Stable Lewis Base Adducts of Tetrahalodiboranes: Synthetic Methods and Structural Diversity


Abstract: A series of 22 new bis(phosphine), bis(carbene) and bis(isonitrile) tetrahalodiborane adducts have been synthesized, either by direct adduct formation with highly sensitive B-X precursors (X = Cl, Br, I) or by ligand exchange at stable B₂X₄(SMe₂)₂ precursors (X = Cl, Br) with labile dimethylsulfide ligands. The isolated compounds have been fully characterized using NMR spectroscopic, (C,H,N)-elemental and, for 20 of these compounds, X-ray crystallographic analysis, revealing an unexpected variation in the bonding motifs. Besides the classical B₂X₄L₂ diborane(6) adducts, some of the more sterically demanding carbene ligands induce a halide displacement leading to the first halide-bridged monocationic diboron species, [B₂X₄L₂]⁺ (A = BCl₄, Br, I). Furthermore, low-temperature 1:1 reactions of B₂Cl₄ with sterically demanding N-heterocyclic carbene ligands led to the formation of kinetically unstable mono-adducts, one of which was structurally characterized. A comparison of the NMR and structural data of new and literature-known bis-adducts shows several trends pertaining to the nature of the halides and the stereoelectronic properties of the Lewis bases employed.

Introduction

Diboron reagents enjoy a prominent position in organic synthesis, wherever they are used in diboration and borylation reactions.[1] In recent years singly base-stabilized sp²-sp⁵-diboranes(5) have received particular attention, as the polarization of their B-B bond generates an intrinsically nucleophilic boryl moiety, which can be used in uncatalyzed diborations or borylations.[2] While the electrophilic nature of boron makes borylated organic molecules excellent cross-coupling partners,[3] it is also the reason for the intrinsic instability of most diboron(4) (B₂X₄) reagents, unless these are stabilized by strongly π-donating amino or alkoxy substituents, as is the case for all commercially available diboron(4) reagents. The chemistry of tetrahalodiboranes (B₂X₄, X = halide) has been comparatively underexplored despite (and perhaps because of) their reactive B-X bonds, which render both their synthesis and the reduction of BCl₄ by a zinc arc discharge,[5] B₂Cl₄ is a highly pyrophoric liquid that decomposes rapidly at 0 °C. The optimization and scale-up of its synthesis by Schlesinger[6] enabled its use as a precursor for the convenient solution phase syntheses of B₂F₄[7] B₂Br₂[8] and later B₂I₄[9] by halogen exchange. Whereas B₂F₄ is stable up to moderately elevated temperatures, B₂Br₄ has to be stored below −40 °C and B₂I₄ below 0 °C under the exclusion of light. An alternative multi-step synthesis of B₂I₄ from commercially available B₂(NMe₂)₄ via B₂(OMe)₄ was designed later by Nöth[10] and recently provided the basis for the first solution phase synthesis of B₂Cl₄ by our group.[11]

Synthesis and decomposition of unstable B₂X₄L₂ compounds

- a) B₂X₄ + 2 OET₂ → B₂X₄(OET₂)₂ T - 78 °C → B₂X₄(OET₂)₂ T - decomposition X = F, T = 0 °C, X = Cl, T = -23 °C
- b) B₂Cl₄ + 2 PSH₂ → B₂Cl₄(PSH₂)₂ - 80 °C T - 78 °C → B₂Cl₄(PSH₂)₂ 25 °C → B₂Cl₄ + B₂S₃ - SH₂ H₂ + byproducts
- c) B₂Cl₄ + 2 PH₂ → B₂Cl₄(PH₂)₂ 25 °C H₇ - 65 °C → B₂Cl₄(PH₂)₂ - PH₄Cl
- d) B₂X₄ + 2 PX₃ → B₂X₄(PX₃)₂ T - 78 °C X = Cl, Br, X = Cl, -45 °C X = Br, CD₂Cl₂

Synthesis of stable B₂X₄L₂ compounds

- e) B₂Cl₄ + 2 NMe₃ → B₂Cl₄(NMe₃)₂ T - 78 °C 228 °C → melts without decomposition
- f) B₂(NMe₂)₄ → B₂Cl₄(NMe₃)₂ HCl 6 H₂O - 78 °C, - 2 [Me₂NH₃]Cl → B₂Cl₄(NMe₃)₂
- g) B₂X₄ + 2 SMe₂ → B₂X₄(SMe₂)₂ X = Cl, Br, 1 T - 78 °C 4 BX₃(SMe₂)₂ 80 °C → B₂(NMe₂)₄

Scheme 1. Early syntheses of bis(base)-stabilized tetrahalodiboranes(6).

With their two highly Lewis acidic boron atoms, tetrahalodiboranes(4) readily form adducts with neutral Lewis bases. While these are in general more electronically stable than their B₂X₄ precursors, the early days of this chemistry were marked by recurring problems of ligand lability and adduct decomposition. In diethyl ether at −78 °C, for example, B₂F₄ and B₂Cl₄ form isolable bis-adducts with the solvent, which upon warming decompose to the mono(etherates), which in turn decompose by ether cleavage (Scheme 1a).[5][6] With SH₂ and PH₃, B₂Cl₄ forms bis-adducts at −78 °C, which decompose upon decomposition. In diethyl ether at −78 °C, for example, B₂F₄ and B₂Cl₄ form isolable bis-adducts with the solvent, which upon warming decompose to the mono(etherates), which in turn decompose by ether cleavage (Scheme 1a).[5][6] With SH₂ and PH₃, B₂Cl₄ forms bis-adducts at −78 °C, which decompose upon

[a] Institute for Inorganic Chemistry and the Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.
Email: h.braunschweig@uni-wuerzburg.de

Supporting information containing NMR and X-ray crystallographic data for this article can be found under:

CCDC 1904798 – 1904819 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

storage challenging. First obtained in 1925 in poor yields from

the reduction of BCl₄ by a zinc arc discharge,[5] B₂Cl₄ is a highly pyrophoric liquid that decomposes rapidly at 0 °C. The optimization and scale-up of its synthesis by Schlesinger[6] enabled its use as a precursor for the convenient solution phase syntheses of B₂F₄[7] B₂Br₂[8] and later B₂I₄[9] by halogen exchange. Whereas B₂F₄ is stable up to moderately elevated temperatures, B₂Br₄ has to be stored below −40 °C and B₂I₄ below 0 °C under the exclusion of light. An alternative multi-step synthesis of B₂I₄ from commercially available B₂(NMe₂)₄ via B₂(OMe)₄ was designed later by Nöth[10] and recently provided the basis for the first solution phase synthesis of B₂Cl₄ by our group.[11]
diborenes and the linear B$_2$Br$_4$ adducts ([1,3-IMe]$_2$B$_2$Cl$_4$ or [1,3-Me$_2$NMe$_2$]$_2$B$_2$I$_4$) proved surprisingly stable, and upon addition of NMMe$_2$ yielded the first mixed-base diborane(6), [B$_2$Cl$_4$(P$_2$Me$_5$)(NMMe$_2$)]$_3$. With non-protonic nitrogen donors, B$_2$F$_4$ and B$_2$Cl$_4$ form stable mono- and bis-adducts, respectively, [B$_2$Cl$_4$(NMMe$_2$)$_2$]$_3$, in particular, remains stable up to its melting point at 228 °C and was crystallographically characterized as early as 1970 as displaying a centrosymmetric structure (B-B distance ca. 1.71 Å, Scheme 1e). While the reaction of protic HNMe$_2$ with B$_2$Cl$_4$ results in hydrolysis of all four chloride ligands and formation of B$_2$(NMMe$_2$)$_4$, the latter conversely reacts with 6 equivalents HCl to yield the stable bis(ammine) adduct B$_2$Cl$_4$(HNMe$_2$)$_2$, and two equivalents [Me$_2$NH$_2$]Cl as a byproduct (Scheme 1f). More recently, our group showed that stable dimethylsulfide adducts of all three heavier tetrahedral diboranes, B$_2$X$_4$(SMMe$_2$)$_4$ (X = Cl, Br, I), may be accessed by the traditional route of adding SMMe$_2$ to B$_2$X$_4$ at −78 °C, as well as by a high-yielding route from commercially available B$_2$(NMMe$_2$)$_4$, by amine-halogen exchange with BX$_4$(SMMe$_2$) (X = Cl, Br) (Scheme 1g).[10]

![Scheme 2](image)

**Scheme 2.** Reduction of B$_2$Br-LL’ to form compounds containing boron-boron multiple bonds.

Given the numerous synthetic challenges and stability issues exemplified in Scheme 1a-d, the first surge of interest in Lewis base tetrahalodiborane adducts died down in the early 1990s. It was renewed only recently in the wake of Robinson’s landmark isolation of the first N-heterocyclic carbene (NHC)-stabilized diborane, B$_2$H$_2$(Dipp)$_2$ (Dipp = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), in which boron is in the formal oxidation state +1.[11] Following a computational study by Frenking and Jones on the suitability of B$_2$X$_4$(IMe)$_2$ adducts (X = H, Cl; IMe = 1,3-dimethylimidazol-2-ylidene), as precursors for B$_2$X$_4$(IMe)$_2$ diboranes and the linear B$_2$(IMe)$_2$ diboronyne,[12] our group showed that B$_2$Br$_4$(Dipp)$_2$ could indeed be selectively reduced first to the corresponding diboronyne, B$_2$Br$_2$(IDipp)$_2$, and ultimately to the first isolable diboronyne, B$_2$(IDipp)$_2$ (Scheme 2a).[20] Since then a handful of symmetrical low-valent diboron compounds have been synthesized by reduction of B$_2$Br$_4$(CAAC)$_2$ (L = carbene), including a diboracumulene stabilized by strongly π-accepting cyclic (alkyl)(amino)carbene (CAAC) ligands (Scheme 2b).[21][22]

More recently, the group of Kinjo synthesized and structurally characterized the first mono-adduct of B$_2$Br$_4$, using a particularly π-acidic CAAC ligand displaying an endocyclic boron atom, CAAC$_4$ (Scheme 2c).[23] B$_2$Br$_4$(CAAC)$_4$ reacted with IDipp (Scheme 2c) and PMe$_5$ to yield the first unsymmetrical bis-adducts of B$_2$Br$_4$, which were reduced to the corresponding diboronyne (Scheme 2c) and a gernially bis(PMe$_5$)-stabilized neutral allenic diboronyne, respectively.[23][24]

In our quest to expand the scope and tune the steric and electronics of low-valent diboron compounds our group has synthesized and characterized a number of stable tetrahalodiborane Lewis base adducts over the years. Herein we present an overview of the synthetic methods employed and compare the influence of various Lewis bases on the electronic and structural properties of these compounds.

**Results and Discussion**

**Synthesis and NMR characterization**

Following the traditional route, two equivalents of a Lewis base L (L = phosphine, isonitrite, NHC or CAAC) were added to a pentane or hexane solution of B$_2$Cl$_4$ or B$_2$Br$_4$ at −78 °C. For B$_2$I$_4$ the reagents were simply combined in benzene at room temperature. The reaction mixtures were stirred for 1 to 2 hours at room temperature, prior to isolation of the colorless precipitates by filtration, washing with pentane or hexane and drying in vacuo. The resulting B$_2$X$_4$L$_2$ bis-adducts were obtained in moderate to excellent yields (47 to 92%, Scheme 3).

![Scheme 3](image)

**Scheme 3.** Synthesis of B$_2$X$_4$L$_2$ bis-adducts from B$_2$X$_4$ and monodentate Lewis bases.

The solubility of these tetrahalodiborane(6) compounds in benzene increases from virtually insoluble in the case of the chloro-derivatives to fully soluble in the case of the iodo-derivative. The solid-state structures of all eleven compounds were confirmed by X-ray crystallographic analysis (vide infra).
While the majority of these compounds can be stored indefinitely at room temperature under an argon atmosphere and are stable in chlorinated solvents, $\text{B}_2\text{Cl}_i(\text{IPr})_2$ and $\text{B}_2\text{Cl}_i(\text{DIPr})_2$ ($\text{IPr} = 1,3$-disopropylimidazol-2-ylidene; $\text{DIPr} = 1$-(2,6-diisopropylphenyl)-3-isopropylimidazol-2-ylidene) decomposed under these conditions to the imidazolium hydrochloride salts and a number of unidentified boron species. Furthermore, isolated $\text{B}_2\text{Cl}_i(\text{CNBu})_2$ was found to decompose in C$_6$D$_6$ and CD$_2$Cl$_2$ over a period of several days at room temperature into a multitude of unidentifiable boron-containing species (see SI). While a wide variety of decomposition pathways of CNBu-stabilized diboron compounds has been reported, including insertion into the B–B bond, C–C-coupling, C≡N cleavage and isoprene elimination,\textsuperscript{23} it is noteworthy that the heavier homologues, $\text{B}_2\text{Br}_i(\text{CNBu})_2$ and $\text{B}_2\text{I}_i(\text{CNBu})_2$, are indefinitely stable in solution.

