Lewis Adducts

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Dative Bonding between Group 13 Elements Using a Boron-Centered Lewis Base

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Abstract: *An electron-rich monovalent boron compound is used as a Lewis base to prepare adducts with Group 13 Lewis acids using both its boron and nitrogen sites. The hard Lewis acid $AlCl_3$ binds through a nitrogen atom of the Lewis base, while softer Lewis acids GaX_3 (Cl, Br, I) bind at the boron atom. The latter are the first noncluster Lewis adducts between a boron-centered Lewis base and a main-group Lewis acid.*

If one constructs covalent bonds using all of the valence electrons of a Group 13 element, this atom will be two electrons short of a full octet and bear an empty orbital that can potentially be filled by electrons. This fundamental fact colors much of the chemistry of Group 13 elements, but it has also served as a provocation to chemists to fill the empty orbital in unusual ways. Filling this orbital by the addition of anions (X^-) and Lewis bases (L) to Group 13 "anes" (ER_3) can lead to stable four-coordinate "ates" (ER_3X^-) and adducts ($L{\rightarrow}ER_3$), respectively. In stark contrast, however, addition of electrons without the addition of atoms (chemical reduction) in general results in a significant destabilization of the compound. Nevertheless, thanks to the pioneering work on reductions of boron compounds by Berndt, Nöth, and Power,[1] reduction of the central atom or adjacent element–halide bonds has become the method of choice for constructing unprecedented multiple-bond systems, anions, and radicals of boron and other Group 13 elements.[2–4]

For many years the challenge of creating a nucleophilic "boryl" anion fuelled interest in the reduction of boron–halide species,[5] until Yamashita, Nozaki, and co-workers ultimately found success by reducing a 2-bromo-1,3,2-diazaborole and isolating a boryllithium species of the form **I** (Figure 1).[6,7] This compound and its derivatives have since led to an impressive body of work based on its nucleophilic properties and have also inspired the development of a number of different anionic species with boron-centered

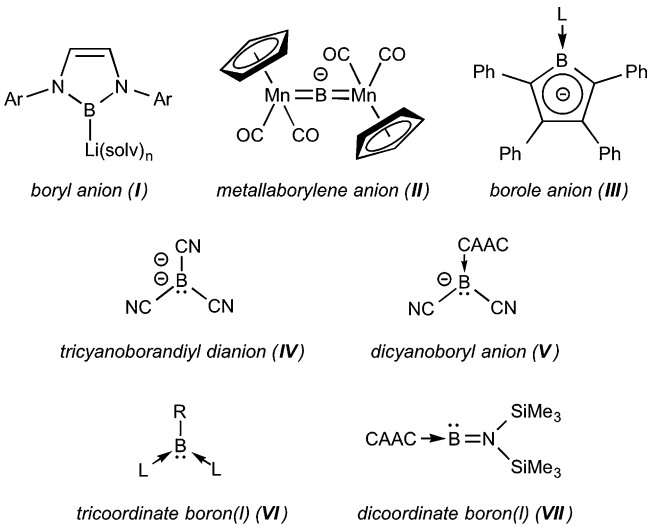

Figure 1. Generic depictions of families of compounds with electron-rich boron atoms discovered in the past decade; solv = ether solvent, L = Lewis donor, CAAC = cyclic (alkyl)(amino)carbene.

nucleophilicity such as metalloborylene anions (**II**),[8] a borole anion (**III**),[9] a tricyanoborandiyl dianion (**IV**),[10] and a carbene-stabilized dicyanoboryl anion (**V**).[11] Doubts have since been cast on the boron-centered nucleophilicity of **II** and **III** with the recent observation of unequivocal radical behavior of **III**;[9c] however, nucleophilic boron-centered anions are clearly no longer the rarity they once were.

In contrast, demonstrating true Lewis basicity of neutral boron species is still a challenge. The lighter elements of Groups 14–16 are well known to act as Lewis bases, while until very recently, analogous basicity of Group 13 species has been restricted to the heavier Group 13 elements,[12] and one nonclassical adduct consisting of a $B{\rightarrow}B$ dative bond from a Lewis basic BC_5Me_5 cluster.[13] However, it was Bertrand's discovery of a reductive route to monovalent boron species of the form RBL_n (**VI** and **VII**, Figure 1; $n = 1, 2$; L = CAAC = cyclic (alkyl)(amino)carbene[14]) that provided the most promising route to potentially Lewis basic, neutral boron species.[15] This possibility was supported the following year in a theoretical study of monovalent boron adducts with Lewis acids [AuCl] and BH_3.[16] While the initial publication of such a boron(I) species lacked definitive proof of the Lewis basicity of the compound, the Brønsted basicity of compounds of the form **VI** was proven by protonation.[15,17] Kinjo's oxazolidene-based borylene species were later shown to form boron–donor complexes with both neutral ($[Cr(CO)_5]$, [CuCl], and [AuCl]) and cationic ($[Au(NHC)]^+$)

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transition-metal fragments,[17] conclusively demonstrating the Lewis basicity of the boron center of boron(I) species **VI**. Kinjo and co-workers have also very recently reported nominally nucleophilic behavior of some neutral but electron-rich boron-containing heterocycles.[18] However, despite this work and the remarkable recent growth of interest in electron-rich boron compounds, classical main-group Lewis acid/base adducts based on boron-centered Lewis bases have remained synthetically elusive. Herein we present the synthesis and characterization of the first all-main-group adduct constructed using a noncluster boron-centered Lewis base.

Recently we reported a new route to doubly donor-stabilized monovalent boron compounds by base-induced liberation of borylene ligands from transition-metal borylene complexes.[19] This new route to B^I compounds contrasts significantly with the reductive routes used by Bertrand[15] and Kinjo,[17] involving only the addition of isonitriles or CO to borylene complexes as the final step, while the harsh reductive step occurs at the earlier synthesis of the borylene complex. Attempts were subsequently made to bind DurB(CNDipp)$_2$ (**1**, Dur = 2,3,5,6-tetramethylphenyl, Dipp = 2,6-diisopropylphenyl) to a number of different Group 13 Lewis acids. In many cases these reactions led to complex mixtures, but when aluminum trichloride ($AlCl_3$) was added to **1**, a more selective reaction took place, with a shift of the ^{11}B NMR resonance of **1** ($\delta = -20.8$) to lower field ($\delta = -8.7$). While the quaternization of tricoordinate boron atoms in general leads to shifts of the ^{11}B NMR resonances to higher field, this process is almost always accompanied by an increase in electron density at the boron atom. Thus, a shift to lower field upon addition of a Lewis acid to the boron atom of **1** (which would presumably result in loss of electron density at boron) would not be altogether surprising. However, this eventuality was ruled out upon further spectroscopic analysis. Yellow crystals of compound **2** (Figure 2) were obtained in moderate yield. ^1H and $^{13}C\{^1H\}$ NMR spectra of this sample indicated three different isopropyl environments in the molecule in a 1:1:2 ratio, a fact that is irreconcilable with a boron-centered Lewis adduct structure.

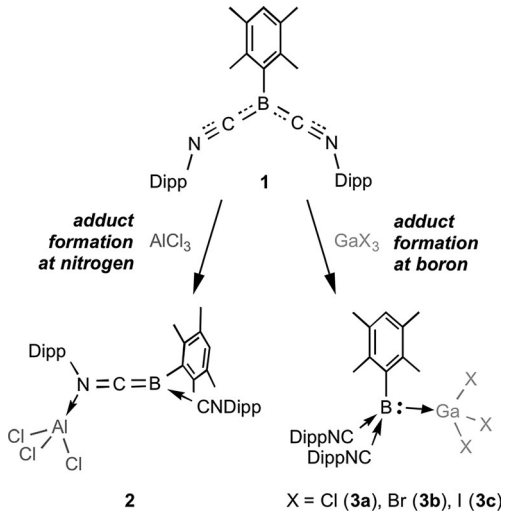

Figure 2. Synthesis of **2** and **3a–c**. Dipp = 2,6-diisopropylphenyl.

Single-crystal X-ray diffraction confirmed the unsymmetrical nature of **2** and indicated the presence of an $AlCl_3$ unit bound to one of the nitrogen atoms of the DurB(CNDipp)$_2$ molecule (Figure 3). The binding of the Lewis acid causes the

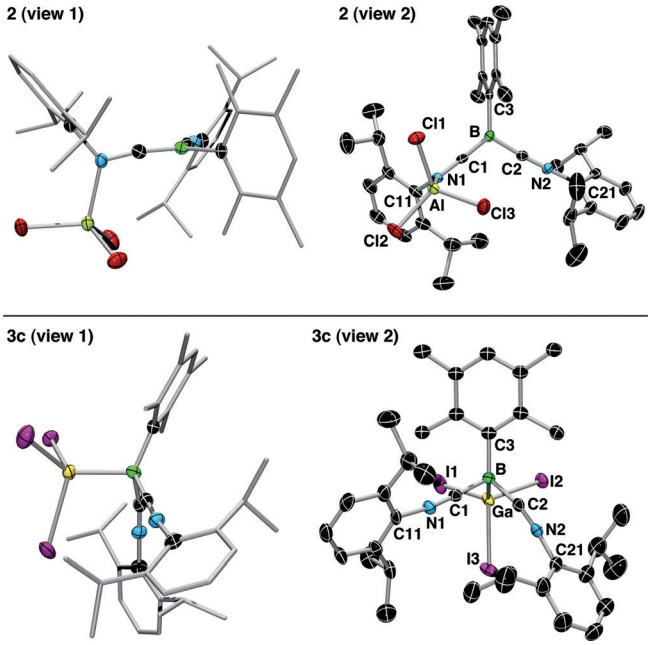

Figure 3. