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Complete List of Authors:	Krempner, Clemens; Texas Tech University, Department of Chemistry and Biochemistry Manankandayalage, Chamila; Texas Tech University, Department of Chemistry & Biochemistry Unruh, Daniel; Texas Tech University, Chemistry and Biochemistry

ARTICLE

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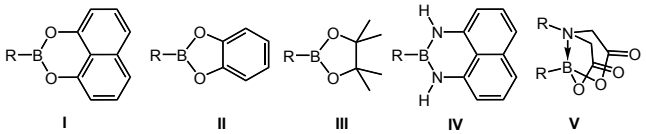
Chamila P. Manankandayalage, Daniel K. Unruh and Clemens Krempner *

The 1,8-naphthalenediolate [1,8-$O_2C_{10}H_8$] supported boronic and boric acid esters of general formula X-B(1,8-$O_2C_{10}H_8$), where X = C_6H_5 (**1a**), C_6F_5 (**2a**), 3,4,5-F_3-C_6H_2 (**3a**), 2,4,6-F_3-C_6H_2 (**4a**), 2,6-F_2-C_6H_3 (**5a**), 2,6-Cl_2-C_6H_2 (**6a**), 2,4,6-Me_3-C_6H_2 (**7a**), 2,6-$(MeO)_2$-C_6H_2 (**8a**), Bu^n (**9a**), MeO (**10a**), OH (**11a**) and Cl (**13a**), were synthesized, NMR spectroscopically characterized, and the solid-state structures of **1a**-**5a**, **8a** and **10a** determined by X-ray crystallography. The acceptor numbers of **1a**-**7a** and **13a** were determined and found to be similar to their catecholate analogues, R-BCat, indicating similar Lewis acidities of these two classes of boronic acid esters. The reaction of $B_2(NMe_2)_4$ with 1,8-naphthalenediol, followed by addtion of HCl furnished the diboronic acid ester $B_2(1,8\text{-}O_2C_{10}H_8)_4$ (**16a**) in ca. 70% yield. Cl-B(1,8-$O_2C_{10}H_8$) (**13a**) was shown to smoothly react with O=PEt_3, DMAP, 1,10-phenanthroline and 2,2'-bipyridine, resp., to give the boronium salts [$(Et_3P{=}O)_2$B(1,8-$O_2C_{10}H_8$)]Cl (**21a**), [$(DMAP)_2$B(1,8-$O_2C_{10}H_8$)]Cl (**22a**), [(2,2'-bipyridine)B(1,8-$O_2C_{10}H_8$)]Cl (**23a**) and [(1,10-phenanthroline)B(1,8-$O_2C_{10}H_8$)]Cl (**24a**), which were characterized by NMR spectroscopy and X-ray crystallography.

Introduction

The last three decades have witnessed the "evolution" of boronic acid ester from ordinary organo element compounds to working horses in organic and organometallic chemistry and catalysis.[1] The seemingly never-ending interest in these types of compounds appears to be fuelled by the high efficiency and broad applicability of the Suzuki-Miyaura coupling [2], specifically in the synthesis of pharmaceutical and agrochemical intermediates and natural products.[3-7] Arguably, pinacol boronic acid esters (**III**), 1,8-diaminonaphthyl boronic acid amides (**IV**) [8] and MIDA-boronates (**V**) [9] (MIDA = N-**m**ethyl-**i**mino**d**iacetic **a**cid) are the most frequently employed reagents in coupling chemistry primarily due to their thermal robustness and hydrolytic stability allowing them to be purified by column chromatography under benchtop conditions (Scheme 1).



Scheme 1. Selected organoboron esters and amides.

However, these undoubtedly favourable properties are at the expense of Lewis acidity of the electron-deficient boron centre limiting the ability of these species to form stable Lewis acid-base adducts for the formation of supramolecular assemblies [10] or to function as active Lewis acid catalysts in organic transformations.[11] Catechol boronic acid esters (**II**), on the other hand, are relatively strong Lewis acids owing to decreased oxygen to boron p-donation resulting from ring strain and competing conjugation with the phenyl ring.[1b] For similar reasons, however, they are more prone to nucleophilic attack at the central boron for example by water, and therefore rapidly hydrolyse when used in combination with "wet" solvents.

We envisioned that boronic acid esters derived from the 1.8-naphthalenediolate scaffold (**I**) should be of similar Lewis acidity as their catechol analogues (**II**) but more thermally robust and less sensitive to hydrolysis due to the larger size of the six-membered dioxaborinane ring. However, apart from Noeth's [12] disclosure of the synthesis of hydroborane (**I**) (R = H), which underwent rhodium catalysed hydroboration of cyclopentene ca. 25 times faster than catechol borane (**II**) (R = H), less is known about these boron compounds.[12-15] Therefore, we wish to report the synthesis, structures and chemical properties of a range of 1,8-naphthalenediolate supported boronic and boric acid esters as well as boronium salts.

Results and Discussion

We initially studied the acid-ester equilibrium of phenyl boronic acid with 1,8-naphthalenediol (1:1 molar ratio) at room temperature in $CDCl_3$ as solvent, which was not pre-dried (Scheme 2). ^{1}H NMR spectroscopic analyses of the reaction mixture revealed rapid and quantitative formation of the boronic acid ester **1a**, confirming the relative stability of **1a** towards hydrolysis in the presence of small amounts of water. To compare the thermodynamic stability of **1a** with those of the

[a] *Department of Chemistry and Biochemistry, Texas Tech University, Memorial Dr. & Boston, Lubbock, TX, 79409, USA. Fax: 806-742-1289; Tel: 806-834-3507; E-mail: clemens.krempner@ttu.edu*

† Footnotes relating to the title and/or authors should appear here.

