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Borophosphonate Cages: Easily Accessible and Constitutionally Dynamic Heterocubane Scaffolds

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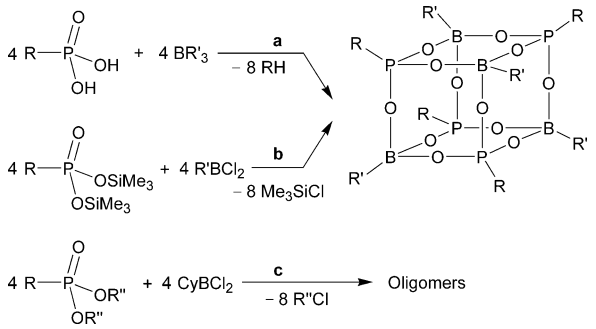
Abstract: A versatile and experimentally facile procedure for the synthesis of borophosphonate cages of the general formula $[t\mathrm{BuPO_3BR'}]_4$ is described. The method involves heating of *tert*-butylphosphonic acid with a boronic acid in toluene to give borophosphonates in [4+4] condensation reactions. The products display a heterocubane structure with bent P-O-B bridges as evidenced by crystallographic analyses. Scrambling experiments show that the borophosphonate cages are constitutionally dynamic scaffolds with exchange reactions occurring on the hour time scale at room temperature. The cages can be decorated with reactive groups such as aldehydes. Our results demonstrate that borophosphonate cages are interesting building blocks for dynamic covalent chemistry.

Keywords: boron · cage compounds · dynamic covalent chemistry · heterocubane · phosphorus

Introduction

Borophosphonates of the general formula $[\mathrm{RPO_3BR'}]_4$ were described for the first time in 1997 in publications by the groups of Roesky[1] and Kuchen.[2] These compounds display a heterocubane structure with P and B atoms at the corner of the cube and bent P-O-B bridges. The cages are isoelectronic to polyhedral silsesquioxanes of the general formula $[(\mathrm{RSi})_8\mathrm{O}_{12}]$ ("POSS"), which have been investigated extensively over the last years as nanometer-scale building blocks for different applications.[3] Compared with cubic silsesquioxanes, the chemistry of borophosphonates cages is hardly explored, and only a few compounds have been prepared and structurally characterized to date.[1,2]

The synthetic pathway used by Roesky and co-workers comprises heating a phosphonic acid with a trialkylborane (mostly $\mathrm{BEt_3}$) in an organic solvent at high temperature (Scheme 1, reaction a).[1] The Kuchen method involves the reaction of *tert*-butylphosphonic bis(trimethylsilyl ester) with $\mathrm{PhBCl_2}$ (Scheme 1, reaction b), but substituents other than R = *tert*-butyl and R′ = Ph were not investigated.[2] A synthetic pathway related to the Kuchen method was later reported by Mortier.[4] It was shown that borophosphonates can be obtained by combining alkylphosphonates (R″ = Me, Et) with $\mathrm{CyBCl_2}$ (Scheme 1, reaction c). However, analytical data of the products suggested the formation of mixtures of oligomers instead of a defined cage structure.



Scheme 1. Reported pathways for the synthesis of borophosphonate cages.[1,2,4]

Below, we describe a versatile and experimentally facile procedure for the synthesis of borophosphonate cages. Direct condensation of *tert*-butylphosphonic acid with boronic acids is shown to give borophosphonates cages in good yields. Furthermore, we demonstrate that borophosphonates are constitutionally dynamic scaffolds that can be decorated with reactive groups. Our results highlight the potential of borophosphonates as building blocks for the thermodynamically controlled synthesis of molecular and polymeric nanostructures.

Results and Discussion

Boronic acids are known to undergo fast and reversible condensation reactions with diols or with themselves to give boronate esters[5] and boroxines.[6] It thus appeared worth-

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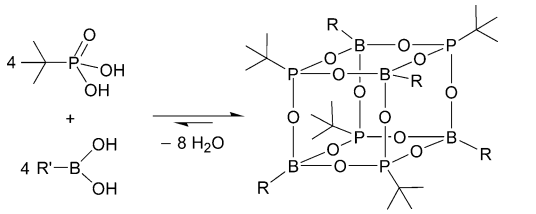
while to attempt the synthesis of borophosphonates by simple condensation reactions of phosphonic acids and boronic acids. As test reaction, we used the condensation of *tert*-butylphosphonic acid with phenylboronic acid, which was expected to give the previously described[2] heterocubane $[t\mathrm{BuPO_3BPh}]_4$ (**1**). When equal amounts of *tert*-butylphosphonic and phenylboronic acid were heated under reflux, using a Dean–Stark trap, the desired [4+4] condensation product was indeed formed (Scheme 2). Isolation led to a yield of 70%, which is clearly superior to the 14% reported by Kuchen.[2]



1 (R = Ph, 70%)
2 (R = *n*Bu, 82%)
3 (R = *n*Pr, 72%)
4 (R = Me, 53%)
5 (R = *p*-Tol, 67%)
6 (R = Cy, 70%)
7 (R = 4-C_6H_4CHO, 70%)
8 (R = 3,5-$C_6H_3(CHO)_2$, 97%)

Scheme 2. Synthesis of borophosphonate cages by [4+4] condensation of phosphonic and boronic acids.

Next, we investigated whether *tert*-butylphosphonic acid could be combined with primary alklboronic acids (R′= *n*Bu, *n*Pr, Me) or another aromatic boronic acid (R′=*p*-Tol). In all cases, a [4+4] condensation reaction was observed to produce the new borophosphonates **2**–**5** in good yields (Scheme 2). Reaction with cyclohexylboronic acid yielded the heterocubane **6**. The formation of **6** with cyclohexyl substituents is interesting in light of the results of Mortier, who obtained oligomers instead of cages upon utilization of $\mathrm{CyBCl_2}$ (Scheme 1, reaction c).[4] Borophosphonate cages with dangling aldehyde functions were obtained by condensation of $t\mathrm{BuPO(OH)_2}$ with 4-formyl- or 3,5-diformylphenylboronic acid, respectively (**7**, **8**). Aldehyde functionalities were chosen because borophosphonates with terminal aldehyde groups are potentially interesting building blocks for the formation of covalent imine networks.[7,8] Attempts to use other phosphonic acids (e.g., Et, Ph, *n*Bu, or *n*-hexyl) instead of $t\mathrm{BuPO(OH)_2}$ were not successful. The condensation products obtained with phenylphosphonic acid displayed very low solubility, regardless of the nature of the boronic acid that was employed. Reactions with *n*-butyl- or *n*-hexylphosphinic acid resulted in the formation of mixtures of different products, which could not be separated. The utilization of a phosphonic acid with a sterically demanding and solubilizing side chain is apparently very important for a controlled condensation reaction.

All new borophosphonates were characterized by multinuclear NMR spectroscopy, elemental analysis, and mass spectrometry. Preliminary low resolution mass spectrometry experiments by chemical ionization with a direct insertion probe revealed the presence of the parent ion species and associated fragments in lower mass range (data not shown). To further validate the identity of the borophosponate compounds, high resolution mass spectrometry experiments were performed on a hybrid 10T FT-ICR instrument. The use of a standard electrospray ionization source (ESI) did not yield detectable signals of the parent ions. However, the compounds were successfully ionized using the atmospheric pressure photo-ionization (APPI) source. Comparison of predicted theoretical and experimental isotopic distributions of the parent ion cluster, coupled with high accuracy mass measurements within a 5 ppm error, allowed confident assignment of the elemental compositions to the parent masses for all the studied borophosphonates. The isotopic distribution of parent ions in the spectra demonstrated the presence of at least 3 atoms of boron in all borophosphonates studied, with the signal-to-noise ratio of the peak for the $^{10}B_4$ isotopomer too low in some cases to assign it directly, albeit its presence can be inferred from the relative abundances of the major isotopomers. A representative MS spectrum is given in Figure 1.

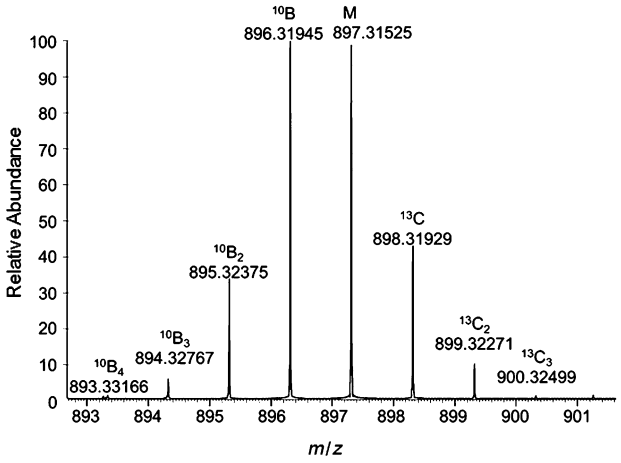


Figure 1. Mass spectrum of the isotopic cluster of the protonated parent ion $[M+\mathrm{H}]^+$ of compound **1** with all significant isotopomers labeled. The mass spectrum clearly indicates the presence of 4 boron atoms in the elemental composition of **1**. Note that the presence of a $^{10}B_4$ isotopomer is expected for all the other compounds, but due to its low S/N ratio, it can not be unambiguously assigned in all cases.

Further structural elucidation was achieved by MS/MS experiments by isolation of the parent ion and irradiation of said ion with a CO_2 laser (IRMPD). Irradiation time and laser power were varied such that the resultant mass spectra demonstrate extended fragmentation patterns. The observed fragmentation pattern is consistent with the tetrameric heterocubane structure as evidenced by extended analysis of compound **5**.

The borophosphonates **3**, **4**, **5**, **7**, and **8** were also characterized by single crystal X-ray diffraction. All the com-

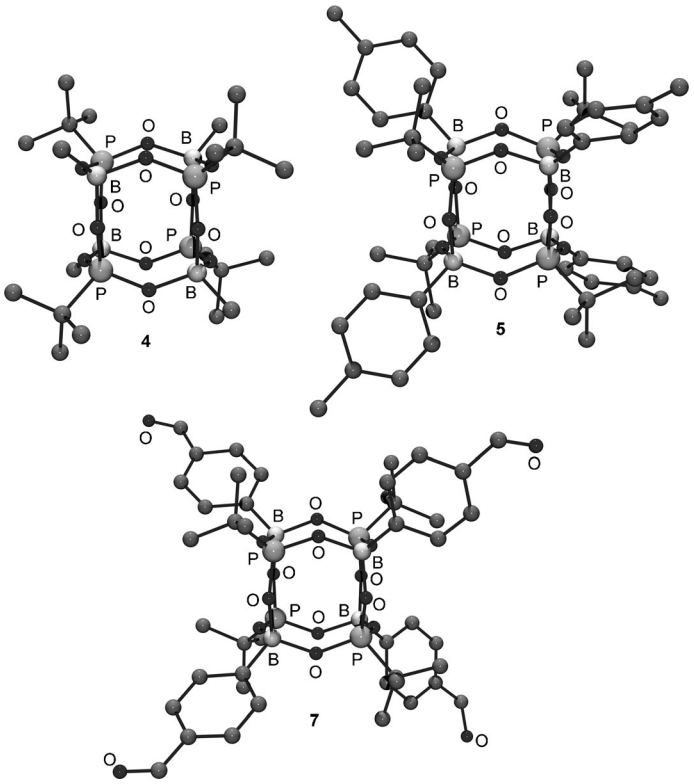


Figure 2. Molecular structures of the borophosphonates **4**, **5**, and **7** in the crystal.

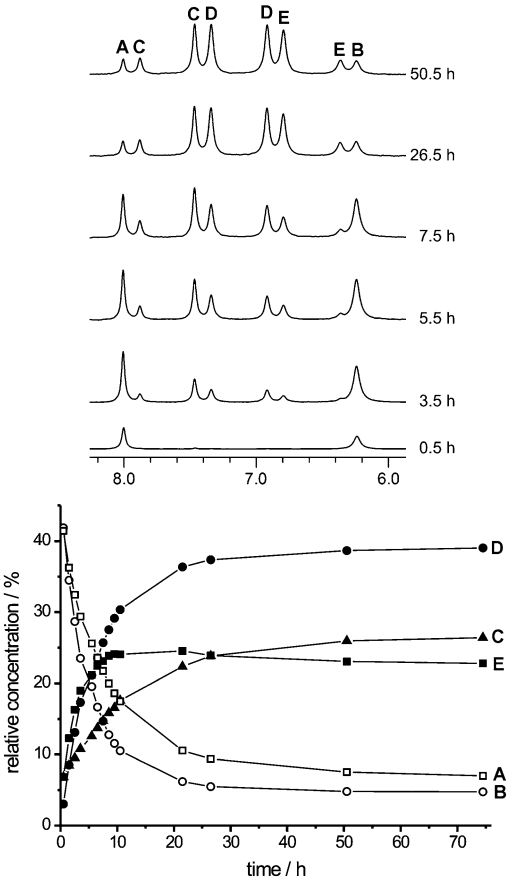


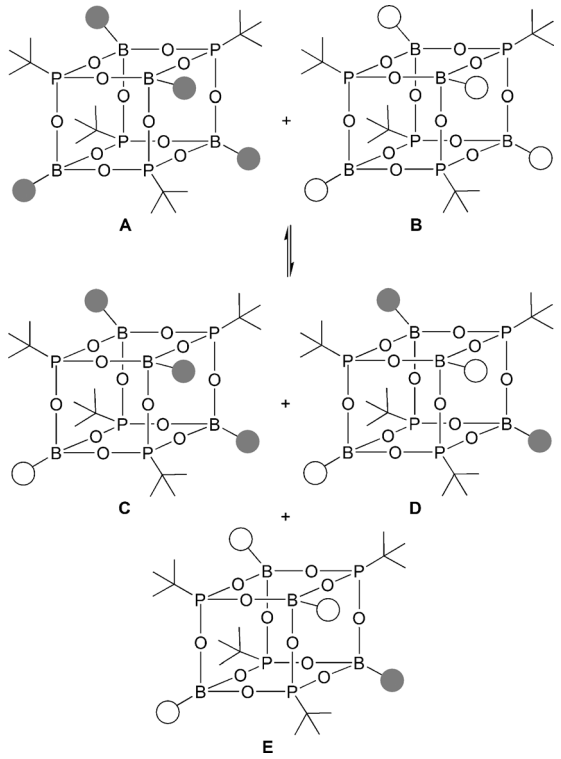
Figure 3. Time-dependent ^{31}P NMR spectrum (top) and species distribution (bottom) for an exchange reaction of **5** and $t\mathrm{Bu_4P_4Et_4B_4O_{12}}$ (6.8 mM each, RT) in $CDCl_3$.

