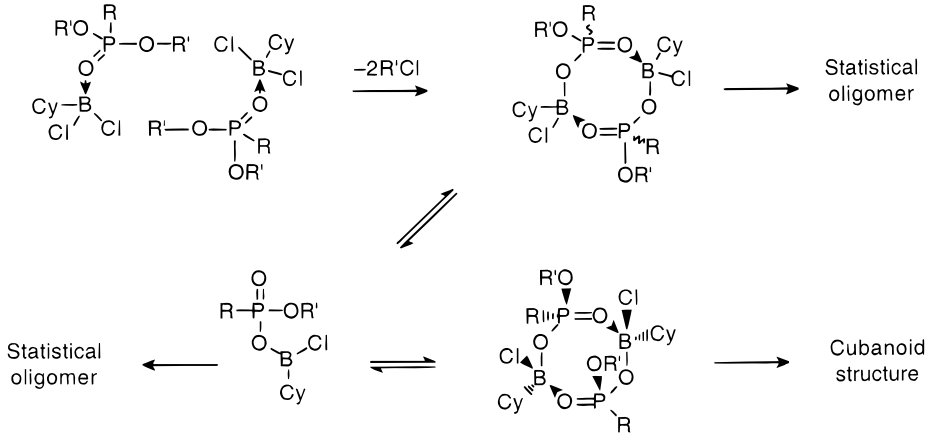
If the elimination of two molecules of alkyl chloride gives a dimer, this may result in synthesis of a cubanoid framework such as those described by Roesky[1] and Kuchen.[2] However, only one isomer among five possible is appropriate for that, whereas the other four would again produce a statistical oligomer (Scheme 5). Therefore, for the selective formation of the cubanoid framework, the all-cis isomer of a dimer should be more stable than the other four, react more quickly, or both. Since all the known examples of cubanoid structures possess a bulky substituent on phosphorus, one can propose that these bulky substituents link the molecules of the all-cis isomer of a dimer in a conformation, where they occupy exclusively equatorial positions. This can result both in stabilization of the all-cis isomer compared with the other four and in higher reactivity, since all chlorine atoms and alkoxy groups are axial and "ready-to-react".

Although the borophosphonates **22**−**26** give in the

Scheme 4



Scheme 5



mass spectra the ions $[RPO_3BC_6H_{11}]_4-C_6H_{11}$, which may be attributed to the cubanoid structures **22′**−**26′** (Scheme 1), their NMR spectra contain broad resonances characteristic for statistical oligomers.[1,14] An interesting structural feature of these compounds is the resemblance of their central $M_4O_{12}P_4$ cubic core to the D4R (double-four-tetrahedral-atom-ring) SBUs found in cloverite, ULM-5,[15] and gallophosphate-A.[16] These compounds can be regarded as potential precursors for the preparation of molecular sieves and ion conductors.

We conclude therefore that structure of the oligomers **22**−**26** is not definite, and the peaks observed in the mass spectra correspond to the lightest molecules present in the mixture. Apparently, the molecules with higher molecular weights are difficult to detect in the EI mass spectra, whereas the measurement of the FAB mass spectra is impossible due to hydrolysis of **22**−**26** by the matrix.

Conclusion

In this article, we have demonstrated the use of phosphonates and organohaloboranes as precursors for framework borophosphonates through a facile haloalkane elimination reaction. Small changes in the bulkiness of the substituents on boron or phosphorus should allow the isolation of borophosphonates with different polyhedral structures. The cage molecules thus obtained will serve us as precursors for the studies of their transformation to three-dimensional borophosphonate materials by nonaqueous routes. Alternatively, the method should provide a convenient new route for effective phosphonate deprotection.

Experimental Section

All operations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Commercially available phosphonates were used without additional purification. Cyclohexyldichloroborane (**6**)[7] and methyldibromoborane (**32**)[13] were prepared according to known procedures. NMR spectra were recorded on Bruker ARX-200, Bruker AC-300, and Bruker WM-300 spectrometers. Chemical shifts in the ^1H and ^{13}C NMR spectra are referenced to internal standard TMS, ^{11}B chemical shifts to external $BF_3{\cdot}Et_2O$, and ^{31}P chemical shifts to external 10% H_3PO_4. Electron impact mass spectra were measured on a Finnigan-MAT instrument at 280−320 °C. Electron microscopy and microprobe analyses were carried out on JEOL instruments.

Reactions of Alkylphosphonates with Cyclohexyldichloroborane (7). General Procedures. Synthesis of Borophosphonates 22−**26.** Neat phosphonate (1 equiv) was quickly added to a solution of cyclohexyldichloroborane (1 equiv) in 50 mL of toluene at −30 °C. The reaction mixture was warmed to ambient temperature. The NMR analysis of the reaction mixtures at this stage indicated the clear and quantitative formation of the corresponding complex **7**−**11**. The subsequent heating of this solution for 12 h at 70 °C (48 h in the case of complex **9**) led to evolution of 2 equiv of alkyl chloride. Then all volatiles were removed under vacuum; the

(14) Only compounds that contain bulky alkyl groups on phosphorus (e.g., *t*-Bu) are reported to be stable. See ref 3a, p 119.
(15) Loiseau, T.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 403.
(16) Merrouche, A.; Patarin, J.; Soulard, M.; Kessler, H.; Angelrot, D. *Synth. Microporous Mater.* **1992**, *1*, 384.

resulting solid oligomers were washed twice with ether and dried under high vacuum.

Detection of Dimers 12−16. If the solution of any complex **7**−**11** was stored for several days at ambient temperature, the corresponding dimers **12**−**16** were observed in the NMR spectra of the reaction mixtures. Only in the case of dimer **15** was the reaction clean and complete. In other cases dimers **12**−**14** and **16** were observed either in equilibria with monomers or together with already formed oligomers.

Hydrolysis of the Mixtures of Oligomers 22−26. A 100 mg portion of a mixture of oligomers was introduced in an NMR tube, and 0.4 mL of CD_3OD was added. Slight heating of the resulting suspension with an air gun gave a clear solution, which according to NMR analysis contained cyclohexylboronic acid **9** and the corresponding phosphonic acids **27**−**31**. Otherwise, 100 mg of an oligomeric borophosphonate was heated for 10 min at 100 °C in 10% HCl. When the resulting clear solution was cooled to room temperature, cyclohexylboronic acid precipitated. The remaining solution contained the corresponding phosphonic acids **27**−**31**.

Reaction of methylphosphonate (**2**; 0.82 g, 5.4 mmol) and cyclohexyldichloroborane (**6**; 0.89 g, 5.4 mmol) gave 0.95 g (94%) of borophosphonate **22**.

Diethyl Methylphosphonate−Cyclohexyldichloroborane Complex (7). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 0.61 (t, 1H, CHB, $^3J_{aa}$ = 11.4 Hz), 1.06 (m, 2H of cyclohexyl), 1.19 (m, 3H of cyclohexyl), 1.44 (t, 6H, $2CH_3$, ^3J = 7.0 Hz), 1.70 (m, 3H of cyclohexyl), 1.81 (m, 2H of cyclohexyl), 2.03 (d, 3H, CH_3P, $^2J_{HP}$ = 18.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$, 300 K): δ 10.97 (d, CH_3P, $^1J_{CP}$ = 139.4 Hz), 16.00 (d, $2CH_3$, $^3J_{CP}$ = 6.5 Hz), 27.26, 27.86, 28.75 ($3CH_2$ of cyclohexyl), 35.5 (br, CHB), 66.58 (d, $2CH_2$, $^2J_{CP}$ = 7.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$, 297 K): δ 37.55. ^{11}B NMR (96 MHz, $CDCl_3$, 297 K): δ 11.5.

Dimer 12. ^{1}H NMR (300 MHz, C_7D_8, 297 K): δ 0.92 (m, 2H, 2CHB), 1.20 (m, 10H of cyclohexyls), 1.25 (m, 6H, $2CH_3$), 1.49 (d, 3H, CH_3, $^2J_{HP}$ = 19.1 Hz), 1.51 (d, 3H, CH_3, $^2J_{HP}$ = 18.8 Hz), 1.98 (m, 10H of cyclohexyls), 4.2 (m, 4H, $2CH_2$). ^{13}C NMR (75 MHz, C_7D_8, 297 K): δ 12.25 (d, CH_3P, $^1J_{CP}$ = 150.2 Hz), 12.31 (d, CH_3P, $^1J_{CP}$ = 154.4 Hz), 15.85 (d, $2CH_3$, $^3J_{CP}$ = 7.3 Hz), 27.18, 27.60, 28.23 ($3CH_2$ of cyclohexyl), 33.5 (br, CHB), 65.18 (d, CH_2O, $^3J_{CP}$ = 8.6 Hz), 65.36 (d, CH_2O, $^3J_{CP}$ = 7.3 Hz). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 24.38 (1P), 24.71 (1P). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ 5.7.

Borophosphonate 22. ^{1}H NMR (300 MHz, C_7D_8, 297 K): δ 1.0−2.2 (unresolved multiplet, cyclohexyl, CH_3P), ^{13}C NMR (75 MHz, C_7D_8, 300 K): δ 13 (br d, CH_3P, $^1J_{CP}$ approximately 150 Hz), 28 (br, cyclohexyl). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 10 (br). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ 3.0. High-resolution EI mass spectrum: *m*/*z* 669 ($[C_7H_{14}PO_3B]_4$ − $C_6H_{11})^+$. HRMS (EI): calcd for $C_{22}H_{45}O_{12}{}^{11}B_4P_4$, 669.22335; found, 669.2237. MS (IE): *m*/*z* 669 (M − C_6H_{11}).

Methylphosphonic Acid (27). ^{1}H NMR (300 MHz, CD_3OD, 297 K): δ 1.44 (d, 3H, CH_3P, $^2J_{HP}$ = 17.6 Hz). ^{13}C NMR (75 MHz, CD_3OD, 297 K): δ 13.03 (d, CH_3P, $^1J_{CP}$ = 140.6 Hz). ^{31}P NMR (121 MHz, CD_3OD, 297 K): δ 30.55.

Reaction of diethyl benzylphosphonate (**2**; 584 mg, 2.56 mmol) with cyclohexyldichloroborane (**6**; 425 mg, 2.56 mmol) gave 0.95 g (94%) of borophosphonate **23**.

Diethyl Benzylphosphonate−Cyclohexyldichloroborane Complex (8). ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): δ 0.72 (t, 1H, CHB, $^3J_{aa}$ = 11.6 Hz), 1.2 (m, 5H of cyclohexyl), 1.40 (t, 6H, $2CH_3$, ^3J = 6.3 Hz), 1.8 (m, 5H of cyclohexyl), 3.82 (d, 2H, CH_2P, $^2J_{HP}$ = 21.9 Hz), 7.5 (m, 5H, C_6H_5). ^{13}C NMR (50 MHz, $CDCl_3$, 300 K): δ 15.86 (d, $2CH_3$, $^3J_{CP}$ = 6.1 Hz), 27.16, 27.78, 28.70 ($3CH_2$ of cyclohexyl), 32.74 (d, CH_3P, $^1J_{CP}$ = 132.1 Hz), 35.5 (br, CHB), 67.33 (d, $2CH_2$, $^2J_{CP}$ = 7.4 Hz), 128.02 (*p*-C), 128.83 (*m*-C), 129.95 (d, *o*-C, $^3J_{CP}$ = 7.0 Hz), C_{quat} not found. ^{31}P NMR (121 MHz, $CDCl_3$, 297 K): δ 30.05. ^{11}B NMR (96 MHz, $CDCl_3$, 297 K): δ 11.3.

Dimer 13. ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): δ 0.40 (m, 2H, 2CHB), 1.07 (t, 3H, CH_3, $^3J_{HH}$ = 6.9 Hz), 1.08 (t, 3H, CH_3, $^3J_{HH}$ = 7.0 Hz), 1.2 (m, 10H of cyclohexyls), 1.6 (m, 10H of cyclohexyls), 3.4 (m, 4H, $2CH_2P$), 4.1 (m, 4H, $2CH_2O$), 7.3 (m, 10H, $2C_6H_5$). ^{13}C NMR (50 MHz, $CDCl_3$, 300 K): δ 15.69 (d, $2CH_3$, $^3J_{CP}$ = 7.1 Hz), 27.24, 27.87, 28.79 ($3CH_2$ of cyclohexyl), 33.50 (d, $2CH_2P$, $^1J_{CP}$ = 150.1 Hz), 34.6 (br, CHB), 66.65 (d, CH_2O, $^3J_{CP}$ = 9.4 Hz), 66.70 (d, CH_2O, $^3J_{CP}$ = 8.3 Hz), 127.45 (d, *p*-C, ^5J = 3.4 Hz), 128.46 (d, *m*-C, ^4J = 3.5 Hz), 129.45 (d, C_{quat}, ^3J = 10.8 Hz), 130.41 (d, *o*-C, ^3J = 7.4 Hz). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 18.51 (1P), 18.68 (1P). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ 5.7.

