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An Iminoboronate Construction Set for Subcomponent Self-Assembly

Marie Hutin,[a] Gérald Bernardinelli,[b] and Jonathan R. Nitschke*[c]

Abstract: Recently we have demonstrated a series of systems in which complex structures were created from simple amine and aldehyde subcomponents by copper(I)-templated imine bond formation. We describe herein the extension of this "subcomponent self-assembly" concept to the generation of structures based upon the iminoboronate ester motif. Equimolar amounts of diol, amine, and 2-formylphenylboronic acid reacted by reversible B–O and C=N bond formation to generate iminoboronate esters, as has recently been reported by James et al. (*Org. Lett.* **2006**, *8*, 609–612). The extent of ester formation was shown to depend upon a number of factors. The exploration of these factors allowed rules and predictions to be formulated governing the self-assembly process. These rules allowed the construction of more complex structures containing multiple boron atoms, including a trigonal cage containing six boron centers, as well as pointing the way to the construction of yet more intricate architectures. The lability of the B–O and C=N bonds also allowed different diol and amine subcomponents to be substituted within these structures. Selection rules were also determined for these substitution reactions, allowing the products to be predicted based upon the electronic properties of the diols and diamines employed. These results thus demonstrate the generality of the subcomponent self-assembly methodology through its application to a new dynamic covalent system.

Keywords: boronic esters · dynamic covalent chemistry · imines · self-assembly · template effects

Introduction

To build complex structures using self-assembly, it is necessary to understand the rules governing the self-assembling system: A deeper understanding of the rules governing a system allows one to predict and create more complex structures, driving a conceptual shift[1] from serendipity[2] towards rational design.[3,4]

Recently it has been demonstrated[5–7] that copper(I) may serve as an excellent template[8] for the formation of imine ligands,[9] allowing the creation of complex structures from simple building blocks.[10] Amine and aldehyde subcomponents are brought together in a well-defined way within the pseudo-tetrahedral coordination environment of the copper(I) ion (Scheme 1a), creating a 90° angle between the two imine ligands. This structure-directing bis(pyridylimine)-copper(I) motif may be incorporated twice into the same subcomponent if 2,9-diformyl-1,10-phenanthroline or 3,6-diformylpyridazine[11] is used, allowing the construction of grids,[6,7] helicates,[7,12] macrocycles,[6,13] and a catenane.[14]

In the present work we describe the use of the iminoboronate ester motif (Scheme 1b) in subcomponent self-assembly. These esters have been developed recently by James and co-workers as an elegant means of determining the enantiopurity of amines[15] and diols.[16] This reaction is inherently multicomponent[4,17,18] in nature, uniting three distinct building blocks in a well-defined fashion: a diol subcomponent is held at 90° to an amine subcomponent around a central pseudotetrahedral boron atom.

In expanding upon the examples presented by James et al.,[15,16] we have investigated the scope and limitations of this reaction, determining which diol and amine subcomponents are mutually compatible. Multitopic[19] subcomponents, which bear multiple binding sites, may be used, allowing the construction of assemblies containing two, three,

[a] Dr. M. Hutin
Department of Organic Chemistry
University of Geneva
30 Quai Ernest Ansermet, 1211 Genève 4 (Switzerland)

[b] Dr. G. Bernardinelli
Laboratory of X-ray Crystallography
University of Geneva
24 Quai Ernest Ansermet, 1211 Genève 4 (Switzerland)

[c] Dr. J. R. Nitschke
Department of Chemistry, University of Cambridge
Lensfield Road Cambridge, CB2 1EW (UK)
Fax: (+44) 1223-336017
E-mail: jrn34@cam.ac.uk

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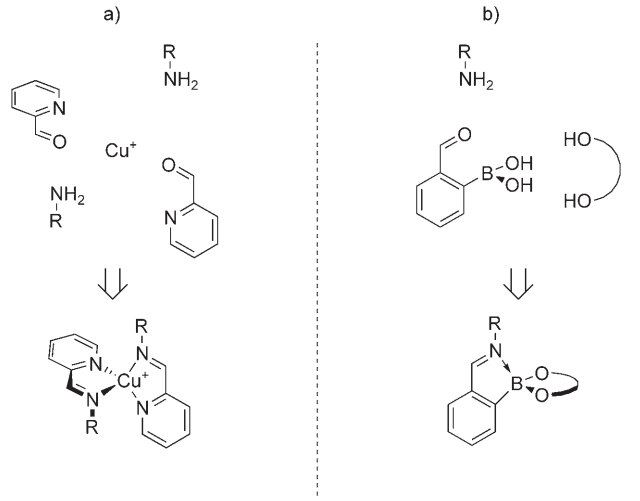


Scheme 1. Self-assembly of a) primary amine and 2-formylpyridine subcomponents with Cu^{I} to form a bis(pyridylimine)copper(I) complex, and b) primary amine, 2-formylphenylboronic acid, and diol subcomponents to form an imino(boronate) ester.

four, or six boron atoms. The dynamic covalent[20] nature of both B–O and C=N bonds[21] allows both diol and amine subcomponents to be independently displaced within these structures in well-defined ways, allowing one structure to be transformed into another. This work thus applies the concepts of subcomponent self-assembly to the rich field of boron-based self-assembly, which includes such recent examples as chemosensors,[22] multicomponent architectures,[18] reversibly formed cages,[23] boroxoaromatics,[21] anionic borate assemblies,[24] borylferrocene structures,[25] macrocycles,[26] as well as self-repairing polymers[27] and porous networks.[28]

Abstract in French: *Nous avons récemment obtenu plusieurs structures complexes par la condensation d'amines et d'aldéhydes en imines, grâce à l'action template de cuivre(*I*). Nous décrivons ici une extension de ce concept par la construction de structures basées sur le motif iminoboronate ester. Des quantités équimolaires de diol, d'amine et d'acide 2-formylphenylboronique réagissent pour former des esters iminoboroniques contenant des liaisons réversibles B–O et C=N, comme l'a récemment démontré Tony James (Org. Lett.* ***2006****, 8, 609–612). La formation de ces esters dépend d'un certain nombre de facteurs. Leur analyse a conduit à l'élaboration des règles dirigeant cette réaction d'autoassemblage. Ces règles ont permis d'obtenir des architectures plus complexes incorporant plusieurs centres boroniques, par exemple une cage trigonale à six bores. La labilité des liaisons B–O et C=N permet à différents sous-composants amine et aldéhyde d'être échangés dans ces structures. Des règles de sélection ont également été déterminées pour ces réactions de substitution, permettant de prédire les produits obtenus sur la base des propriétés électroniques des diols et amines utilisés. Ces résultats démontrent la généralité de la méthodologie d'autoassemblage de sous-composants par son application à un nouveau système dynamique covalent.*

Results and Discussion

This study is divided into three parts. First, the rules governing the self-assembly and solution stability of a set of mononuclear imino(boronate) esters from amine, diol, and 2-formylphenylboronic acid were deciphered and explored. Second, these rules were applied to the generation of more complex structures, incorporating two, three, and four boron centers, as well as a six-boron trigonal cage. The preparation of these structures helped to illuminate the scope and limitations of this reaction. Third, the rules governing the substitution of one subcomponent for another within these structures were investigated. Certain subcomponents were observed to displace others cleanly; the observed selectivities were analyzed in terms of the electronic properties of both amine and diol subcomponents.

