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Bidentate boron Lewis acids: synthesis by tin boron exchange reaction and host–guest complex formation†

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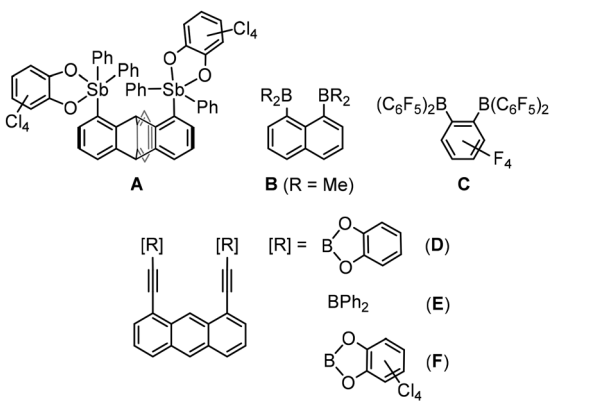
Four bidentate boron Lewis acids based on the 1,8-diethynylanthracene backbone have been synthesized by a tin–boron exchange reaction with various chloroboranes, yielding the products in good to excellent yields. Complexation experiments of the host compounds with pyridine, pyrimidine and TMEDA demonstrated striking differences in terms of formation and solubility of the supramolecular adducts. The host–guest complexes were investigated by multinuclear NMR spectroscopy and structurally characterized by X-ray diffraction experiments, illustrating the adaptation of the host system upon adduct formation with different neutral guest molecules.

Introduction

While poly-Lewis bases (*e.g.* crown ethers or cryptands) have been extensively studied for decades, their phenomenological counterparts, poly-Lewis acids (PLAs), have attracted increasing interest in recent years.[1–3] Like their Lewis base counterparts, PLAs find applications in catalysis,[4–8] anion sensing[9–20] or small molecule recognition.[21–23] PLAs combine multiple Lewis acid functions *via* a mostly organic backbone. Although a wide variety of elements are used in PLAs, such as silicon,[24] tin,[25,26] antimony[11,27,28] or mercury,[29] a high percentage of PLAs contain group 13 elements – particularly boron[12,21,30–33] – due to their natural electron deficiency.

Most PLAs are bidentate and therefore bind the corresponding guest molecule or ion in a pincer-like μ(1,2)-chelating mode. A rigid organic scaffold is required to ensure selective complexation of the guest molecule. To provide this rigidity, they are usually based on aromatic backbones such as phenylene,[22] naphthalene[13] or anthracene.[33] The element which serves as Lewis acid component in such systems as well as the distance between the functions is crucial for their host–guest chemistry, as it determines the selectivity towards potential guest molecules. For example, the triptycene-based antimony (v) Lewis acid **A** (Scheme 1) by Gabbaï *et al.* can effectively bind fluoride ions in a chelating fashion.[11] Among the bidentate boron Lewis acids, the naphthalene derivative **B** of Katz, commonly known as 'hydride sponge', is a prominent representative. This host system can chelate not only hydride ions, as the name suggests, but also fluoride and hydroxide ions.[13] The perfluorinated system **C** of Collins and Piers, which has also been studied in detail in the context of isobutene polymerization, has been found to cooperatively complex chloride, fluoride, hydroxide, methanolate and azide ions.[34–38]

The organic backbone is sometimes substituted and extended with alkynyl spacers, which offers three advantages. First, the semi-rigid alkynes allow the Lewis acid functions to adapt to the spatial requirements of the guest molecule. Second, they prevent steric repulsion between the complexed guest molecule and the backbone, which can occur in some



Scheme 1 Various bidentate Lewis acids with antimony and boron.