Borophosphonate 23. ^{1}H NMR (300 MHz, C_7D_8, 297 K): δ 0.6−1.6 (unresolved multiplet, cyclohexyl), 2.8−3.6 (br, CH_2P), 7.0−7.4 (br, C_6H_5). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 3.5 ($\nu_{1/2}$ = 1000 Hz). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ −1 ($\nu_{1/2}$ = 900 Hz). Cubic tetramer **23′** was mainly observed in MS (IE). HRMS (IE): calcd for $C_{46}H_{61}O_{12}{}^{11}B_4P_4$, 973.34855; found, 973.3486. MS (IE): *m*/*z* 973 (M − C_6H_{11}).

Benzylphosphonic Acid (28). ^{1}H NMR (200 MHz, CD_3OD, 300 K): δ 3.11 (d, 2H, CH_2P, ^1J = 21.7 Hz), 7.1−7.4 (m, 5H, C_6H_5). ^{13}C NMR (50 MHz, CD_3OD, 300 K): δ 34.44 (d, CH_2P, ^1J = 135.0 Hz), 126.12 (d, *p*-C, ^5J = 3.4 Hz), 127.95 (d, *m*-C, ^4J = 2.9 Hz), 129.48 (d, *o*-C, ^3J = 6.3 Hz), 132.89 (d, C_{quat}, ^3J = 9.3 Hz). ^{31}P NMR (121 MHz, CD_3OD, 297 K): δ 25.3.

Reaction of diethyl vinylphosphonate (**3**; 470 mg, 2.89 mmol) with cyclohexyldichloroborane (**6**; 480 mg, 2.89 mmol) gave 435 mg (75%) of borophosphonate **24**.

Diethyl Vinylphosphonate−Cyclohexyldichloroborane Complex (9). ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): δ 1.21 (m, 6H of cyclohexyl), 1.39 (t, 6H, $2CH_3$, ^3J = 7.0 Hz), 1.75 (m, 3H of cyclohexyl), 1.89 (m, 2H of cyclohexyl), 6.2−6.8 (m, 3H, $CH{=}CH_2$). ^{13}C NMR (50 MHz, $CDCl_3$, 300 K): δ 15.87 (d, $2CH_3$, $^3J_{CP}$ = 6.4 Hz), 27.02, 27.87, 28.53 ($3CH_2$ of cyclohexyl), 37.2 (br, CHB), 67.22 (d, $2CH_2$, $^2J_{CP}$ = 7.2 Hz), 120.08 (d, CH=, $^1J_{CP}$ = 192.8 Hz), 141.05 (CH_2=). ^{31}P NMR (121 MHz, $CDCl_3$, 297 K): δ 18.7. ^{11}B NMR (96 MHz, $CDCl_3$, 297 K): δ 11.3.

Dimer 14. ^{13}C NMR (75 MHz, C_7D_8, 297 K): δ 67.95 (d, CH_2O, $^3J_{CP}$ = 7.4 Hz), 68.37 (d, CH_2O, $^3J_{CP}$ = 7.4 Hz), 119.12 (d, =CHP, $^1J_{CP}$ = 189.0 Hz), 119.31 (d, =CHP, $^1J_{CP}$ = 193.0 Hz), 143.33 (CH_2=). ^{31}P NMR (121 MHz, $CDCl_3$, 297 K): δ 16.96 (1P), 17.61 (1P). ^{11}B NMR (96 MHz, $CDCl_3$, 297 K): δ 5.4.

Borophosphonate 24. ^{1}H NMR (300 MHz, C_7D_8, 297 K): δ 1.0−2.2 (unresolved multiplet, cyclohexyl), 6.0−6.8 (br, $CH{=}CH_2$). ^{13}C NMR (75 MHz, C_7D_8, 300 K): δ 26−29 (br, cyclohexyl), 123 (br doublet, *C*H=), 137 (br, CH_2=).; ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 0.7 ($\nu_{1/2}$ = 1000 Hz). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ −0.5 ($\nu_{1/2}$ = 1000).