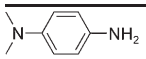
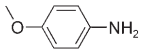
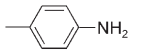
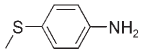
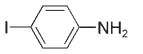
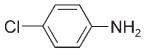
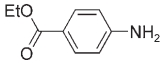
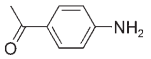
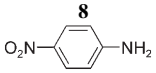
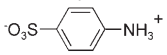
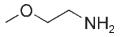
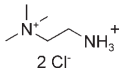
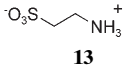
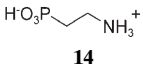
Rules governing iminoboronate ester formation: To investigate the scope and limitations of imino(boronate) ester[29] formation in the context of subcomponent self-assembly, we first prepared a series of mononuclear structures incorporating a variety of different diol and amine subcomponents. A modified version of the procedure described by James et al.[15,16] was employed: The reactions noted in Table 1 were carried out by mixing equimolar amounts of 2-formylphenylboronic acid, diol, and amine in $[D_4]$methanol. This solvent was best able to dissolve the polyols investigated, which showed poor solubility in nonpolar solvents. To avoid possible competition between diol subcomponents and methanol solvent (see below),[30] all samples were dried under dynamic vacuum and all products were characterized by NMR spectroscopy in $CDCl_3$.

Five broad trends became apparent from the data presented in Table 1. First, charged amines did not form well-defined, soluble iminoboronate esters with any of the three diols. For positively charged **12** and negatively charged **10**, **13**, and **14**, this appeared to be a result of the poor solubility of the starting materials and products in chloroform and methanol.

Second, more electron-rich amines led to more complete iminoboronate formation. We attribute this to the greater nucleophilicity of more electron-rich imines, as has been explored in copper-templated systems.[31]

Third, catechol **A** produced more stable boronate esters than the more electron-rich aliphatic diols **B** and **C**. We suspect that this is a consequence of the greater Pauling electronegativity of hydrogen (2.2) than boron (2.0) and the greater (resonance) stabilization of the catecholate dianion than the ethylene glycolate dianion. Since a diolate residue bound to an electropositive boron atom will have more anionic character than the protonated diol, factors stabilizing the anion should also stabilize boron complexes. Ligand-to-boron charge-transfer interactions from the more polariz-

Table 1. Amines and diols investigated in the iminoboronate-forming reaction of Scheme 1b.[a]

Amine	 **A** Yield [%]	 **B** Yield [%]	 **C** Yield [%]
 **1**	**100** *100*	**92** *92*	**92** *85*
 **2**	**100** *100*	**96** *95*	**91** *88*
 **3**	**100** *100*	**99** *98*	**90** *83*
 **4**	**100** *100*	**89** *87*	**88** *82*
 **5**	**100** *100*	**84** *80*	**67** *50*
 **6**	**100** *100*	**90** *81*	**80** *72*
 **7**	**97** *96*	**77** *75*	**68** *70*
 **8**	**93** *93*	**78** *55*	**57** *50*
 **9**	**82** *86*	**X**	**X**
 **10**	Insol.	Insol.	Insol.
 **11**	**100** *100*	**100** *100*	**100** *100*
 **12**	Insol.	Insol.	Insol.
 **13**	Insol.	Insol.	Insol.
 **14**	Insol.	Insol.	Insol.

[a] Yields [%] are given as determined by ^{1}H NMR integration for the products of imine condensation (in boldface) and boronic ester formation (in italics) in $CDCl_3$. Reactions that gave multiple unidentified products are indicated by an "X", and reactions that produced chloroform-insoluble products are noted as "Insol." Triethylamine (1 equiv) was added to neutralize protonated amines **10**, **12**, **13** and **14**.

able π system of the catecholate anion to the boron center, in analogy to what is observed for d^0 transition-metal catecholates,[32] might also lend an additional degree of stabilization to catechol boronate esters.

Fourth, the presence of a catechol (**A**) residue also enhanced imine formation, and the presence of a more electron-rich amine residue also stabilized the boronate ester. This mutualistic effect may be explained in terms of template[8] stabilization: Binding to a catecholate makes the boron center more electron-deficient, thus rendering a dative bond between nitrogen and boron more stabilizing to the system as a whole. This mutual stabilization of ester and imine moieties is reflected in Table 1: A high yield of one condensation is strongly correlated with a high yield of the other condensation.

Fifth, among anilines and aliphatic diols, quantitative ester formation is observed only in the case of *p*-toluidine **3** and ethylene glycol **B**. Electron-electron repulsion around the boron center may result in destabilization in cases where the highly electron-rich anilines **1** and **2** are present with electron-rich diols **B** and **C**.

In a recent paper, Anslyn et al. investigated the structures of a set of amino(boronate)ester compounds in solution and in the solid state,[30] and were able to correlate ^{11}B chemical shifts with the coordination environments of boron centers. Comparison of the ^{11}B chemical shifts of selected compounds from Table 1 with this prior work shed light upon the coordination environments of the boron centers of this series of compounds, which in turn helped to explain the observed mutualism between imine and ester formation.

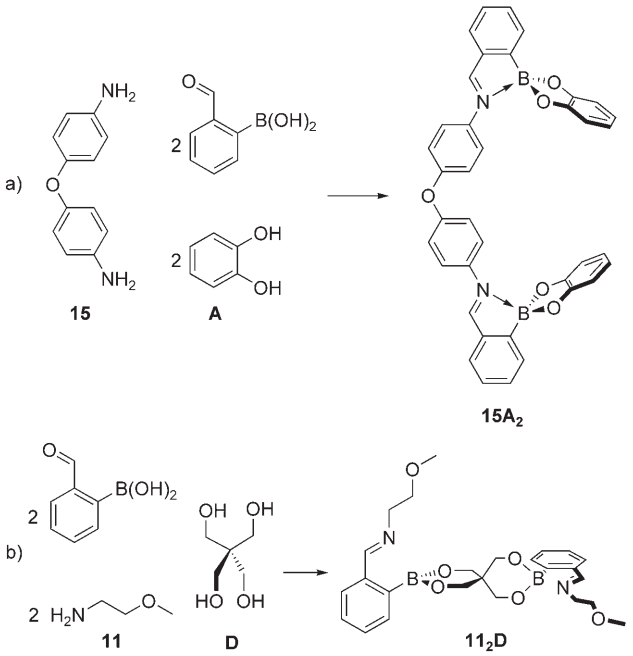
First, the ^{11}B chemical shifts of **3A**, **3B**, and **3(OMe)$_2$**[33] coincided at $\delta = 14.7$ ppm in methanol, whereas they were observed at $\delta = 15.1$, 22.9, and 21.6 ppm, respectively, in chloroform. This was consistent with the conclusion that these diols did not compete effectively with the solvent in methanol,[30] disfavoring the formation of their boronic esters.

