Heteroelement Analogues of Benzoxaborole

Subjects: Chemistry, Organic | Chemistry, Medicinal | Biochemistry & Molecular Biology

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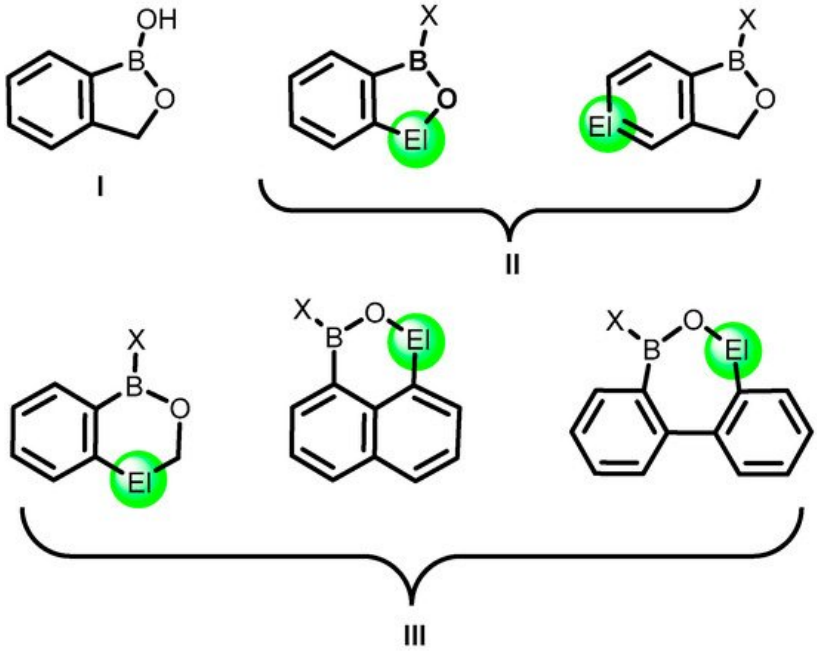
Heteroelement analogues of benzoxaboroles constitute an interesting class of boracyclic compounds and may offer the opportunity for various applications while retaining high stability arising from the presence of a strong B-O bond in the ring structure. The replacement of a carbon atom in the boracycle or an adjacent benzene ring with a heteroatom may result in a significant change of structural behaviour. Moreover, physicochemical properties, including solubility, lipophilicity, hydrolytic stability, boron Lewis acidity, and others, can be modified. The aim of this review is to highlight several emerging groups of boracyclic systems which comprise various heteroelement atoms such as another boron, silicon, tin, nitrogen, phosphorus, and iodine. The information on synthesis and properties of such systems is complemented by presentation of their practical potential encompassing especially organic synthesis and catalysis as as medicinal chemistry.

Keywords: boron ; heterocycles ; benzoxaborole ; Lewis acidity ; antimicrobial activity

1. Introduction

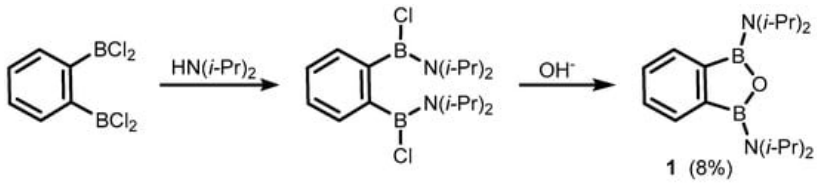
Recently, benzoxaboroles (Scheme 1, structure I) constitute one of the leading groups of organoboron compounds. This is mainly due to their promising biological properties, which have been exploited for the past 20 years in medicinal and bioanalytical chemistry [1][2][3][4]. Benzoxaboroles are strongly predestined for such applications due to their improved thermodynamic stability, resulting from the presence of a strong covalent boron-oxygen bond. Overall, they are rather stable to air and water and, in general, do not undergo rapid degradation under in vivo conditions. Therefore, heteroelement analogues of benzoxaboroles (Scheme 1, general structures II) constitute an interesting alternative and may offer the opportunity for various novel applications while retaining high stability arising from the presence of a strong B-O bond in the ring structure. The replacement of a carbon atom in the boracycle or an adjacent benzene ring with a different atom may result in a significant change of structural behaviour, e.g., a tendency to aggregation involving dative interactions of a heteroatom with the boron atom. Moreover, the presence of a heteroatom may result in modified physicochemical properties, including solubility, lipophilicity, hydrolytic stability, boron Lewis acidity, and others. The aim of this review is to highlight several emerging groups of boracyclic systems which comprise various heteroelement atoms such as another boron, silicon, tin, nitrogen, phosphorus, and iodine. Some ring expanded analogues (Scheme 1, general structures III), including compounds based on naphthalene and biphenyl-scaffold, are also included. Overall, the review is divided into sections based on type of heteroelement and heterocyclic ring as the primary and secondary classification criteria, respectively. The synthesis and physicochemical properties as well as applications of compounds of interest are consecutively presented in each section.