Vinylphosphonic Acid (29). ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): δ 5.8−6.3 (m, 3H, $CH{=}CH_2$). ^{13}C NMR (50 MHz, $CDCl_3$, 300 K): δ 128.25 (d, CH=, $^1J_{CP}$ = 184.3 Hz), 132.72 (CH_2=).

Reaction of dimethyl allylphosphonate (**4**; 135 mg, 0.90 mmol) with cyclohexyldichloroborane (**6**; 150 mg, 0.90 mmol) gave 150 mg (78%) of borophosphonate **25**.

Dimethyl Allylphosphonate−Cyclohexyldichloroborane Complex (10). ^{1}H NMR (200 MHz, C_7D_8, 300 K): δ 1.09 (m, 1 H, CHB), 1.50 (m, 5H of cyclohexyl), 2.05 (m, 3H of cyclohexyl), 2.30 (m, 2H of cyclohexyl), 2.99 (dd, 2H, CH_2P, $^2J_{HP}$ = 22.7 Hz, $^3J_{HH}$ = 7.2 Hz), 3.76 (d, 6H, $2CH_3$, $^3J_{HP}$ = 11.5 Hz) 5.20 (m, 2H, $CH{=}CH_2$), 5.68 (m, 1 H, *CH*=CH_2). ^{13}C NMR (50 MHz, C_7D_8, 300 K): δ 28.02, 29.31, 30.16 ($3CH_2$ of cyclohexyl), 30.50 (d, CH_3P, $^1J_{CP}$ = 137.3 Hz), 37.6 (br, CHB), 57.38 (d, $2CH_3$, $^2J_{CP}$ = 8.1 Hz); 123.83 (d, CH_2=, $^3J_{CP}$ = 15.9 Hz), 124.53 (d, CH=, $^2J_{CP}$ = 12.6 Hz). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 34.31. ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ 11.6.

Dimer 15. ^{1}H NMR (300 MHz, C_7D_8, 297 K): δ 0.92 (m, 1 H, CHB), 1.50 (m, 5H of cyclohexyl), 2.08 (m, 5H of cyclohexyl), 2.97 and 2.98 (2 AB systems, 4H, $2CH_2P$, $^2J_{HP}$ = 23.7 Hz, $^2J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 6.9 Hz), 3.80 (d, 3H, CH_3, $^3J_{HP}$ = 11.8 Hz),

3.81 (d, 3H, CH_3, $^3J_{HP}$ = 11.8 Hz), 5.22 (m, 2H, CH=CH_2), 5.80 (m, 1 H, C*H*=CH_2). ^{13}C NMR (50 MHz, C_7D_8, 300 K): δ 28.69, 29.17, 29.51 ($3CH_2$ of cyclohexyl), 32.66 (d, CH_3P, $^1J_{CP}$ = 151.5 Hz), 32.70 (d, CH_3P, $^1J_{CP}$ = 151.2 Hz), 34.5 (br, CHB), 56.80 (d, $2CH_3$, $^2J_{CP}$ = 8.7 Hz), 122.57 (d, $2CH_2$=, $^3J_{CP}$ = 15.3 Hz), 126.35 (d, 2CH=, $^2J_{CP}$ = 13.1 Hz). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 21.27 (1P), 21.29 (1P). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ 8.1. HRMS: calcd for $C_{14}H_{27}O_6{}^{11}B_2P_2{}^{35}Cl_2$, 445.08459; found, 445.0831. MS (IE): *m*/*z* 493 (M − Cl), 445 (M − C_6H_{11}).

Borophosphonate 25. ^{1}H NMR (300 MHz, C_7D_8, 297 K): δ 0.6−1.6 (unresolved multiplet, cyclohexyl), 2.4 (br, CH_2P), 4.9−5.2 (br, CH=CH_2), 5.4−5.8 (br, *C*H=). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 0.7 ($\nu_{1/2}$ = 1000 Hz). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ 0 ($\nu_{1/2}$ = 600 Hz). The ion $M^+ - C_6H_{11}$ corresponding to tetramer **25′** was detected by high-resolution EIMS spectroscopy: HRMS: calcd for $C_{30}H_{53}O_{12}{}^{11}B_4P_4$, 773.28595; found, 773.2867. MS (IE): *m*/*z* 773 (M − C_6H_{11}).

Allylphosphonic Acid (30). ^{1}H NMR (200 MHz, CD_3OD, 300 K): δ 2.70 (dddd, 2H, CH_2P, $^2J_{HP}$ = 22.1 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz), 5.30 (m, 2H, CH=CH_2), 6.00 (m, 1 H, C*H*=CH_2). ^{13}C NMR (50 MHz, CD_3OD, 300 K): δ 32.74 (d, CH_2P, $^1J_{CP}$ = 137.0 Hz), 118.65 (d, CH_2=, $^3J_{CP}$ = 14.3 Hz), 128.39 (d, CH=, $^2J_{CP}$ = 11.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$, 297 K): δ 26.9.

Reaction of diethyl azidomethylphosphonate (**5**;[17] 294 mg, 1.52 mmol) with cyclohexyldichloroborane (**6**; 260 mg, 1.52 mmol) gave 330 mg (95%) of borophosphonate **26**.

Diethyl Azidomethylphosphonate−Cyclohexyldichloroborane Complex (11). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 0.64 (tt, 1 H, CHB, $^3J_{aa}$ = 11.7 Hz, $^3J_{ae}$ = 2.7 Hz), 1.06 (m, 2H of cyclohexyl), 1.19 (m, 4H of cyclohexyl), 1.45 (t, 6H, $2CH_3$, ^3J = 7.1 Hz), 1.70 (br m, 4H of cyclohexyl), 1.81 (m, 2H of cyclohexyl), 4.17 (d, 2H, CH_2P, ^2J = 11.4 Hz), 4.55 (m, 4H, $2CH_2O$). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 16.19 (d, $2CH_3$, $^3J_{CP}$ = 5.4 Hz), 27.20, 27.79, 28.72 ($3CH_2$ of cyclohexyl), 35.5 (br, CHB), 45.07 (d, CH_3P, $^1J_{CP}$ = 155.8 Hz), 66.5 (br, $2CH_2O$). ^{31}P NMR (121 MHz, $CDCl_3$, 297 K): δ 24.53. ^{11}B NMR (96 MHz, $CDCl_3$, 297 K): δ 11.7. ^{14}N NMR (22 MHz, $CDCl_3$, 297 K): δ −332 (br), −164.8, −135.3.

Dimer 16. ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 0.64 (tt, 1H, CHB, $^3J_{aa}$ = 11.7 Hz, $^3J_{ae}$ = 2.7 Hz), 1.06 (m, 2H of cyclohexyl), 1.19 (m, 4H of cyclohexyl), 1.45 (t, 6H, $2CH_3$, ^3J = 7.1 Hz), 1.70 (br m, 4H of cyclohexyl), 1.81 (m, 2H of cyclohexyl), 3.84 (ABX system, 2H, CH_2P, δ_A 3.81, δ_B 3.87, $^2J_{AB}$ = 15.5 Hz, $^2J_{AP}$ = 13.2 Hz, $^2J_{BP}$ = 12.2 Hz), 3.86 (ABX system, 2H, CH_2P, δ_A 3.82, δ_B 3.90, $^2J_{AB}$ = 15.3 Hz, $^2J_{AP}$ = 13.2 Hz, $^2J_{BP}$ = 12.6 Hz), 4.42 (m, 4H, $2CH_2O$). ^{13}C NMR (50 MHz, C_7D_8, 300 K): δ 16.01 (d, 4 CH_3, $^3J_{CP}$ = 6.1 Hz), 27.65, 28.15, 29.10 ($3CH_2$ of cyclohexyl), 32.5 (br, CHB), 44.51 (d, CH_2P, $^1J_{CP}$ = 172.1 Hz), 45.93 (d, CH_2P, $^1J_{CP}$ = 174.6 Hz), 67.86 (d, $2CH_2$, $^2J_{CP}$ = 9.1 Hz). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 13.55 (1P), 13.48 (1P). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ 8.1. ^{14}N NMR (22 MHz, $CDCl_3$, 297 K): δ −332 (br), −164.8, −135.3.