pounds display a heterocubane structure. Graphical representations of three selected structures (**4**, **5**, and **7**) are given in Figure 2, and key structural data are summarized in Table 1. As observed for other cubic group 13 phosphonates,[1,2,9] the P–O distances are all very similar with an average value of 1.53 Å. The average B–O bond length of 1.50 Å is comparable to what is found for other compounds containing tetragonal $RB(OR')_4$ units such as boron-capped clathrochelates.[10] The values found for the P-O-B angles (α(av.) = 140.0°) are also within the expected range.[1,2,7]

The B-O-C linkage of boronate esters is thermodynamically highly stable.[11] Yet, boronate esters are dynamic compounds that undergo rapid exchange reactions, for example, with alcohols. This feature allows the synthesis of boronate esters under thermodynamic control, which has enabled the construction of molecular nanostructures, polymers and networks.[12,13] The dynamic behavior of borophosphonate cages has not been investigated so far. To examine whether these heterocubanes are constitutionally dynamic compounds, we have performed scrambling experiments. An equimolar mixture of **1** and **4** (14 mM each) in $CDCl_3$ was examined by time-dependent ^{31}P NMR spectroscopy. After a few hours, new signals appeared in the spectrum (Figure 3). Assuming that borophosphonates undergo exchange reactions, one would predict the formation of three new different species (Scheme 3, **C**–**E**). The mixed species **C** and **E** should display two ^{31}P NMR signals with a ratio of 3:1, whereas **D** should show two signals with a ratio of 1:1. Indeed, we observed the formation of six new peaks, the relative ratios of which are in line with the formation of the mixed species **C**–**E**. The time course of the reaction showed that equilibrium was established after approximately 70 h. By integration of the ^{31}P NMR signals, we were able to estimate an equilibrium distribution of A/B/C/D/E = 4.8:7.0:39:26.4:22.8. These values are not too far from a statistical distribution of A/B/C/D/E = 11.1:11.1:33.3:22.2:22.2:, which is, of course, expected because the different B–R side chains point away from each other. Similar results were obtained from scrambling experiments with **5** and $[t\mathrm{BuPO_3BEt}]_4$:[1] the equilibrium was established after approximately 50 h and a nearly statistical species distribution was finally observed.

Table 1. Average bond lengths [Å] and angles [°] of compounds **3**, **4**, **5**, **7**, and **8**.

	3	**4**	**5**	**7**	**8**
P–O	1.527	1.527	1.535	1.532	1.536
B–O	1.496	1.496	1.498	1.494	1.492
P–C	1.804	1.802	1.805	1.793	1.805
P-O-B	140.37	139.14	140.14	140.18	140.19
O-P-O	111.67	111.65	111.45	111.18	111.14
O-B-O	108.49	108.31	108.71	109.00	109.15



Scheme 3. Two borophosphonate cages **A** and **B** undergo exchange reactions to give a mixture of five different heterocubanes (**A**–**E**). The grey and white circles symbolize the side chains at boron and phosphorous.

For the combination of **5** and $[t\mathrm{BuPO_3BEt}]_4$, we have also investigated the effect of variation of the temperature and the concentration. When the temperature was increased from 25 to 40 °C, the exchange reactions became faster. For a semi-quantitative analysis, we have fitted the conversion of the starting material **5** with an exponential decay function. The resulting half-life was 76 min at 25 °C and 25 min and 40 °C. Surprisingly, the exchange became slower when the concentration of the borophosphonates was increased (the half-life increased from 56 to 72 min when going from 13 to 33 mM). This result indicates that the rate-limiting step is the dissociation of the heterocubane structure, which should become more favorable at lower concentrations.

Conclusion

We have demonstrated that borophosphonates of the general formula $[t\mathrm{BuPO_3BR'}]_4$ can be obtained by condensation of *tert*-butylphosphonic acid with boronic acids. The possibility to use simple condensation reactions substantially facilitates the synthesis of borophosphonates, because boronic acids are easily accessible and easy to handle. Scrambling experiments provide clear evidence for a constitutionally dynamic behavior of the borophosphonate cage compounds.

The condensation of boronic acids with tetraols allows the dynamic covalent connection of two boronic acids, whereas condensation reactions with hexaols allow the linking of three boronic acids. Borophosphonates offer a means to link four boronic acids in a dynamic fashion. Boronate esters have been used extensively for the formation of molecular nanostructures, polymers, and networks (e.g., covalent organic frameworks) under thermodynamic control.[12,13] Borophosphonates are expected to find applications in related areas.