A comparison of the $^{11}$B NMR resonances of analogous tetrachloro-, -bromo- and -iodo $\text{B}_2\text{X}_i\text{L}_2$ derivatives, both new and literature-known, shows increasing upfield shifts down the group (Table 1). $\text{B}_2\text{Cl}_i(\text{CNBu})_2$, for example, displays an $^{11}$B NMR shift of $-43.1$ ppm, ca. $27$ ppm upfield of $\text{B}_2\text{Br}_i(\text{CNBu})_2$ at $-16.5$ ppm.\textsuperscript{25} A comparably large shift difference of $20$ to $24$ ppm is observed for $\text{B}_2\text{I}_i(\text{SMez})_2$ ($\delta_{11B} = -20.0$ ppm) and $\text{B}_2\text{Br}_i(\text{SMez})_2$ ($\delta_{11B} = -3.3$ ppm),\textsuperscript{26} as well as $\text{B}_2\text{I}_i(\text{PCy})_2$ ($\delta_{11B} = -28.0$ ppm) and $\text{B}_2\text{Br}_i(\text{PCy})_2$ ($\delta_{11B} = -4.3$ ppm).\textsuperscript{26} A smaller upfield shift of $5$ to $8$ ppm is observed between pairs of $\text{B}_2\text{Cl}_i\text{L}_2$ and $\text{B}_2\text{Br}_i\text{L}_2$ analogues, e.g. for $\text{B}_2\text{Cl}_i(\text{SMez})_2$ ($\delta_{11B} = 7.3$ ppm) and $\text{B}_2\text{Br}_i(\text{SMez})_2$ ($\delta_{11B} = 0.3$ ppm),\textsuperscript{26} $\text{B}_2\text{Cl}_i(\text{PMe})_2$ ($\delta_{11B} = 0.3$ ppm) and $\text{B}_2\text{Br}_i(\text{PMe})_2$ ($\delta_{11B} = -7.3$ ppm) and $\text{B}_2\text{Cl}_i(\text{CAAC})_2$ ($\delta_{11B} = -2.3$ ppm) and $\text{B}_2\text{Br}_i(\text{CAAC})_2$ ($\delta_{11B} = -2.3$ ppm).\textsuperscript{26} This is in line with the greater increase in relative electronegativity from I to Br (ca. $11\%$) than from Br to Cl (ca. $7\%$).\textsuperscript{29} For a given halogen the $^{11}$B NMR shifts of $\text{B}_2\text{X}_i\text{L}_2$ derivatives are particularly sensitive to the overall electron donor strength of the ligands. A comparison of the compounds shown in Scheme 1 with literature data provides the following order of overall electron donor strength: $\text{SMez} < \text{IDip} < \text{CAAC}^{\text{Me}} < \text{IDip} < \text{PCy} < \text{IPr} < \text{PMe} < \text{CN Dip} < \text{CN Bu}$ (Table 1).

For the adduct formation of $\text{B}_2\text{I}_4$ with CAAC$^{\text{Me}}$ an ionic species, $[\text{B}_2\text{I}_4(\text{CAAC})_2]^2$\textsuperscript{2}I, was obtained by displacement of one of the iodides. The compound displays a single, very broad $^{11}$B NMR $\delta_2$ resonance at $\sim 5.9$ ppm, significantly downfield from that expected for a classical $\text{B}_2\text{I}_4(\text{CAAC})_2$ diborane(6) bis-adduct, which would appear slightly downfield of that of $\text{B}_2\text{I}_4(\text{PCy})_2$ at $\sim 28$ ppm. The solid-state structure of $[\text{B}_2\text{I}_4(\text{CAAC})_2]^2$ shows that one of the iodide ligands of the diboron cation occupies a bridging position (\textit{vide infra}). It is the first example of such a structural motif for Lewis base-stabilized tetravalodiboranes.

![Figure 1](image-url)
<table>
<thead>
<tr>
<th>Compound type</th>
<th>Formula</th>
<th>$^{13}$B NMR shifts (ppm) $^a$</th>
<th>Bond lengths (Å)</th>
<th>Torsion angle (L.B.B.L.) ($^\circ$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_3\text{X}_3\text{L}$</td>
<td>$\text{B}_2\text{Cl}(\text{IMes})_2$</td>
<td>68.5, $-4.6$</td>
<td>1.719(4), 1.861(1), 1.868(1)</td>
<td>1.976(1)</td>
<td>180 $^a$</td>
</tr>
<tr>
<td>$\text{B}_3\text{Cl}(\text{IDip})_2$</td>
<td>68.7, $-4.1$</td>
<td>1.72(2)</td>
<td>$^{sp^3}$B 2.03(1), 2.058(9)</td>
<td>$^{sp^3}$B 1.80(1), 1.910(8)</td>
<td>1.61(1) $^a$</td>
</tr>
<tr>
<td>$\text{B}_3\text{Br}($CAAC$)^2$</td>
<td>67.3, $-6.3$</td>
<td>1.72(2)</td>
<td>$^{sp^3}$B 2.03(1), 2.058(9)</td>
<td>$^{sp^3}$B 1.80(1), 1.910(8)</td>
<td>1.61(1) $^a$</td>
</tr>
</tbody>
</table>

| $\text{B}_3\text{X}_3\text{L}^\text{b}$ | $\text{B}_2\text{Cl}($SMes$)_2$ | 3.7 | 1.753(5), 1.763(3) | 1.873(3) | 1.941(2) | 1.686(3) | 1.683(4) | 178.1(2), 179.0(2) $^a$ |
| $\text{B}_2\text{Cl}($PEcy$)_2$ | 4.8 | 1.735(8) | 1.884(6) | 1.907(5) | 2.035(5) | 162.2(3) $^a$ |
| $\text{B}_2\text{Cl}($PPh$)_2$ | 3.5 | 1.754(6) | 1.910(3) | 1.915(3) | 1.633(4) | 180 $^a$ |
| $\text{B}_2\text{Cl}($Dip$)$ | 2.4 | 1.757(4) | 1.886(3) | 1.925(3) | 1.630(4), 1.641(3) | 154.1(2) $^a$ |
| $\text{B}_2\text{Cl}($Mes$)$ | 2.7 | 1.760(4) | 1.874(3) | 1.912(3) | 1.645(3), 1.646(3) | 154.7(2) $^a$ |
| $\text{B}_2\text{Cl}($Silmes$)$ | 1.1 | – | – | – | – | – $^a$ |
| $\text{B}_2\text{Cl}($CAAC(chi)$)^2$ $^f$ | 2.6 | 1.758(5), 1.763(3) | 1.873(3) | 1.941(2) | 1.686(3) | 1.683(4) | 178.1(2), 179.0(2) $^a$ |
| $\text{B}_2\text{Br}($SMes$)_2$ | –0.3 | 1.715(4) | 2.026(2), 2.051(2) | 1.961(2) | 180 $^a$ |
| $\text{B}_2\text{Br}($PPh$)_2$ | –7.3 | 1.713(4) | 2.059(2), 2.068(2) | 1.956(2) | 180 $^a$ |
| $\text{B}_2\text{Br}($Dip$)$ | –6.7 | 1.708(7) | 2.061(5) | 2.071(5) | 1.974(5), 1.977(5) | 170.3(2) $^a$ |
| $\text{B}_2\text{Br}($Dip$)$ | –5.2 | 1.748(3) | 2.064(3) | 2.081(3) | 2.033(3), 2.050(3) | 167.1(1) $^a$ |
| $\text{B}_2\text{Br}($PCy$)_2$ | –4.3 | 1.746(7) | 2.052(4) | 2.073(5) | 2.019(5), 2.026(5) | 163.1(2) $^a$ |
| $\text{B}_2\text{Br}($Mes$)$ | –6.8 | 1.718(5) | 2.069(2), 2.054(3) | 1.975(3) | 180 $^a$ |
| $\text{B}_2\text{Br}($Dpp$)$ | –5.0 | 1.752(6) | 2.051(4) | 2.064(5) | 2.008(6), 2.018(4) | 50.5(5) $^a$ |
| $\text{B}_2\text{Br}($Dpp$)$ | –6.7 | 1.714(7) | 2.027(5) | 2.042(5) | 1.980(5), 1.995(5) | 32.7(3) $^a$ |
| $\text{B}_2\text{Br}($Dpp$)$ | –7.0 | – | – | – | – | – $^a$ |
| $\text{B}_2\text{Br}($Dpp$)$ | –7.2 | 1.713(3) | 2.058(2), 2.068(2) | 1.956(2) | 22.6(1) $^a$ |
| $\text{B}_2\text{Br}($CNBu$)_2$ | –16.5 | 1.716(5) | 2.027(4), 2.034(4) | 1.570(5), 1.592(5) | 177.7(3) $^a$ |
| $\text{B}_2\text{Br}($CNDip$)_2$ | –15.7 | 1.732(3) | 2.016(3) | 2.044(2) | 1.581(4), 1.579(4) | 172.9(2) $^a$ |
| $\text{B}_2\text{Br}($Dip$)$ | –2.2 | 1.764(4) | 2.048(3) | 2.116(3) | 1.637(3), 1.638(3) | 151.4(2) $^a$ |
| $\text{B}_2\text{Br}($Dep$)_2$ | 0.8 $^{[10]}$ | 1.736(6) $^{[11]}$ | 2.053(4) | 2.086(4) $^{[11]}$ | 1.663(5), 1.664(5) $^{[11]}$ | 159.3(3) $^{[11]}$ |
| $\text{B}_2\text{Br}($Dip$)_2$ | –4.8 | – | – | – | – | – $^{[11]}$ |
| $\text{B}_2\text{Br}($CAAC(chi)$)^2$ | –2.3 | 1.754(5) | 2.058(3) | 2.136(3) | 1.660(4), 1.667(4) | 177.3(3) $^{[11]}$ |
| $\text{B}_2\text{Br}($SMes$)_2$ | –20.0 | 1.714(7) | 2.250(3), 2.280(3) | 1.955(4) | 180 $^a$ |
| $\text{B}_2\text{Br}($PyMes$)_2$ | –27 | 1.727(7) | 2.290(5), 2.298(5) | 1.958(5) | 180 $^a$ |
| $\text{B}_2\text{Br}($PCy$)_2$ | –28 | 1.766(6) | 2.293(4) | 2.313(4) | 2.013(4), 2.027(4) | 163.1(2) $^a$ |
| $\text{B}_2\text{Br}($PCy$)_2$ | –26 | 1.759(5) | 2.281(3) | 2.306(3) | 1.980(4), 1.981(4) | 167.2(2) $^a$ |
| $\text{B}_2\text{Br}($CNBu$)_2$ | –43.1 | 1.675(16) | 2.259(8), 2.287(8) | 1.560(10) | 180 $^a$ |

$^a$ At 25 $^\circ$C; $^b$ structural data for both hexane and toluene co-crystals; $^c$ X = terminal X, X$_a$ = bridging X; $^d$ disorder preventing discussion of structural parameters; $^e$ two molecules present in the asymmetric unit; $^f$ this work.
Furthermore, the reaction of IMes or IDip with one equivalent of B$_2$Cl$_4$ at $-78 \, ^\circ\text{C}$ led to the formation of the mono-adducts B$_2$Cl$_4$(IMes) and B$_2$Cl$_4$(IDip), respectively, as well as small amounts of the corresponding B$_2$Cl$_4$(NHC)$_2$ bis-adducts (Scheme 5). These highly unstable compounds were identified by low-temperature $^{11}$B NMR spectroscopy by their two major broad resonances around $-69$ and $-5$ ppm, alongside several minor side products. These resonances are similar to those observed for the only other reported B$_2$Cl$_4$ mono-adduct, B$_2$Cl$_4$(P(SiMe$_3$)$_2$), at 69.5 (sp$^3$-B) and $-0.9$ (sp$^3$-B) ppm. An X-ray crystallographic experiment on single crystals of B$_2$Cl$_4$(IMes) obtained by diffusion of pentane into a saturated difluorobenzene solution at $-30 \, ^\circ\text{C}$ confirmed the formation of the 1:1 adduct (vide infra).

![Figure 2. Crystallographically-derived molecular structures of (from left to right, top) B$_2$Br$_4$(PMe$_2$L)$_2$, B$_2$Br$_4$(PE$_2$L)$_2$, B$_2$Br$_4$(PP$_2$L)$_2$, B$_2$Cl$_4$(PCy$_3$L)$_2$, B$_2$Cl$_4$(PCy$_3$L)$_2$.](Image 48x534 to 387x753)

Scheme 5. Low-temperature formation of a B$_2$Cl$_4$-mono-NHC adducts.

Warming of these reaction mixtures to room temperature resulted in decomposition into the ionic, chloride-bridged compounds [B$_2$Cl$_4$(IMes)$_2$][BCl$_4$] and [B$_2$Cl$_4$(IDip)$_2$][BCl$_4$], respectively, both structurally confirmed by X-ray crystallographic analysis (vide infra). Both compounds display a sharp $^{11}$B NMR singlet at 6.9 ppm for the BCl$_4^-$ counteranion, which is likely formed by the addition of the expelled chloride anion to free BCl$_4$, resulting from the inevitable disproportionation of excess B$_2$Cl$_4$ upon warming the reaction mixture to room temperature. The broad $^{11}$B NMR B$_2$ resonances of the [B$_2$Cl$_4$(NHC)$_2$] cations (13.6 and 36.6 ppm for NHCl = IMes and IDip, respectively) are downfield-shifted from those of their B$_2$Cl$_4$(NHC)$_2$ diboranate(6) counterparts (2.7 and 1.5 ppm, respectively). The surprisingly low-field $^{11}$B NMR shift of the IDip- versus the IMes-analogue may be caused by reversible ligand dissociation in solution. This hypothesis was supported by the fact that the $^{11}$B NMR shift of [B$_2$Cl$_4$(IDip)$_2$][BCl$_4$] was highly concentration- and solvent-dependent, varying between 25 and 40 ppm at room temperature. Due to the poor solubility of the species, however, and the fact that it could not be separated from B$_2$Cl$_4$(IDip)$_2$, no qualitative analysis of its fluxional solution behavior could be carried out. It is noteworthy that these ionic compounds were not observed as products of the 1:2 reactions of B$_2$Cl$_4$ with IMes or IDip, which suggests that it may only be accessible from the decomposition of the mono-adducts. While cationic monoboron(III) species, which are significantly more Lewis acidic than neutral boranes, are well-known and have found applications in catalysis, in particular, cationic diboron species like these remain relatively rare. Most known examples are dicatonic bis(base)-stabilized sp$^2$-sp$^2$- or sp$^3$-sp$^3$-diboron(II) compounds, in which the electron-deficient boron centers are stabilized through π donation by neutral and/or anionic nitrogen ligands, while Kinjo reported a unique tetrakis(carbene)-stabilized sp$^3$-sp$^3$-diboron dication. Prior to the [B$_2$X$_4$L$_2$]A compounds presented herein, only a couple of examples of monocationic sp$^2$-sp$^2$-diboron(II) compounds had been reported, which were obtained by adding a single equivalent of IMes or IDip to B$_2$Br$_2$(NMe$_2$)$_2$, resulting in the displacement of one bromide ligand.

Attempts to obtain mixed-base adducts by adding a second Lewis base L to in-situ-formed B$_2$Cl$_4$(NHC) at low temperature all resulted in statistical mixtures of B$_2$Cl$_4$(NHC)$_2$L, B$_2$Cl$_4$L$_2$ and B$_2$Cl$_4$(NHC)L as determined by $^{11}$B NMR spectroscopic analysis.
diboranes are magnetically inequivalent, with regards to their coupling to each of the $^{31}$P nuclei. This leads to higher order effects for the $^1$H and $^{13}$C($^1$H) resonances exhibiting $^3$P-coupling. In the case of $\text{BrB}(\text{PEt}_3)_2$ shown in Fig. 3, for example, the $^1$H NMR PCH$_2$ resonance at 2.10 ppm appears as a well-defined doublet of quartets overlapping with a broad virtual quartet. This unusual splitting pattern is owed to the existence of a complex ABXMMX’VB’A’ spin system (A’A’ = CH$_3$, B’B’ = CH$_3$, XX’ = P1/P2, M'/M = B1/B2) with strong coupling between the magnetically inequivalent pair of $^{31}$P nuclei, as well as $^3$J(H-H) and $^3$J(H-B1) couplings of similar magnitudes. The line broadening of the virtual signal is caused by the additional coupling to the fast-relaxing quadrapolar boron nuclei in the B-B bridge. In this spin system the virtual $^1$H-$^{31}$P coupling $N$, defined as the apparent peak separation of the two outer peaks, provides $[J_{\text{H,B1}}]+[J_{\text{H,B2}}] = 10.9$ Hz. Conversely, the corresponding $^{13}$C($^1$H) NMR PCH$_2$ resonance at 13.5 ppm appears as a sharp doublet displaying a broad virtual resonance at its center, while the CH$_3$ resonance at 7.7 ppm appears as a virtual triplet. Here we have two AXMMX’A’ spin systems (A’A’ = CH$_3$ or CH$_3$, XX’ = P1/P2, M'/M = B1/B2), in which the virtual $^{13}$C-$^3$P coupling $N$, defined as the separation between the two outer peaks, provides $[J_{\text{H,B1}}]+[J_{\text{H,B2}}] = 38.6$ Hz and $[J_{\text{H,B1}}]+[J_{\text{H,B2}}] = 5.4$ Hz. Similar higher order effects can be observed in the $^1$H and $^{13}$C($^1$H) NMR spectra of all the $\text{BrB}(\text{PR}_3)_2$ and $\text{BrB}(\text{dppa})_2$ diboranes.

To circumvent the numerous challenges associated with the synthesis, storage and handling of $\text{BrB}(\text{PEt}_3)_2$ and $\text{BrB}(\text{dppa})_2$, we sought to replace them with their dimethylsulfide bis-adducts, which are stable solids at room temperature under inert atmosphere and can be synthesized on a multigram scale from commercially available $\text{B}_2(\text{NMMe}_2)_4$ and $\text{BX}_2(\text{SMe}_2)$ ($X = \text{Cl}$ and $\text{Br}$), respectively.\textsuperscript{[36]} It was hoped that the weakly binding SMe$_2$ ligands could be easily displaced by stronger donor ligands to afford new $\text{BrB}$ bis-adducts in higher yields. Indeed, ligand exchange reactions of $\text{BrB}(\text{SMe}_2)_2$ with two equivalents of a trialkylphosphine proceeded quantitatively to $\text{BrB}(\text{PR}_3)_2$ in benzene at room temperature over the course of 3 h (Scheme 6a). Under the same conditions, $\text{BrB}(\text{SMe}_2)_2$ underwent quantitative ligand exchange with various amino- and ferrocenyl-bridged bis(phosphines) at room temperature (Scheme 6b). The corresponding tetrachlorodiborane(6) analogues could also be obtained in a similar fashion but proved virtually insoluble in all suitable NMR and crystallization solvents, thus precluding further analysis.

Although chemically equivalent, the substituents of each of the two phosphine moieties in the $\text{BrB}(\text{PR}_3)_2$ and $\text{BrB}(\text{dppa})_2$ diboranes are magnetically inequivalent, with regards to their coupling to each of the $^{31}$P nuclei. This leads to higher order effects for the $^1$H and $^{13}$C($^1$H) resonances exhibiting $^3$P-coupling. In the case of $\text{BrB}(\text{PEt}_3)_2$ shown in Fig. 3, for example, the $^1$H NMR PCH$_2$ resonance at 2.10 ppm appears as a well-defined doublet of quartets overlapping with a broad virtual quartet. This unusual splitting pattern is owed to the existence of a complex ABXMMX’VB’A’ spin system (A’A’ = CH$_3$, B’B’ = CH$_3$, XX’ = P1/P2, M'/M = B1/B2) with strong coupling between the magnetically inequivalent pair of $^{31}$P nuclei, as well as $^3$J(H-H) and $^3$J(H-B1) couplings of similar magnitudes. The line broadening of the virtual signal is caused by the additional coupling to the fast-relaxing quadrapolar boron nuclei in the B-B bridge. In this spin system the virtual $^1$H-$^{31}$P coupling $N$, defined as the apparent peak separation of the two outer peaks, provides $[J_{\text{H,B1}}]+[J_{\text{H,B2}}] = 10.9$ Hz. Conversely, the corresponding $^{13}$C($^1$H) NMR PCH$_2$ resonance at 13.5 ppm appears as a sharp doublet displaying a broad virtual resonance at its center, while the CH$_3$ resonance at 7.7 ppm appears as a virtual triplet. Here we have two AXMMX’A’ spin systems (A’A’ = CH$_3$ or CH$_3$, XX’ = P1/P2, M'/M = B1/B2), in which the virtual $^{13}$C-$^3$P coupling $N$, defined as the separation between the two outer peaks, provides $[J_{\text{H,B1}}]+[J_{\text{H,B2}}] = 38.6$ Hz and $[J_{\text{H,B1}}]+[J_{\text{H,B2}}] = 5.4$ Hz. Similar higher order effects can be observed in the $^1$H and $^{13}$C($^1$H) NMR spectra of all the $\text{BrB}(\text{PR}_3)_2$ and $\text{BrB}(\text{dppa})_2$ diboranes.

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Interestingly, the outcome of the ligand exchange reaction of B₂Br₄(SMes)₂ with CAAC₄Mo exclusively yielded bromide-bridged [B₂Br₄(CAAC₄Mo)₂]Br (δ₁H = 7.8 ppm, Scheme 7c), whereas the direct addition of CAAC₄Mo to B₂Br₄ affords the classical diborane(6) only (δ₁H = -2.3 ppm, Scheme 2b). Gratifyingly, the reduction of [B₂Br₄(CAAC₄Mo)₂]Br with four equivalents of sodium naphthalenide in THF yields the diboracumulene B₂(CAAC₄Mo)₂ (Scheme 7d) in similar yields to the reduction of B₂Br₄(CAAC₄Mo)₂ (Scheme 2b).  

The synthesis of B₂X₂L₂ (or [B₂X₂L₂]₂) from B₂X₄(SMe)₂ (X = Cl, Br), room-temperature-stable solids, obtained in a single step and excellent yield from two commercial reagents, B₂(NMe)₄ and BX₄(SMe₂) (Scheme 1f),[10] is particularly attractive as all these compounds are potential precursors for low-valent diboron species. Until now, the synthesis of such compounds relied on multi-step, low-yielding syntheses of pyrophoric and thermally unstable B₂X₄, also starting from commercial B₂(NMe)₄.[10] This new synthetic route also facilitates the scaling-up of syntheses, thus opening up new horizons for reactivity studies on these compounds.

X-ray crystallographic analyses

Colorless single crystals suitable for X-ray crystallographic analyses were obtained for the majority of the new tetrahalodiborane Lewis base adducts described above. The resulting solid-state structures are displayed in Figs. 1, 2, 4, 5 and 7 (see Figs. S68 – S70 in the SI for the solid-state structures of B₂Br₄(PMe₂Ph)₂, [B₂Cl₂(Dip)₂][BCl] and [B₂Br₄(CAAC₄Mo)₂]Br[27] while relevant bond lengths and angles are provided in Table 1.

Figure 4. Crystallographically-derived molecular structure of B₂Cl₂(IMes). Thermal ellipsoids drawn at 50% probability level. Ellipsoids on the ligand peripheries and most hydrogen atoms omitted for clarity.

A tetrahalodiborane(5). X-ray crystallographic analysis of the mono-adduct B₂Cl₂(IMes) (Fig. 4) confirmed the unsymmetrical nature of the compound, which displays one planar sp²-borane moiety at B₂ (Z₁(B₂) 359.8(2)°) and one tetrahedral sp³-borane moiety at B₁ (B₂-B₁-C₁ 103.45(19); B₂-B₁-C₂ 111.8(2); B₂-B₁-C₁ 116.4(2)°). Accordingly, the B₂-Cl bonds (1.753(3), 1.764(4) Å) are significantly shorter than the B₁-Cl bonds (1.882(3), 1.893(3) Å), similarly to the variation in B-Br bond lengths in Kinjo’s tetrabromodiborane(5), B₂Br₄(CAAC₄Mo).[23] Comparison with the corresponding bis(IMes) adduct, B₂Cl₂(IMes)₂ (Fig. 1), shows much shorter B-B and B-Cl bonds in B₂Cl₂(IMes) (1.719(4) and 1.619(4) Å, respectively) versus B₂Cl₂(IMes)₂ (1.760(4) and 1.645(3), 1.646(3) Å, respectively) as expected for the lower coordination number. In recent years sp²-sp²-diboranes have gained in popularity due to their potential as sources of a nucleophilic boryl moiety[20] and numerous examples have now been structurally characterized.[28] However, besides B₂Br₄(CAAC₄Mo)[23] B₂Cl₂(IMes) is only the second example of a crystallographically characterized tetrahedral diborane(5).

Diborane(6) adducts of monodentate ligands. For a given halogen X the B-B bond length of the B₂X₂L₂ diborane(6) compounds seems more dependent on the steric than the electronic properties of L. Thus the B-B bond in B₂Br₄(CNDip): (1.732(3) Å) is significantly longer than in B₂Br₄(CNBu): (1.716(5) Å) despite CNBu being the stronger donor, while B₂Cl₂(SMes): and B₂Cl₂(PMe₃): display identical B-B bond lengths (1.719(2) and 1.718(3) Å, respectively), despite PMe₃ being a significantly stronger donor than SMes. As expected, the B-B bonds in these B₂X₂L₂ compounds are significantly shorter than in the few structurally characterized B₂H₂L₂ tetrahydrodiborane(6) counterparts (L = IMes: 1.795(5) Å[39] iDip: 1.828(4) Å[37] PPh₃: 1.76(2) Å)[60] due to the more electronegative halides drawing electron density out of the B-B bond.

Interestingly, there is little B-B bond length variation for a given ligand L when varying the halogen X. This is best exemplified by the virtually identical B-B bond lengths in B₂X₄(SMes): of 1.719(2), 1.715(4) Å and 1.714(7) Å for X = Cl, Br and I, respectively. The same observation can be made for bis(phosphine) adducts such as B₂X₄(PMe₃): (B-B 1.718(3), 1.713(3) and 1.727(7) Å for X = Cl, Br and I, respectively), bis(NHC) adducts such as B₂X₄(Dip)₂: (B-B 1.757(4) and 1.764(4) Å for X = Cl and Br, respectively) and the bis(CAAC₄Mo) adducts (B-B 1.758(5) – 1.763(3) and 1.754(5) Å for X = Cl and Br, respectively). The only significant outlier is the tetraiododiborane(6) bis(isonitrile) adduct B₂I₄(CNBu): (Fig. 4), which displays a very short B-B bond length of 1.675(16) Å, ca. 0.04 Å shorter than that of its bromide analogue (1.716(5) Å). Among classical diborane(6) compounds there are few examples of shorter B-B single bonds, including a bipyridine-bridged bis(benzene1,2-dithiolate) diborane (B₂I₂(1.655(5) Å)[38] in which the shortening of the B-B bond is enforced by the bridging ligand.

All the B₂X₂L₂ diboranes(6) in which L is a monodentate donor ligand display a staggered anti-conformation of the ligands. For the smallest ligands (e.g. SMes, PMe₃, NMe₃, CNBu), the structure tends to be centroymmetric, with an (L,B,B,L) torsion angle of 180° (Fig. 6), which then widens with the steric demands of the ligands. This is best exemplified by the extensive series of B₂Br₄L₂ analogues, in which the torsion angle α follows the increase in steric demands of L: SMes > PMe₃ > NMe₃ > CNBu > CNDip.
(180°) = CN/But (177.7(3)°) < CNDip (172.9(2)°) < PrPr3 (167.1(1)°) < PCy3 (163.1(2)°) < IDep (159.2(3)°) < IDepPr (151.4(2)°). The only outlier in this series is BzBr(Imes)2, which displays a (C,B,B,C) torsion angle of 177.3(3)° despite the high steric demands of the CAAC\(^{26}\) ligand. Similarly, the (C,B,C) torsion angle of B2Cl4(Imes)2 is close to 180°, which suggests that electronic factors override steric for this particular ligand. Moreover, with the exception of B2Cl4(Imes)2, in which the two NHC rings are coplanar, the mean planes of the NHC or CAAC rings in the other bis-carbene adducts form an angle β from 57° in BzBr(Imes)2 to ca. 79° in B2Cl4(Imes)2, albeit without any obvious steric-dependent trend, suggesting an interplay between steric and packing forces. Furthermore, again with the exception of BzCl(CIrPr)2 and BzCl(Imes)2, one of the B-X bonds at each boron center tends to align with the π framework of the adjacent carbene ligand, as seen by the relatively small (X,B,C,N) torsion angles γ, ranging from 0° and 4° in BzCl(CIrPr)2 to 9° and 14° in BzCl(Imes)2, presumably to maximize orbital overlap with the π electrons of the halide ligand.

It is noteworthy that, with the exception of the recently published BzBr(PCY3)2,\(^{28}\) the tetrabromodiborane bis(phosphine) adducts presented herein are among the first crystallographically characterized compounds of their kind. Furthermore, BzBr(CN/But)2 is the first structurally characterized tetraiododiborane bis(isonitrile) adduct.

Diborane(6) adds of bridging diphosphine ligands. Here again, the B-B distance is governed by the steric of the diphosphine spacer: while BzBr(dppa\(^{pr}\)) (dppa\(^{pr}\) = bis(diphenylphosphino)isopropylamine) and BzBr(dppm\(^{pf}\)) (dppm\(^{pf}\) = bis(diphenylphosphino)p-fluoroaniline), with their small amino spacer, display identical B-B bond lengths (1.714(7) and 1.713(3) Å, respectively), similar to those of the less sterically demanding BzBr(PrPh\(^{3}\)) adducts (R2 = Me3, Et3, MesPh: B-B 1.708(7) – 1.7185(6) Å, BzBr(dppm) (dppm = 1,1'-bis(diphenylphosphino)ferrocene), with its large ferrocene spacer, displays a much longer B-B bond of 1.752(6) Å. Furthermore, the (P,B,B,P) torsion angle widens with the size of the spacer, from NPhF (22.6(1)°) over NPr (32.7(3)°) to Fc (50.5(5)°), as the molecule strives to reach a staggered gauche conformation with minimal ligand repulsion. The effect of the ligand electronics is seen in the two dppa analogues: the B-Br bonds of the more electron-withdrawing dppa\(^{p}Pr\) derivative (2.058(2), 2.066(2) Å) are slightly longer than in the dppa\(^{pr}\) derivative (2.027(5) – 2.042(5) Å) while the B-P bonds in the former (1.956(2) Å) are significantly shorter than in the latter (1.980(5), 1.995(5) Å). While bridging diphosphines have been employed to stabilize cyclic cis-1,2-diaryl-diborinates,\(^{43}\) the diphosphine-bridged diboranes presented herein are the first to have been structurally characterized.

**Figure 7.** Crystallographically-derived molecular structures of the halide-bridged ionic bis-carbene adducts [BzCl(Imes)2]BCl4 (top) and [BzCl(CAAC\(^{26}\))2]BCl4 (bottom). Thermal ellipsoids drawn at 50% probability level. Ellipsoids on the ligand peripheries and most hydrogen atoms omitted for clarity.