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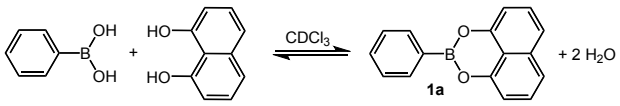
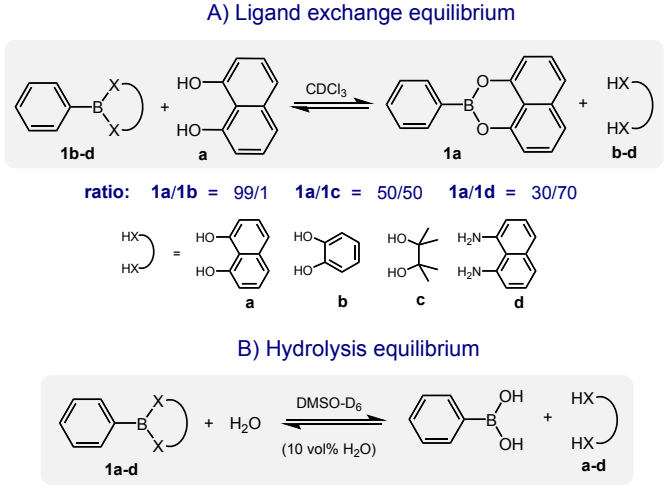
phenyl boronic acid esters **1b**-**d**, ligand exchange experiments were undertaken.



Scheme 2. Reaction of 1,8-naphthalenediol with phenyl boronic acid.

Equimolar amounts of 1,8-naphthalenediol were treated with **1b**-**d**, resp., in $CDCl_3$ as solvent (Figure 1A), and the resulting mixtures analysed by ^1H NMR spectroscopy after reaching equilibrium. Upon adding 1,8-naphthalenediol, the catechol ester **1b** within minutes quantitatively converted into **1a** at room temperature confirming our hypothesis that owing to its lower ring strain **1a** is thermodynamically significantly more stable than **1b**. In case of the bulkier pinacol ester **1c**, heating at 50°C overnight was required to reach equilibrium resulting in the formation of 50% **1c** and 50% **1a**. In contrast, several days of heating 50°C were required to equilibrate a $CDCl_3$ solution of **1d** and 1,8-naphthalenediol to a mixture of **1a** and **1d** in a 30/70 ratio. Note that treating ester **1a** with the corresponding diols **b**-**d**, resp., in $CDCl_3$ as solvent gave the same equilibrium mixtures, which confirms the validity of the approach and the following order in stability with respect to ligand exchange: **1b** << **1c** ≈ **1a** < **1d**.

The results from the ligand exchange experiments are in good agreement with the obtained hydrolysis data of **1a-d**, showing the hydrolytic stability but also the rate of hydrolysis in DMSO-D_6/water (10 vol% H_2O) to be in the following order **1b** >> **1c** > **1a** >> **1d** (Figure 1B). Thus, while 1,8-diaminonaphthalene compound **1d** did not hydrolyse at all even after 12 days under the conditions applied, catechol ester **1b** quantitatively hydrolysed within 5 minutes. Astonishingly, also ester **1a** proved to be significantly more stable than **1b**; after ca. 5 min. only 15% and after 18 hrs. ca 70% of **1a** converted into 1,8-naphthalenediol, reaching equilibrium after ca. 3 days with a 1,8-naphthalenediol/**1a** ratio of ca. 73/27. Pinacol ester **1c** hydrolysed at a much lower rate than **1a**, reaching equilibrium after ca. 9 days with a pinacol/**1c** ratio of ca. 65/35.



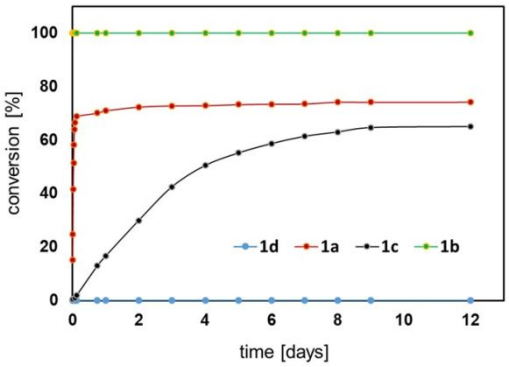
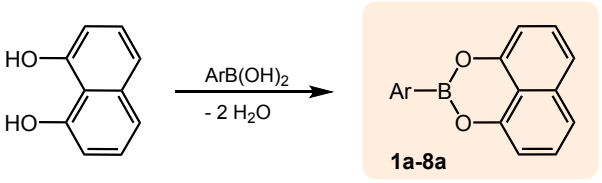


Figure 1. Ligand exchange experiments (A) and hydrolysis (B) of **1a-d** in DMSO-D_6/H_2O (10 vol% H_2O).

Encouraged by the high stability and ease of formation of **1a**, various 1,8-naphthalenediol derived aryl boronic acid esters were prepared (Scheme 3). Thus, the reaction of 1,8-naphthalenediol with the respective aryl boronic acids in acetonitrile at room temperature gave crystalline precipitates of the boronic esters **1a, 3a-5a** and **8a** in good to excellent isolated yields. The esters **2a**, **6a** and **7a** were synthesized by a slightly modified procedure (see supporting information for details) as they did not crystallize from acetonitrile. Isolated **1a**-**8a** were fully characterized by multi nuclear NMR spectroscopy and combustion analysis.



1a Ar = C_6H_6 (84%) **2a** Ar = C_6F_5 (60%)
3a Ar = 3,4,5-F_3-C_6H_2 (95%) **4a** Ar = 2,4,6-F_3-C_6H_2 (92%)
5a Ar = 2,6-F_2-C_6H_3 (85%) **6a** Ar = 2,6-Cl_2-C_6H_3 (84%)
7a Ar = 2,4,6-Me_3-C_6H_2 (63%) **8a** Ar = 2,6-$(MeO)_2$-C_6H_3 (75%)

Scheme 3. Synthesis of the aryl boronic acid esters **1a**-**8a**.

