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Synthesis of Borophosphonate Cage Compounds: Influence of Substituent and Concentration Effects on Product Distribution in Condensation Reactions of Aryl Phosphonic Acids and Boronic Acids

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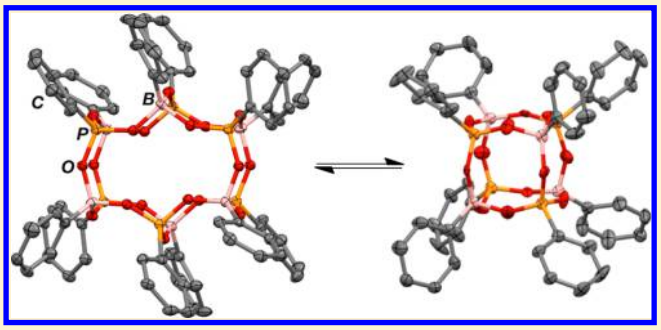
Supporting Information

ABSTRACT: Aryl borophosphonate cage compounds $[ArPO_3BAr']_n$ with n = 4 or 6 were synthesized by condensation reactions of $ArP(O)(OH)_2$ and $Ar'B(OH)_2$. (3,5-^{t}Bu$_2$-Ph)P(O)(OH)$_2$ (**1**) reacts with arylboronic acids that contain electron-withdrawing substituents to form borophosphonate tetramers $[Ar^1PO_3BAr^2]_4$ (Ar^1 = 3,5-^{t}Bu$_2$-Ph; Ar^2 = *o*-Br-Ph, *o*-CF_3-Ph, *p*-CF_3-Ph, *p*-CHO-Ph; **3a−d**) and hexamers $[Ar^1PO_3BAr^2]_6$ (Ar^2 = *p*-CF_3-Ph, *p*-CHO-Ph; **4c−d**) in 80−93% NMR yield. For Ar^2 = *p*-CF_3-Ph and *p*-CHO-Ph, both products were observed, with the tetramer being favored under dilute reaction conditions and the hexamer favored under concentrated reaction conditions. Interconversion between tetramer (**3c** or **3d**) and hexamer (**4c** or **4d**) was observed at room temperature and above in toluene. The phosphine phosphonic acid (2-PPh$_2$-Ph)P(O)(OH)$_2$ (**6**) reacts with arylboronic acids that contain electron-withdrawing substituents to form tetramers $[Ar^1PO_3BAr^2]_4$ (Ar^1 = 2-PPh$_2$-Ph; Ar^2 = *p*-CF_3-Ph, *p*-CHO-Ph; **7c−d**) in 70−75% NMR yield. The reactions of **1** or **6** with (*p*-tolyl)B(OH)$_2$ (**2f**), and the reaction of **6** with (*o*-CF_3-Ph)B(OH)$_2$ (**2b**), yield only trace amounts of borophosphonate cage compounds and instead afford the corresponding $[ArBO]_3$ boroxines and condensation products with unknown structures.

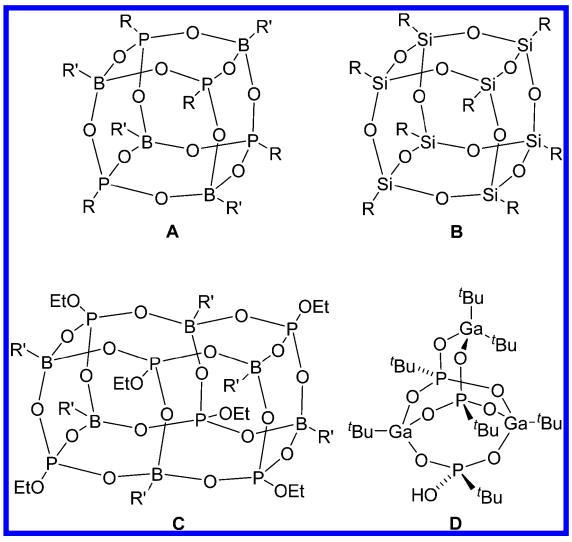


INTRODUCTION

Borophosphonates of general formula $[RPO_3BR']_4$ adopt three-dimensional cubic cage structures (Chart 1, **A**), in which the edges are formed by B−O−P bonds.[1] These compounds, which are isoelectronic and isostructural with polyhedral oligomeric silsesquioxanes $(RSi)_8O_{12}$ (**B**, POSS),[2,3] have attracted interest due to their potential applications as building blocks for more complex structures and materials and as scaffolds for multicenter catalysts. Several borophosphate compounds of general formula $[EtOPO_3BR']_6$ (**C**) have also been reported and adopt hexameric cage structures that are similar to the cubanoid structure observed for borophosphonates and POSSs.[4]

Borophosphonate cages have been synthesized by several methods (Scheme 1). Roesky and co-workers reported that alkyl (R = ^{t}Bu, Me, Et) and phenyl phosphonic acids react with trialkylboranes (R′ = Et, ^{s}Bu) by alkane elimination to generate borophosphonates in 66−95% yield (Scheme 1, route a).[1] Roesky, Mason, and their co-workers used this method to generate analogous structures with other Group 13 metals (Al, Ga, In).[1a,5,6] The reaction of ^{t}BuP(O)(OH)$_2$ with GaMe$_3$ under mild conditions (room temperature in THF) yields the tetrameric gallophosphonate cage $[^t$BuPO$_3$GaMe$]_4$. In contrast, the reaction of ^{t}BuP(O)(OH)$_2$ with the bulkier gallium alkyl Ga^{t}Bu$_3$ yields different condensation products depending on the reaction conditions and provides insight into the stepwise nature of the growth process. The single-ring dimer [^{t}Bu-

Chart 1



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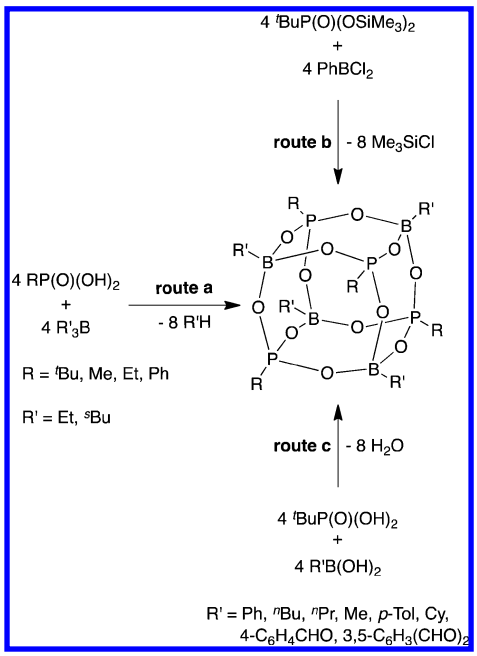
Scheme 1