Scheme 1. Structures of benzoxaborole, I; its heteroelement congeners, II; and related ring-expanded systems, III. El stands for heteroatom or heteroatom-based fragment.

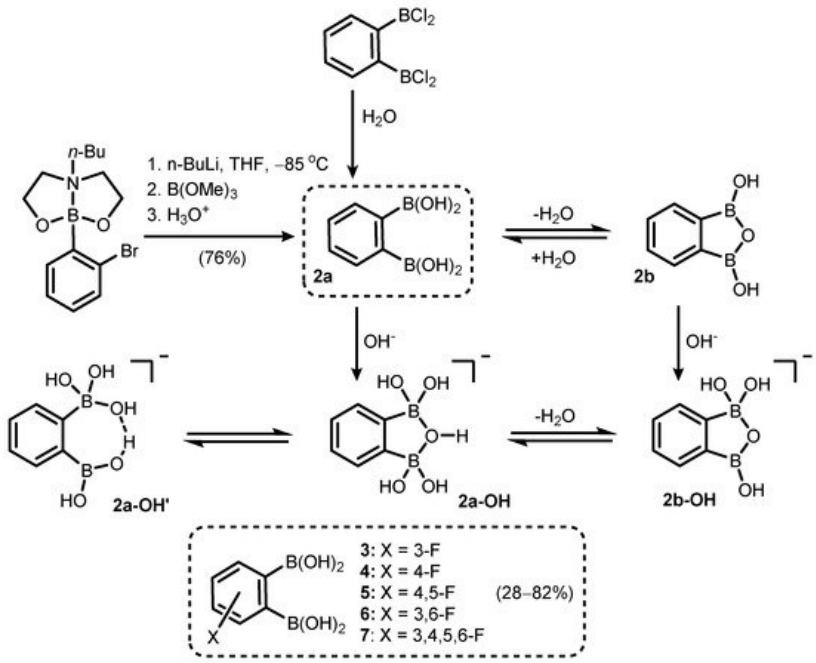
2. Benzoxadiboroles and Related Ring-Expanded Systems Comprising B-O-B Linkage

The formal substitution of the C3 carbon atom in benzoxaborole results in a benzoxadiborole framework featuring a B-O-B linkage within the five-membered ring. An example of such a well-defined boracyclic system (**1**) was reported by Kaufmann et al. in 1994 [5]. It was isolated in a low yield by aminolysis of 1,2-bis(dichloroboryl)benzene [6] followed by ring closure with hydroxide anion (Scheme 2).



Scheme 2. Synthesis of 1,3-bis(diisopropylamino)-1,3-dihydro-2,1,3-benzooxadiborole.

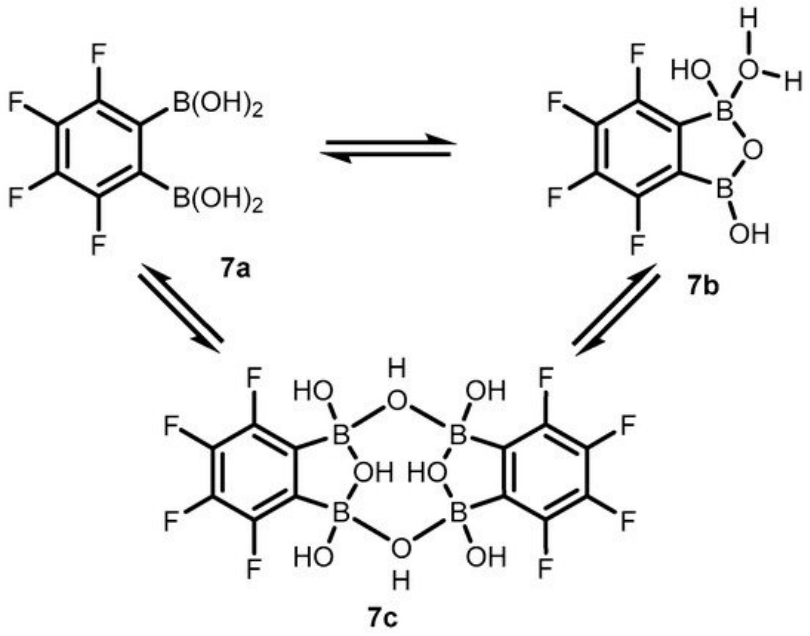
Phenylene-1,2-diboronic acid (**2a**) was found to be a useful precursor of benzooxadiborole derivatives (Scheme 3). It can be readily obtained by careful hydrolysis of 1,2-bis(dichloroboryl)benzene [6] or a Br/Li exchange reaction of 2-(2-bromophenyl)butyl[1,3,6,2]dioxazaborocan, followed by quenching the aryllithium intermediate with $B(OMe)_3$ (Scheme 3) [7]. Subsequent studies on the structural behaviour of **2** and its fluorinated derivatives (**3**–**7**) revealed that those compounds tend to equilibrate in solution with respective cyclic semi-anhydrides, i.e., 1,3-dihydroxy-1,3-dihydro-2,1,3-benzoxadiboroles (Scheme 3). ^{1}H and ^{13}C NMR analyses in various dry deuterated solvents (acetone, THF, DMSO) revealed that cyclization (**2a**→**2b**) occurs to a significant extent. Moreover, the ^{11}B NMR spectrum showed that boron atoms (**2**) are slightly deshielded (by ca. 4 ppm) with respect to free acid. However, the B-O-B linkage is readily cleaved upon the addition of water (or D_2O), shifting the equilibrium towards free acid (**2b**).



Scheme 3. Synthesis of phenylene-1,2-diboronic acid (**2a**). Cyclization and acid-base equilibria involving **2a** and 1,3-dihydroxybenzoxadiborole (**2b**).

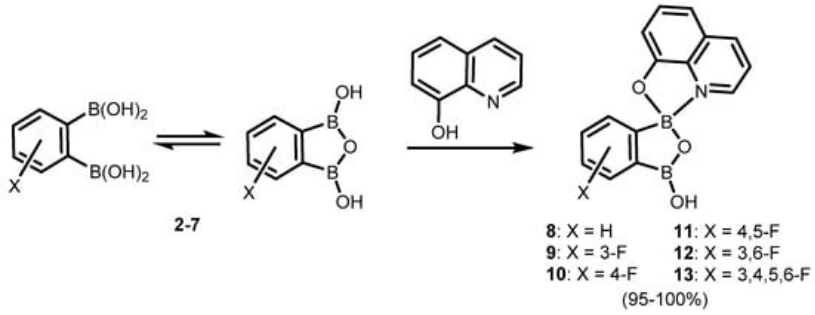
The formation of 1,3-dihydroxybenzoxadiborole scaffold (**2b**) (Scheme 3) clearly accounts for the apparent stronger acidity (pK_a = 6.0) of the entire equilibrium system compared to related acyclic meta- and para-substituted phenylenediboronic acids [8][9]. Theoretical (DFT B3LYP) studies indicate that the relative stabilization the anionic form (**2b-OH**) is important in this respect, although the persistence of its hydrated forms, i.e., a cyclic species (**2a-OH**) with a bridging hydroxyl anion bound simultaneously by two boronic groups in a bidentate fashion and an unsymmetrical form (**2a-OH'**), stabilized by charge-assisted intramolecular H-bond, should also be taken into account.

Subsequent studies revealed that 3,4,5,6-tetrafluorophenylene-1,2-diboronic acid **7** shows a stronger tendency to intramolecular cyclization. X-ray diffraction analysis confirmed the formation of perfluorinated benzoxadiborole (**7b**), complexed with water molecules (Scheme 4) [8]. Interestingly, a unique dimeric form of **7c** was also obtained by crystallization in toluene. The molecule consists of two benzoxadiborole frameworks fused by means of two B-OH-B bridges and additionally stabilized by π-π interactions of aromatic rings, resulting in a general chair-type conformation. Overall, the impact of perfluorination results in the strong acidity enhancement of **7** compared to **2**, leading to an apparent pK_a of 3.0, which is among the lowest figures for boronic acids and related species.