Borophosphonate 26. ^{1}H NMR (300 MHz, C_7D_8, 297 K): δ 1.0−2.2 (unresolved multiplet, cyclohexyl), 3.9−4.2 (br, CH_2P). ^{13}C NMR (75 MHz, C_7D_8, 300 K): δ 26−29 (br, cyclohexyl), 45 (br doublet, CH_2P), 137 (br, CH_2). ^{31}P NMR (121 MHz, C_7D_8, 297 K): δ 3.7 ($\nu_{1/2}$ = 300 Hz), −6.2 (sharp). ^{11}B NMR (96 MHz, C_7D_8, 297 K): δ −4 ($\nu_{1/2}$ = 180 Hz). ^{14}N NMR (22 MHz, $CDCl_3$, 297 K): δ −332 (br), −164.8, −135.3.

Azidomethylphosphonic Acid (31). ^{1}H NMR (300 MHz, CD_3OD, 300 K): δ 3.40 (d, 2H, CH_2P, $^2J_{HP}$ = 12.0 Hz). ^{13}C NMR (50 MHz, CD_3OD, 300 K): δ 45.37 (d, CH_2P, $^1J_{CP}$ = 157.1 Hz), 118.65 (d, CH_2=, $^3J_{CP}$ = 14.3 Hz). ^{31}P NMR (81 MHz, CD_3OD, 297 K): δ 15.29.

Reaction of Diethyl Benzylphosphonate (2) with Dimethylbromoborane (34). Diethyl benzylphosphonate (**2**; 187 mg, 0.82 mmol) was quickly added to a solution of Me_2BBr (**34**; 100 mg, 0.82 mmol) in 1 mL of deuteriotoluene. The reaction mixture was warmed to room temperature and left overnight. The NMR analysis showed the clear formation of equivalent amounts of ethyl bromide and an equilibrium mixture of **35a−c**. Evaporation of the volatiles under vacuum gave 180 mg (91%) of a slightly yellow viscous oil.

Equilibrium Mixture 35a−c. ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 0.61 (t, 1H, CHB, $^3J_{aa}$ = 11.4 Hz), 0.35 (s, 6H, $2CH_3B$), 0.85 (t, CH_3CH_2O, ^3J = 6.9 Hz), 2.90 (d, 2H, CH_2P, $^2J_{HP}$ = 22.4 Hz), 3.64 (br 2H, CH_3CH_2O), 6.9−7.2 (m, 5H, C_6H_5). ^{13}C NMR (75 MHz, C_7D_8, 300 K): 9.89 (br, $2CH_3B$), 15.90 (d, CH_3CH^2O, $^3J_{CP}$ = 6.5 Hz), 34.30 (d, CH_3P, $^1J_{CP}$ = 148.1 Hz), 63.96 (br, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$, 297 K): 17.66. ^{11}B NMR (96 MHz, $CDCl_3$, 297 K): 11.2. The high-resolution mass spectrum supports the structure.

Methanolysis of **35** gave the benzylphosphonic acid monoethyl ester **18**.

Benzylphosphonic Acid Monoethyl Ester (18). ^{1}H NMR (200 MHz, C_7D_8 + CD_3OD, 300 K): δ 1.32 (td, 3H, CH_3, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.4 Hz), 3.25 (d, 2H, CH_2P, $^1J_{HP}$ = 21.6 Hz), 4.08 (dq, 2H, CH_2O, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 0.7 Hz), 7.40 (m, 5H, C_6H_5). ^{13}C NMR (50 MHz, C_7D_8 + CD_3OD, 300 K): δ 33.20 (d, CH_2P, $^1J_{CP}$ = 136.5 Hz), 61.63 (d, CH_2O, $^2J_{CP}$ = 6.6 Hz), 126.46 (d, *p*-C, $^5J_{CP}$ = 3.6 Hz), 128.15 (d, *m*-C, $^4J_{CP}$ = 3.1 Hz), 129.62 (d, *o*-C, $^3J_{CP}$ = 6.5 Hz), 132.11 (d, C_{quat}, $^2J_{CP}$ = 9.3 Hz). ^{31}P NMR (121 MHz, C_7D_8 + CD_3OD, 297 K): δ 25.5.

OM000067V

(17) **5** was obtained by treatment of diethyl α-iodophosphonate (Lancaster) with sodium azide in DMSO: Berté-Verrando, S.; Nief, F.; Patois, C.; Savignac, P. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *103*, 91.