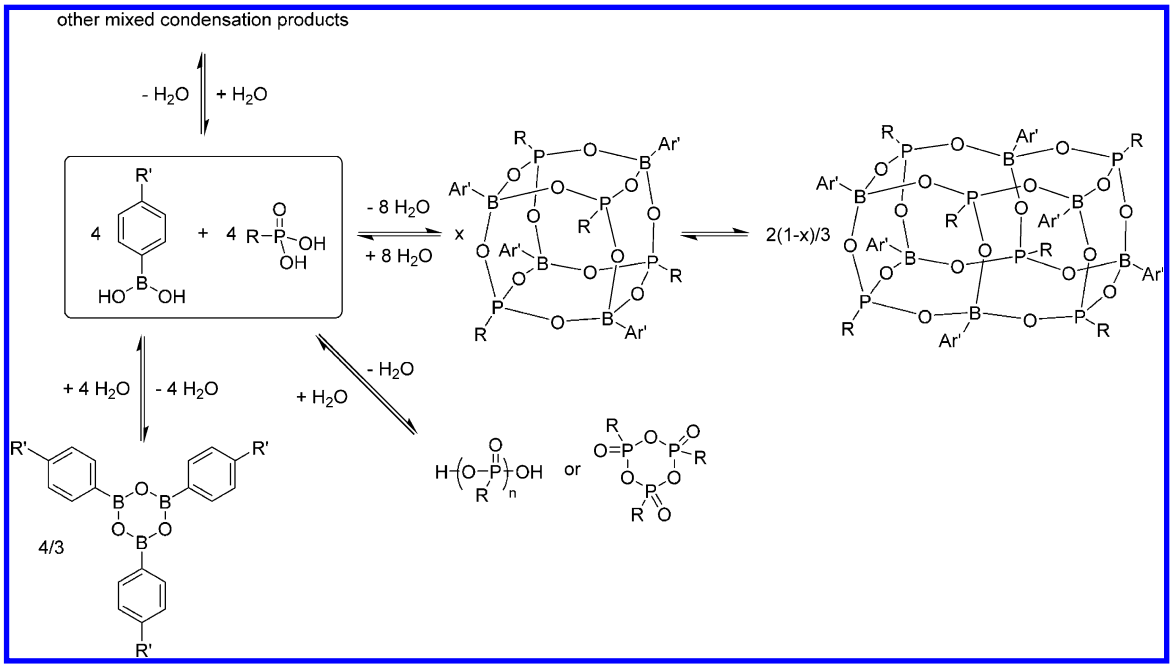
$(OH)PO_2Ga^tBu_2]_2$ is formed at −50 °C in THF, the trimer $(^tBuGa)_2(^tBu_2Ga)(O_3P^tBu)_2\{O_2P(OH)^tBu\}$ (Chart 1, **D**) is observed after 15 h in refluxing toluene, and the tetrameric cage $[^tBuPO_3Ga^tBu]_4$ is ultimately formed after 2 h in refluxing digyme.[6b,7,8] A mixture of tetrameric and hexameric aluminophosphonate cages, $[^tBuPO_3AlMe]_4$ and $[^tBuPO_3AlMe]_6$, is formed when the small trialkylaluminum $AlMe_3$ is used.[9] In a similar system, in addition to tetrameric and hexameric cages, $[MePO_3Al^tBu]_4$ and $[MePO_3Al^tBu]_6$, an interesting $[MePO_3Al^tBu]_{10}$ decamer consisting of two tetramers (each with an open edge) linked through a cyclic dimer was also observed.[5b,c] Kuchen reported that $^tBuP(O)(OSiMe_3)_2$ reacts with $PhBCl_2$ by Me_3SiCl elimination to form the corresponding tetrameric borophosphonate cage (Scheme 1, route b), though the yield was only 14%.[10,11]

Recently, Severin and co-workers reported that condensation reactions of $^tBuP(O)(OH)_2$ and $R'B(OH)_2$ in refluxing toluene, using a Dean−Stark trap to remove the H_2O byproduct, generate tetrameric borophosphonate cages in high yield (Scheme 1, route c).[12] A wide range of $R'B(OH)_2$ reactants are converted to cage products, including alkyl (R′ = ^{n}Bu, ^{n}Pr, Me, Cy) and sterically undemanding aryl (R′ = Ph, *p*-tol, *p*-CHO-Ph, 3,5-$(CHO)_2$-Ph) boronic acids. However, similar reactions of the sterically smaller alkylphosphonic acids $^nBuP(O)(OH)_2$ and $^nHexP(O)(OH)_2$ with boronic acids produced mixtures of condensation products that could not be separated and were not characterized. Reactions of $PhP(O)(OH)_2$ with boronic acids gave insoluble products which were also not characterized. Severin concluded that phosphonic acids that are both sterically demanding and solubilizing are required for a controlled condensation reaction.

Scheme 2 illustrates several possible condensation pathways of phosphonic acids with boronic acids. In addition to tetrameric cages $[RPO_3BR']_4$, 1:1 borophosphonate products with different structures and degrees of oligomerizations are possible. In particular, hexameric cages analogous to **C** (Chart 1) may be expected when sterically small $RP(O)(OH)_2$ and $R'B(OH)_2$ reactants are used. Boronic acids are well-known to reversibly and rapidly self-condense to boroxines $(R'BO)_3$, with condensation being particularly favored for electron-donating R′ groups.[13] Arylboroxines are destabilized by *ortho* substituents, which distort the planar structure[14] and reduce the overlap between the π-orbitals of the aryl ring and the empty boron p orbital. Finally, phosphonic acids are also known to self-condense to linear or cyclic phosphonic acid anhydrides $(H[OP(=O)R]_nOH$ or $[RP(=O)O]_n)$.[15]

This paper describes the synthesis of $[ArPO_3BAr']_4$ and $[ArPO_3BAr']_6$ borophosphonate cages that contain aryl substituents at both P and B via Severin-type condensation reactions. The product distribution is influenced by the steric

Scheme 2



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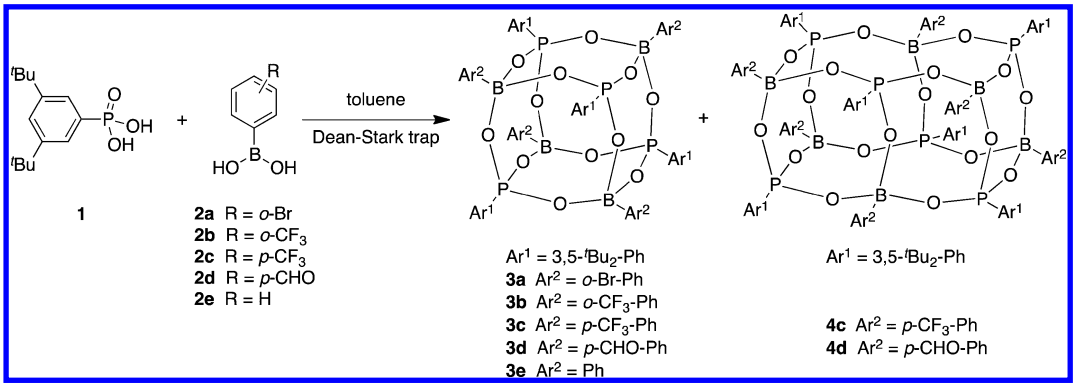
Scheme 3



properties and solubility of the phosphonic acid, the steric and electronic properties of the boronic acid, and the concentrations of the reactants.

RESULTS AND DISCUSSION

Reaction of (3,5-^{t}Bu$_2$-Ph)P(O)(OH)$_2$ (1) with Arylboronic Acids That Contain Electron-Withdrawing Substituents. Based on the guidelines outlined by Severin noted above, (3,5-^{t}Bu$_2$-Ph)P(O)(OH)$_2$ (**1**), which incorporates solubilizing ^{t}Bu groups and is not sterically hindered at the phosphorus center, is an attractive candidate for controlled condensation reactions with boronic acids. Compound **1** reacts in toluene with (*o*-Br-Ph)B(OH)$_2$ (**2a**) and (*o*-CF$_3$-Ph)B(OH)$_2$ (**2b**), which contain electron-withdrawing substituents in the *ortho* position, to generate the tetrameric cages [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*o*-Br-Ph)]$_4$ (**3a**) and [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*o*-CF$_3$-Ph)]$_4$ (**3b**) in 84% and 93% yield, respectively, as determined by ^{31}P{^{1}H} NMR. Compounds **3a** and **3b** were isolated in 48−50% yield by recrystallization from hexane. High-resolution mass spectral data, multinuclear NMR data, and an X-ray crystallographic analysis of **3a** (*vide infra*) established that **3a** and **3b** have tetrameric cage structures as shown in Scheme 3.

The reactions of **1** with (*p*-CF$_3$-Ph)B(OH)$_2$ (**2c**) and (*p*-CHO-Ph)B(OH)$_2$ (**2d**), which contain electron-withdrawing substituents in the *para* position, are less selective. These sterically unhindered boronic acids react to form mixtures of tetrameric and hexameric borophosphonate cages, and interestingly, the concentration of the reactants strongly influences the product distribution. The reaction of **1** with **2c** at low initial concentration ([**1**]$_0$ = [**2c**]$_0$ = 2.5 mM) generates [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*p*-CF$_3$-Ph)]$_4$ (**3c**) as the major product, along with a small amount of [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*p*-CF$_3$-Ph)]$_6$ (**4c**) as shown by ^{31}P{^{1}H} NMR analysis of the product mixture (Figure 1a). The yields of **3c** and **4c** were determined to be 81% and 7%, respectively, by ^{1}H NMR. **4c** is less soluble than **3c** and was removed by precipitation with hexane followed by filtration. **3c** was isolated in analytically pure form by removing the solvent from the filtrate and washing with hexane. However, the isolated yield of **3c** was low (12%), due in part to competitive conversion to **4c** during workup. In contrast, the reaction of **1** with **2c** at high initial concentration ([**1**]$_0$ = [**2c**]$_0$ = 25 mM) produces **4c** as the major product (72%, vs 16% **3c**) (Figure 1b). **4c** was isolated by recrystallization from toluene in 49% yield.

Similar results were obtained for the reaction of **1** with **2d**. At low initial concentration ([**1**]$_0$ = [**2d**]$_0$ = 2.5 mM), the tetramer [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*p*-CHO-Ph)]$_4$ (**3d**) was the major product (81%, ^{1}H NMR), and only a small amount (5%) of the hexamer [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*p*-CHO-Ph)]$_6$ (**4d**) was formed. Compound **3d** was isolated by precipitation from the reaction

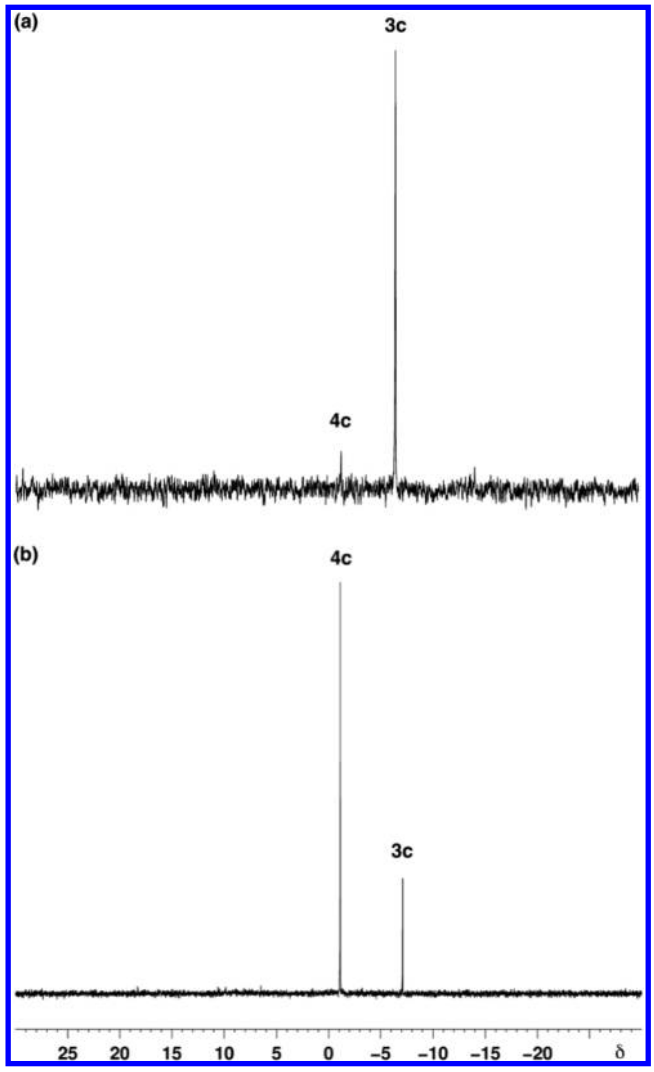


Figure 1. ^{31}P{^{1}H} NMR spectra of product mixtures from the reaction of (3,5-^{t}Bu$_2$-Ph)P(O)(OH)$_2$ (**1**) and (*p*-CF$_3$-Ph)B(OH)$_2$ (**2c**) in toluene. (a) Low initial concentration of reactants: ([**1**]$_0$ = [**2c**]$_0$ = 2.5 mM); NMR solvent = C_6D_6. Peak assignments: [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*p*-CF$_3$-Ph)]$_4$ (**3c**): δ −6; [(3,5-^{t}Bu$_2$-Ph)PO$_3$B(*p*-CF$_3$-Ph)]$_6$ (**4c**): δ −1. (b) High initial concentration of reactants: ([**1**]$_0$ = [**2c**]$_0$ = 25 mM); NMR solvent = toluene. Peak assignments: **3c**: δ −7; **4c**: δ −1.

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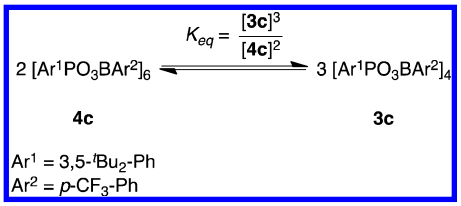
mixture in 44% yield. At high initial concentration ($[\mathbf{1}]_0$ = $[\mathbf{2d}]_0$ = 25 mM), a mixture of **3d** (44%) and **4d** (36%) is formed. The conversion of **3d** to **4d** is slower than the conversion of **3c** to **4c** noted above, but **4d** was enriched to 52% when the product mixture from the high concentration reaction was cooled and left at room temperature for 18 h and was isolated by recrystallization from toluene in 36% yield. Similarly, NMR studies show that **1** reacts with $PhB(OH)_2$ (**2e**) at low initial concentration ($[\mathbf{1}]_0$ = $[\mathbf{2e}]_0$ = 2.5 mM) to yield $[(3,5\text{-}^t\mathrm{Bu}_2\text{-Ph})PO_3BPh]_4$ (**3e**) as the major product (73%, ^{1}H NMR).

Interconversion of Hexameric and Tetrameric Cages. To probe the hexamer/tetramer interconversion further, the isomerization of pure **4c** was studied by ^{1}H NMR. Heating a solution of **4c** in toluene-d_8 at 105 °C results in slow (3 weeks) formation of an equilibrium mixture of **3c** and **4c** (K_{eq} = $[\mathbf{3c}]^3/[\mathbf{4c}]^2$ = 2.4(1) × 10^{-3} M, Scheme 4). This equilibrium shifts toward **4c** at room temperature (K_{eq} = $[\mathbf{3c}]^3/[\mathbf{4c}]^2$ = 1.2(1) × 10^{-3} M), which is consistent with the expectation (based on stoichiometry) that **3c** should be entropically favored. The conversion of pure **4c** to the equilibrium **4c**/**3c** mixture is much slower than the interconversion of **3c** and **4c** observed in the **1**/**2c** reaction mixture, suggesting that the latter process is catalyzed by other species in the mixture (e.g., $RP(O)(OH)_2$, H_2O, other condensation products).

Scheme 4



The product mixture from the dilute **1**/**2c** reaction ($[\mathbf{1}]_0$ = $[\mathbf{2c}]_0$ = 2.5 mM) is enriched in **3c** relative to the expected equilibrium concentration ($[\mathbf{3c}]/[\mathbf{4c}]$: obs, 17; calcd, 2.6; see the Supporting Information for details). Conversely, the product mixture from the concentrated reaction ($[\mathbf{1}]_0$ = $[\mathbf{2c}]_0$ = 25 mM) is enriched in **4c** ($[\mathbf{3c}]/[\mathbf{4c}]$: obs, 0.33; calcd, 1.0). These deviations from the equilibrium ratios suggest that kinetic factors influence the product distribution. The high reactant concentrations favor intermolecular condensations relative to intramolecular reactions and produce larger (hexameric) aggregates.

Reaction of 1 with (*p*-tolyl)B(OH)$_2$. The reaction of **1** with (*p*-tolyl)$B(OH)_2$ (**2f**), which contains an electron-donating methyl substituent, results in complete consumption of the starting materials but generates a mixture of products (Scheme 5). The ^{31}P{^{1}H} NMR spectrum of the reaction mixture contains a sharp signal at δ −8.0, in the range expected for $[(3,5\text{-}^t\mathrm{Bu}_2\text{-Ph})PO_3B(p\text{-tolyl})]_4$ (**3f**), and a broad resonance at δ 20 to −10 (Figure 2a). The presence of **3f** was confirmed by MALDI-MS, but ions derived from other mixed condensation products were also observed by MALDI-MS and APCI-MS analysis of the reaction mixture. For comparison, the self-condensation of **1** under the same reaction conditions in the absence of boronic acid generates products that exhibit broad ^{31}P{^{1}H} resonances at δ ca. 15, 9, and 0 (Figure 2b). These results suggest that the reaction of **1** and **2f** generates, in addition to **3f**, other mixed borophosphonate condensation products as well as condensation products derived from **1**. The ^{1}H NMR spectrum of the product mixture contains prominent resonances for *p*-tolylboroxine (**5f**), corresponding to a 20% yield.

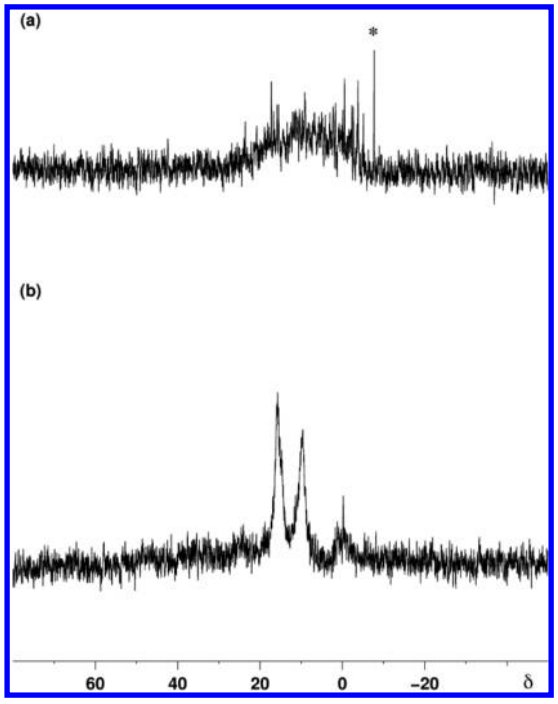
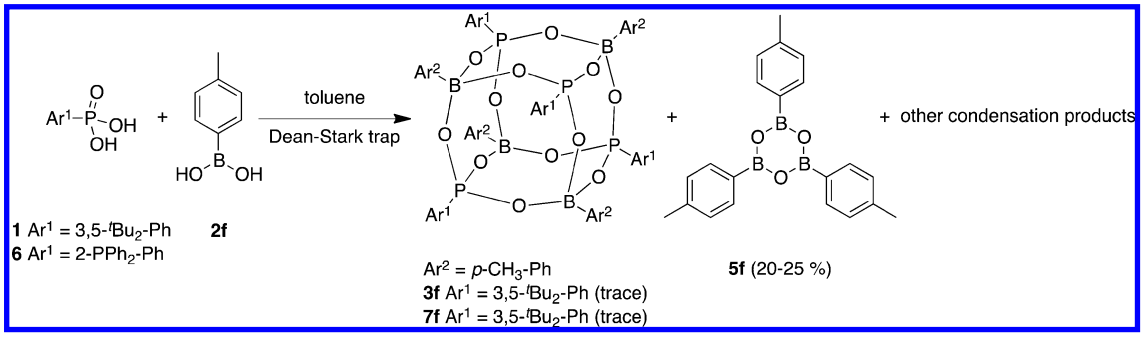


Figure 2. ^{31}P{^{1}H} NMR spectra (in C_6D_6) of product mixtures from (a) the reaction of (3,5-^{t}Bu$_2$-Ph)P(O)$(OH)_2$ (**1**) and (*p*-tolyl)$B(OH)_2$ (**2f**) and (b) the self-condensation of (3,5-^{t}Bu$_2$-Ph)P(O)$(OH)_2$ (**1**). * = $[(3,5\text{-}^t\mathrm{Bu}_2\text{-Ph})PO_3B(p\text{-tolyl})]_4$ (**3f**, δ −8).

Scheme 5



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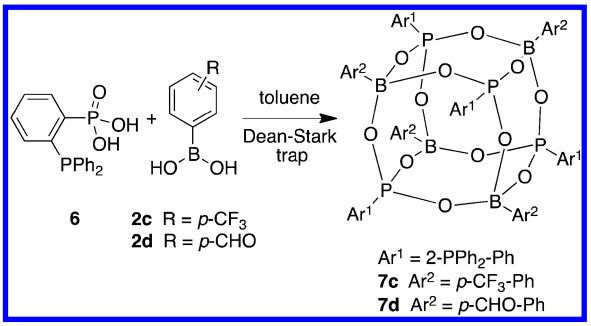
Reaction of (2-PPh_2-Ph)P(O)$(OH)_2$ (6) with Arylboronic Acids. The reactions of (2-PPh_2-Ph)P(O)$(OH)_2$ (**6**)[16] with boronic acids were explored because the corresponding cages are potentially interesting as ligands. Compound **6** reacts cleanly with (*p*-CF_3-Ph)B$(OH)_2$ (**2c**) and (*p*-CHO-Ph)B$(OH)_2$ (**2d**) to afford the tetrameric products [(2-PPh_2-Ph)PO_3B(*p*-CF_3-Ph)]$_4$ (**7c**) and [(2-PPh_2-Ph)PO_3B(*p*-CHO-Ph)]$_4$ (**7d**), even at high concentration (Scheme 6). **7c** and **7d**

Scheme 6



are formed in 75% and 70% NMR yield, respectively, and were isolated by recrystallization from toluene in 34−40% yield. The $^{31}P\{^1H\}$ NMR spectra of **7c** and **7d** each contain phosphonate resonances in the range δ −9 to −10 and a phosphine resonance at δ −14. The diphenylphosphino substituent is thus able to solubilize the reaction intermediates and is sufficiently sterically demanding to favor the selective formation of tetramers.

The reaction of **6** with (*p*-tolyl)B$(OH)_2$ (**2f**) is similar to that of **1**. The reactants are fully consumed, but only a trace amount of [(2-PPh_2-Ph)PO_3B(*p*-tolyl)]$_4$ (**7f**) is formed, as determined by $^{31}P\{^1H\}$ NMR and confirmed by MALDI-MS. The major products are *p*-tolylboroxine (25%) and condensation products of unknown structures.

Role of Boroxine Formation. As noted above, **1** and **6** react with PhB$(OH)_2$ and aryl boronic acids that contain electron-withdrawing substituents (Br, CHO, CF_3) to afford high yields of tetrameric or hexameric cages, but when *p*-tolylboronic acid is used, only low yields of cage products are formed and *p*-tolylboroxine is the major boron-containing product. In principle, phosphonic acids can also condense with boroxines to form borophosphonate cages. Indeed, the reaction of **1** with *o*-CF_3-phenylboroxine generates tetrameric cage **3b** in high yield (85% by ^{19}F NMR). In contrast, the reaction of **1** with *p*-tolylboroxine yields cage **3f** in only 10% NMR yield, with 20% of the *p*-tolylboroxine remaining after the reaction.

These results suggest that the relative stabilities of borophosphonate cages and boroxines influence the product distribution. Electron-withdrawing substituents on the boron aryl group stabilize the "borate-like" four-coordinate boron centers in the borophosphonate cages and destabilize the three-coordinate boron centers in the boroxines.[13] In contrast, electron-donating groups have the opposite effect, and so cage formation is disfavored in these cases. This effect is less important when alkylphosphonic acids rather than arylphosphonic acids are used. Severin reported high yields of cage when ^{t}BuP(O)$(OH)_2$ was reacted with (*p*-CHO-Ph)B$(OH)_2$ (70%) or (*p*-tolyl)B$(OH)_2$ (67%). The ^{t}Bu group is more electron-donating than aryl groups, so it better-stabilizes the "phosphonium-like" four-coordinate RPO_3 centers in the cage structure.

Steric Limitations on Cage Formation. The reaction of **6** with (*o*-CF_3-Ph)B$(OH)_2$ (**2b**) is unselective, generating a mixture of products. The reactants are fully consumed, but multiple species are observed by $^{31}P\{^1H\}$ NMR (multiple resonances in the range δ 51 to −15). A weak $[M + H]^+$signal for [(2-PPh_2-Ph)PO_3B(*o*-CF_3-Ph)]$_4$ (**7b**) is observed in the APCI mass spectrum of the reaction mixture, and (*o*-CF_3-Ph)-boroxine is formed in 40% yield, as determined by ^1H NMR. It is likely that the presence of *ortho* substituents on both the phosphonic acid and boronic acid disfavors cage formation in this case.

Solid-State Structures. The solid-state structure of **3a** (Figure 3) is similar to those of [^{t}BuPO_3BAr′]$_4$ (Ar′ = *p*-tol, *p*-

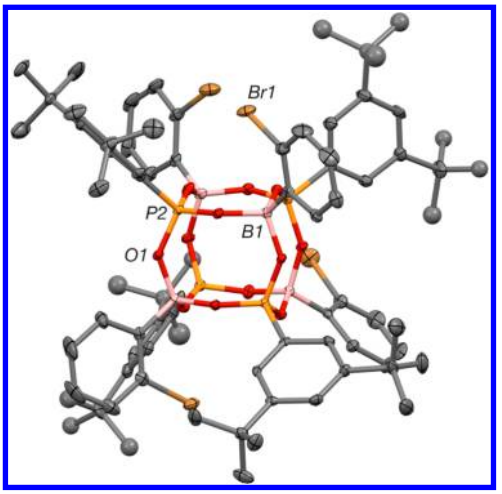


Figure 3. Molecular structure of **3a**. Hydrogen atoms are omitted. Four of the ^{t}Bu groups are disordered over several positions; in these cases, the positions of the methyl carbons were refined isotropically, and one position of the methyl carbons is shown as a sphere. Average bond lengths (Å) and angles (°) (number of data, range): P−O: 1.522(7) (12, 1.511(2)−1.533(2)); B−O: 1.483(7) (12, 1.472(3)−1.496(3)); P−C_{ipso}: 1.766(2) (4, 1.766(3)−1.767(2)); B−C_{ipso}: 1.600(3) (4, 1.595(4)−1.603(3)); P−O−B: 141.2(4.5) (12, 135.7(1)−149.1(2)); O−P−O: 111.39(1.05) (12, 113.39(9)−119.62(9)); O−B−O: 108.7(0.8) (12, 107.6(2)−110.8(2)).