Second, in $CDCl_3$ the ^{11}B chemical shifts of **3(OMe)$_2$** and **3B** noted above were consistent with a trigonal-planar geometry at boron,[30] whereas the chemical shift of **3A** suggested a tetrahedral geometry in which a N→B bond was present. Boron centers coordinated by alkoxides thus appeared to be sufficiently electron-rich to gain no stabilization by accepting a fourth, imine, ligand. Template stabilization[8,9] would thus not be operative in these cases, which could explain the lower yields associated with diols **B** and **C**.

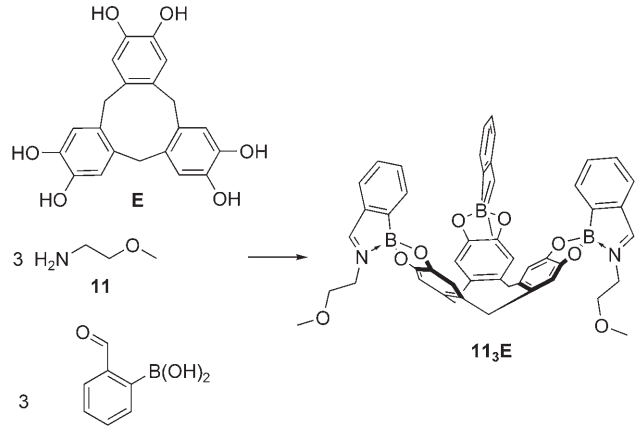
More complex structures via bridging subcomponents: Having thus clarified the rules governing imino(boronate) ester formation, we investigated how greater structural complexity might be created by using this methodology. We reasoned that the use of multitopic[19] diol or amine subcomponents, capable of bridging two or more boron centers, could provide a route to more complex structures.

The use of bis(4-aminophenyl) ether **15** as a subcomponent thus allowed construction of product **15A$_2$**, as shown in Scheme 2a. As shown in Scheme 2b, pentaerythritol (**D**) provided a different geometry of ditopic linkage, joining two imino(boronate) esters orthogonally by a central spiro-linkage.[27] The initial use of methanol as a solvent, followed by evaporation and NMR spectroscopic characterization of the product in $CDCl_3$, was undertaken to circumvent the very low solubility of **D** in non-hydrogen-bonding solvents.

Compounds **15A$_2$** and **11$_2$D** were both synthesized quantitatively; no aldehyde or free alcohol resonances were ob-



Scheme 2. Preparation of di-boron structures a) $\mathbf{15A_2}$ and b) $\mathbf{11_2D}$.



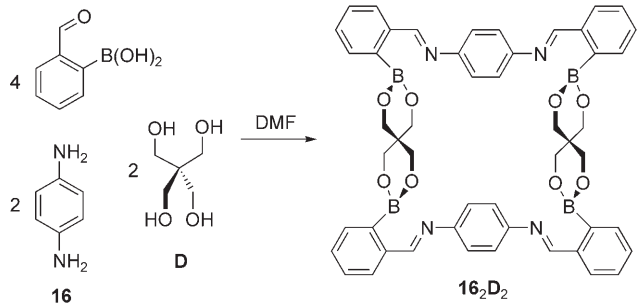
Scheme 3. Synthesis of compound $\mathbf{11_3E}$, of which only one possible conformer is shown.

served in the ^{1}H NMR spectra (see the Supporting Information). The rules defined previously for mononuclear compounds could thus be extrapolated to dinuclear compounds: The formation of stable dinuclear iminoboronate ester $\mathbf{15A_2}$ could be predicted based upon the successful participation of subcomponents **2** and **A** (Table 1) in this condensation reaction. The successful preparation of $\mathbf{11_2D}$ could likewise be predicted based upon the observation of the quantitative formation of **11C**. No diastereotopic splitting of the ethylene protons of the **11** residues of $\mathbf{11_2D}$ was observed, which was consistent with a lack of N→B interactions and thus free rotation about the B–C bonds. This lack of N→B interactions was in turn consistent with the electron-rich character of **D**, following the rules deciphered above.

Cyclotricatechylene-type molecules similar to **E** have been employed as tritopic linkers in the generation of a variety of complex self-assembled architectures.[23,34] The reaction of cyclotricatechylene **E** (1 equiv) with 2-formylphenylboronic acid and amine **11** (3 equiv each) led to the formation of trinuclear $\mathbf{11_3E}$ (Scheme 3). Again, the prior observation of **11A** allowed us to predict that the structurally similar $\mathbf{11_3E}$ would be stable.

When the sample was cooled, the NMR spectrum of $\mathbf{11_3E}$ showed features that we attributed to the presence of at least three conformational isomers at low temperature. The calculated[35] energetic barrier of about 60 kJ mol^{-1} for the interconversion of these conformers was consistent with a process involving rupture of the predicted N→B bond[36] followed by free rotation about the B–C_{phenyl} bond. A more in-depth discussion of the low-temperature behavior of $\mathbf{11_3E}$ is presented in the Supporting Information.

Carrying this methodology further, we reasoned that the use of rigid, difunctional subcomponents might allow the construction of macrocycles having well-defined geometries. The product of the reaction of Scheme 4, in which **16** and **D** were employed as subcomponents, was thus predicted to be four-boron macrocycle $\mathbf{16_2D_2}$.



Scheme 4. Formation of the macrocycle $\mathbf{16_2D_2}$.

Such a macrocycle was indeed observed experimentally. When *para*-diaminobenzene **16**, bis-diol **D**, and 2-formylphenylboronic acid were heated in DMF at 50 °C overnight (Scheme 4), crystals of the product $\mathbf{16_2D_2}$ suitable for X-ray analysis were obtained (Figure 1). Crystalline $\mathbf{16_2D_2}$ displayed a very low solubility in all solvents tried, which precluded this product's characterization by NMR spectroscopy. NMR spectra of the crystallization supernatant showed a complex mixture of products. The solubility of $\mathbf{16_2D_2}$ was sufficient, however, in a mixture of chloroform and THF to allow its identification by APCI mass spectrometry.