Experimental Section

General: All the reactions were performed under an atmosphere of dry dinitrogen using standard Schlenk and vacuum-line techniques. The solvents toluene and chloroform were dried using a solvent purification system from Innovative Technologies, Inc., dry acetonitrile 99.9% was purchased from Acros Organics. *n*-Butylboronic acid (98%), 4-formylphenylboronic acid (97%), and *tert*-butylphosphonic acid were purchased from Acros, *p*-tolylboronic acid (97%) and 3,5-diformylboronic acid (no purity declaration by the producer) were purchased from Sigma Aldrich, *n*-propylboronic acid (98%) and methylboronic acid (97%) were purchased from Alfa Aesar, and cyclohexylboronic acid (97%) was purchased from ACBR. All boronic acids were recrystallized from water prior to use. The borophosphonate $[t\mathrm{BuPO_3BEt}]_4$ was synthesized according to a published procedure.[1] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 spectrometer with the residual solvents as internal standards or $BF_3{\cdot}OEt_2$ (^{11}B) as an external standard. ^{31}P NMR spectra were recorded on a Bruker Avance 200 spectrometer with 85% H_3PO_4 as external standard. $CDCl_3$ was dried over P_2O_5 and C_6D_6 was dried with 4 Å molecular sieves. All spectra were recorded at room temperature. Elemental analyses were performed on an EA 1110 CHN instrument.

Synthesis of $[t\mathrm{BuPO_3BPh}]_4$ (1): A suspension of phenylboronic acid (47.6 mg, 39 μmol) and *tert*-butylphosphonic acid (55.1 mg, 39 μmol) in toluene (120 mL) was heated under reflux for 3.5 h using a Dean Stark trap. Subsequently, the solvent was removed under vacuum and the residue was dissolved in dry toluene (2 mL). Upon addition of CH_3CN (10 mL), the product precipitated in the form of a white powder, which was isolated and dried under vacuum. Yield: 70% (62.5 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.07$ (d, $^3J = 18.9$ Hz, 9H), 7.30–7.36 (m, 1H), 7.43–7.49 (m, 2H), 7.94–8.00 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): $\delta = 24.20$ (d, $^3J = 2.2$ Hz), 30.76 (d, $^2J = 168.9$ Hz), 127,13, 127.37, 130.71, 144.37 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): $\delta = 2.08$ ppm; ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 8.35$ ppm; elemental analysis calcd (%) for $C_{40}H_{56}B_4O_{12}P_4$ (896.31): C 53.62, H 6.30; found: C 52.69, H 6.49; MS (CI): *m*/*z* (%): 897 (90); HRMS (*m*/*z*): 897.3153.

Synthesis of $[t\mathrm{BuPO_3B}(n\mathrm{Bu})]_4$ (2): The condensation of *n*-butylboronic acid (31.4 mg, 274 μmol) with *tert*-butylphosphonic acid (42.6 mg, 274 μmol) was achieved as described for **1**. After evaporation of the solvent, the residue was dissolved in chloroform (2 mL). Upon addition of CH_3CN (10 mL), the product precipitated in the form of a white powder, which was isolated and dried under vacuum. Yield: 82% (50.7 mg). ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 0.78$–0.86 (m, 2H), 1.11 (t, $^3J = 7.1$ Hz, 3H), 1.17 (d, $^3J = 18.2$ Hz, 9H), 1.56–1.71 ppm (m, 4H); ^{13}C NMR (C_6D_6, 101 MHz): $\delta = 14.66$, 22.87, 24.13 (d, $^3J = 2.8$ Hz), 26.59, 28.01, 30.46 ppm (d, ^{2}J = 171.1 Hz); ^{11}B NMR (C_6D_6, 128 MHz): $\delta = 4.20$ ppm; ^{31}P NMR (81 MHz, C_6D_6): $\delta = 6.73$ ppm; elemental analysis calcd (%) for $C_{32}H_{72}B_4O_{12}P_4$ (816.43): C 47.1, H 8.89; found: C 47.09, H 8.63; MS (CI): *m*/*z* (%): 817 (90). Single crystals were obtained by layering a solution of **2** in toluene with CH_3CN in an NMR tube and storage at −18 °C.

Synthesis of $[t\mathrm{BuPO_3B}(n\mathrm{Pr})]_4$ (3): The condensation of *n*-propylboronic acid (48.6 mg, 54 μmol) with *tert*-butylphosphonic acid (42.5 mg, 54 μmol) was achieved as described for **1**. After evaporation of the solvent, the residue was dissolved in toluene (1.5 mL). Upon addition of CH_3CN (10 mL), the product precipitated in the form of a white powder, which was isolated and dried under vacuum. Yield: 72% (74.8 mg). ^{1}H NMR

(400 MHz, [D$_6$]benzene): δ = 0.78–0.86 (m, 2H), 1.11 (t, ^3J = 7.1 Hz, 3H), 1.17 (d, ^3J = 18.2 Hz, 9H), 1.56–1.71 ppm (m, 4H); ^{13}C NMR (101 MHz, [D$_6$]benzene,): δ = 14.66, 22.87, 24.13 (d, ^3J = 2.8 Hz), 26.59, 28.01, 30.46 ppm (d, ^{2}J = 171.1 Hz); ^{11}B NMR (128 MHz, [D$_6$]benzene): δ = 4.20 ppm; ^{31}P NMR (81 MHz, [D$_6$]benzene): 6.73 ppm; elemental analysis calcd (%) for $C_{28}H_{64}B_4O_{12}P_4$ (759.94): C 44.25, H 8.49; found: C 44.16, H 9.27; MS (CI): *m*/*z* (%): 718 (80) $[M-Pr]^{\bullet+}$. Crystals of **3** were obtained by dissolution in hot hexane and subsequent storage at −18 °C.