CHO-Ph, and 3,5-$(CHO)_2$-Ph).[12] The $P_2B_2O_4$ rings that comprise the faces of the cubic core adopt a flattened chair−chair conformation,[17] and the B−O and P−O distances and the P−O−B, P−O−P, and B−O−B angles are similar to those observed in previous studies.[12]

3d also adopts a cubic cage structure. In this case, two types of cages with the same atom connectivity but different spatial orientation of the oxygen bridges are cocrystallized, one of which is shown in Figure 4. These conformational isomers result from the flexibility of the oxygen bridges. While the cages are relatively rigid and the boron and phosphorus atoms occupy essentially the same positions in the two conformers, the oxygen atoms may lie in or out of the plane passing through the B−P−B atoms (Figure 5, see the Supporting Information for further details).

The solid-state structure of **4d** is shown in Figure 6. The hexameric cage features two 12-membered rings and six 8-membered rings. The 12-membered $P_3B_3O_6$ rings adopt a [6′6′] conformation,[18] in which four O atoms pucker into the cage (e.g., O6), while two pucker out (e.g., O7). The inward pucker generates close contact between the B-aryl and P-aryl groups that flank the inward-puckered oxygen, forcing these

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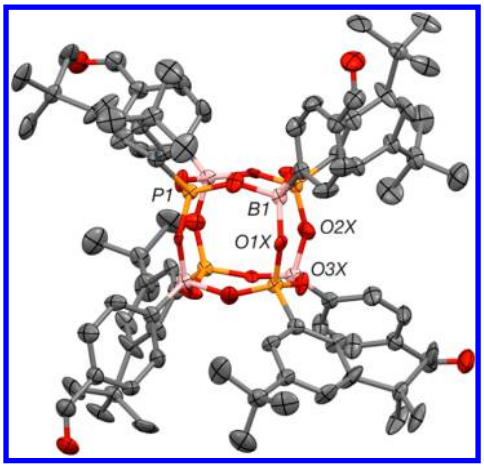

Figure 4. Molecular structure of **3d**. Hydrogen atoms are omitted. The oxygen atoms are disordered over two positions, only one of which is shown. One ^{t}Bu group is disordered over two positions, only one of which is shown. Average bond lengths (Å) and angles (°) (number of data, range): P−O: 1.51(5) (3, 1.48(1)−1.57(9)); B−O: 1.47(8) (3, 1.46(1)−1.482(9)); P−C_{ipso}: 1.767(3); B−C_{ipso}: 1.602(4); P−O−B: 142.8(6.9) (3, 135.9(6)−149.7(7)); O−P−O: 110.9(3.1) (3, 107.4(5)−112.8(5)); O−B−O: 108.3(19.9) (3, 87.4(5)−127.1(6)).

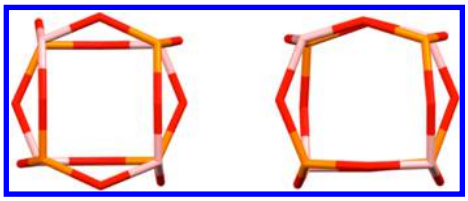

Figure 5. Core structures of the two cocrystallized conformational isomers of **3d**. Red = O, orange = P, pink = B.

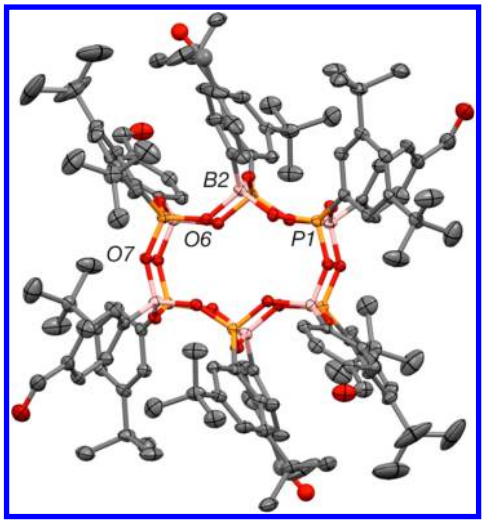

Figure 6. Molecular structure of **4d**·C_6H_6·$2C_7H_8$. Hydrogen and solvent atoms are omitted. The formyl group is disordered over two positions, only one of which is shown. Average bond lengths (Å) and angles (°) (number of data, range): P−O: 1.524(7) (9, 1.514(3)−1.536(3)); B−O: 1.489(6) (9, 1.479(5)−1.495(6)); P−C_{ipso}: 1.769(5) (3, 1.767(5)−1.771(4)); B−C_{ipso}: 1.591(7) (3, 1.588(7)−1.593(6)); P−O−B: 137.5(5.1) (9, 127.8(3)−144.2(3)); O−P−O: 110.6(2.8) (9, 104.9(2)−114.2(2)); O−B−O: 107.7(2.4) (9, 102.5(3)−110.1(3)).

flanking groups to adopt nearly mutually parallel conformations, as illustrated in Figure 7. This arrangement, in turn, generates close steric interactions between the B-aryl and P-aryl groups that flank the outward-puckered oxygens. Such steric interactions would be particularly severe if either the B-aryl or P-aryl groups contain *ortho* substituents, which provides an explanation for the observation that only tetrameric structures are formed in these cases.

CONCLUSIONS

Tetrameric $[ArPO_3BAr']_4$ and hexameric $[ArPO_3BAr']_6$ borophosphonate cages that contain aryl groups at B and P were synthesized by the condensation reactions of aryl phosphonic acids and aryl boronic acids using Severin's method. Aryl boronic acids that contain electron-withdrawing substituents afford cages with the highest yields, while aryl boronic acids with electron-donating groups form mixtures of condensation products and boroxines. Steric effects strongly influence the product distribution and yield. When both starting acids are *ortho*-substituted, the reaction produces only trace amounts of tetrameric cages. When either the aryl phosphonic acid or the aryl boronic acid has an *ortho* substituent, the reaction selectively produces the tetrameric cage. When neither reactant is *ortho*-substituted, the reaction produces a mixture of tetramer and hexamer. In this case, the tetramer is favored at low reactant concentrations, and the hexamer is favored at high reactant concentrations, reflecting the relative rates of intramolecular and intermolecular condensation reactions as the cages are formed. The sensitivity of hexamer formation to the steric profile of the B and P aryl groups is attributed to the inward puckering of some of the oxygen atoms in the molecular structure, which places these aryl groups in close proximity. The hexameric and tetrameric cages can interconvert in solution.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed under a nitrogen atmosphere using drybox or Schlenk techniques. Nitrogen was purified by passage through Q-5 oxygen scavenger and activated molecular sieves. Toluene and hexanes were purified by passage through BASF R3-11 oxygen scavenger and activated alumina. Compound **6** was prepared by the literature route.[16] Arylboroxines were prepared by azeotropic distillation of the corresponding arylboronic acids with toluene for 6 h.[19] The following materials were obtained from commercial sources and used without further purification: 1-bromo-3,5-di-*tert*-butylbenzene (Aldrich, 97%), ^{n}BuLi solution (Aldrich, 2.5 M in hexanes), diethyl chlorophosphate (Aldrich, 97%), and bromotrimethylsilane (Aldrich, 97%). Phenylboronic acid (Aldrich, 95%), 4-tolylboronic acid (Matrix, 97%), 2-bromophenylboronic acid (Matrix, 98%), 2-(trifluoromethyl)-phenylboronic acid (Matrix, 98%), 4-(trifluoromethyl)phenylboronic acid (Matrix, 97%), and 4-formylphenylboronic acid (Acros, 97%) were recrystallized from H_2O prior to use. Elemental analyses were performed by Robertson Microlit Laboratories. The solvent content in elemental analysis samples was quantified by ^{1}H NMR. NMR spectra were acquired on Bruker DRX-500 or Bruker DRX-400 spectrometers at ambient temperature unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and are internally referenced to residual ^{1}H and ^{13}C solvent resonances. ^{31}P chemical shifts are reported relative to externally referenced 85% H_3PO_4. ^{19}F spectra were referenced to external BF_3·Et_2O, and ^{19}F chemical shifts are reported relative to $CFCl_3$. ^{11}B chemical shifts are reported relative to externally referenced BF_3·Et_2O. Coupling constants are reported in Hz. NMR signals were assigned based on COSY, HMQC, and ^{1}H{^{31}P} experiments as well as trends in chemical shifts and coupling constants derived from these experiments. C_6D_6, THF-d_8, and toluene-d_8 were dried over Na/benzophenone. CD_2Cl_2 was dried over P_2O_5. Mass spectrometry was performed on an Agilent 6224 TOF-MS