To obtain more soluble macrocyclic products, several other diamines[37] were investigated in concert with **D** as subcomponents. NMR spectra in all cases indicated mixtures of products. We suspect that the failures of these systems to produce single macrocyclic products may be linked to the poor ability of pentaerythritol **D** to form boronate esters: Only aliphatic amine **11** quantitatively formed iminoboronates with **D** or with its congener **C**. Furthermore, the failure of aliphatic diols to form boronate esters containing

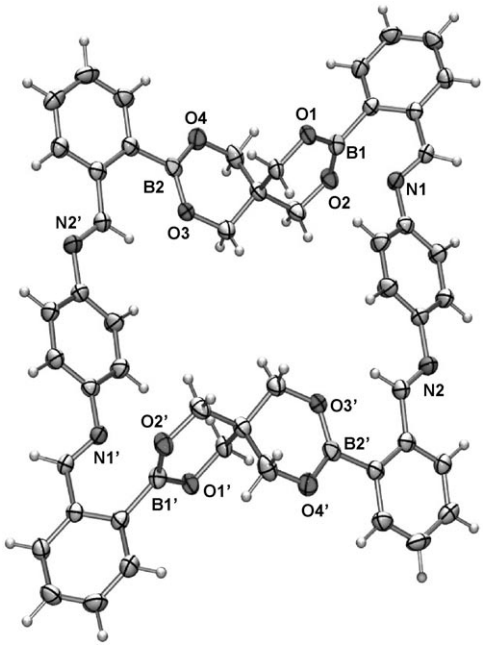


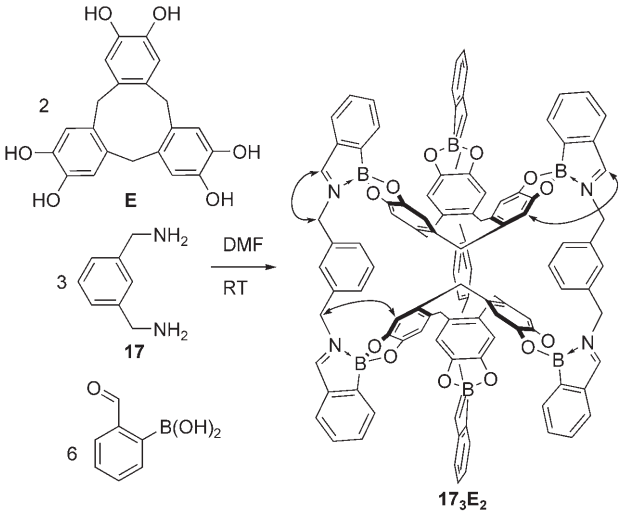
Figure 1. Crystal structure of centrosymmetric macrocycle $\mathbf{16_2D_2}$.

N→B bonds, as indicated by NMR spectroscopy (see above) and crystallography (see below), deprives these assemblies of an important structure-determining element. The resulting systems may possess too many degrees of freedom to be able to select a unique product from the diverse dynamic combinatorial libraries[38] formed by the starting subcomponents.

The crystal structure of $\mathbf{16_2D_2}$ showed a centrosymmetric macrocycle with trigonal-planar geometries for the boron atoms, in accordance with our expectations for aliphatic alcohol **D**. Half of the nitrogen atoms' lone pairs were directed away from the closest boron atoms, whereas the others showed an N···B distance of 2.392(4) Å. This is substantially longer than expected for a N→B coordinative interaction (<1.75 Å).[30]

We therefore concluded that no template effect[8] was stabilizing these imine bonds, in keeping with our NMR results with aliphatic diols. We attribute thus the driving force for the formation of this macrocycle to its lack of solubility in the reaction mixture: the lack of imine templation would lead to a lack of structural definition, resulting in the formation of a diverse mixture of cyclic and linear products in solution, which is consistent with our NMR observations.

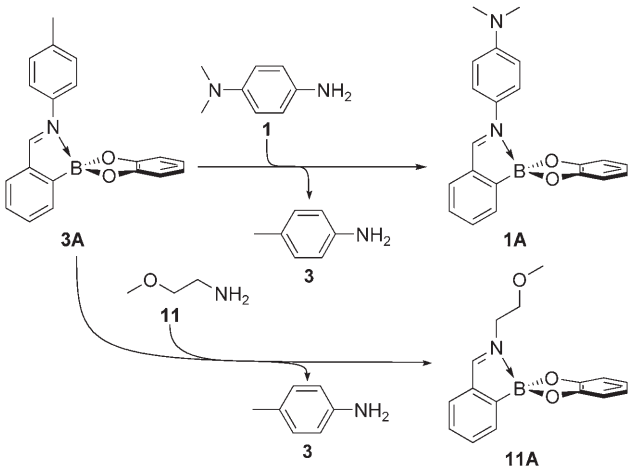
In contrast with aliphatic tetrol **D**, aromatic subcomponent **E** might be expected to produce better-defined cage-type[23] architectures due to the possibility of N→B coordinative interactions. This prediction was borne out by the preparation of trigonal cage $\mathbf{17_3E_2}$ (Scheme 5) upon mixing cyclotricatechylene **E** with *m*-xylylenediamine **17** and 2-formylphenylboronic acid in deuterated DMF under argon. After one night at room temperature, ^{1}H NMR spectroscopy showed the clean formation of the cage $\mathbf{17_3E_2}$. Although we were not able to obtain X-ray quality crystals of $\mathbf{17_3E_2}$, the



Scheme 5. Formation of the cage $\mathbf{17_3E_2}$; double-headed arrows indicate key observed NOE correlations between protons

proposed structure is entirely consistent with MALDI-MS and 2D-NMR measurements. ROESY ^{1}H spectra were particularly instructive, showing NOE correlations (indicated by arrows in Scheme 5) that were consistent with the indicated high-symmetry cage structure. The successful preparation of $\mathbf{17_3E_2}$ validated the use of iminoboronate subcomponent self-assembly to generate well-defined, complex architectures based upon the rules detailed above, acting in concert with the symmetries and numbers of linking functional groups present in the starting subcomponents.[39]

Subcomponent substitution reactions: Within structures containing copper(I)-templated imine ligands it has been shown that an electron-rich amine may displace a more electron-poor amine residue.[31] The same driving force may be harnessed for substitution within imino(boronate)-containing structures (Scheme 6), allowing the clean transformation of one structure into another.

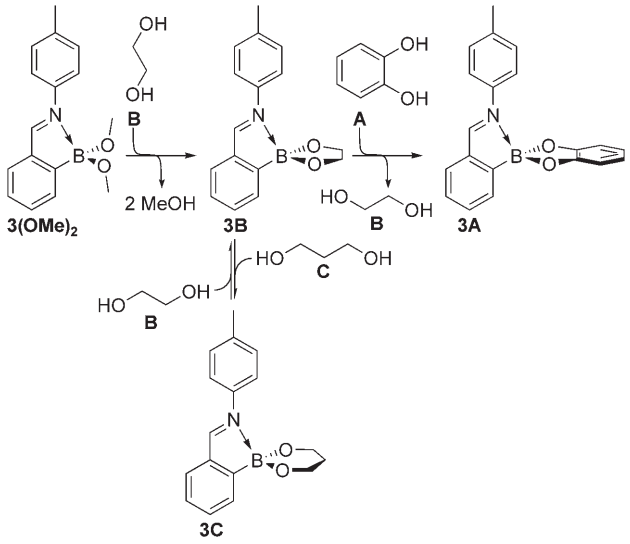


Scheme 6. Substitution reactions of amines **1** and **11** with iminoboronate **3A** in $CDCl_3$.

The addition of *p*-dimethylaminoaniline (**1**; 1 equiv) to a chloroform solution of iminoboronate **3A** (1 equiv) led to the clean substitution of the *p*-toluidine residue of **3A**, giving **1A** as the unique product. We attribute the driving force of this reaction to the greater stabilization of the electron-poor boron center by the more electron-rich imine ligand formed by subcomponent **1**.[31]

Substitution was also observed when amine **11** (1 equiv) was added to a chloroform solution of compound **3A** (1 equiv). The driving force of the reaction was again attributed to the formation of a more electron-donating, and thus stabilizing, ligand in the case of aliphatic amine **11**. In both cases the substitution reaction was complete after 3 h at room temperature, as determined by NMR monitoring.

In addition to their dynamic-covalent imine bonds, the labile boron–oxygen bonds of iminoboronate esters may serve as points of reassembly (Scheme 7).[21] Substitutions carried out at these bonds may occur independently of substitutions involving the imine bonds: The two kinds of linkages are chemically orthogonal, allowing particularly rich substitution chemistry.



Scheme 7. Transformation of **3(OMe)$_2$** into **3B** and subsequently into **3A**.

The addition of ethylene glycol **B** to a chloroform solution of iminoboronate ester **3(OMe)$_2$** led to its complete conversion into **3B** (Scheme 7, left). We attribute the driving force of this reaction to the gain in entropy associated with the chelate effect.[40] The addition of an equimolar amount of 1,3-propanediol to **3B** resulted in the establishment of an equilibrium between **3B** and **3C** with neither predominating (45% **3B** and 55% **3C** at equilibrium), in similar fashion to what Philp et al. have observed in boroxoaromatic systems.[21] The addition of catechol A to a chloroform solution of **3B** or **3C**, however, resulted in the quantitative displacement of the aliphatic diol subcomponent to produce **3A**. We reasoned that the driving force for this displacement was identical to the reason that catechol esters are more stable than aliphatic diol esters: the partial negative charge on the oxygen atoms in these esters is better stabilized by the presence of an aromatic ring.

Conclusion

The iminoboronate motif[15,16] thus serves as an excellent tecton[41] for the creation of new architectures by subcomponent self-assembly within the confines of the rules outlined herein. A wide variety of structures are accessible, incorporating an extensive array of diol and amine subcomponents. These building blocks may be multitopic,[19] allowing access to architectures such as macrocycles and cages. Selective substitution is possible within these structures at both diols and amines, again following logical rules. This new set of subcomponents includes diols, which should not interact with the subcomponents employed in our previous copper(I)/diimine system,[10] and would thus not be expected to interfere with the formation of copper complexes. Both copper and boron systems might act together to co-direct the formation of a more complex structure by the simultaneous application of two distinct sets of self-assembly rules.

Experimental Section

General: All reactions were carried out using reagents of the highest commercially available purity. *p*-Toluidine (**3**) was sublimed prior to use. NMR spectra were assigned with the help of COSY, NOESY, and HSQC measurements.[35] All ^{11}B chemical shifts were referenced to $BF_3{\cdot}Et_2O$ at $\delta = 0$ ppm as an external standard in a sealed capillary. Methods A and B, described below, were used in the preparation of many of the new compounds, as noted. All experiments were carried out at room temperature (RT) = (296 ± 2) K unless otherwise indicated.

Method A: Into a NMR tube with a Teflon screw-cap were added the indicated quantities of diol, amine, and 2-formylphenylboronic acid, to which was added deuterated methanol (0.4 mL). All starting materials dissolved within 5 min. After four hours, NMR spectra showed the complete condensation of amine with aldehyde to form imine. The solvent was removed under dynamic vacuum and the residue was dissolved in $CDCl_3$. NMR spectroscopy indicated the clean formation of a single product.

Method B: Into a NMR tube with a Teflon screw-cap were added the indicated quantities of polyol, amine, and 2-formylphenylboronic acid, to which was added deuterated methanol (0.4 mL). After one night at 50 °C, NMR spectra showed the complete condensation of amine with aldehyde to form imine and all polyol had dissolved. The solvent was removed under dynamic vacuum and the residue was dissolved in $CDCl_3$. NMR spectroscopy indicated the clean formation of a single product.

3(OMe)$_2$: Into a NMR tube with a Teflon screw-cap was added *p*-toluidine (0.031 mmol, 1 equiv), 2-formylphenylboronic acid (0.031 mmol, 1 equiv), and MeOH (0.35 mL). After one hour at room temperature, the solvent was removed and $CDCl_3$ (0.35 mL) was added. NMR spectroscopy indicated the clean formation of a single product. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.62$ (s, 1H, imine), 7.54 (m, 5H, 3-iminophenylboronic ester + 5-iminophenylboronic ester + 6-iminophenylboronic ester + aniline next to imine), 7.40 (dt, $J = 7.5$ Hz, $J' = 1$ Hz, 1H, 4-iminophenylboronic ester), 7.26 (d, overlap with $CHCl_3$, 2H, aniline next to methyl), 3.28 (s, 6H, -OCH_3), 2.40 ppm (s, 3H, -CH_3); ^{11}B NMR (641.85 MHz, 298 K) $CDCl_3$: $\delta = 21.6$; MeOD: $\delta = 14.8$; ^{13}C NMR (100.62 MHz, 298 K,

$CDCl_3$): $\delta = 159.9$, 138.2, 132.4, 130.8, 128.2, 128.1, 121.3, 121.2, 51.1, 21.3; EI-MS: 267 $[\mathbf{3(OMe)_2}]^+$.

11A (Method A): Pyrocatechol **A** (3.16 mg, 0.029 mmol, 1 equiv), 2-methoxyethylamine (**11**; 2.15 mg, 0.029 mmol, 1 equiv), 2-formylphenylboronic acid (4.29 mg, 0.029 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.34$ (s, 1H, imine), 7.65 (d, $J = 7$ Hz, 1H, 6-iminophenylboronic ester), 7.54 (m, 2H, 3-iminophenylboronic ester + 5-iminophenylboronic ester), 7.38 (dt, $J = 7.5$ Hz, $J' = 1$ Hz, 1H, 4-iminophenylboronic ester), 6.88 (m, 2H, catecholate), 6.77 (m, 2H, catecholate), 3.65 (m, 2H, -CH=N-CH_2CH$_2$OCH$_3$), 3.58 (m, 2H, -CH=N-CH$_2$CH_2OCH$_3$), 3.35 ppm (s, 3H, -CH=N-CH$_2$CH$_2$OCH_3); ^{11}B NMR (641.85 MHz, 298 K) $CDCl_3$: $\delta = 13.3$ ppm; MeOD: $\delta = 10.9$ ppm; ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 170.1$, 152.4, 137.9, 134.2, 131.1, 128.8, 26.9, 119.4, 110.3, 69.3, 59.1, 49.7 ppm; EI-MS: 281 $[\mathbf{11A}]^+$, 250 $[\mathbf{11A}-CH_3O]^+$, 236 $[\mathbf{11A}-CH_3OCH_2]^+$, 222 $[\mathbf{11A}-CH_3OCH_2CH_2]^+$, 209 $[\mathbf{11A}-CH_3OCH_2CH_2N]^+$.

11B (Method A): 1,2-Ethanediol **B** (1.8 μL, 0.032 mmol, 1 equiv), 2-methoxyethylamine (**11**; 2.40 mg, 0.032 mmol, 1 equiv), 2-formylphenylboronic acid (4.78 mg, 0.032 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.30$ (s, 1H, imine), 7.57 (d, $J = 7$ Hz, 1H, 6-iminophenylboronic ester), 7.45 (m, 2H, 3-iminophenylboronic ester + 5-iminophenylboronic ester), 7.28 (t, $J = 8$ Hz, 1H, 4-iminophenylboronic ester), 4.13 (s, 4H, -OCH_2CH_2O-), 3.80 (t, $J = 5$ Hz, 2H, -CH=N-CH_2CH$_2$OCH$_3$), 3.74 (t, $J = 5$ Hz, 2H, -CH=N-CH$_2$CH_2OCH$_3$), 3.37 ppm (s, 3H, -CH=N-CH$_2$CH$_2$OCH_3); ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 168.8$, 137.9, 133.4, 130.5, 127.9, 126.2, 69.9, 65.5, 59.1, 50.4 ppm; EI-MS: 233 $[\mathbf{11B}]^+$, 203 $[\mathbf{11B}-CH_3O]^+$, 188 $[\mathbf{11B}-CH_3OCH_2]^+$, 161 $[\mathbf{11B}-CH_3OCH_2CH_2N]^+$.

11C (Method A): 1,3-Propanediol **C** (2.8 μL, 0.039 mmol, 1 equiv), 2-methoxyethylamine **11** (2.93 mg, 0.039 mmol, 1 equiv), 2-formylphenylboronic acid (5.85 mg, 0.039 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.50$ (s, 1H, imine), 7.60 (m, 2H, 6-iminophenylboronic ester + 3-iminophenylboronic ester), 7.41 (dt, $J = 7$ Hz, $J' = 1$ Hz, 1H, 5-iminophenylboronic ester), 7.32 (dt, $J = 7.5$ Hz, $J' = 1.5$ Hz, 1H, 4-iminophenylboronic ester), 4.14 (t, $J = 5.5$ Hz, 4H, -OCH_2CH$_2$CH_2O-), 3.87 (t, $J = 6$ Hz, 2H, -CH=N-CH_2CH$_2$OCH$_3$), 3.74 (t, $J = 5.5$ Hz, 2H, -CH=N-CH$_2$CH_2OCH$_3$), 3.39 (s, 3H, -CH=N-CH$_2$CH$_2$OCH_3), 2.04 ppm (quint., $J = 5.5$ Hz, 2H, -OCH$_2$CH_2CH$_2$O-); ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 165.9$, 139.0, 131.9, 131.2, 128.6, 127.4, 71.6, 62.0, 59.1, 57.1, 28.3 ppm; EI-MS: 247 $[\mathbf{11C}]^+$, 217 $[\mathbf{11C}-CH_3O]^+$, 202 $[\mathbf{11C}-CH_3OCH_2]^+$, 188 $[\mathbf{11C}-CH_3OCH_2CH_2]^+$, 175 $[\mathbf{11C}-CH_3OCH_2CH_2N]^+$.

1A (Method A): Pyrocatechol (**A**; 2.84 mg, 0.026 mmol, 1 equiv), 4-amino-*N*,*N*-dimethylaniline (**1**; 3.50 mg, 0.025 mmol, 1 equiv), 2-formylphenylboronic acid (3.86 mg, 0.026 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.46$ (s, 1H, imine), 7.64 (d, $J = 7$ Hz, 1H, 6-iminophenylboronic ester), 7.55 (m, 2H, 3-iminophenylboronic ester + 5-iminophenylboronic ester), 7.38 (dt, $J = 7.5$ Hz, $J' = 1$ Hz, 1H, 4-iminophenylboronic ester), 7.23 (d, $J = 9$ Hz, 2H, aniline next to imine), 6.88 (m, 2H, catecholate), 6.78 (m, 4H, catecholate), 6.52 (d, $J = 9$ Hz, 2H, aniline next to NMe_2), 2.93 ppm (s, 6H, -N(CH$_3$)$_2$); ^{11}B NMR (641.85 MHz, 298 K) $CDCl_3$: $\delta = 15.0$ ppm; MeOD: $\delta = 13.6$ ppm.; ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 161.6$, 152.3, 150.8, 137.6, 133.9, 131.0, 129.7, 128.9, 126.6, 122.9, 119.4, 112.3, 110.3, 40.3 ppm; ES-MS: 372 $[\mathbf{1A}+MeO]^-$.

2A (Method A): Pyrocatechol (**A**; 2.65 mg, 0.024 mmol, 1 equiv), 4-methoxyaniline (**2**; 3.01 mg, 0.025 mmol, 1 equiv), 2-formylphenylboronic acid (3.61 mg, 0.024 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.50$ (s, 1H, imine), 7.67 (d, $J = 7$ Hz, 1H, 6-iminophenylboronic ester), 7.60 (m, 2H, 3-iminophenylboronic ester + 5-iminophenylboronic ester), 7.42 (dt, $J = 7.5$ Hz, $J' = 1$ Hz, 1H, 4-iminophenylboronic ester), 7.30 (d, $J = 9$ Hz, 2H, aniline next to imine), 6.84 (m, 2H, catecholate), 6.77 (m, 4H, aniline next to -OMe + catecholate), 3.76 ppm (s, 3H, -OCH$_3$); ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 165.1$, 160.3, 152.1, 137.3, 134.7, 134.0, 131.2, 129.1, 127.3, 123.4, 119.5, 114.9, 110.4, 55.6 ppm; EI-MS: 329 $[\mathbf{2A}]^+$, 314 $[\mathbf{2A}-CH3]^+$.

3A (Method A): Pyrocatechol (**A**; 2.33 mg, 0.021 mmol, 1 equiv), *p*-toluidine (**3**; 2.28 mg, 0.021 mmol, 1 equiv), 2-formylphenylboronic acid (3.18 mg, 0.021 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.53$ (s, 1H, imine), 7.68 (d, $J = 7$ Hz, 1H, 6-iminophenylboronic ester), 7.64 (d, $J = 7.5$ Hz, 1H, 3-iminophenylboronic ester), 7.60 (dt, $J = 7.5$ Hz, $J' = 1$ Hz, 1H, 5-iminophenylboronic ester), 7.42 (dt, $J = 7.5$ Hz, $J' = 1$ Hz, 1H, 4-iminophenylboronic ester), 7.25 (d, $J = 8$ Hz, 2H, aniline next to imine), 7.09 (d, $J = 8$ Hz, 2H, aniline next to -Me), 6.85 (m, 2H, catecholate), 6.75 (m, 2H, catecholate), 2.30 ppm (s, 3H, -CH$_3$); ^{11}B NMR (641.85 MHz, 298 K) $CDCl_3$: $\delta = 15.1$ ppm; MeOD: $\delta = 14.7$ ppm; ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 166.2$, 152.2, 139.6, 138.6, 137.3, 134.9, 131.3, 130.3, 129.1, 127.5, 121.9, 119.5, 110.3, 21.2 ppm. EI-MS: 313 $[\mathbf{3A}]^+$.

3B (Method A): 1,2-Ethanediol (**B**; 21.70 mg, 0.345 mmol, 1 equiv), *p*-toluidine (**3**; 37.46 mg, 0.345 mmol, 1 equiv), 2-formylphenylboronic acid (52.42 mg, 0.345 mmol, 1 equiv), and MeOH (4 mL). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.60$ (s, 1H, imine), 7.71 (dd, $J = 8$ Hz, 2H, 3-iminophenylboronic ester + 6-iminophenylboronic ester), 7.50 (t, $J = 7.5$ Hz, 1H, 5-iminophenylboronic ester), 7.41 (t, $J = 7.5$ Hz, 1H, 4-iminophenylboronic ester), 7.31 (d, $J = 8$ Hz, 2H, aniline nexte to imine), 7.23 (d, $J = 8$ Hz, 2H, aniline next to -Me), 4.15 (brs, 4H, -OCH_2CH_2O-), 2.40 ppm (s, 3H, -CH$_3$); ^{11}B NMR (641.85 MHz, 298 K) $CDCl_3$: $\delta = 22.9$ ppm; MeOD: $\delta = 14.7$ ppm; ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 163.1$, 139.4, 137.7, 132.7, 132.4, 130.1, 129.4, 127.7, 121.8, 65.6, 21.4 ppm; EI-MS: 265 $[\mathbf{3B}]^+$.

4A (Method A): Pyrocatechol (**A**; 2.80 mg, 0.025 mmol, 1 equiv), 4-(methylmercapto)aniline (**4**; 3.54 mg, 0.025 mmol, 1 equiv), 2-formylphenylboronic acid (3.81 mg, 0.025 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.55$ (s, 1H, imine), 7.63 (m, 3H, 3-iminophenylboronic ester + 5-iminophenylboronic ester + 6-iminophenylboronic ester), 7.42 (t, $J = 7.5$ Hz, 1H, 4-iminophenylboronic ester), 7.27 (d, overlapped signal with $CHCl_3$, 2H, aniline next to imine), 7.11 (d, $J = 8.5$ Hz, 2H, aniline next to -SMe), 6.86 (m, 2H, catecholate), 6.77 (m, 2H, catecholate), 2.43 ppm (s, 3H, -SCH_3); ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 165.8$, 152.0, 140.9, 137.8, 137.2, 134.9, 131.3, 129.2, 127.6, 126.7, 122.4, 119.6, 110.4, 15.4; EI-MS: 345 $[\mathbf{4A}]^+$, 330 $[\mathbf{4A}-CH_3]^+$.

5A (Method A): Pyrocatechol (**A**; 2.65 mg, 0.024 mmol, 1 equiv), 4-iodoaniline (**5**; 5.28 mg, 0.024 mmol, 1 equiv), 2-formylphenylboronic acid (3.61 mg, 0.024 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.55$ (s, 1H, imine), 7.65 (m, 5H, 3-iminophenylboronic ester + 5-iminophenylboronic ester + 6-iminophenylboronic ester + aniline nexte to imine), 7.43 (t, $J = 7$ Hz, 1H, 4-iminophenylboronic ester), 7.08 (d, $J = 8.5$ Hz, 2H, aniline next to -I), 6.86 (m, 2H, catecholate), 6.78 ppm (m, 2H, catecholate); ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 167.2$, 151.8, 140.7, 138.8, 137.0, 135.3, 131.4, 129.3, 128.0, 123.8, 120.8, 119.8, 110.5, 94.9 ppm; EI-MS: 425 $[\mathbf{5A}]^+$.

6A (Method A): Pyrocatechol (**A**; 2.65 mg, 0.024 mmol, 1 equiv), 4-chloroaniline (**6**; 3.06 mg, 0.024 mmol, 1 equiv), 2-formylphenylboronic acid (3.61 mg, 0.024 mmol, 1 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.58$ (s, 1H, imine), 7.70 (m, 3H, 3-iminophenylboronic ester + 5-iminophenylboronic ester + 6-iminophenylboronic ester), 7.48 (t, $J = 7.5$ Hz, 1H, 4-iminophenylboronic ester), 7.32, (m, 4H, aniline), 6.90 (m, 2H, catecholate), 6.81 ppm (m, 2H, catecholate);. ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 167.1$, 151.9, 139.6, 137.1, 135.3, 131.5, 129.9, 129.3, 127.9, 123.5, 119.8, 110.5 ppm. EI-MS: 333 $[\mathbf{6A}]^+$.

$\mathbf{11_2D}$ (Method B): Pentaerythritol (**D**; 3.20 mg, 0.023 mmol, 1 equiv), 2-methoxyethylamine (**11**; 3.54 mg, 0.047 mmol, 2 equiv), 2-formylphenylboronic acid (7.06 mg, 0.047 mmol, 2 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.37$ (s, 1H, imine), 7.69 (d, $J = 7$ Hz, 1H, 6-iminophenylboronic ester), 7.50 (d, $J = 7.5$ Hz, 1H, 3-iminophenylboronic ester), 7.45 (t, $J = 7.5$ Hz, 1H, 5-iminophenylboronic ester), 7.29 (t, $J = 7.5$ Hz, 1H, 4-iminophenylboronic ester), 4.09 (s, 4H, -OCH_2CCH_2O-), 3.93 (t, $J = 5$ Hz, 2H, -CH=N-CH_2CH$_2$OCH$_3$), 3.77 (t, $J = 5$ Hz, 2H, -CH=N-CH$_2$CH_2OCH$_3$), 3.39 ppm (s, 3H, -CH=N-CH$_2$CH$_2$OCH_3); ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): $\delta = 168.3$, 137.8, 132.8, 130.6, 127.9, 127.0, 70.5, 66.1 (two overlapping peaks), 59.1, 53.1 ppm; EI-MS: 478 $[\mathbf{11_2D}]^+$, 447 $[\mathbf{11_2D}-OCH_3]^+$, 443 $[\mathbf{11_2D}-CH_3OCH_2]^+$, 419 $[\mathbf{11_2D}-CH_3OCH_2CH_2]^+$.

$\mathbf{15A_2}$ (Method B): Pyrocatechol (**A**; 2.30 mg, 0.021 mmol, 2 equiv), bis(4-amino)diphenyl ether (**15**; 4.18 mg, 0.010 mmol, 1 equiv), 2-formylphenyl-

boronic acid (3.13 mg, 0.021 mmol, 2 equiv). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): $\delta = 8.52$ (s, 2H, imine), 7.69 (d, $J = 7$ Hz, 2H, 6-iminophenylboronic ester), 7.61 (m, 4H, 3-iminophenylboronic ester + 5-iminophenylboronic ester), 7.43 (dt, $J = 7.5$ Hz, $J' = 1$ Hz, 2H, 4-iminophenylboronic ester), 7.30 (d, $J = 9$ Hz, 4H, aniline next to the oxygen), 6.85 (m, 8H, aniline next to imine + catecholate), 6.74 ppm (m, 4H, catecholate); ^{13}C NMR (100.62 MHz, 298 K, $CDCl_3$): δ = 166.2, 157.2, 152.0, 137.2, 136.7, 135.1, 131.4, 129.2, 127.7, 123.8, 119.8, 119.7, 110.4 ppm; EI-MS: 612 $[\mathbf{15A_2}]^+$.