Further confirmation of the structural connectivity of **1a**-**5a** and **8a** was obtained from single-crystal X-ray analyses; the results are shown in Figures 2-7. Owing to extensive π-stacking the aromatic ring systems in **1a**-**4a** are co-planar with respect to each other, similar to what is seen for the analogous catechol esters **1b**-**5b**.[16,17] Only compounds **5a** and **8a** show in the solid state twisted structures with a C1-C2-B1-O2 dihedral angle of 60° for **5a** and a C16-C11-B1-O2 dihedral angle of 73° for **8a**. For comparison, selected bond parameter of **1a-5a** and the analogous catechol esters **1b-5b** are summarized in table 1. As expected, due to their larger ring size, **1a**-**5a** have larger O-B-O angles (122°-123°) then the respective five-membered ring catechol derivatives **1b-5b** with angles of ca. 112°. While the C-O distances are fairly similar for both classes of compounds ranging from 1.385 to 1.395 Å, the B-O distances of **1a**-**5a** are somewhat shorter and the B-C distances are slightly longer (both by only 0.01-0.02 Å) than those of **1b-5b**.

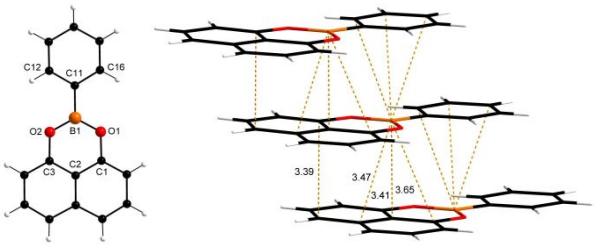


Figure 2. Solid-state structure of C_6H_5-BNad (**1a**).

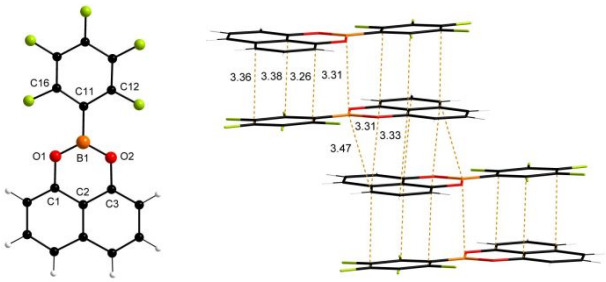


Figure 3. Solid-state structure of C_6F_5-BNad (**2a**) (green = fluorine).

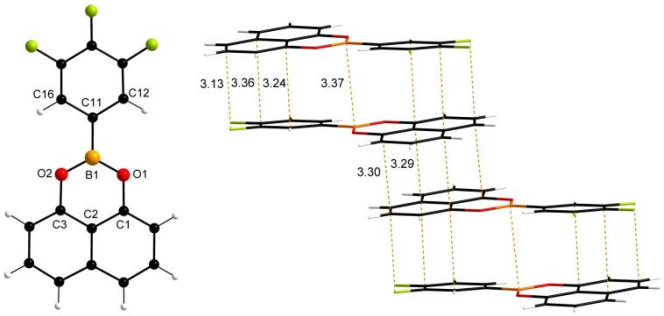


Figure 4. Solid-state structure of 3,4,5-F_3-C_6H_2-BNad (**3a**) (green = fluorine).

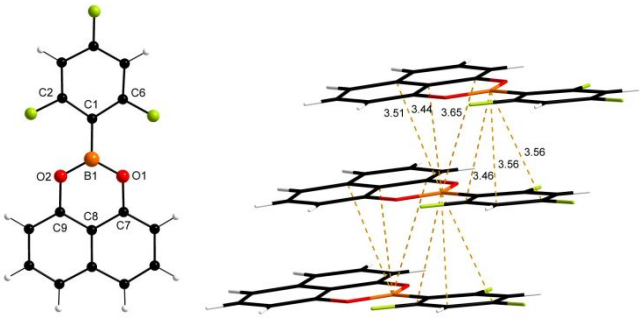


Figure 5. Solid-state structure of 2,4,6-F_3-C_6H_2-BNad (**4a**) (green = fluorine).

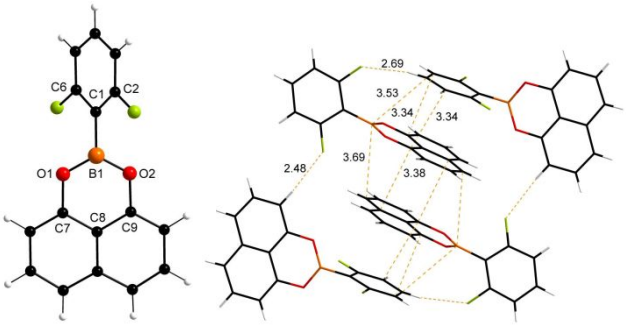


Figure 6. Solid-state structure of 2,6-F_2-C_6H_3-BNad (**5a**) (green = fluorine).

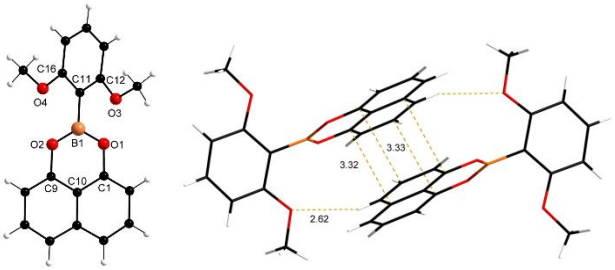


Figure 7. Solid-state structure of 2,6-$(MeO)_2$-C_6H_3-BNad (**8a**).

This becomes particularly evident by comparing individual pairs of boronic acid esters with identical X-aryl groups and can be attributed to a slightly increased π-donating ability of the oxygen's to boron in the six-membered ring structures as opposed to the smaller five-membered rings present in **1b-5b**. However, caution should be taken as the C-O, B-O and B-C distances for both classes of boronic acid ester are generally very similar.

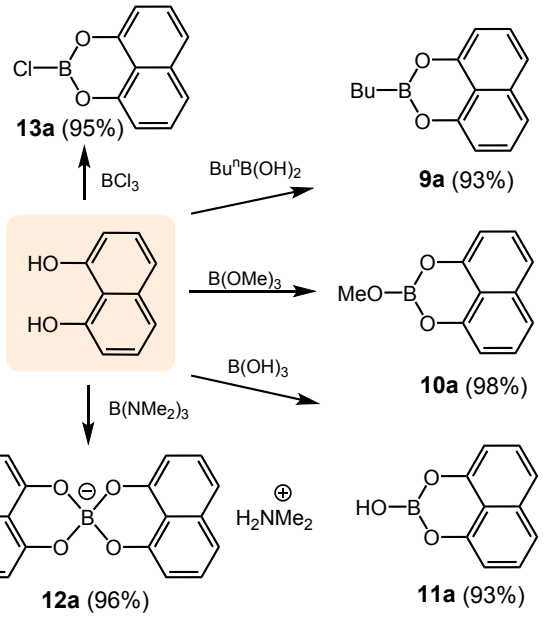
Table 1. Selected bond lengths [Å] and angles [°] of **1a-5a** and **1b-5b**.