Synthesis of [*t*BuPO$_3$BMe]$_4$ (4): The condensation of methylboronic acid (49.4 mg, 81 μmol) with *tert*-butylphosphonic acid (111.86 mg, 81 μmol) was achieved as described for **1**. After evaporation of the solvent, the residue was dissolved in a minimum amount of hot hexane. Small amounts of solid were filtered off and the solution was stored at −18 °C. A first crop of crystals formed (69.4 mg, 53 %). The solvent of the remaining solution was removed in vacuum, and a second crystallization from hexane gave further product (21.5 mg). Total yield: 91.9 mg (70 %). ^{1}H NMR (400 MHz [D$_6$]benzene): δ = 0.78–0.85 (m, 2H), 1.15 (d, ^3J = 18.2 Hz, 9H), 1.24 (t, ^3J = 7.4 Hz, 3H), 1.64–1.76 ppm (m, 2H); ^{13}C NMR (101 MHz, [D$_6$]benzene): δ = 18.38, 19.00, 24.08 (d, ^3J = 2.6 Hz), 26.10, 29.57, 30.42 ppm (d, ^2J = 170.9 Hz); ^{11}B NMR (128 MHz, [D$_6$]benzene): δ = 3.96 ppm; ^{31}P NMR (81 MHz, [D$_6$]benzene): 6.92 ppm; elemental analysis calcd (%) for $C_{20}H_{48}B_4O_{12}P_4$ (647.73): C 37.09, H 7.47; found: C 37.25, H 8.02. MS (CI): *m*/*z* (%): 648 (100); HRMS (*m*/*z*): 649.2541.

Synthesis of [*t*BuPO$_3$B(*p*-Tol)]$_4$ (5): The condensation of *p*-tolylboronic acid (47.6 mg, 20 μmol) with *tert*-butylphosphonic acid (55.1 mg, 20 μmol) was achieved as described for **1**. After evaporation of the solvent, the residue was dissolved in hot hexane and filtered hot. Evaporation of the solvent under vacuum gave a white powder, which was washed with small amounts of cold hexane. Yield: 67 % (62.5 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.13 (d, ^3J = 18.8 Hz, 9H), 2.26 (s, 3H), 7.27–7.31 (m, 2H), 7.89–7.93 ppm (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 21.52, 24.22 (d, ^3J = 2.4 Hz), 30.72 (d, ^2J = 169.04), 128.12, 130.77, 136.38, 141.10 ppm; ^{11}B NMR (128 MHz, CDCl$_3$): δ = 2.33 ppm; ^{31}P NMR (81 MHz, CDCl$_3$): δ = 8.15 ppm; elemental analysis calcd (%) for $C_{44}H_{64}B_4O_{12}P_4$ (952.11): C 55.51, H 6.78; found: C 52.37, H 6.64 ppm; MS (CI): *m*/*z* (%): 953 (70); HRMS (*m*/*z*): 953.3825. Single crystals were obtained by layering a solution of **5** in toluene with CH$_3$CN in an NMR tube and storage at −18 °C.

Synthesis of [*t*BuPO$_3$B(cy-Hex)]$_4$ (6): The condensation of cyclohexylboronic acid (63.6 mg, 40 μmol) with *tert*-butylphosphonic acid (55.1 mg, 40 μmol) was achieved as described for **1**. After evaporation of the solvent, the residue was dissolved in toluene (2 mL). Upon addition of CH$_3$CN (10 mL), the product precipitated in the form of a white powder, which was isolated and dried under vacuum. Yield: 79.8 mg (70 %).^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.33 (m, 1H), 1.0 (m, 2H), 1.14 (m, 3H), 1.20 (m, 9H). 1.69 ppm (m, 5H); ^{13}C NMR(101 MHz, CDCl$_3$): δ = 27.80 (d, ^3J = 7.65 Hz), 28.29, 28.56 30.09, 31.8 ppm; ^{11}B NMR (128 MHz, CDCl$_3$): δ = 6.70 ppm; ^{31}P NMR (81 MHz, CDCl$_3$): δ = 5.92 ppm; elemental analysis calcd (%) for $C_{40}H_{82}B_4O_{16}P_4$ (922.51): C 52.10, H 8.96; found: C 48.31, H 8.53; MS (CI): *m*/*z* (%): 922 (100); HRMS (*m*/*z*): 921.5044.

Synthesis of [*t*BuPO$_3$B(*p*-C$_6$H$_5$CHO)]$_4$ (7): The condensation of 4-formylboronic acid (41.2 mg, 27 μmol) with *tert*-butylphosphonic acid (38.7 mg, 27 μmol) was achieved as described for **1**. After evaporation of the solvent, the residue was dissolved in toluene (2 mL). Upon addition of hexane (10 mL), the product precipitated in the form of a white powder, which was isolated and dried under vacuum. Yield: 70 % (49.3 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.22 (d, ^3J = 19.1 Hz, 9H), 7.71–7.76 (m, 2H,), 7.82–7.89 (m, 2H), 10.03 ppm (s, 1H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 24.12 (d, ^3J = 2.3 Hz), 30.86 (d, ^3J = 167.1 Hz), 129.12, 131.04, 135.86, 151.35, 192.94 ppm; ^{11}B NMR (128 MHz, CDCl$_3$): δ = 2.26 ppm; ^{31}P NMR (81 MHz, CDCl$_3$): δ = 9.28 ppm; elemental analysis calcd (%) for $C_{44}H_{56}B_4O_{16}P_4$ (1008.04): C 52.43, H 5.60; found: C 52.48, H 5.70; MS (CI): *m*/*z* (%): 953 (70); MS (CI): *m*/*z* (%): 1009 (25); HRMS (*m*/*z*): 1009.2960. Single crystals were obtained by the slow diffusion of pentane into a solution of **7** in chloroform.

Synthesis of [*t*BuPO$_3$B(C$_6$H$_5$-3,5-CHO)]$_4$ (8): The condensation of 3,5-diformylboronic acid (79.2 mg, 44 μmol) and *tert*-butylphosphonic acid (62.7 mg, 44 μmol) was achieved as described for **1**. After evaporation of the solvent, the residue was dissolved in toluene (2 mL). Upon addition of hexane (10 mL), the product precipitated in the form of a white powder, which was isolated and dried under vacuum. Yield: 122.4 mg (97 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.26 (d, ^3J = 19.4 Hz, 9H), 8.30–8.33 (m, 2H), 8.37–8.38 (m, 2H), 10.14 ppm (s, 2H); ^{13}C NMR(101 MHz, CDCl$_3$): δ = 24.18 (^3J = 2.2 Hz), 30.97 (^2J = 165.5 Hz), 131.33, 136.50, 136.64, 146.67, 191.76 ppm; ^{11}B NMR (128 MHz, CDCl$_3$): δ = 2.43 ppm; ^{31}P NMR (81 MHz, CDCl$_3$): δ = 10.22 ppm; elemental analysis calcd (%) for $C_{48}H_{56}B_4O_{20}P_4$ (1120.27): C 51.47, H 5.04; found: C 53.65, H 5.49; MS (CI): *m*/*z* (%): 1120 (10); HRMS (*m*/*z*): 1121.2757. Single crystals were obtained by the slow diffusion of pentane into a solution of **7** in benzene.

Mass spectrometry: Mass spectrometry (MS) and tandem mass spectrometry (MS/MS) experiments were performed on a hybrid linear ion trap Fourier transform ion cyclotron resonance mass spectrometer (LTQ FT-ICR MS, Thermo Scientific, Bremen, Germany) equipped with a 10 T superconducting magnet (Oxford Instruments Nanoscience, Abingdon, UK). Samples were dissolved at a concentration of 0.1 mg mL^{-1} in toluene and analyzed using the atmospheric pressure photo-ionisation (APPI) ion source at a flow rate of 10 μL min^{-1}. The nebulizer temperature was set to 300 °C. Mass measurements were performed with a resolution of 100000 at *m*/*z* 400, with 50 to 100 scans averaging. Precursor ion selection was performed in the linear ion trap using a typical isolation window of 10 *m*/*z* units. Accumulated ions were transferred to the ICR ion trap for MS/MS experiments with infrared multiphoton dissociation (IRMPD) using a CO_2 IR laser at power comprised in the 10 to 20 W range and for irradiation periods of 50 to 150 ms. Data analysis was carried out using XCalibur software (Thermo Scientific, Bremen, Germany). Chemical Ionization mass spectrometry analyses were performed on a 1200 L Triple Quadrupole instrument (Varian Inc.) using ammonia as reactant gas was ammonia. 1 mL of sample (1 mg mL^{-1} in CHCl3) was deposited on the direct insertion probe and introduced into the mass spectrometer. Graphics showing the fragmentation pattern can be obtained on request from the authors.

Scrambling experiments: Equimolar solutions of **1** and **4** as well as **5** and (*t*BuPO$_3$BEt)$_4$ were prepared in different concentrations and at different temperatures. The NMR tubes were melted off and the reactions were observed by ^{31}P NMR. Integration of the corresponding signals gave the relative concentration of each species in solution.

Crystallographic analyses: Intensity data were collected using an Oxford Diffraction KM-4 CCD diffractometer (**3**, **4**), a Bruker APEX II CCD system (**5**, **8**), or a marμx system (Marresearch) (**7**), using graphite monochromatized $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) at low temperature. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table 2. Data reduction was carried out with CrysAlis PRO[14] (**3**, **4**) and EvalCCD[15] (**5**, **8**) and automar.[16] Structure solution and refinement were performed with the SHELXTL software package.[17] The structures were refined using the full-matrix least-squares routines on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included to the models in calculated positions using the riding model. CCDC-866106 (**3**), CCDC-866107 (**4**), CCDC-866108 (**5**), CCDC-866109 (**7**), and CCDC-866110 (**8**) contain the supplementary crystallographic data for this paper (excluding structure factors). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 2. Crystallographic data for the complexes **3**, **4**, **5**, **7**, and **8**.

Complex	**3**	**4**	**5**	**7**	**8**
empirical formula	$C_{28}H_{64}B_4O_{12}P_4$	$C_{20}H_{48}B_4O_{12}P_4$	$C_{44}H_{64}B_4O_{12}P_4$	$C_{44}H_{56}B_4O_{16}P_4$	$C_{48}H_{56}B_4O_{20}P_4$
mol. weight [g mol^{-1}]	759.91	647.70	952.07	1008.01	1120.05
crystal size [mm^3]	0.30×0.27×0.20	0.36×0.30×0.25	0.50×0.47×0.34	0.44×0.18×0.13	0.43×0.42×0.25
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*P*2/*n*	*Pna*2$_1$	*Pccn*	*P*2$_1$/*n*	*C*2/*c*
A [Å]	13.6934(17)	12.2896(3)	12.2050(16)	12.558(3)	24.222(9)
B [Å]	10.4815(10)	15.6665(3)	18.512(5)	43.898(9)	21.747(5)
c [Å]	15.0471(15)	18.0952(4)	22.243(3)	18.411(4)	24.833(10)
α [°]	90	90	90	90	90
β [°]	94.935(10)	90	90	92.83(3)	117.170(17)
γ [°]	90	90	90	90	90
volume [Å^3]	2151.7(4)	3483.94(13)	5025.6(16)	10137(4)	11637(7)
Z	2	4	4	8	8
density [g cm^{-3}]	1.173	1.235	1.258	1.321	1.279
T [K]	140(2)	140(2)	100(2)	140(2)	100(2)
absorption coeff. [mm^{-1}]	0.225	0.266	0.207	0.215	0.200
Θ range [°]	2.86 to 27.18	3.08 to 27.47	3.31 to 27.54	1.98 to 25.61	3.07 to 27.50°
index ranges	−15 γ 16, −13 γ 13, −19 γ 17	−14 γ 15, −19 γ 19, −23 γ 22	−15 γ 15, −24 γ 24, −28 γ 28	−15 γ 15, −53 γ 53, 0 γ 22	−31 γ 31, −27 γ 28, −32 γ 32
reflns collected	14020	25535	90271	18457	90355
independent reflns	4509 (R_{int}=0.0423)	7300 (R_{int}=0.0187)	5778 (R_{int}=0.0863)	18457 (R_{int}=0.0000)	12936 (R_{int}=0.0923)
absorption correction	semi-empirical	semi-empirical	semi-empirical	none	semi-empirical
max. and min. transmission	1.0000 and 0.6035	1.0000 and 0.9399	0.7456 and 0.6746		0.7456 and 0.6639
data/restraints/parameters	4509/0/217	7300/1/362	5778/0/289	18457/63/1254	12936/49/713
goodness-of-fit on F^2	1.061	1.047	1.141	1.125	1.120
final *R* indices [$I>2s(I)$]	*R*1=0.0517, *wR*2=0.1301	*R*1=0.0228, *wR*2=0.0620	*R*1=0.0450, *wR*2=0.0898	*R*1=0.1141, *wR*2=0.3211	*R*1=0.0759, *wR*2=0.1470
R indices (all data)	*R*1=0.0704, *wR*2=0.1405	*R*1=0.0251, *wR*2=0.0626	*R*1=0.0663, *wR*2=0.0984	*R*1=0.1640, *wR*2=0.3574	*R*1=0.1186, *wR*2=0.1649
larg. diff. peak/hole [eÅ^{-3}]	0.607 and −0.346	0.318 and −0.232	0.488 and −0.370	0.533 and −0.858	0.579 and −0.370

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Cage Compounds

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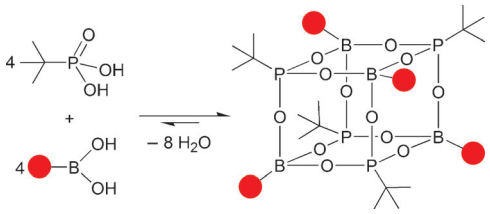
Borophosphonate Cages: Easily Accessible and Constitutionally Dynamic Heterocubane Scaffolds



Dynamic covalent chemistry: Direct condensation of *tert*-butylphosphonic acid with boronic acids gives borophosphonate cages of the general formula $[t\mathrm{BuPO_3BR'}]_4$ in good yields. Furthermore, it is demonstrated that borophosphonates are constitutionally dynamic scaffolds that can be decorated with reactive groups (see scheme).

Dynamic cubes…
… in this case borophosphonate cages with P-O-B linkages, can be obtained in [4+4] condensation reactions of *tert*-butylphosphonic acid and boronic acids. The cages are constitutionally dynamic scaffolds that can be decorated with reactive groups. These features make borophosphonates attractive building blocks for the thermodynamically controlled synthesis of molecular and polymeric nanostructures. For more details see the Full Paper by K. Severin et al. on page ■■ ff.