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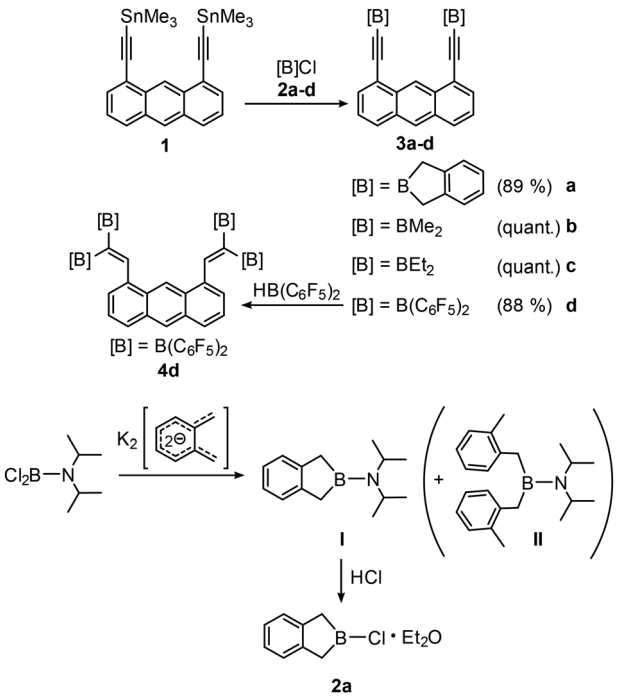
cases, such as with the 1,8-anthracenyl backbone. Finally, the alkynes can be easily substituted with various Lewis acid functions such as boryl[33] and stibanyl[39] groups. Some of these substitution reactions are not accessible for direct functionalization of aromatic systems. An established route for introducing such Lewis acid functions is either by lithiation, as used by Katz to synthesize the host system **D**,[40] or, more elegantly, by a tin-element exchange reaction, as used to synthesize the anthracene-based diboranyl compounds **D**, **E** and **F**.[33] A direct comparison of the two routes for the synthesis of **D** highlighted the advantages of the tin–boron exchange reaction.

The phenyl derivative **E** was found to form a 1 : 1-adduct with pyrimidine and TMEDA. Attempts to obtain a host with a significantly higher Lewis acidity in the form of the perchlorocatecholato derivative **F** were hampered by the insolubility of this compound.

Since the synthesis and host–guest chemistry with anthracene derivatives is well established in our group,[3,23,30,33,39] we chose the 1,8-diethinylanthracene backbone as a test system for our subsequent work, in which we tried to introduce other boranyl functions by a tin–boron exchange reaction, which offer additional properties such as an easier purification process, less steric repulsion of the substituents, better solubility or a higher Lewis acidity. We then investigated the host–guest chemistry of these new host systems.



Scheme 2 Synthesis of the bidentate boron host systems **3a–d**, subsequent hydroboration of **3d** and characterized intermediates **I** and **II** in the synthesis of **2a**.

Results and discussion

Tin–boron exchange reactions

The bidentate Lewis acids **3a–d** were synthesized in good to excellent yields by a transmetallation reaction with the chloroboranes **2a–d** (Scheme 2). A tin–boron exchange reaction with the chloroborane **2a**[41] gave product **3a** in 89% yield. In the synthesis of **2a**, the precursor compound **I** and the by-product **II** were structurally characterized (Scheme 2, for solid state structures see the ESI†). As reported, chloroborane **2a** is unstable and was therefore used as a stabilized diethyl etherate; however, the product **3a** was found to be stable for months as a solid under inert conditions at ambient temperature and for weeks as a solution in dry $CDCl_3$.

For the dialkylborane derivatives **3b** and **3c**, comparable exchange reactions of stannylalkynes with Me_2BBr and Et_2BCl, respectively, are known from the literature.[42,43] Since a reaction of stannane **1** with Me_2BBr did not yield diborane **3b**, Me_2BCl (**2b**) was used instead. **2b** was conveniently prepared in an analogous approach to the reported synthesis of Et_2BCl (**2c**) by Breher *et al.*[44] by reacting trimethylborane with boron trichloride in the presence of catalytic amounts of $NaBH_4$.

Dimethylalkynylboranes have been reported to be highly unstable,[43] and although we were able to isolate **3b**, the reaction was found to be sensitive to reaction time. Longer reaction times (>30 min) lead to complete decomposition of the product, presumably due to ligand redistribution reactions of methyl and ethynyl groups. However, after removal of the formed chlorotrimethylstannane and excess Me_2BCl (**2b**), the isolated compound **3b** is stable for months as a solid under inert conditions at ambient temperature and for weeks as a solution in dry $CDCl_3$. The transmetallation reaction with Et_2BCl (**2c**) was found to be much more insensitive to unwanted ligand redistribution reactions. As the products **3b** and **3c** are non-volatile, purification was conveniently achieved by removal of the volatile reactants, giving both systems in quantitative yield.

A tin–boron exchange reaction with $(C_6F_5)_2BCl$ (**2d**[45,46]), as reported by Piers *et al.*[47] could be applied to bisstannane **1** to give the highly electrophilic bidentate borane **3d**, which could be further functionalized by hydroboration with two equivalents of Piers' borane ($(C_6F_5)_2BH$),[46,48] leading to the tetraboranyl compound **4d**. Further hydroboration of the CH=C[B$(C_6F_5)_2$]$_2$ groups does not occur even with an excess of $(C_6F_5)_2BH$. This had already been observed by Piers for the hydroboration of diphenylacetylene, which also yielded the olefin without further hydroboration. This is due to either steric or electronic reasons, since both ethynyl functions in 1,8-diethynylanthracene undergo double hydroboration with Piers' borane, ultimately forming the 1,8-diethylderivative bearing two CH_2–CH[B$(C_6F_5)_2$]$_2$ groups.[30] This again correlates with the observations regarding a feasible twofold hydroboration of phenylacetylene.[46] As already mentioned by Piers, unsaturated CH=C[B$(C_6F_5)_2$]$_2$ groups such as in **4d** do not undergo β-elimination or retrohydroboration, which consistently was also not observed for compound **4d** at ambient temperature.

The solid state structures of **3a**, **3d** and **4d** have been determined by single crystal X-ray diffraction (Fig. 1). The boron

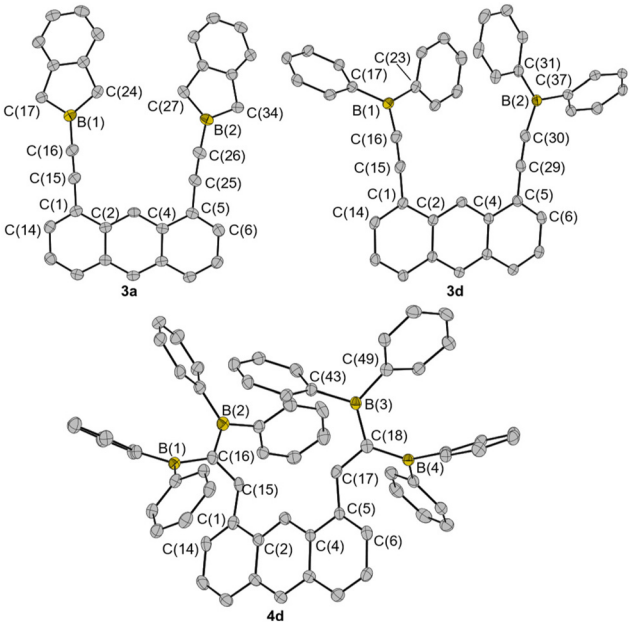


Fig. 1 Molecular structures of **3a**, **3d** and **4d** in the solid state. Hydrogen atoms, fluorine atoms and solvent molecules are omitted for clarity and ellipsoids are set to 50% probability. Selected distances [Å] and angles [°] of **3a**: B(1)···B(2) 5.941(2), B(1)–C(16) 1.520(2), B(1)–C(17) 1.575(2), B(1)–C(24) 1.571(2), B(2)–C(26) 1.515(2), B(2)–C(27) 1.574(2), B(2)–C(34) 1.572(2); C(17)–B(1)–C(24) 108.2(1), C(17)–B(1)–C(16) 126.5(1), C(24)–B(1)–C(16) 125.4(1), C(27)–B(2)–C(34) 108.4(1), C(27)–B(2)–C(26) 126.7(1), C(34)–B(2)–C(26) 125.0(1); of **3d**: B(1)···B(2) 5.968(2), B(1)–C(16) 1.501(2), B(1)–C(17) 1.570(2), B(1)–C(23) 1.580(2), B(2)–C(30) 1.504(2), B(2)–C(31) 1.570(2), B(2)–C(37) 1.579(2); C(17)–B(1)–C(23) 121.5(1), C(17)–B(1)–C(16) 119.8(1), C(23)–B(1)–C(16) 118.7(1), C(31)–B(2)–C(37) 122.7(1), C(31)–B(2)–C(30) 122.7(1), C(37)–B(2)–C(30) 114.6(1); of **4d**: B(1)···B(2) 2.770(6), B(3)···B(4) 2.754(6), B(3)–C(18) 1.554(5), B(3)–C(43) 1.594(5), B(3)–C(49) 1.575(5); C(1)–C(15)–C(16) 126.1(3), C(15)–C(16)–B(1) 118.6(3), B(1)–C(16)–B(2) 125.1(3), B(3)–C(18)–B(4) 124.1(3).

atoms in **3d** and **4d** are approximately trigonally planar with C–B–C angles ranging from 114.6(1)° to 125.1(3)° and angle sums of 360.0(3)°. In **3a**, the deviation from the ideal 120° is most pronounced due to the bridging *o*-xylylene group: the five-membered ring causes the angles C(17)–B(1)–C(24) and C(27)–B(2)–C(34) to be significantly smaller than 120°, resulting in the other two C–B–C angles being larger than 120°. Despite this distortion, the boron atoms have trigonal planar geometry (*d*(B(1)···C(16)–C(17)–C(24)-plane) = 0.001(1) Å).

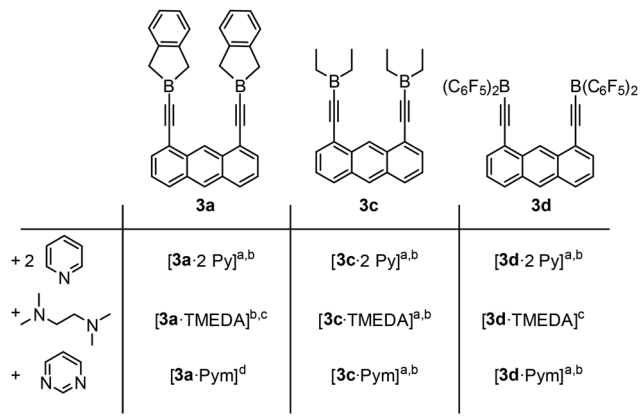
In **3d**, the ethynyl spacer C(15)≡C(16)–B(1) is strongly distorted (angle C(15)–C(16)–B(1) = 166.8(2)°; torsion angle B(1)–C(1)–C(5)–C(8) = 156.6(1)°). This is most likely due to packing effects of the C_6F_5 groups. For example, one C_6F_5 group of the deformed ethynyl spacer shows an intramolecular parallel-displaced aryl stacking interaction with one C_6F_5 group of the other boranylalkynyl group (*d*(centroid–centroid) = 3.575(1) Å).

Additionally, the other C_6F_5 group of this deformed ethynyl spacer shows an intermolecular aryl stacking interaction with the anthracene backbone of another molecule (*d*(centroid–centroid) = 3.725(1) Å). Apart from these, there are several intermolecular aryl stacking interactions between the anthracene backbones. In **4d**, the CH═C[B(C_6F_5)$_2$]$_2$ groups are rotated away from each other due to steric repulsion. In addition, the vinyl groups are distorted and not in plane with the anthracenyl backbone. This is indicated by the torsion angle C(15)–C(1)–C(5)–C(17) of 22.2(3)°. Similar to **3d**, there are also several intra- and intermolecular aryl stacking interactions in **4d**.

Host–guest chemistry of the Lewis-acids

The adduct formation of the host systems was then investigated in detail. The hydroborated species **4d** was found to be unsuitable for the formation of distinguishable adducts, probably for steric reasons or due to strong aryl stacking interactions of the eight C_6F_5 groups. Furthermore, the host chemistry of **3b** was found to be similar to that of **3c**, but since the ethyl derivative **3c** is easier accessible, this system was selected for further investigation. The adduct formation of **3a**, **3c** and **3d** with pyridine (Py) and the bifunctional bases pyrimidine (Pym) and tetramethylethylenediamine (TMEDA) was analysed by means of NMR spectroscopy, single crystal X-ray diffraction and elemental analyses (Scheme 3). In general, the coordination sphere of the boron atoms of each adduct in the solid state is distorted tetrahedral by coordination of a nitrogen atom of the respective amine. Consistent with this, the adduct formation of each adduct in solution (except the insoluble ones) is indicated by a chemical shift in the ^{11}B NMR spectra between −7 and +2 ppm, which is the typical shift range for tetracoordinated boron species. All three host systems formed the expected 1 : 2-adduct with pyridine. The signals in the ^{1}H NMR spectra were shifted with respect to the corresponding free host system (Fig. 2).

In contrast to the free host, the methylene protons of the adducts [**3a**·2Py] and [**3c**·2Py] become diastereotopic, resulting in a prominent doublet in the ^{1}H NMR spectra. In the ^{19}F NMR spectrum of [**3d**·2Py], the signals of the C_6F_5 groups are shifted with respect to the free host compound (Fig. 3).



Scheme 3 Adduct formation of hosts **3a**, **3c** and **3d** with pyridine, pyrimidine and TMEDA. [a] NMR spectra confirm the adduct formation; [b] a solid state structure was determined (see Fig. 4); [c] the formed adduct precipitates quantitatively, therefore no NMR data could be collected; [d] the ^{1}H NMR spectrum is strongly broadened, indicating oligomers or a dynamic exchange of different species in solution.

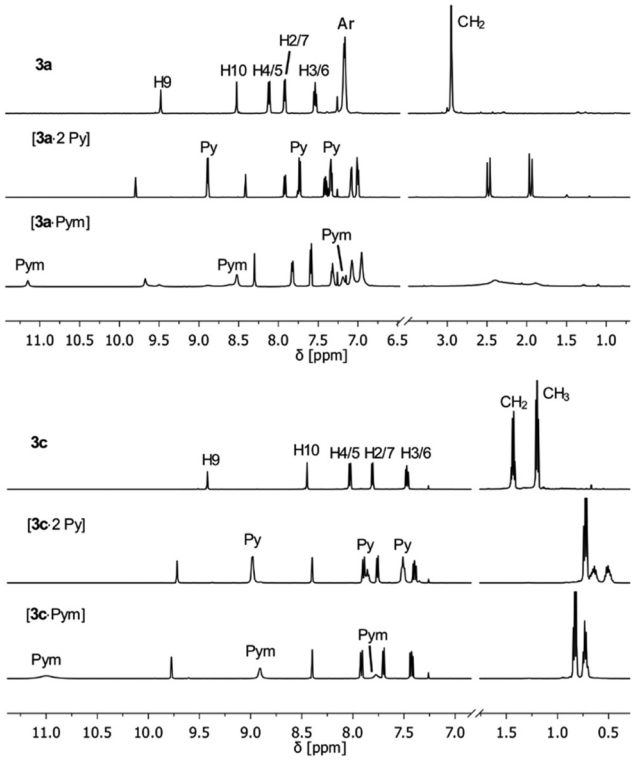


Fig. 2 ^{1}H NMR spectra of diboranes **3a** (top) and **3c** (below) as free host systems and adducts with pyridine (Py) and pyrimidine (Pym) in $CDCl_3$.