11_3E: Into a NMR tube with a Teflon screw-cap were added triscatechylene **E** (2.9 mg, 0.008 mmol), 2-methoxyethylamine (1.8 mg, 0.024 mmol), 2-formylphenylboronic acid (5.2 mg, 0.024 mmol), methanol (0.4 mL), and $[D_6]$DMSO (0.1 mL). After one night at room temperature, solvents were removed under dynamic vacuum and the residue was dissolved in $CDCl_3$. NMR spectroscopy indicated the clean formation of a single product. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): $\delta = 8.32$ (s, 3H, imine), 7.57 (d, $J = 7$ Hz, 3H, 6-iminophenylboronic ester), 7.49 (m, 6H, 3-iminophenylboronic ester + 5-iminophenylboronic ester), 7.32 (t, $J = 7$ Hz, $J' =$ 7.5 Hz, 3H, 4-iminophenylboronic ester), 6.88 (brs, 6H, catecholate), 4.85 (d, $J = 13.5$ Hz, 3H, -catecholate-CH_2-catecholate-), 3.50 (m, 15H, -catecholate-CH_2-catecholate- + -CH=N-CH_2CH$_2$OCH$_3$ + -CH=N-CH$_2$CH_2OCH$_3$), 3.31 ppm (brs, 9H, -CH=N-CH$_2$CH$_2$OCH_3); ^{13}C NMR (125.77 MHz, 298 K, $CDCl_3$): δ = 170.1, 150.9, 137.8, 134.0, 131.0, 130.7, 128.6, 126.7, 111.5, 69.5, 59.0, 49.3 (br), 37.2 ppm; APCI-MS ($CHCl_3$) = 880.4 $[\mathbf{11_3E}]^+$.

Macrocycle 16_2D_2: Into a NMR tube with a Teflon screw-cap were added pentaerythrytol (5.4 mg, 0.040 mmol), 1,4-diaminobenzene (4.3 mg, 0.040 mmol), 2-formylphenylboronic acid (11.9 mg, 0.080 mmol), and $[D_7]$DMF (0.35 mL). All starting materials dissolved within 1 h at 50 °C. After two days at this temperature, yellow crystals suitable for X-ray analysis had formed within the tube. NMR spectra of the supernatant solution or of the crystals suspended in THF and DMF showed mixtures of products. APCI-MS (THF/$CHCl_3$): 872.5 $[\mathbf{16_2D^2}]^+$.

Crystallographic data for 16_2D_2 ($C_{50}H_{44}B_4N_4O_8$) ; $M_r = 872.2$, monoclinic, $P\bar{1}$, $a = 9.9854(11)$, $b = 11.3648(11)$, $c = 11.7149(11)$ Å; $\alpha = 68.199(11)$, $\beta =$ 78.892(12), $\gamma = 65.704(11)°$; $V = 1123.8(2)$ Å^3; $Z = 1$, $\mu = 0.086$ mm^{-1}, $\rho_{calcd} = 1.289$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); 14696 reflections measured at 150 K on a STOE IPDS diffractometer, 5023 unique reflections of which 2616 with $|F_o| > 4\sigma(F_o)$. Data were corrected for Lorentz and polarization effects and for absorption (T_{min}, $T_{max} = 0.9837$, 0.9907). The structure was solved by direct methods (SIR97).[42] All calculations were performed with the XTAL system.[43] Full-matrix least-squares refinement based on F using weights of $1/(\sigma^2(F_o) + 0.0002(F_o^2))$ gave final values $R = 0.042$, $\omega R = 0.038$ and $S = 1.33(2)$ for 298 variables and 2751 contributing reflections. CCDC-653019 (**16_2D_2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Cage 17_3E_2: Into a NMR tube with a Teflon screw-cap were added cyclotricatechylene **E** (7.77 mg, 0.021 mmol), freshly distilled *m*-xylylenediamine (**17**; 4.04 mg, 0.030 mmol), 2-formylphenylboronic acid (8.88 mg, 0.060 mmol), and $[D_7]$DMF (0.7 mL) under argon. After one night at room temperature, proton NMR spectrum showed the clean formation of **17_3E_2**. ^{1}H NMR (500 MHz, 298 K, $[D_7]$DMF): $\delta = 8.56$ (s, 6H, imine), 7.63 (d, $J = 7$ Hz, 6H, 6-iminophenylboronic ester), 7.55 (m, 9H, 5 *m*-xylylenediimine + 3-iminophenylboronic ester), 7.41 (m, 15H, 4-iminophenylboronic ester, 5-iminophenylboronic ester + 2 *m*-xylylenediimine), 7.29 (d, $J = 7.5$ Hz, 6H, 4 *m*-xylylenediimine + 6 *m*-xylylenediimine), 7.06 (s, 12H, aromatic protons from cyclotricatechylene subcomponent), 4.97 (d, $J = 13$ Hz, 6H, aliphatic protons from cyclotricatechylene subcomponent), 4.21 (s, 12H, aliphatic protons from *m*-xylylenediamine subcomponent), 3.63 ppm (d, $J = 13.5$ Hz, aliphatic protons from cyclotricatechylene subcomponent); ^{13}C NMR (125.77 MHz, 298 K, $[D_7]$DMF): $\delta =$ 170.7, 151.9, 138.90, 134.9, 133.6, 133.5, 130.9, 130.7, 130.4, 128.8, 127.7, 111.1, 51.1, 37.1 ppm; MALDI-MS: 1716.63 $[C_{108}H_{78}B_6N_6O_{12}]^+$.

Preparation of 11A by amine substitution: Following Method A, compound **3A** (or compound **1A**) (0.030 mmol) was prepared in an NMR tube. Solvents were subsequently removed under dynamic vacuum; 2-methoxyethylamine (**11**; 2.27 mg, 0.030 mmol, 1 equiv) and $CDCl_3$ (0.35 mL) were then added. NMR spectra indicated the complete conversion of **1A** into **11A** and **1** (or **3**) following three hours at room temperature. No further evolution was observed following heating of the tube to 323 K during three days.

Preparation of 3A by diol substitution: Following Method A, compound **3B** (16.89 mg, 0.064 mmol) was prepared in an NMR tube. Solvents were subsequently removed under dynamic vacuum; catechol (**A**; 7.01 mg, 0.064 mmol, 1 equiv) and $CDCl_3$ (0.35 mL) were then added. NMR spectra indicated the complete conversion of **3B** into **3A** and **B** after one hour at room temperature. No further evolution was observed following heating of the tube to 323 K during three days.

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