-	B-C	B-O [c]	C-O [c]	O-B-O
C_6H_5Bnad (**1a**)	1.561(2)	1.375(2)	1.384(1)	122.0(1)
C_6H_5Bcat (**1b**)[a]	1.537(5)	1.394(3)	1.395(4)	109.8[d]
C_6F_5Bnad (**2a**)	1.578(2)	1.367(1)	1.389(1)	122.9(1)
C_6F_5Bcat (**2b**)[b]	1.558(2)	1.382(2)	1.389(2)	112.4(1)
3,4,5-F_3-C_6H_2Bnad (**3a**)	1.558(3)	1.370(3)	1.395(2)	122.7(2)
3,4,5-F_3-C_6H_2Bcat (**3b**)[b]	1.546(2)	1.381(2)	1.386(2)	112.2(1)
2,4,6-F_3-C_6H_2Bnad (**4a**)	1.573(2)	1.370(1)	1.385(1)	122.3(1)
2,4,6-F_3-C_6H_2Bcat (**4b**)[b]	1.553(2)	1.383(2)	1.385(2)	112.1(1)
2,6-F_2-C_6H_3Bnad (**5a**)	1.574(2)	1.366(1)	1.388(1)	123.2(1)
2,6-F_2-C_6H_3Bcat (**5b**)[b]	1.553(2)	1.386(2)	1.385(2)	111.7(1)

nad = 1,8-**na**phthalene**d**iolate; [a] ref. 16; [b] ref. 17; [c] average distances; [d] standard deviation unavailable.

We next investigated the synthetic potential of 1,8-naphthalenediol as a supporting ligand for boron with various electronic and coordination environments (Scheme 4). For example, refluxing a equimolar amounts of $Bu^nB(OH)_2$ and 1,8-naphthalenediol in acetonitrile gave after vacuum distillation the aliphatic boronic acid ester **9a** in almost quantitative yields

as an air and moisture-stable, colourless liquid (Scheme 5). Heating a hexanes solution of 1,8-naphthalenediol in the presence of a 3-fold excess of $B(OMe)_3$ gives the boric ester **10a** as a colourless solid in excellent isolated yields; its solid-state structure is depicted in Figure 8. The corresponding hydroxy borate **11a** was synthesized in 93% yield from refluxing 1,8-naphthalenediol with a twofold excess of boric acid in acetonitrile. To our surprise, **11a** proved to be remarkably thermally robust as elimination of water and condensation reactions did not occur at 100°C under vacuum. The reaction of stochiometric amounts of 1,8-naphthalenediol with $B(NMe_2)_3$ did not give the targeted amino borate Me_2N-BNad; rather the spirocyclic ammonium borate **12a** was rapidly formed as the sole product. Even the use of an excess of $B(NMe_2)_3$ at low temperatures did not produce Me_2N-BNad. However, almost quantitative yields of **12a** were obtained when two equivalents of 1,8-naphthalenediol were treated with one equivalent of $B(NMe_2)_3$ at room temperature.



Scheme 4. Synthesis of **9a**-**13a**.

The addition of an two-fold excess of BCl_3 to a CH_2Cl_2 solution of 1,8-naphthalenediol quantitatively generated after removal of solvent under vacuum chloro borate **13a** in 95% yield (Scheme 4). In contrast to the above described compounds, **13a** is an extremely air and moisture sensitive colourless solid that can be stored under nitrogen for a few weeks without showing notable signs of decomposition. However, when solutions of **13a** in dry C_6D_6 were exposed air and moisture, crystals slowly formed over time, which by NMR spectroscopy and X-ray analysis were identified as a mixture of boroxane **14a** (Figure 9) and hydroxy borate **11a**.

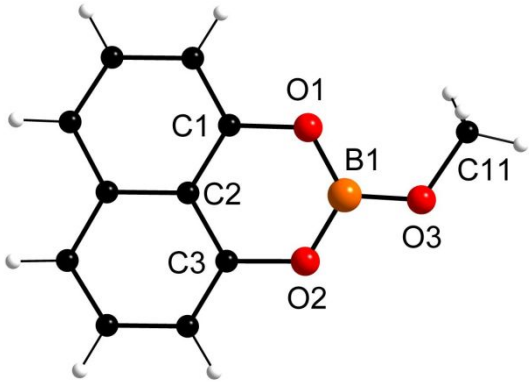


Figure 8. Solid-state structure of **10a**. (Only one of the three independent molecules in the unit cell is shown for clarity). Selected bond lengths [Å] and angles [°]: O1 B1 1.380(1), O1 C1 1.381(1), O2 B1 1.375(1), O2 C3 1.379(1), O3 B1 1.349(1), O3 C11 1.439(1), O3 B1 O2 116.34(10), O3 B1 O1 121.40(10), O2 B1 O1 122.26(10), B1 O1 C1 119.87(9).

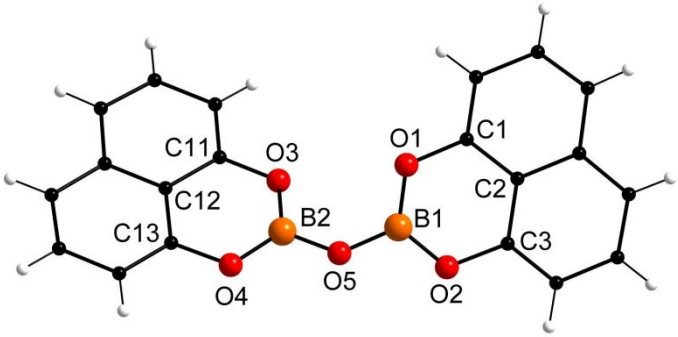
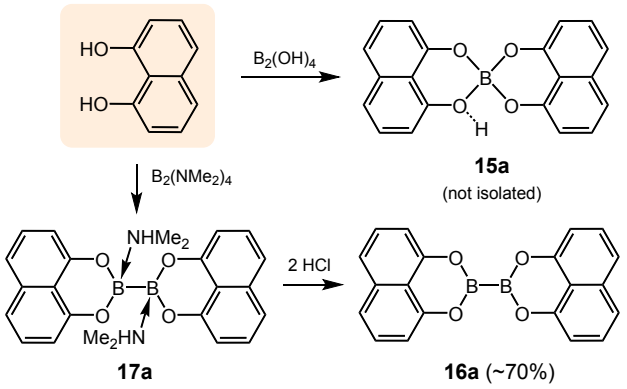


Figure 9. Solid-state structure of **14a**. Selected bond lengths [Å] and angles [°]: O1 B1 1.370(1), O1 C1 1.388(1), O2 B1 1.365(2), O2 C3 1.381(1), O3 B2 1.374(1), O3 C11 1.382(1), O4 B2 1.370(1), O4 C13 1.379(1), O5 B2 1.352(1), O5 B1 1.364(1), B2 O5 B1 133.03(9), O5 B1 O2 116.09(9), O5 B1 O1 120.13(10), O2 B1 O1 123.75(10), O5 B2 O4 116.60(10), O5 B2 O3 120.12(10), O4 B2 O3 123.19(10).

Diboronic esters such as B_2Pin_2 and B_2Cat_2 have been utilized extensively as borylating reagents in organic reactions involving the formation of C-B bonds.[18] Initial attempts to synthesize the corresponding diborane **16a** directly via the reaction of 1,8-naphthalenediol with $(HO)_2B$-$B(OH)_2$ failed; instead the protonated spirocyclic borate **15a** was formed as the major product along with $B(OH)_3$ according to NMR spectroscopic studies (Scheme 5). Following an alternative protocol reported by Marder and co-workers[19], 1,8-naphthalenediol was reacted with $(Me_2N)_2B$-$B(NMe_2)_2$ to give a white precipitate of the diborane dimethylamine adduct **17a**. Subsequent treatment of **17a** with ethereal HCl gave rise to the formation to the donor free diboronic ester **16a** in overall yields of ca. 70%. Compound **16a** is a thermally stable colourless solid that is insoluble in aliphatic and aromatic hydrocarbons and diethyl ether, sparingly soluble in THF but shows good solubility in DMSO.



Scheme 5. Synthesis of **16a**.

The solid-state structures of **16a** (Figure 10) and **17a** (Figure 11) were determined by X-ray crystallography; suitable single-crystals were grown from THF, resp. For **16a**, each Bnad moiety is virtually planar and, the two of them in each molecule are coplanar (O1-B1-B1-O1, 0°). As expected, the B-B distance **16a** with 1.699(3) Å is significantly shorter than that of **17a** with 1.739(2) Å, where both boron centres are tetra-coordinated. Note also that the B-B distances of **16a** is comparable to those of other oxy-functionalized diboranes such as $B_2(OH)_4$ [1.715 Å][20], B_2neop_2 [1.712 Å][21], B_2pin_2 [1.704 Å][22] and B_2cat_2 [1.678 Å].[23]

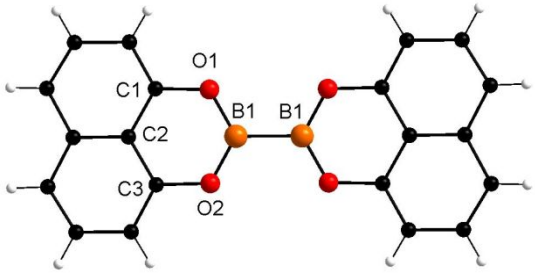


Figure 10. Solid-state structure of **16a** (for clarity positional disorder not shown). Selected bond lengths [Å] and angles [°]: B1 B1 1.699(3), O1 B1 1.373(2), O2 B1 1.376(2), O1 C1 1.385(2), O2 C3 1.386(2), C1 C2 1.415(2), C2 C3 1.416(2), B1 O1 C1 120.43(12), B1 O2 C3 120.19(12), O1 C1 C2 118.55(13), O1 B1 O2 121.69(13), O1 B1 B1 119.20(16), O2 B1 B1 119.11(16).

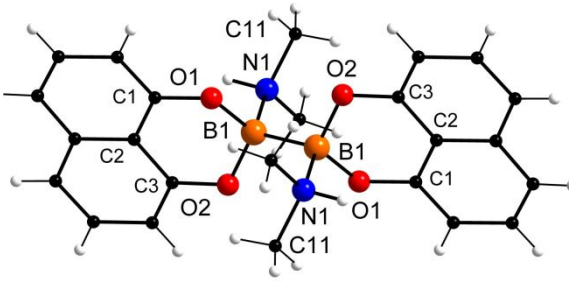


Figure 11. Solid-state structure of **17a**. Selected bond lengths [Å] and angles [°]: B1 B1 1.739(2), O1 C1 1.352(1), O1 B1 1.482(1), O2 C3 1.352(1), O2 B1 1.470(1), N1 C11 1.482(2), N1 C12 1.487(2), N1 B1 1.680(2), O2 B1 B1 112.61(11), O1 B1 B1 112.03(11), N1 B1 B1 112.05(11), O2 B1 O1 112.74(9), O2 B1 N1 103.21(8), O1 B1 N1 103.51(8).

All borate esters have been characterized by multi nuclear NMR spectroscopy and combustion analysis. For comparison, the ^{11}B NMR chemical shifts are listed in Table 2. The ^{11}B NMR chemical shifts of **1a-11a** and **14a** are in the typical range for tri-coordinate boron compounds with central OBO_2 and CBO_2 units. The ^{11}B NMR signals of **1a**-**9a** appear within the relatively narrow range of 27-32 ppm, and are slightly shifted to higher field relative to their catechol ester analogues **1b**-**9b**. Likewise, the tri-coordinate borates **10a**, **11a** and **14a** display ^{31}B NMR signals within a narrow range (17-18 ppm), and are high-field shifted relative to their catechol analogues **10b**, **11b** and **14b**.

Table 2. ^{11}B NMR chemical shifts [δ in ppm] of R-BNad (**1a**-**17a**) and RBCat (**1b**-**17b**).[a]

R-BNad	δ_{11B}	R-BCat	δ_{11B}
C_6H_5-Bnad (**1a**)	27.9	C_6H_5-Bcat (**1b**)	30.7[c]
C_6F_5-Bnad (**2a**)	27.9	C_6F_5-Bcat (**2b**)	29.1[c]
3,4,5-F_3-C_6H_2-Bnad (**3a**)	27.0	3,4,5-F_3-C_6H_2-Bcat (**3b**)	30.8[c]
2,4,6-F_3-C_6H_2-Bnad (**4a**)	27.2	2,4,6-F_3-C_6H_2-Bcat (**4b**)	29.7[c]
2,6-F_2-C_6H_3-Bnad (**5a**)	27.2	2,6-F_2-C_6H_3-Bcat (**5b**)	29.9[c]
2,6-Cl_2-C_6H_3-Bnad (**6a**)	27.5	2,6-Cl_2-C_6H_3-Bcat (**6b**)	30.7
2,4,6-Me_3-C_6H_2-Bnad (**7a**)	29.8	2,4,6-Me_3-C_6H_2-Bcat (**7b**)	32.9[d]
Bu^n-Bnad (**9a**)	32.0	Bu^n-Bcat (**9b**)	-
MeO-Bnad (**10a**)	17.8	MeO-Bcat (**10b**)	23.4[e]
HO-Bnad (**11a**)	18.4	HO-Bcat (**11b**)	22.9[f]
$[H_2NMe_2][B(nad)_2]$ (**12a**)	0.5[b]	$[H_2NMe_2][B(cat)_2]$ (**12b**)	14.0[g]
Cl-Bnad (**13a**)	24.8	Cl-Bcat (**13b**)	28.8[h]
nadB-O-Bnad (**14a**)	17.0	catB-O-Bcat (**14b**)	22.4[i]
nadB-BNad (**16a**)	5.4[b]	catB-Bcat (**16b**)	31.6[j]
$[Bnad(HNMe_2)]_2$ (**17a**)	1.4[b]	$[Bcat(HNMe_2)]_2$ (**17b**)	-

nad = 1,8-**na**phthalene**di**olate; [a] measured in $CDCl_3$ if not otherwise stated; [b] DMSO-D_6; [c] ref. 24; [d] ref. 25; [e] ref. 26, C_6D_6; [f] ref. 27, C_6D_6; [g] ref. 19; C_6D_6/CH_3CN; [h] CD_2Cl_2; [i] ref. 26, C_6D_6; [j] ref. 19, CD_2Cl_2;

We next set out to determine the relative Lewis acid strength of the newly prepared esters **1a**-**7a** via the classical Gutmann-Beckett method.[24, 28-30] In this method, O=PEt_3 is combined with the corresponding Lewis acid in benzene and the change in ^{31}P NMR chemical shift for O=PEt_3 is measured and the acceptor numbers (ANs) are then calculated according to the formula shown in Table 3. Generally, higher ANs indicate higher Lewis acid strength. For comparison, the results for **1a-7a** as well as for the respective catechol derivatives **1b-7b** are listed in Table 3 for C_6D_6 as solvent (for more details see Tables S1 and S2). Both classes of compounds display similar ANs, suggesting similar electronic contributions from both the catecholate and the 1,8-naphthalenediolate ligand toward the central electron deficient boron. Furthermore, the Lewis acidity appears to correlate reasonably well with the electronic properties of the X-aryl group, e. g. electron-withdrawing X groups increase the AN, while electron donating groups lower it. As expected, and as is the case for both classes of boronic acid esters the AN increases with increasing the number of electron-withdrawing fluorine atoms attached to the aryl substituent. However, some discrepancies were also noted demonstrating the limitation of

using ANs as a means of quantifying the Lewis acidity of boranes.

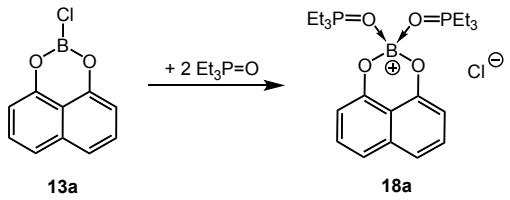
Table 3. Acceptor numbers (ANs)[a] of selected boronic acid esters.

R-BNad	AN	R-BCat	AN
C_6H_5-Bnad (**1a**)	59.6	C_6H_5-Bcat (**1b**)	62.5
C_6F_5-Bnad (**2a**)	80.9	C_6F_5-Bcat (**2b**)	78.9
3,4,5-F_3-C_6H_2-Bnad (**3a**)	72.7	3,4,5-F_3-C_6H_2-Bcat (**3b**)	75.2
2,4,6-F_3-C_6H_2-Bnad (**4a**)	73.8	2,4,6-F_3-C_6H_2-Bcat (**4b**)	73.4
2,6-F_2-C_6H_3-Bnad (**5a**)	72.3	2,6-F_2-C_6H_3-Bcat (**5b**)	73.0
2,6-Cl_2-C_6H_3-Bnad (**6a**)	53.7	2,6-Cl_2-C_6H_3-Bcat (**6b**)	64.8
2,4,6-Me_3-C_6H_2-Bnad (**7a**)	11.8	2,4,6-Me_3-C_6H_2-Bcat (**7b**)	12.2
Cl-Bnad (**13a**)	89.7	Cl-Bcat (**13b**)	87.5

nad = 1,8-**na**phthalene**d**iolate; [a] The ^{31}P NMR chemical shifts were measured in C_6D_6. The respective acceptor numbers were calculated as follows: AN = (δ_{31P} – 41.0) × (100/(86.1 – 41.0).[29]

For example, the 2,6-dichlorophenyl substituted esters **6a** and **6b** show significantly lower ANs than the 2,6-difluorophenyl derivatives **5a** and **5b**. Note also that **5a** (AN = 72.3) and **5b** (73.0) have almost identical ANs, while the ANs for **6a** (AN = 53.7) and **6b** (AN = 64.8) are markedly different. The reason for these inconsistencies appears to be steric in nature, and it may very well be concluded that the 1,8-naphthalenediolate ligand requires somewhat more space than its catecholate counterpart.

Apparently, due to the lack of appreciable levels of steric hindrance, fairly similar ANs were found for the chloro borates **13a** (AN = 89.7) and **13b** (AN = 87.5). Note also that both values are significantly higher than those of the strong and relatively "soft" Lewis acid $B(C_6F_5)_3$ (AN = 77.6)[30,31] but similar to that of the "hard" Lewis acid $B(OC_6F_5)_3$ (AN = 86.5)[32] and markedly lower than Ingleson's adduct [CatBOTf(O=PEt_3)] with a ^{31}P NMR chemical shift of δ_{31P} = 85.4 ppm (CH_2Cl_2) (AN = 98).[27] We further noticed that upon adding two equivalents of O=PEt_3 to a C_6D_6 solution of **13a**, a crystalline precipitate formed, which by multi-nuclear NMR spectroscopy and X-ray analysis was identified as the boronium salt **18a** (Scheme 6). Comparison of the integrals of the aromatic signals with those of the ethyl signals of O=PEt_3 in the ^1H NMR spectrum of **18a** indeed confirmed the presence of two molecules of O=PEt_3 per 1,8-naphthalenediolate unit.



Scheme 6. Formation of boronium chloride **18a**.

The observed ^{31}P and ^{11}B NMR chemical shifts of 83.9 ppm and 0.1 ppm (CD_2Cl_2), respectively, suggest a tetrahedral coordination environment for the central boron cation with two O=PEt_3 coordinating. It is worthwhile noting that its ^{31}P NMR chemical shift is fairly close to that of the in situ generated boronium salts $[F_2B(O=PEt_3)_2]OTf$[33] (84.8 ppm in $CDCl_3$) and $[CatB(O=PEt_3)_2]OTf$[27] (83.9 ppm in CH_2Cl_2) suggesting similar Lewis acidities of the cationic boron centres in all three species. On the other hand, the ^{31}P NMR signal of O=PBu_3 in [9-BBN(O=PBu_3)$_2$]NTf_2[34] with 71.9 ppm (CH_2Cl_2) is markedly up-field shifted relative to **18a**. This may be attributed to the more sterically crowded BBN framework resulting in weaker donor-acceptor interactions of two the O=PEt_3 units with the boron cation. On the other hand, the ^{31}P NMR signal of O=PEt_3 in [8-Ph_2P-$C_{10}H_6B(O=PEt_3)_2][NTf_2]_2$[35] with 90.8 ppm ($CD_2Cl_2$) is significantly down-field shifted relative to **18a**, which can be well understood in terms of the "dicationic" nature of the boron centre. The results of the X-ray analysis of **18a** (Figure 12) further corroborated the structural assignment of a tetrahedral boronium cation with a fully charge separated chloride anion. Nonetheless, despite the formally positive charge at boron, the B-O ring distances with 1.447(2) and 1.443(2) Å are longer than those of the esters **2a**-**5a** with trigonal planar coordination environment for boron. Only in the tetra-coordinated diborane **17a**, are the B-O ring distances [1.482(1) and 1.470(1) Å] somewhat longer.

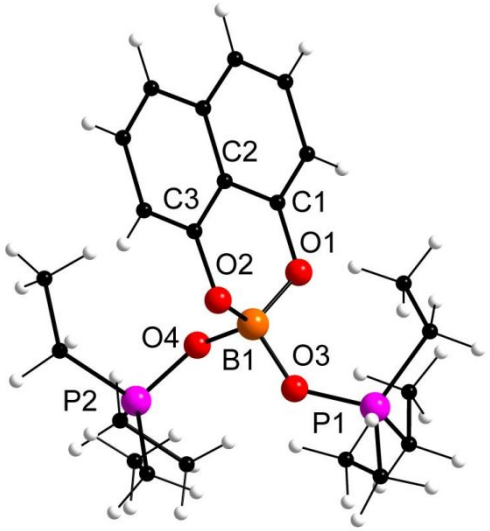
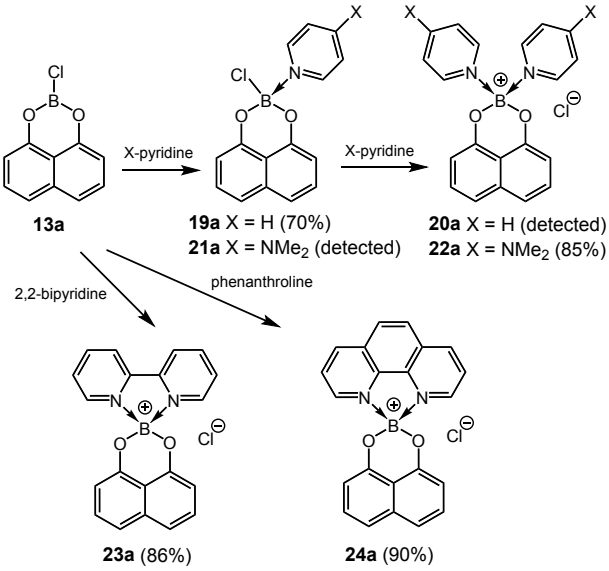


Figure 12. Solid-state structure of **18a** (chloride anion omitted for clarity). Selected bond lengths [Å] and angles [°]: O2 B1 1.447(2), O3 B1 1.471(2), O4 B1 1.499(2), O1 B1 1.443(2), P1 O3 1.551(1), P2 O4 1.547(1), O1 C1 1.365(2), O2 C3 1.364(2), B1 O3 P1 136.14(10), B1 O4 P2 134.79(11), O1 B1 O2 115.53(14), O1 B1 O3 109.61(13), O2 B1 O3 107.70(14), O1 B1 O4 106.75(13), O2 B1 O4 109.31(12), O3 B1 O4 107.70(13).

The rapid formation of the boronium salt prompted us to investigate the Lewis acid-base behaviour of **13a** (Scheme 7). Thus, upon adding one equivalent of dry pyridine to **13a**, the expected Lewis acid-base adduct **19a** was obtained as a colourless solid material in almost quantitative yields. Addition of a second equivalent of pyridine gave rise to a change of the NMR spectroscopic features of **19a** indicating the formation of the boronium species **20a** being in equilibrium with **19a**. Adding a large excess of pyridine fully shifted the equilibrium towards the boronium salt **20a**, which could not be isolated but was characterized in solution by NMR spectroscopy. Astonishingly,

reacting two equiv. of the stronger donor DMAP with **13a**, enabled the formation and isolation of boronium salt **22a** as a colourless solid in good yields. However, **22a** is thermally and moisture sensitive and susceptible to partial loss of DMAP with formation of **21a** upon drying under vacuum for extensive periods of time. Hoping to circumvent the loss of donor from the boronium cation, **13a** was reacted with equimolar amounts of 2,2'-bipyridine and 1,10-phenanthroline, resp., in toluene as solvent. In both reactions reddish-orange crystals precipitated, which by multi-nuclear NMR spectroscopy were identified as the boronium salts **23a** and **24a**. As in the previous case, both compounds are heat and moisture sensitive but can be stored at room temperature under nitrogen over several weeks without decomposition.



Scheme 7. Lewis acid base reactions of **13a** with nitrogen based donor molecules.

Surprisingly few examples of well-characterized boronium salts[36] supported by chelating diolate ligands are documented in the literature. Among those, most notable are $[CatB(bipy)]ClO_4$[37], $[PinB(DMAP)_2]Br$[38], $[PinB(py)_2]OTf$[39], and the boroxine-derived salt $[(py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$[40], of which only the latter two compounds have been structurally characterized by X-ray crystallography. Attempts to grow crystals of the boronium salts **22a**-**24a** suitable for X-ray analysis were complicated by their extreme moisture sensitivity and tendency to form microcrystalline materials or powders. Only for **23a** was it possible to determine its solid state structure by X-ray crystallography (Figure 13); suitable crystals were grown from benzene. Due to partial hydrolysis during crystal growth, the unit cell contains two molecules of **23a** and one molecule of highly disordered **11a**. Nonetheless, the results of the X-ray analysis clearly confirmed chelation of the 2,2'-bipyridine unit to the boron cation, and the chloride anion being fully dissociated. This leads to a distorted tetrahedral coordination environment for boron with an average B-O ring distance of ca. 1.42 Å being slightly shorter than that of the boronium salt **18a** with ca. 1.46 Å.

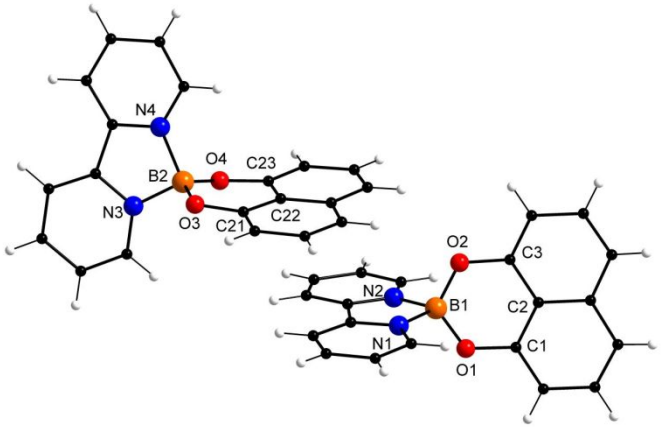


Figure 13. Solid-state structure of **23a** (chloride anions and disordered **11a** omitted for clarity). Selected bond lengths [Å] and angles [°]: O1 B1 1.418(2), O2 B1 1.422(2), O3 B2 1.423(2), O4 B2 1.416(2), N1 B1 1.610(2), N2 B1 1.585(2), N3 B2 1.582(2), N4 B2 1.615(2), O1 C1 1.371(2), O2 C3 1.365(2), O3 C21 1.364(2), O4 C23 1.368(2), O5 B3 O6 117.7(4), O5 B3 O7 121.0(4), O6 B3 O7 121.3(5), O1 B1 O2 118.62(14), O1 B1 N2 110.67(15), O2 B1 N2 108.76(14), O1 B1 N1 110.04(14), O2 B1 N1 111.25(15), N2 B1 N1 94.95(11), O4 B2 O3 117.86(14), O4 B2 N3 111.44(15), O3 B2 N3 108.35(14), O4 B2 N4 109.07(14), O3 B2 N4 112.42(15), N3 B2 N4 95.45(12).

Conclusions

Inspired by the design of robust Lewis acids for potential applications in Lewis acid catalysed transformations, the 1,8-naphthalenediolate-supported boronic and boric acid esters **1a**-**11a** and **13a** as well as diboronic ester **16a** were prepared from reactions of commercially available boron compounds with 1,8-naphthalendiol. In addition, a series of highly sensitive but room temperature stable boronium salts were synthesized via treatment of chloro borate **13a** with the neutral donors $O=PEt_3$, DMAP, 1,10-phenanthroline and 2,2'-bipyridine, resp. A comparison of the hydrolytic stability of boronic acid ester **1a** with its catechol counterpart **1b** and ligand exchange experiments suggest the 1,8-naphthalenediolate esters to have greater thermodynamic and hydrolytic stabilities than their catecholate analogues, most likely owing to differences in ring sizes resulting in different ring strain. The lower ring strain in the 1,8-naphthalenediolate esters does not seem to negatively affect their Lewis acidities, as the acceptor numbers determined by the Gutman-Beckett method showed similar values for both classes of boronic acid esters. Applications of these new boron-containing Lewis acids in catalytic organic transformations are currently undergoing in our lab.

Conflicts of interest

There are no conflicts to declare.

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TOC

New 1,8-Naphthalenediolate supported Boronic, Diboronic and Boric Acid Esters and Boronium salts have been synthesized and structurally characterized.