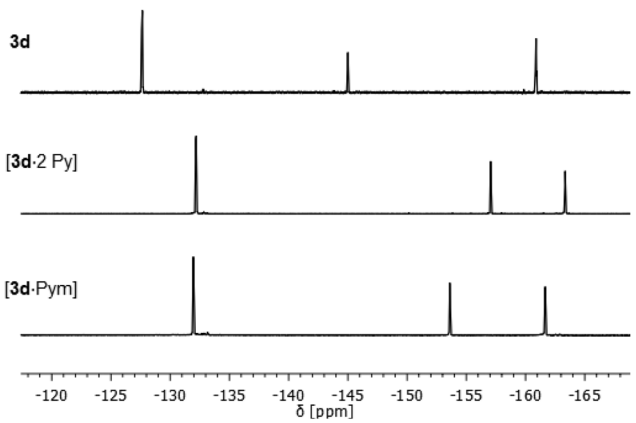


Fig. 3 ^{19}F NMR spectra of diborane **3d** as free host system and adducts with pyridine (Py) and pyrimidine (Pym) in C_6D_6.

Structural evidence for a 1 : 2-adduct formation of the pyridine adducts could be obtained by single crystal X-ray diffraction for the adducts of each host (Fig. 4). Among the pyridine adducts, [**3d**·2Py] shows the most pronounced distortion of the ethynyl spacers. This is expressed by the widest B···B distance among the adducts observed herein, by B(1)–C(1)–C(5) and B(2)–C(5)–C(1) angles well above 90° (indicating a strong lateral bending) and by a torsion angle B(1)–C(1)–C(5)–B(2) of 18.3(1)°, additionally indicating twisting of the alkyne units relative to the backbone (Table 1). This result can be explained by the higher steric demand of the C_6F_5 groups. Despite the higher Lewis acidity of the $B(C_6F_5)_2$ functions, the B···N distances in [**3d**·2Py] are not significantly shorter than in [**3a**·2Py] or [**3c**·2Py].

The formation of supramolecular complexes was then tested with the flexible bifunctional base TMEDA, which can adapt to the (mostly) fixed B···B distance in the host system. All three host systems quantitatively form an adduct with 1 : 1 composition in the form of a poorly soluble or insoluble precipitate. Even when a large excess of TMEDA was applied, the 1 : 1 adducts remained precipitated. Elemental analyses confirmed the 1 : 1 composition of the three TMEDA adducts.

While [**3a**·TMEDA] and [**3d**·TMEDA] are completely insoluble in $CDCl_3$, the adduct [**3c**·TMEDA] remains partially dissolved. This corresponds to the observation, that the adducts of the ethyl derivative **3c** are the most soluble ones studied here. In case of [**3c**·TMEDA], the ^{1}H and ^{11}B NMR spectroscopic data additionally support the existence of a stable adduct in solution. For [**3a**·TMEDA] and [**3c**·TMEDA], the precipitation process provided single crystals suitable for X-ray diffraction. The molecular structures in the solid state confirm the presence of chelate-like 1 : 1-adducts, in which the two amine functions of one TMEDA molecule are coordinated by the two boron atoms of a host molecule.

The pincer-like complexation of TMEDA results in less bent alkyne spacers and consequently a smaller B···B distance compared to the pyridine adducts (Table 1). Although the results for [**3c**·TMEDA] confirm a chelate-like 1 : 1-adduct and strongly suggest such an adduct for [**3a**·TMEDA], it cannot be conclusively ruled out for [**3d**·TMEDA] whether it is a chelate-like 1 : 1-adduct or a polymer with a 1 : 1 composition.

At least the formation of supramolecular adducts was tested with pyrimidine, which is a more rigid guest molecule and has a smaller N···N distance than TMEDA. When added to a solution of **3a**, a strong broadening of the signals in the NMR spectra is observed (Fig. 2). The appearance of only one ^{11}B NMR signal at 0.7 ppm of a 1 : 1 mixture of **3a** and pyrimidine confirms the saturation of each boron atom with an amine function. The broadening of the ^{1}H NMR resonances indicates the formation of oligomers with a 1 : 1 composition. Despite all attempts, single crystals of such an adduct could not be obtained.

Both **3c** and **3d** bind pyrimidine in a pincer-like fashion, as confirmed by the solid-state structures of the adducts [**3c**·Pym] and [**3d**·Pym]. Since the N···N distance in pyrimidine is smaller than in TMEDA, the B···B distances in the pyrimidine adducts are the shortest observed in this study. The alkyne spacers of the pyrimidine adducts are also the least distorted, as indicated by angles B(1)–C(1)–C(5) and B(2)–C(5)–C(1) close to 90° and a small torsion angle B(1)–C(1)–C(5)–B(2) (Table 1).

A doublet of the diastereotopic methylene protons can be observed in the ^{1}H NMR spectrum of [**3c**·Pym] (Fig. 2), similar but shifted with respect to [**3c**·2Py]. The ^{1}H and ^{19}F NMR spectroscopic data of [**3d**·Pym] are also consistent with the formation of a 1 : 1-adduct. Comparable to the ^{19}F NMR spectrum of the pyridine adduct of **3d**, the signals of the C_6F_5 groups in

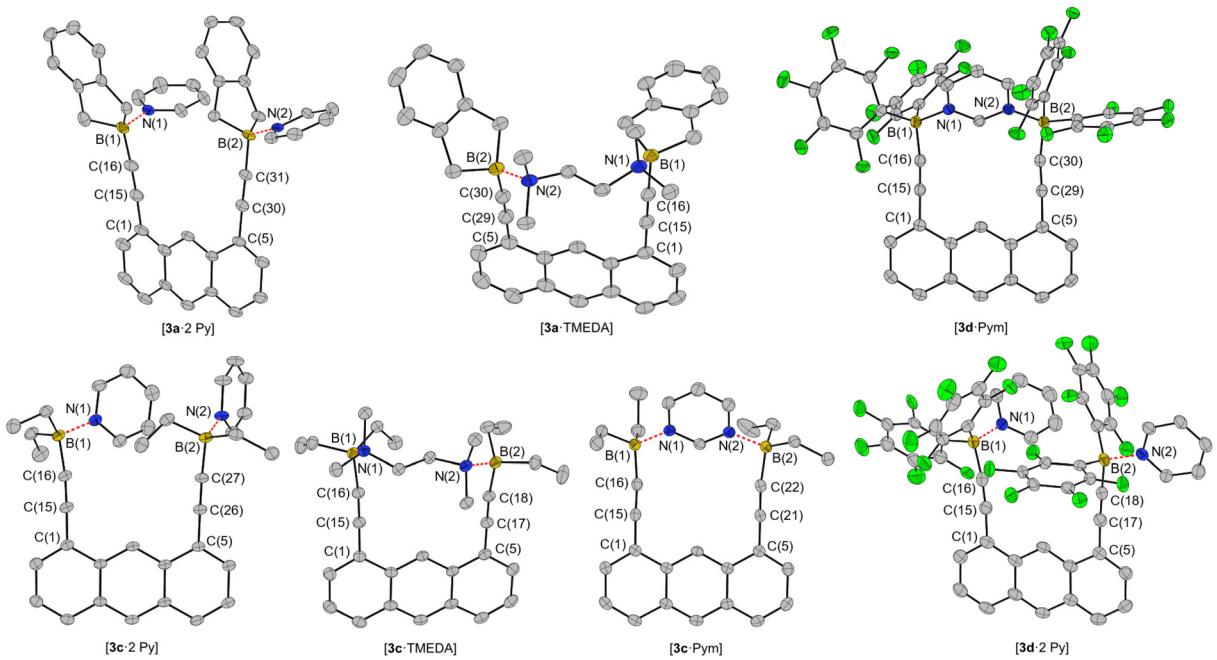


Fig. 4 Molecular structures of the adducts [**3a**·2Py], [**3a**·TMEDA], [**3d**·Pym], [**3c**·2Py], [**3c**·TMEDA], [**3c**·Pym] and [**3d**·2Py] in the solid state. B···N interactions are shown as red dotted lines. Hydrogen atoms, solvent molecules (in case of [**3d**·2Py] and [**3c**·Pym]) and one disordered C_6F_5 group (in case of [**3d**·2Py]) are omitted for clarity. For [**3a**·2Py], one of two independent molecules in the asymmetric unit is shown. Ellipsoids are set at 50% probability. Relevant data for these structures are listed in Table 1.

Table 1 Selected distances [Å] and angles [°] of the solid-state structures of the adducts [**3a**·2Py], [**3c**·2Py], [**3d**·2Py], [**3a**·TMEDA], [**3c**·TMEDA], [**3c**·Pym] and [**3d**·Pym] depicted in Fig. 4

Adduct	d(B(1)···B(2))	d(B(1)–N(1))	d(B(2)–N(2))	∢(B(1)–C(1)–C(5))	∢(B(2)–C(5)–C(1))	τ(B(1)–C(1)–C(5)–B(2))
[**3a**·2Py]	5.706(7)	1.638(6)	1.638(5)	98.8(1)	90.0(1)	13.7(1)
[**3c**·2Py]	5.808(1)	1.645(1)	1.636(1)	95.4(1)	92.8(1)	21.6(1)
[**3d**·2Py]	6.403(6)	1.596(6)	1.629(5)	101.9(1)	95.8(1)	18.3(1)
[**3a**·TMEDA]	5.453(2)	1.659(2)	1.678(2)	92.0(1)	92.6(1)	17.1(1)
[**3c**·TMEDA]	5.494(1)	1.717(1)	1.719(1)	93.7(1)	92.1(1)	13.9(1)
[**3c**·Pym]	5.231(2)	1.680(2)	1.673(2)	90.7(1)	92.5(1)	8.5(1)
[**3d**·Pym]	5.085(3)	1.669(2)	1.671(3)	91.3(1)	90.7(1)	4.7(1)

[**3d**·Pym] are shifted with respect to the free host **3d** (Fig. 3). When more than 1.0 equivalents of pyrimidine are added, signals of [**3d**·2Pym] can be observed in addition to [**3d**·Pym] as a distinct second species in solution. In the solid state, the B···B distance is even smaller than for [**3c**·Pym], despite the higher steric demand of C_6F_5 groups compared to ethyl groups.

Conclusions

The tin–boron exchange reaction with the chloroboranes **2a–d** allowed the efficient synthesis of four bidentate Lewis acids based on the 1,8-diethynylanthracene backbone. In addition, host **3d** was hydroborated to give tetraborane **4d**, with which no further hydroboration reaction was possible. Host–guest experiments with pyrimidine and TMEDA in solution and in the solid state demonstrated the formation of supramolecular chelate-like host–guest complexes. In the solid state structures, different steric requirements of the substituents were expressed by different degrees of bending of the alkyne spacers. This backbone distortion allows the host system to adapt to the guest molecules to a certain extent. The different substituents of the boranyl functions resulted in significantly different solubilities of the adducts. While the partially fluorinated system **3d** and its adducts were moderately soluble, the adducts of the ethyl derivative **3c** were the most soluble. The TMEDA adducts were completely or nearly insoluble in chloroform or benzene and immediately precipitated as 1 : 1 adducts. For **3c** and **3d**, pincer-like host–guest complexes with the smaller pyrimidine were observed in solution and the solid state. In contrast to **3c** and **3d**, system **3a**, despite its similarity to **3c**, did not form a distinct adduct with pyrimidine, but rather showed a dynamic exchange of different species in solu-

tion. The highly Lewis-acidic system **3d** forms a 1 : 1 adduct with pyrimidine, but also shows two distinguishable species ([**3d**·Pym] and [**3d**·2Pym]) upon addition of more than one equivalent pyrimidine.

Author contributions

J. L. Beckmann: synthesis, data analysis, writing the manuscript. H.-G. Stammler, B. Neumann and J.-H. Lamm: determination of SC-XRD structures, XRD data analysis. N. W. Mitzel: writing, reviewing, and editing the manuscript, supervision, project administration.

Conflicts of interest

There are no conflicts to declare.

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