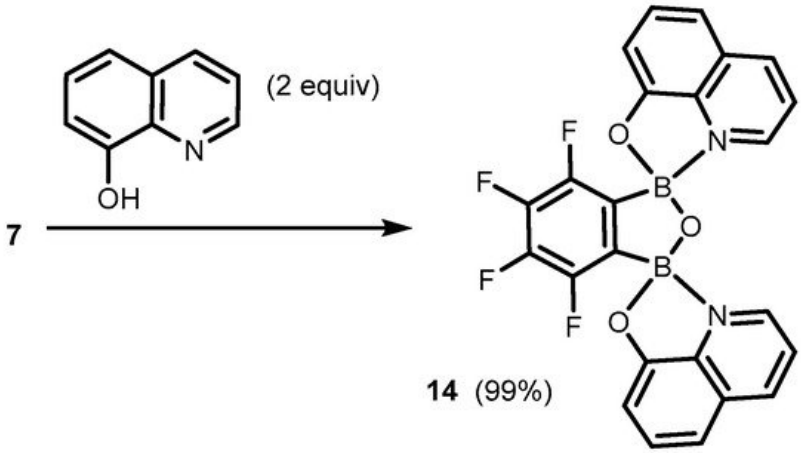


Scheme 4. Structural diversity of 3,4,5,6-tetrafluorophenylene-1,2-diboronic acid (**7**) involving the standard open form (**7a**), the benzoxadiborole tautomer (**7b**) and the cyclic dimer (**7c**).

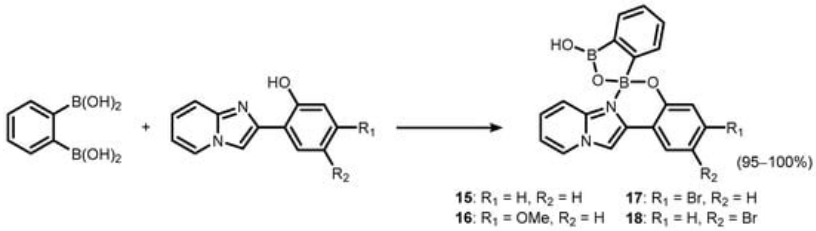
It was found that the benzoxadiborole scaffold is strongly stabilized upon treatment with -8-hydroxyquinoline (Scheme 5) [10]. The reactions of **2a/2b** and its fluorinated derivatives **3**–**7** afforded respective chelate complexes **8**–**13**, both in solution and under mechanochemical conditions. The most Lewis acidic **7** also bound readily two 8-oxyquinolinato ligands, yielding bis(chelate) (**14**) (Scheme 6) [10]. All of the obtained complexes exhibit green luminescence in acetonitrile solution (λ_{em} = ca. 525 nm, Φ = 13–15%), resembling other organoboron 8-oxyquinolinato complexes. Interestingly, it is blue-shifted in solid state (λ_{em} = ca. 500 nm), which was ascribed to the effect of H-bonding and other polar interactions of discrete molecules in the crystal lattice. Importantly, the electroluminescence properties of complexes **8** and **14** was proved by testing OLEDs containing those compounds as emitters [10]. Later on, complex **8** became the subject of in-depth structural characterization, which included interesting solvatomorphic behaviour [11] as well as high resolution single-crystal X-ray diffraction electron density studies performed for the first time in the case of a luminescent oxyquinolinato organoboron complex [12]. Furthermore, **2** was also employed for the synthesis of a series of luminescent (*O*,*N*)-chelate complexes (**15**–**18**) with 2-(imidazo[1,2-a]pyridin-2-yl)phenol ligands (Scheme 7) [13]. The products were also characterized by single crystal X-ray diffraction, which revealed formation of H-bonded dimers in the solid state.



Scheme 5. Synthesis of benzoxadiborole 8-oxyquinolinato complexes **8**–**13**.