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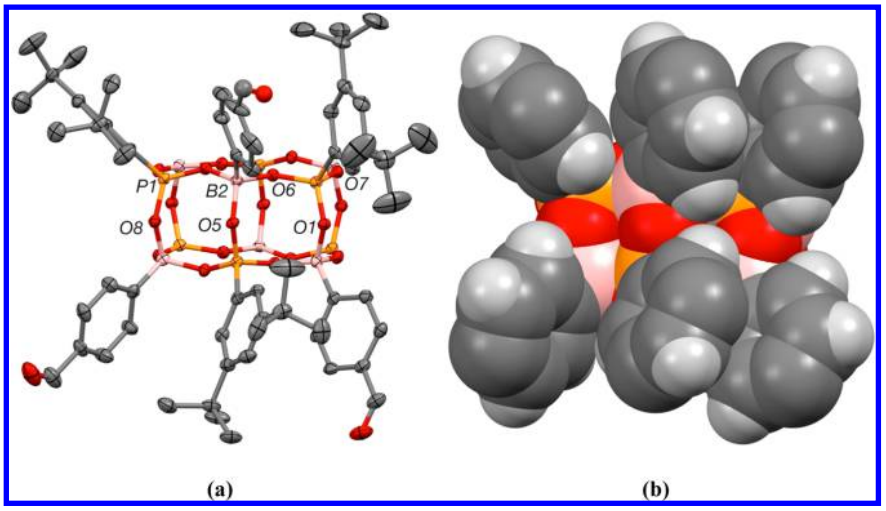
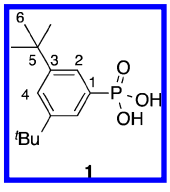


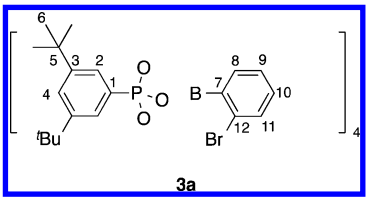
Figure 7. Alternate view of **4d** that illustrates key steric interactions. (a) Side view of **4d** in which hydrogen atoms and the aryl groups at the back are omitted. O6 is inward-puckered and O1, O5, O7, and O8 are outward-puckered. (b) Space-filling view in the same perspective as in (a), in which the aryl-hydrogen atoms are shown but the formyl and ^{t}Bu substituents are omitted.

instrument (high resolution) or an Agilent 6130 LCMS (low resolution).

*(3,5-^{t}Bu$_2$-Ph)P(O)(OH)$_2$ (**1**).* A Schlenk flask was charged with 1-bromo-3,5-di-*tert*-butylbenzene (5.384 g, 20.00 mmol) and Et_2O (120 mL) and cooled to 0 °C. ^{n}BuLi solution (2.5 M, 8.0 mL, 20 mmol) was added via syringe over 5 to 10 min. The mixture was stirred at 0 °C for 30 min and then warmed to room temperature for another 1 h. The clear colorless solution was cooled to −78 °C, and a solution of diethyl chlorophosphate (2.9 mL, 20 mmol) in Et_2O (30 mL) was added. The mixture was stirred at room temperature for 18 h to yield a cloudy colorless solution. The reaction mixture was transferred to a separatory funnel that contained H_2O (50 mL). The aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic fractions were washed with brine (20 mL) and dried over $MgSO_4$, and the volatiles were removed under vacuum to yield a colorless oil. The crude product was purified by silica gel chromatography, using a 2:1 hexanes:ethyl acetate mixture as the eluent. The product was isolated as a clear oil and directly dissolved in CH_2Cl_2 (150 mL). Bromotrimethylsilane (8.5 mL, 64 mmol) was added at room temperature, and the reaction mixture was stirred at room temperature for 2 days. The volatiles were removed under vacuum, and the crude product was dissolved in MeOH (100 mL) and stirred for 2 h. The MeOH was removed under vacuum to yield a viscous oil. Hexane was added to the oil to afford **1** as a white solid. **1** was dried in vacuum oven (3.721 g, 69%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 24.2. ^1H NMR (CD_2Cl_2): δ 11.44 (s, 2H, O*H*), 7.74 (d, $^3J_{PH}$ = 15, 2H, H^2), 7.68 (s, 1H, H^4), 1.34 (s, 18H, H^6). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 151.5 (d, $^3J_{PC}$ = 15, C^3), 127.7 (d, $^4J_{PC}$ = 2, C^4), 126.9 (d, $^1J_{PC}$ = 192, C^1), 125.4 (d, $^2J_{PC}$ = 11, C^2), 35.3 (s, C^5), 31.4 (s, C^6). HRMS (*m*/*z*): calcd for $[C_{14}H_{23}PO_3 + H]^+$, 271.1463; found, 271.1456.



*[(3,5-^{t}Bu$_2$-Ph)PO$_3$B(o-Br-Ph)]$_4$ (**3a**).* A Schlenk flask equipped with a Dean−Stark trap was charged with **1** (324 mg, 1.20 mmol), 2-bromophenylboronic acid (241 mg, 1.20 mmol), and toluene (48 mL). The mixture was refluxed for 3 h. The volatiles were removed under vacuum to afford a white solid. This material was recrystallized from hot hexane to afford **3a** as a white crystalline solid, which was dried under vacuum (250 mg, 48%). X-ray quality crystals were grown by slow evaporation of a hexane solution of **3a**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −9.6. ^1H NMR (C_6D_6): δ 8.31 (dd, $^3J_{PH}$ = 17, $^4J_{HH}$ = 2; 2H, H^2), 7.96 (dd, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H^8), 7.64 (d, $^4J_{HH}$ = 1, 1H, H^4), 7.53 (dd, $^3J_{HH}$ = 8, $^4J_{HH}$ = 0.5; 1H, H^{11}), 6.96 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 0.5; 1H, H^9), 6.81 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2; 1H, H^{10}), 1.16 (s, 18H, H^6). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 151.4 (d, $^3J_{PC}$ = 18, C^3), 143.0 (broad, C^7), 134.6 (s, C^{B-Ar}), 133.6 (s, C^{B-Ar}), 129.5 (s, C^{B-Ar}), 127.3 (d, $^4J_{PC}$ = 4, C^4), 127.1 (d, $^2J_{PC}$ = 13, C^2), 126.4 (s, C^{B-Ar}), 126.1 (d, $^1J_{PC}$ = 236, C^1), 35.2 (d, $^4J_{PC}$ = 2, C^5), 31.3 (s, C^6), the C^{B-Ar} resonance is obscured by the solvent peak (δ 127.8−128.9). $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 3.7. HRMS (*m*/*z*): calcd for $[C_{80}H_{100}B_4P_4O_{12}Br_4 + H]^+$, 1741.3308; found, 1741.3348. EA: calcd for $C_{80}H_{100}B_4P_4O_{12}Br_4$, %: C, 55.21; H, 5.79. Found: C, 55.09; H, 5.79.



