Angewandte
Highlights

Lewis Acidic Cyclophanes

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Incorporation of Boron in the Walls of an “All-Carbon” Cyclophane: A Novel Approach to Lewis Acidic Macrocycles**

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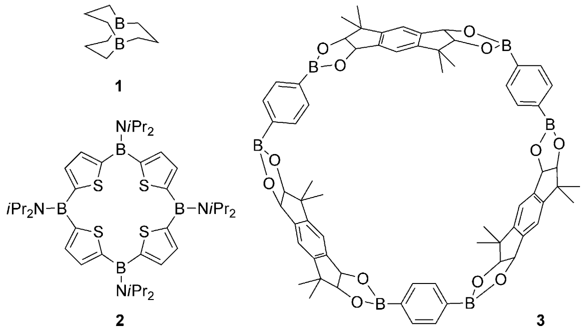
The incorporation of Lewis-acidic centers in macrocyclic structures is one of the most coveted synthetic targets for those interested in polyfunctional Lewis acids. While various motivations can be invoked, the desire to obtain charge-reverse analogues of well-known Lewis-basic macrocyclic ligands has prompted much of the existing efforts.[1] Original success in this line of research has come in the form of several organometallic mercury[2] and tin[3] macrocylces that have been used for the complexation of both anionic and neutral electron-rich species. A key “enabler” in this chemistry is undoubtedly the stability of Hg–C and Sn–C bonds, which facilitates all steps involved in the synthesis and isolation of the macrocyclic Lewis acids.

By contrast to the above organometallic macrocycles, organoboron macrocycles have remained extremely scarce, a situation that possibly reflects the inherent reactivity of these compounds toward water and oxygen. One of the earliest contributions in this field of research is a 1964 paper describing 1,5-diborabicyclo[3,3,3]undecane (**1**) as a product of the reaction of triallylborane with Et_3NBH_3 (Scheme 1).[4] Although the synthesis of this compound was never reproduced and its properties were not experimentally explored, this early account inspired many researchers, thereby leading to isolation of organoboron macrocycles, such as **2**[5] and **3**.[6] One of the common features of these existing systems is the use of stabilizing amino or alkoxy groups, which unfortunately limits, if not compromises, the Lewis acidity of the boron centers.

Another approach to electron-deficient hosts consists in the design of cyclophanes, the inner cavities of which are defined by π-acidic functionalities such as, for example, pyridinium units.[7] In an integrative approach that marries the field of polyfunctional Lewis acid and cyclophane chemistry, Chen and Jäkle have now reported the synthesis, electrochemical properties, and anion affinity of the first bora-cyclophane.[8] Realizing that the trigonal coordination geometry of an organoboron compound would be compatible with six-fold symmetry, these authors decided to target a hexameric structure with a boron atom at each corner. The macrocycle was skillfully “stitched” together by a series of rigorously controlled ligand-exchange reactions involving silylated and stannylated fluorene units and boron bromide reagents. The overall structure is kinetically stabilized through the use of the bulky 1,3,5-tri-*iso*-propyl-phenyl substituent, which caps each boron atom. The resulting bora-cyclophane (Scheme 2) displays a hexagonal ring structure and has been characterized by a combination of methods, thus leaving no doubts as to its identity. In addition to an aesthetically pleasing structure, this new compound also displays an intense blue fluorescence.



Scheme 1. Early examples of boron-containing cyclic and macrocyclic structures.

The electron-deficient character of this hexafunctional Lewis acid is enhanced by the equal contribution of the vacant p orbitals of all six boron atoms to the lowest unoccupied molecular orbital (LUMO). Owing to this evenly distributed LUMO, the compound undergoes an apparent two-electron reduction process (redox potential $E_{1/2} = -2.06$ V vs. ferrocene/ferrocenium (Fc/Fc^+)), which occurs at significantly more anodic potential than that measured for the one-electron reduction of the mononuclear analogue **5** ($E_{1/2} = -2.35$ vs. Fc/Fc^+).[9] Because of charge confinement, further reduction to the hexaanion becomes increasingly difficult as illustrated by the observation of well-defined reduction waves in the cyclic voltammogram of **4**.[8] Some of these features are

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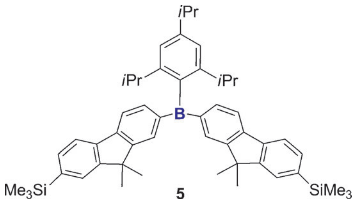

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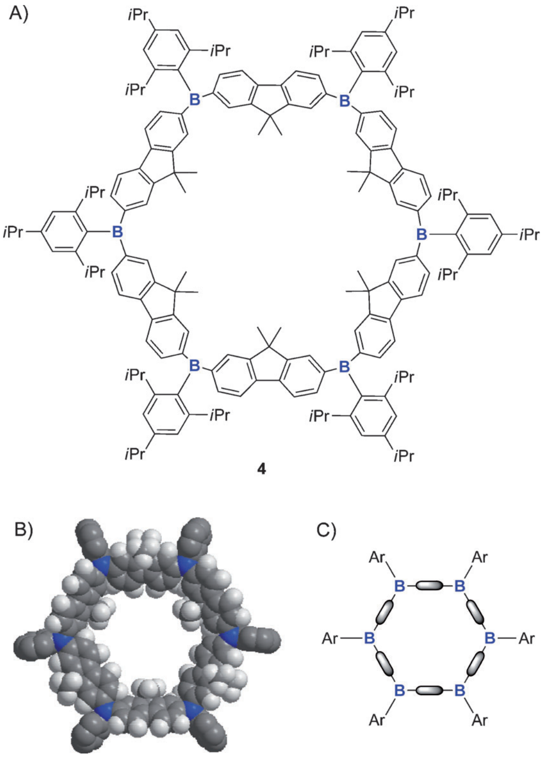
reminiscent of the behavior of C_{60}, which can also become charged with six electrons.[10] The accessible two-electron reduction potential of **4** combined with the circular delocalization of charge suggests that such bora-cyclophanes may serve as electron acceptors in organic light-harvesting materials.

The overall charge of this molecule can also be altered by coordination of anions to the boron centers. Despite the presence of bulky substituents and negative cooperative effects between each of the anion binding sites, **4** can be converted into the corresponding hexaborate species ($[\mathbf{4}\text{-}X_6]^{6-}$; X = F, CN; Scheme 3), which has been confirmed by solution studies. In the case of the cyanide complex, the hexacyanoborate anion was observed by electrospray mass spectrometry as an aggregate with tetrabutyl ammonium counter ions. Because anion coordination changes the electronic structure of the host, the formation of the fluoride and cyanide complexes is accompanied by a turn-off of the blue fluorescence of the cyclophane, thus providing a response that could be monitored for sensing purposes. An interesting facet of this photophysical response is the fact that binding of the first anion induces a nonproportional response showing a larger than expected quenching of the fluorescence intensity. Hence, this cyclophane should not be taken as a simple collection of six independent boron-centered chromophores. Instead, the observed amplification[11] suggests extensive communication between each unit, with a single anion binding event disrupting the electronic structure of the whole molecule. Finally, anion binding provides a simple way for converting an electron-poor host (**4**) into an electron-rich macrocyclic species ($[\mathbf{4}\text{-}X_6]^{6-}$). Because of the accumulation of negative charges, the latter should display a large affinity for cationic guest molecules. This facile switching of the macrocycle's character may provide a strategy for the triggered release of supramolecularly encapsulated guests through anion coordination/decoordination at the boron centers.



Scheme 2. A) Line drawings showing the bora-cyclophane **4.** B) Arbitrary space-filling representation of **4** (H atoms and *i*Pr groups of the 1,3,5-(*i*Pr)C_6H_2 groups omitted for clarity). C) Simplified representation of **4**.

In summary, this brief account highlights the synthesis of the first all-organoelement bora-cyclophane (**4**). Because of the absence of donor substituents, the boron centers of this derivative retain their inherent electron deficiency. Although the presence of bulky substituents significantly dampens the Lewis acidity of the boron centers, the bora-cyclophane displays appealing electrochemical properties and also binds small nucleophilic anions. These unique characteristics suggest that this class of compounds may find applications in organic light-harvesting materials and host–guest chemistry.

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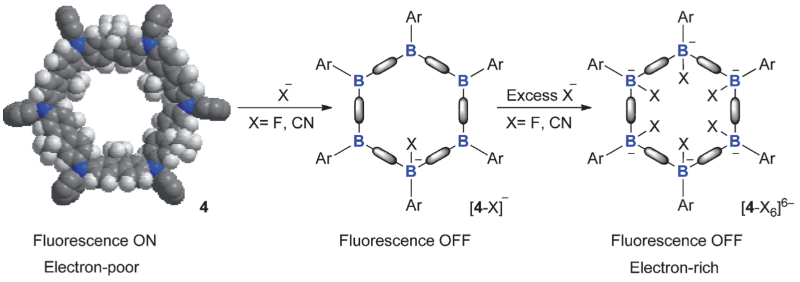

Scheme 3. Anion complexation by **4**.

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