Ionic [BzXIL2]A compounds. While hydrodiboranes are well-known to form \(\mu^2\)-hydride-bridged structures displaying three-center-two-electron bonding, examples of \(\mu^2\)-halogen-bridged diboranes are much rarer. To date only a handful of such structures, albeit of neutral, mono(base)-stabilized halodiboranes, have been reported: a series of \(\mu^2\)-halide-bridged phosphine adducts of BzXClMes2 (X = Cl, Br, I; Mes = 2,4,6-Me3C6H2)\(^{43}\) a series of \(\mu^2\)-chloro-bridged pyridine adducts of BzClAr2 (Ar = Mes, Dur = 2,3,5,6-Me4C6H2) and a \(\mu^2\)-iodo-bridged 1,2,3-azadiborolidine.\(^{44}\) Similarly to these two analogues, the two boron, terminal halogen and carbene carbon atoms in [BzCl(Imes)2]BCl4 and [BzCl(CAAC\(^{26}\))2]BCl4 (Fig. 7) are quasi-coplanar, with a maximum deviation from the mean Bz(X)2C2 plane of 0.15 and 0.24 Å, respectively. In both cases, the Bz(X)2C2 plane lies perpendicular to that of the BzX-heterocycle (X2 = bridging halide)\(^{45}\) and presents a trans arrangement of the halide and carbene ligands, the latter being rotated such that the bridging halide is flanked on either side by one aryl group. A comparison of BzCl(Imes)2 and its chlorine-bridged analogue [BzCl(Imes)2]BCl4 shows considerable shortening of the B-B bond from 1.760(4) to 1.667(3) Å,

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**Figure 6.** Schematic representation of the (L,B,L) torsion angle α in BzXIL2 compounds, as well as the angle β between the mean planes of the carbene rings and the (X,B,C,N) torsion angle γ in BzX(Imes)2 compounds.
concomitant with a ca. 4% shortening of the B-Cl and B-Cas3 bonds, due to the bridging halide effectively lowering the coordination number of the boron atoms to less than four. Despite the much larger size of the iodide ligand compared to the chloride, the B-B bond length in [B2I2(CAAC3)]2 (1.678(8) Å) is not significantly longer than in [B2Cl2(IMes)]2BCl4 (1.667(3) Å). The B-X bonds are elongated by ca. 13% in [B2Cl2(IMes)]2BCl and 7% in [B2I2(CAAC3)]2 compared to the B-X bonds (Table 1). Unlike the two previously reported unsymmetrically halide-bridged diborane mono-adducts,[39][44] the presence of the two Lewis bases in the iodine [B2X2L]-A species generates a pseudo-C2v symmetry around the axis passing through the bridging halide and the center of the B-B bond, leading to two relatively similar B-X bond lengths (B-Cl 2.033(2), 2.078(3) Å; B-I 2.400(5), 2.422(5) Å) and B-X angles (B-B-Cl 64.66(12), 67.51(12)°; B-B-I 69.0(3), 70.3(3)°) in each case, suggesting that the two electrons are equally shared between the two B-X bonds.

Conclusions

To conclude, we have synthesized, isolated and characterized a series of new bis(base)-stabilized tetrahalodiboranes through the addition of two equivalents of phosphines, isonitriles, NHCs and CAACs to B3X4 precursors (X = Cl, Br, I). For the majority of these ligands classical B2X2L2 diborane(6) adducts were obtained, but for some of the most sterically demanding carbene ligands (L = IMes, IDip, CAAC3), ionic halide-bridged compounds of the form [B2X2L]A (X = Cl, A = BCl4; X = Br, I) were isolated, which in reduction reactions yield the same products as their B2X4L2 diborane(6) counterparts. At ~70 °C the 1:1 addition of IMes and IDip to B2Cl4 afforded the unsymmetrical diborane(5) mono-adducts, B2ClL1, one of which was crystallographically characterized. Upon warming these highly unstable compounds disproportionated to the corresponding ionic [B2X2L]A species. Furthermore, we showed that L/SMe2 ligand exchange at stable B2X4(SMe2)2 precursors (X = Cl, Br) provides a more facile and scalable route towards bis(base)-stabilized tetrahalodiboranes.

The 11B NMR shifts of the new and literature-known B2X2L2 species show a strong dependency on the nature of both X and L. While a relatively small upfield shift of 5 to 8 ppm is observed upon moving from Cl to Br for a given ligand L, a much higher upfield shift of 20 to 25 ppm is observed upon replacing Br with I, in line with the relative decrease in electronegativity down the halogen group. For a given halogen, the 11B NMR shift is dependent on the overall donor ability of L, with a ca. 16 ppm upfield shift between the weakest (SMe2) and strongest donor employed (CNBu2). Furthermore, 1H and 13C NMR spectroscopic analysis of bis(phosphine)- and amino-bridged diphosphine-stabilized tetraboromodiboranes revealed higher order effects caused by the existence of complex ABXMM’X’BA’ and AXMM’X’A’ spin systems, involving the 1H and 13C nuclei, respectively, as well as the two magnetically inequivalent 31P nuclei, which strongly couple to each other via the quadrupolar B-B bridge.

Of the 22 isolated tetrahalodiborane bis-adducts, 20 were crystallographically characterized. Structural analyses of new and literature-known B2X2L2 compounds, in which L is a monodentate ligand, show a strong preference for a staggered anti-conformation of the ligands with respect to the B-B axis.

While the nature of the halogens has seemingly little effect on the geometry of the molecules, the electronic and steric properties of L greatly influences the B-B bond length and the ligand conformation, respectively. In theionic [B2X2L2]-A species the B-X-B bridge displays symmetrical three-center-two-electron bonding and lies perpendicular to the near-planar B2X2L2 core.

While tetrahalodiborane Lewis base adducts have long been neglected because of the lengthy, low-yielding syntheses and instability of their B3X4 precursors, the new synthetic route via ligand exchange with the readily scalable and easy-to-handle B2X4(SMe2)2 precursors now opens up the possibility of studying these compounds on a larger scale. Having already proven their worth as precursors for mono- and zero-valent diborion species, their reactivity in anion exchange, salt metathesis, B-B-bond cleavage and addition reactions remains to be explored.

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Conflict of interest

The authors declare no conflict of interest.

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22 new tetrahalodiborane bis(base) adducts and two unstable mono(base) adducts were synthesized by the addition of carbenes, phosphines and isonitriles to highly sensitive B$_2$X$_4$ or by ligand exchange at stable B$_2$X$_4$(SMe$_2$)$_2$ precursors. NMR-spectroscopic and crystallographic studies reveal a variety of structural motifs, from sp$^2$-sp$^3$-diboranes(5) and sp$^3$-sp$^3$-diboranes(6) in staggered anti and gauche conformations to novel halide-bridged diboron cations.