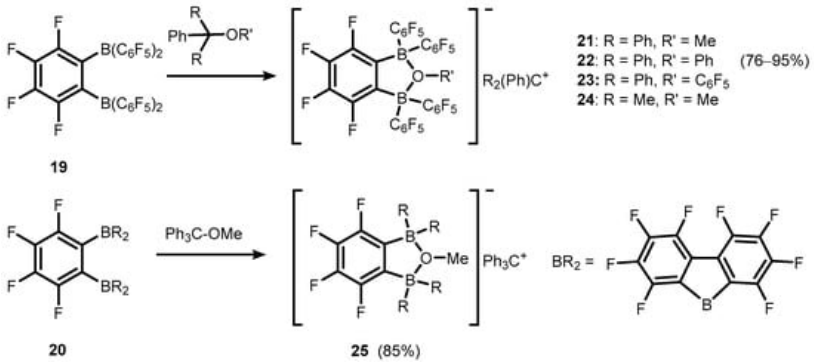


Scheme 6. Synthesis of benzoxadiborole bis(8-oxyquinolinato) complex **14**.

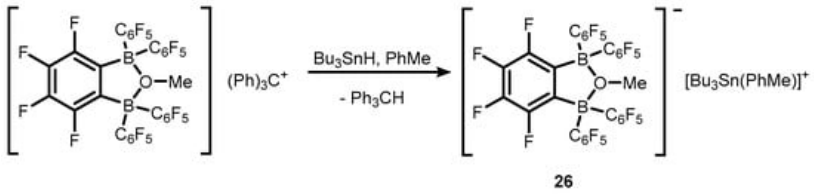


Scheme 7. Synthesis of benzoxadiborole (*O*,*N*)-chelate complexes **15**–**18** with 2-(imidazo[1,2-a]pyridin-2-yl)phenol.

Transformations of strong bidentate Lewis acids of a general formula *o*-C6F4(BR2)2, R = C_6F_5 (**19**), and BR_2 = $BC_{12}F_8$ (**20**) gave rise to various anionic or neutral boracyclic species structurally closely related to **7b**/**7c** (Scheme 8) [14][15][16][17]. However, it should be noted that most of them are formed, at least in a formal sense, by means of dative O→B interactions. Specifically, weakly-coordinating borate anions *o*-C6F4[B(C_6F_5)2]2(*μ*-OR), R = Me, Ph, C_6F_5, and C6F4[$BC_{12}F_8$]2(*μ*-OMe) were employed for stabilization of selected tertiary carbocations in respective ion-pair compounds (**21**–**24** and **25**, respectively) (Scheme 8) [15][16][17][18]. It was found that trityl salts (**21**–**23**) are effective co-catalysts of ethylene polymerization due to activation of dimethyl zirconocene (Cp_2ZrMe_2), resulting in corresponding products with Cp_2ZrMe^+ cation [15][18]. Compound **21** was also used for generation of stannylium cationic species **26** (Scheme 9) [19].

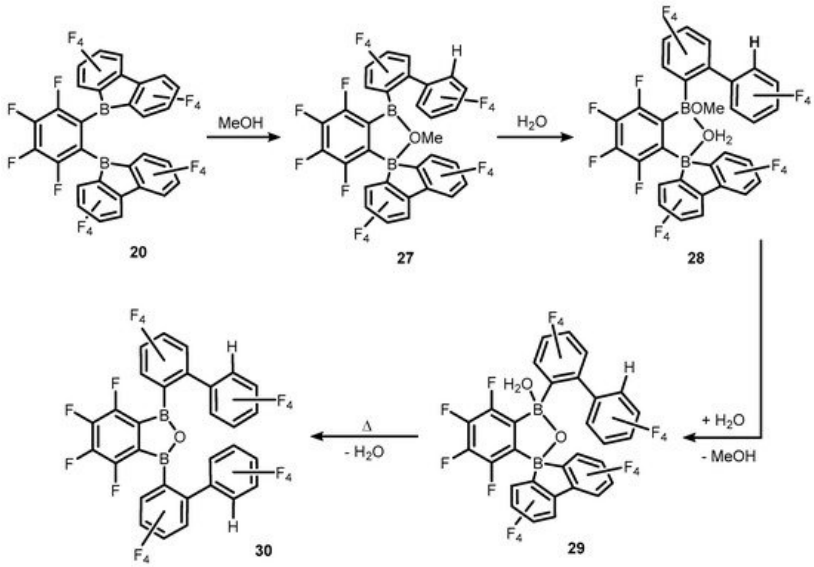


Scheme 8. Synthesis of ion-pair compounds **21**–**25**, comprising tertiary carbocations and weakly-coordinating anions based on perfluorinated benzoxadiborole backbones.



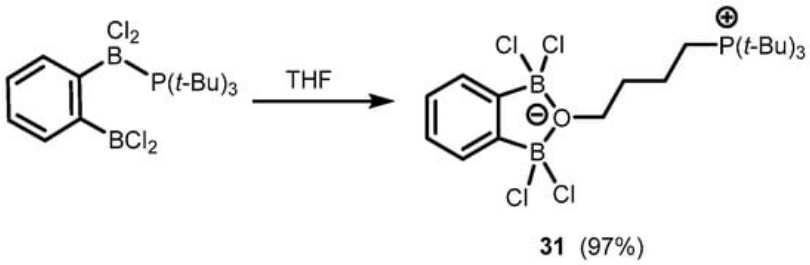
Scheme 9. Synthesis of stannylium cationic species **26**.

The analogous oxonium salt with $(Et_2O)_2H^+$ counterion was also obtained [19]. Similarly, related Bronsted acids based on solvated protons were generated from reactions of **19**–**20** with an excess of protic reagents (MeOH, H_2O) (Scheme 10) [20]. It should be noted that such species are generally prone to protolytic cleavage of B-C, which results in fragmentation of a boracyclic anions derived from **19**. On the other hand, controlled treatment of **20** with MeOH/H_2O gives rise to various neutral species such as cyclic borinic ester (**27**) obtained upon protonolysis of one B-C bond in the borafluorene ligand, the unique system (**28**) with water molecule bridging two boron centres, water-coordinated borinic acid (**29**) as well as the benzoxadiborole (**30**) arising from the cleavage of another B-C bond. The molecular structures of compounds **27**–**30** were determined by X-ray diffraction. The studies on the reactivity of **19**–**20** towards water were directly connected to their use as potent initiators of isobutene polymerization. They were aimed at shedding light on the plausible role of dissolved water as a chain transfer agent in polymerizations involving **19**–**20** that give rise to weakly-coordinating counteranions. It was suggested that species featuring bridging water molecule such as compound **28** are active as a strong Brønsted acid that is able to protonate isobutene which initiates the polymer chain growth [20].



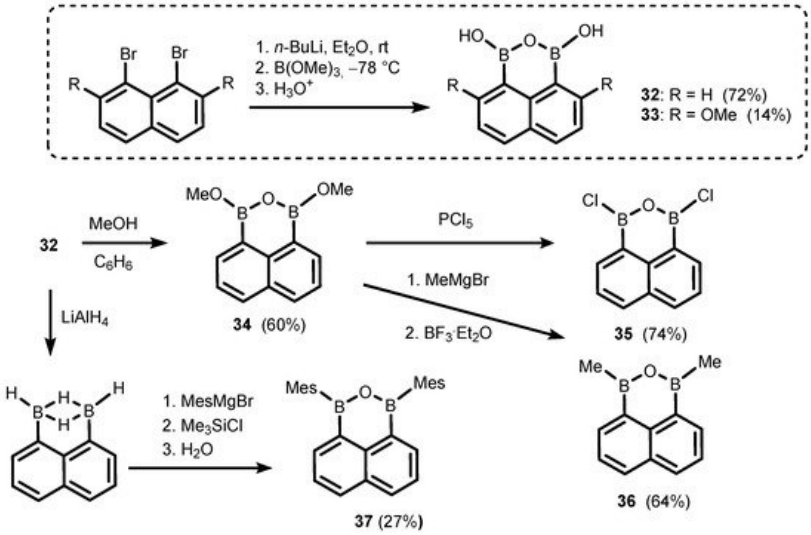
Scheme 10. Transformations of **20** to various boracyclic systems (**27**–**30**) upon interactions with MeOH and H_2O.

In addition, one can also mention herein the synthesis of a zwitterionic system (**31**) based on an anionic benzoxadiborole framework with a C_4-chain attached to an oxygen atom and decorated with a cationic phosphonium end group. This was obtained by the ring opening of the THF molecule due to interaction with a Frustrated Lewis Pair system composed of 1,2-bis(dichloroboryl)benzene and tris(*tert*-butyl)phosphine (Scheme 11) [21].



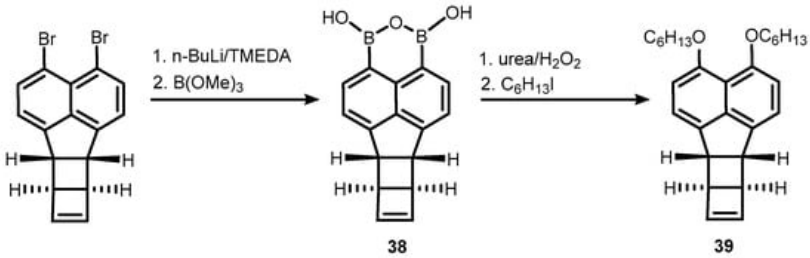
Scheme 11. Synthesis of a zwitterionic system **31** based on an anionic benzoxadiborole framework.

The ring-expanded benzoxadiborole analogues are based on naphthalene and biphenyl scaffolds. Thus, 1,3-dihydroxy-1*H*,3*H*-naphth[l,8-*cd*][l,2,6]oxadiborin (**32**) (Scheme 12) is easily accessible by diboronation of 1,8-dilithionaphthalene with $B(OMe)_3$ [22][23][24]; 4,9-Dimethoxy derivative (**33**) was obtained analogously and characterized by single-crystal X-ray diffraction [25]. Compound **32** was successfully used as a coupling partner in selected Suzuki–Miayura cross-coupling reactions, resulting in the formation of new aryl-aryl bonds [26][27][28]. Thus, its behaviour seems to be rather typical of arylboronic acids and their derivatives. However, unlike benzoxadiboroles, the B-O-B linkage in **32** seems to be rather stable as there are no data which might indicate that a reversible hydrolysis to naphthalene-1,8-diboronic acid occurs to any appreciable extent. Compound **32** was used as a starting material for synthesis of a few 1*H*,3*H*-naphth[l,8-*cd*][l,2,6]oxadiborin derivatives (**34**–**37**) where hydroxyl groups were replaced with OMe, Cl, Me [23], or mesityl (Mes) substituents [24], respectively.



Scheme 12. Synthesis of 1,3-dihydroxy-1*H*,3*H*-naphth[l,8-*cd*][l,2,6]oxadiborins (**32**–**33**) and conversion of **32** to **34**–**37**.

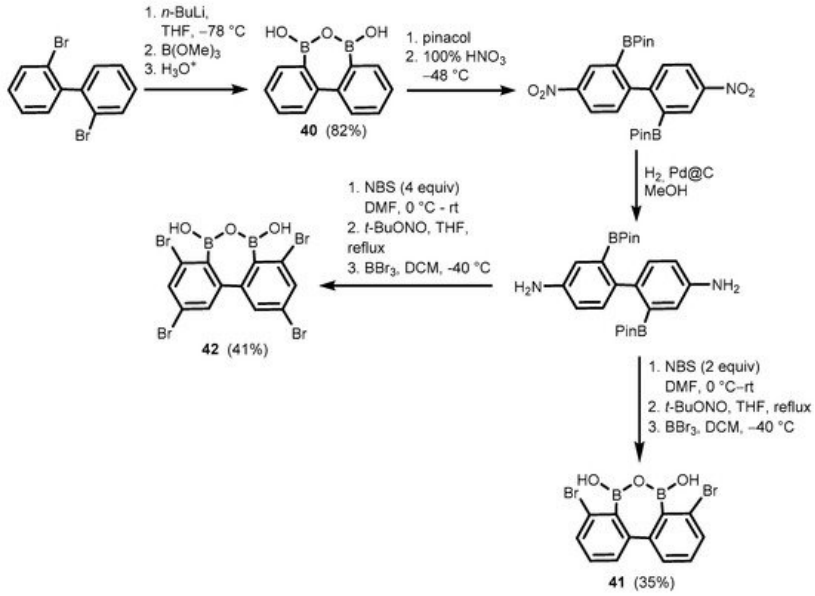
Very recently, a structurally extended analogue of **32** based on bicyclohexene-*peri*-naphthalene framework **38** was obtained using an analogous protocol involving bromine-lithium exchange in an appropriate dibromide, followed by boronation. It should be stressed that the system features a significant ring strain arising from the presence of two C4 and one C5-ring fused with the naphthalene core. Nevertheless, **38** was used successfully for the synthesis of peri-substituted bis(hexyl ether) (**39**)via oxidation of B-C bonds followed by alkylation (Scheme 13) [29].



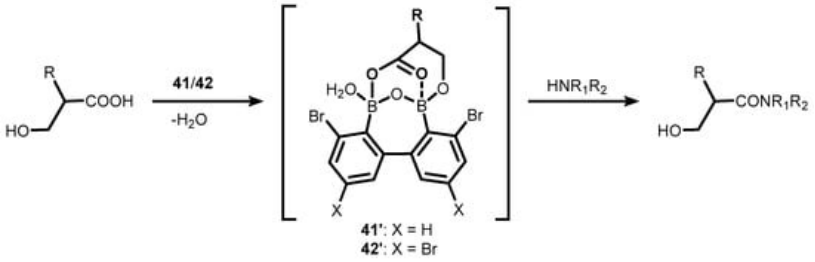
Scheme 13. Synthesis and transformation of a boracyclic system (**38**) featuring B-O-B linkage attached to bicyclohexene-peri-naphthalene scaffold.

Related oxadiborepins, i.e., 7-membered boracyclic systems comprising B-O-B linkage and 2,2′-biphenyl core, were also obtained [30][31][32]. It should be noted that the plausible equilibrium between biphenyl-2,2′-diboronic acid and its cyclic semi-anhydride (**40**) has not been studied to date, although its synthesis was reported already in 2002 [30], followed by crystallographic determination of **38** in 2011 [31]. Compounds **41**–**42** were obtained in a multistep protocol starting with

2,2′-dibromobiphenyl (Scheme 14). Remarkably, **41**–**42** were reported as efficient catalysts of dehydrative amidation of carboxylic acids with amine substrates. Initially, they were employed for efficient preparation of various α- and β-hydroxy substituted amides [32] but thereafter also proved effective in catalyzing the formation of Weinreb amides [33][34] as well as various oligopeptides [35]. In the former case, the proposed mechanism of the catalytic process involves the cooperation of the two boron atoms in **41**–**42**, which enables the formation of a cyclic mixed anhydride with carboxylic acid molecule, as evidenced by the ESI MS spectrum; this is followed by an attack of amine on the activated carbonyl group (Scheme 15) [32]. It should be noted that the performance of **42** is impressive, as evidenced by low catalyst loading (even a 0.01 mol% turnover number (TON) parameter up to 7500).

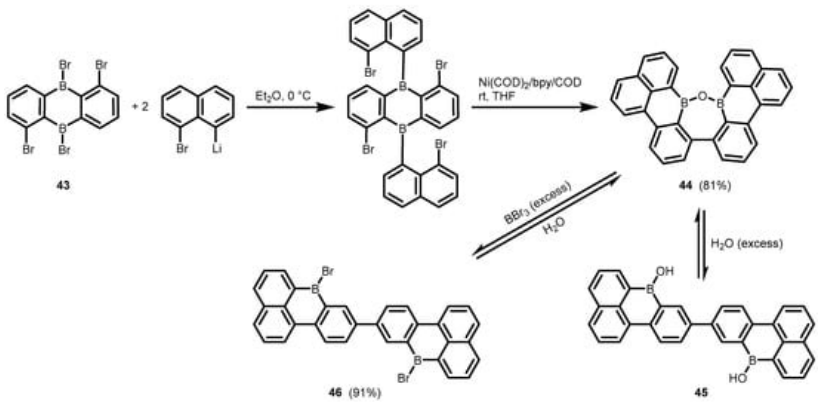


Scheme 14. Synthesis of oxadiborepins **40**–**42**.



Scheme 15. Direct amidation of β-hydroxy substituted carboxylic acids with amines in the presence of bromo-substituted oxadiborepins **41**–**42**.

One can also mention the unexpected synthesis of the fused polycyclic oxadiborepin (**44**) from the diboraanthracene precusor (**43**) which involved double arylation with 8-bromo-1-naphthyllithium followed by successful debromination/C–C coupling using $Ni(COD)_2$/bpycatalyst (Scheme 16) [36]. The formation of a third C–C bond and the cleavage of two B–C bonds was observed when THF was used as the solvent. The ^1H NMR studies on the structural behaviour of **44** revealed that it exists in equilibrium with the respective diborinic acid (**45**) upon the addition of water, whereas complete conversion to the dibromo derivative (**46**) occurs upon heating with an excess of BBr_3. Compound **46** is readily reconverted back to **44** upon the addition of water.



Scheme 16. Synthesis and cleavage of the fused polycyclic oxadiborepin **44**.

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