*[(3,5-^{t}Bu$_2$-Ph)PO$_3$B(o-CF$_3$-Ph)]$_4$ (**3b**).* **3b** was synthesized analogously to **3a** from **1** (811 mg, 3.00 mmol) and 2-(trifluoromethyl)-phenylboronic acid (569 mg, 2.99 mmol) in toluene (120 mL). The volatiles were removed under vacuum to afford a white solid. This material was recrystallized from hot hexane to afford **3b** as a white crystalline solid, which was dried under vacuum (640 mg, 50%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −9.5. ^1H NMR (C_6D_6): δ 8.23 (d, $^3J_{HH}$ = 7, 1H, H^8), 8.04 (dd, $^3J_{PH}$ = 12, $^4J_{HH}$ = 2; 2H, H^2), 7.65 (d, $^4J_{HH}$ = 1, 1H, H^4), 7.62 (d, $^3J_{HH}$ = 8, 1H, H^{11}), 7.11 (t, $^3J_{HH}$ = 8, 1H, H^9), 7.00 (t, $^3J_{HH}$ = 8, 1H, H^{10}), 1.09 (s, 18H, H^6). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 151.3 (d, $^3J_{PC}$ = 17, C^3), 141.5 (broad, C^7), 134.6 (s, C^8), 133.3 (q, $^2J_{FC}$ = 31, C^{12}), 130.9 (s, C^9), 127.3 (d, $^4J_{PC}$ = 4, C^4), 126.6 (d, $^2J_{PC}$ = 13, C^2), 126.4 (q, $^3J_{FC}$ = 6, C^{11}), 126.1 (q, $^1J_{FC}$ = 273, C^{13}), 125.8 (d, $^1J_{PC}$ = 236, C^1), 35.0 (d, $^4J_{PC}$ = 2, C^5), 31.1 (s, C^6), the C^{10} resonance is obscured by the solvent peak (δ 127.8−128.9). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −56.9. $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 3.6. HRMS (*m*/*z*): calcd for $[C_{84}H_{100}B_4P_4O_{12}F_{12} + H]^+$, 1697.6424; found: 1697.6484. EA: calcd for $C_{84}H_{100}B_4P_4O_{12}F_{12}$·0.2 THF, %: C, 59.46; H, 5.94. Found: C, 59.24; H, 6.03.

*[(3,5-^{t}Bu$_2$-Ph)PO$_3$B(p-CF$_3$-Ph)]$_4$ (**3c**).* **3c** was synthesized analogously to **3a** from **1** (81 mg, 0.30 mmol) and 4-(trifluoromethyl)-phenylboronic acid (57 mg, 0.30 mmol) in toluene (120 mL). The volatiles were removed with a rotovap to afford a yellow solid. The crude product was redissolved in toluene (1 mL), hexane (10 mL) was added, and a white precipitate formed. The mixture was filtered. The

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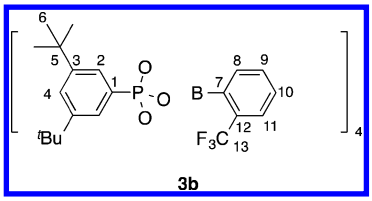
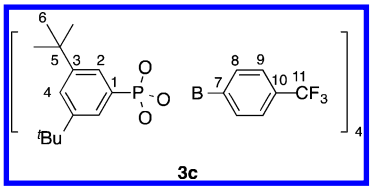
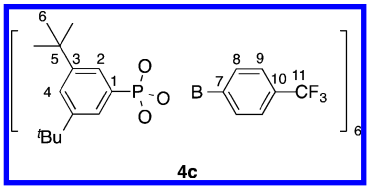


filtrate was taken to dryness under vacuum to afford **3c** as a yellow solid. The solid was washed with hexane and dried under vacuum (15 mg, 12%). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −6.9. ^1H NMR (THF-d_8): δ 7.79 (d, $^3J_{HH}$ = 8, 2H, H^8), 7.75 (s, 1H, H^4), 7.72 (dd, $^3J_{PH}$ = 16, $^4J_{HH}$ = 2; 2H, H^2), 7.52 (d, $^3J_{HH}$ = 8, 2H, H^9), 1.22 (s, 18H, H^6). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 152.5 (d, $^3J_{PC}$ = 17, C^3), 132.0 (s, C^8), 130.2 (q, $^2J_{FC}$ = 32, C^{10}), 128.8 (d, $^4J_{PC}$ = 4, C^4), 125.9 (d, $^2J_{PC}$ = 13, C^2), 125.8 (d, $^1J_{PC}$ = 234, C^1), 125.5 (q, $^1J_{FC}$ = 271, C^{11}), 124.7 (q, $^3J_{FC}$ = 4, C^9), 35.6 (d, $^4J_{PC}$ = 2, C^5), 31.2 (s, C^6); the C^7 resonance was not observed. $^{19}F\{^1H\}$ NMR (THF-d_8): δ −62.9. $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 3.4. HRMS (m/z): calcd for $[C_{84}H_{100}B_4P_4O_{12}F_{12} + H]^+$, 1697.6424; found, 1697.6522.

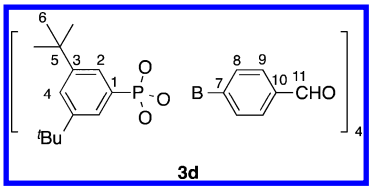


*[(3,5-^{t}Bu$_2$-Ph)PO$_3$B(p-CF$_3$-Ph)]$_6$ (**4c**).* **4c** was synthesized analogously to **3a** from **1** (81 mg, 0.30 mmol) and 4-(trifluoromethyl)-phenylboronic acid (57 mg, 0.30 mmol) in toluene (12 mL). The volatiles were removed under vacuum to afford a yellow solid. This material was recrystallized from hot toluene to afford **4c** as a white powder, which was dried under vacuum (63 mg, 49%). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 0.3. ^1H NMR (THF-d_8): δ 7.48 (d, $^3J_{HH}$ = 8, 2H, H^8), 7.45 (s, 1H, H^4), 7.42 (dd, $^3J_{PH}$ = 16, $^4J_{HH}$ = 2; 2H, H^2), 7.12 (d, $^3J_{HH}$ = 8, 2H, H^9), 1.15 (s, 18H, H^6). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 151.5 (d, $^3J_{PC}$ = 16, C^3), 132.0 (s, C^8), 129.4 (q, $^2J_{FC}$ = 32, C^{10}), 128.0 (d, $^4J_{PC}$ = 3, C^4), 125.7 (d, $^1J_{PC}$ = 214, C^1), 125.6 (d, $^2J_{PC}$ = 12, C^2), 125.2 (d, $^1J_{FC}$ = 271, C^{11}), 124.3 (d, $^3J_{FC}$ = 4, C^9), 35.2 (d, $^4J_{PC}$ = 1, C^5), 31.1 (s, C^6); the C^7 resonance was not observed. $^{19}F\{^1H\}$ NMR (THF-d_8): δ −62.8. $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 3.7. HRMS (m/z): calcd for $[C_{126}H_{150}B_6P_6O_{18}F_{18} + H]^+$, 2545.9597; found, 2545.9663.

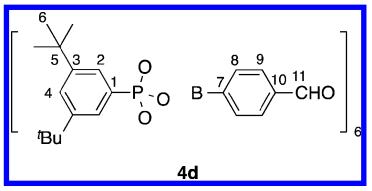


*[(3,5-^{t}Bu$_2$-Ph)PO$_3$B(p-CHO-Ph)]$_4$ (**3d**).* **3d** was synthesized analogously to **3a** from **1** (75 mg, 0.28 mmol) and 4-formylphenylboronic acid (41 mg, 0.27 mmol) in toluene (110 mL). The volatiles were removed under vacuum to afford a white solid. This material was redissolved in toluene (2 mL), hexane (10 mL) was added, and a white precipitate formed. The solid **3d** was collected by filtration, washed with hexane, and dried under vacuum (46 mg, 44%). X-ray quality crystals were grown by layering hexane onto a toluene solution of **3d** at −40 °C. $^{31}P\{^1H\}$ NMR (THF-d_8): δ −6.9. ^1H NMR (THF-d_8): δ 9.92 (s, 1H, H^{11}), 7.82 (d, $^3J_{HH}$ = 8, 2H, H^9), 7.77−7.74 (m, 5H, H^2, H^4, H^8), 1.23 (s, 18H, H^6). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 192.0 (s, C^{11}), 152.5 (d, $^3J_{PC}$ = 18, C^3), 150.9 (broad, C^7), 137.3 (s, C^8), 132.0 (s, C^{10}), 129.1 (s, C^9), 128.8 (d, $^4J_{PC}$ = 4, C^4), 125.9 (d, $^1J_{PC}$ = 234, C^1), 125.9 (d, $^2J_{PC}$ = 13, C^2), 35.6 (d, $^4J_{PC}$ = 2, C^5), 31.2 (s, C^6). $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 3.5. HRMS (m/z): calcd for $[C_{84}H_{104}B_4P_4O_{16} + H]^{+\cdot}$ 1537.6725; found, 1537.6785. ESI-MS (1:1 CH_2Cl_2:acetonitrile, LiCl, positive ion scan): 1543.9 ($[M + Li]^+$ = 1543.6).

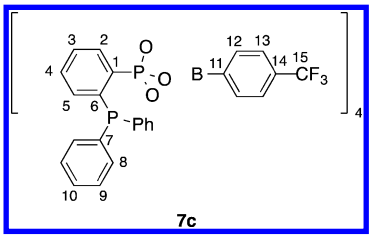
*[(3,5-^{t}Bu$_2$-Ph)PO$_3$B(p-CHO-Ph)]$_6$ (**4d**).* **4d** was synthesized analogously to **3a** from **1** (811 mg, 3.00 mmol), 4-formylphenylboronic acid



(450 mg, 3.00 mmol), and toluene (120 mL). The reaction mixture was cooled and left at room temperature for 18 h. The volatiles were removed under vacuum to afford a white solid. This material was redissolved in toluene (25 mL), hexane (20 mL) was added, and a white precipitate formed. The precipitate was recrystallized from toluene to afford **4d** as white powder, which was dried under vacuum (410 mg, 36%). X-ray quality crystals were grown by slow evaporation of a toluene solution of **4d** at −40 °C. $^{31}P\{^1H\}$ NMR (THF-d_8): δ −1.6. ^1H NMR (THF-d_8): δ 9.72 (s, 1H, H^{11}), 7.51 (d, $^3J_{HH}$ = 8, 2H, H^9), 7.44−7.41 (m, 3H, H^2 and H^4), 7.35 (d, $^3J_{HH}$ = 8, 2H, H^8), 1.14 (s, 18H, H^6). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 191.7 (s, C^{11}), 151.5 (d, $^3J_{PC}$ = 17, C^3), 149.8 (broad, C^7), 136.5 (s, C^8), 132.1 (s, C^{10}), 128.7 (s, C^9), 128.0 (d, $^4J_{PC}$ = 3, C^4), 125.9 (d, $^1J_{PC}$ = 214, C^1), 125.6 (d, $^2J_{PC}$ = 12, C^2), 35.2 (d, $^4J_{PC}$ = 2, C^5), 31.2 (s, C^6). $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 4.1. HRMS (m/z): calcd for $[C_{126}H_{156}B_6P_6O_{24} + H]^+$, 2306.0049; found, 2306.0107.



*[(2-PPh$_2$-Ph)PO$_3$B(p-CF$_3$-Ph)]$_4$ (**7c**).* **7c** was synthesized analogously to **3a** from **6** (103 mg, 0.301 mmol) and 4-(trifluoromethyl)-phenylboronic acid (57 mg, 0.30 mmol) in toluene (12 mL). The volatiles were removed under vacuum to afford a yellow solid. This material was recrystallized by diffusion of hexane into a toluene solution of **7c** to afford **7c** as a white powder, which was collected by filtration and dried under vacuum (60 mg, 40%). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −9.9, −15.1. ^1H NMR (THF-d_8): δ 7.81 (dd, $^3J_{PH}$ = 16, $^3J_{HH}$ = 8; 1H, H^2), 7.53 (dt, $^3J_{HH}$ = 8, $^4J_{PH}$ = 2; 1H, H^4), 7.41 (t, $^3J_{PH}$ = $^3J_{HH}$ = 7, 1H, H^5), 7.40−7.32 (m, 3H; H^3 and H^{12}), 7.12 (t, $^3J_{HH}$ = 7, 2H, H^{10}), 7.06 (d, $^3J_{HH}$ = 8, 2H, H^{13}), 6.92 (t, $^3J_{HH}$ = 8, 4H, H^9), 6.77 (t, $^3J_{PH}$ = $^3J_{HH}$ =7, 4H, H^8). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 147.7 (broad, C^{11}), 143.3 (m, C^6), 138.6 (d, $^2J_{PC}$ = 19, C^5), 138.0 (d, $^3J_{PC}$ = 14, C^3), 133.9 (m, J_{PC} is obscured due to overlap, C^2, C^4, C^8), 133.6 (dd, $^1J_{PC}$ = 236, $^2J_{PC}$ = 36; C^1), 132.3 (s, C^{12}), 129.8 (d, $^1J_{PC}$ = 17, C^7), 129.1 (q, $^2J_{FC}$ = 31, C^{14}), 128.7 (m, J_{PC} is obscured due to overlap, C^9, C^{10}), 125.7 (q, $^1J_{FC}$ = 272, C^{15}), 124.3 (q, $^3J_{FC}$ = 4, C^{13}). $^{19}F\{^1H\}$ NMR (THF-d_8): δ −62.5. $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 3.4. HRMS (m/z): calcd for $[C_{100}H_{72}B_4P_8O_{12}F_{12} + H]^{+\cdot}$ 1985.3184; found, 1985.3161.



*[(2-PPh$_2$-Ph)PO$_3$B(p-CHO-Ph)]$_4$ (**7d**).* **7d** was synthesized analogously to **3a** from **6** (103 mg, 0.301 mmol) and 4-formylphenylboronic acid (45 mg, 0.30 mmol) in toluene (12 mL). The volatiles were removed under vacuum to afford a white solid. This material was recrystallized from hot toluene to afford **7d** as a white powder, which was dried under vacuum (46 mg, 34%). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −9.7, −14.9. ^1H NMR (THF-d_8): δ 9.85 (s, 1H, H^{15}), 7.80 (dd, $^3J_{PH}$ = 17, $^3J_{HH}$ = 8; 2H, H^2), 7.51 (t, $^3J_{HH}$ = 8, 1H, H^4), 7.42 (t, $^3J_{PH}$ = $^3J_{HH}$ = 6, 1H, H^5), 7.37 (d, $^3J_{HH}$ = 8, 2H, H^{13}), 7.34−7.30 (m, 3H, H^3 and

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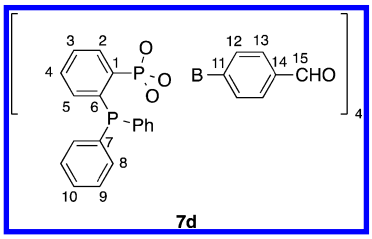
H^{12}), 7.09 (t, $^3J_{HH}$ = 7, 2H, H^{10}), 6.88 (t, $^3J_{HH}$ = 8, 4H, H^9), 6.78 (t, $^3J_{PH}$ = $^3J_{HH}$ = 6, 4H, H^8). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 192.3 (s, C^{15}), 143.4 (m, C^6), 138.6 (d, $^2J_{PC}$ = 19, C^5), 138.2 (d, $^3J_{PC}$ = 15, C^3), 136.6 (s, C^{12}), 134.1 (dd, $^1J_{PC}$ = 231, $^2J_{PC}$ = 50; C^1), 133.9 (m, J_{PC} is obscured due to overlap, C^2, C^4, C^8), 132.5 (s, C^{14}), 129.8 (d, $^1J_{PC}$ = 17, C^7), 128.7 (m, J_{PC} is obscured due to overlap, C^9, C^{10}), 128.7 (s, C^{13}); the C^{11} resonance was not observed. $^{11}B\{^1H\}$ NMR (toluene-d_8): δ 2.5. HRMS (m/z): calcd for $[C_{100}H_{76}B_4P_8O_{16} + H]^+$, 1825.3485; found, 1825.3476. ESI-MS (1:1 CH_2Cl_2:acetonitrile, LiCl, positive ion scan): 1831.5 ($[M + Li]^+$ = 1831.3).



7d

Interconversion of 4c and 3c. Two J-Young NMR tubes were charged with **4c** (2.7 mg and 3.3 mg, respectively) and toluene-d_8 (0.5 mL) and sealed under nitrogen in a glovebox. The tubes were brought out of the glovebox and heated in a 105 °C oil bath. NMR spectra were obtained periodically at room temperature. Equilibrium was reached after 3 weeks. The equilibrium constant $K_{eq} = [\mathbf{3c}]^3/[\mathbf{4c}]^2 = 2.4(1) \times 10^{-3}$ M. The tubes were cooled to room temperature and NMR spectra were obtained periodically. Equilibrium was reached after 4 weeks. The equilibrium constant $K_{eq} = [\mathbf{3c}]^3/[\mathbf{4c}]^2 = 1.2(1) \times 10^{-3}$ M.

X-ray Data Collection and Structure Refinement. The diffraction data for **3a**, **3d**, and **4d** were measured at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). Data reduction and integration were performed with the Bruker APEX2 software package. Data were corrected for absorption effects using the empirical methods as implemented in SADABS. The structures were solved and refined by full-matrix least-squares procedures using the Bruker SHELXTL software package. Crystallographic data and details of the data collection and structure refinement are provided in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Crystal structure report for compounds **3a**, **3d**, and **4d** and combined cif file; Procedures for borophosphonate synthesis and self-condensation of **1**; Interconversion of **4c** and **3c**; $^{11}B\{^1H\}$ NMR background subtraction; NMR spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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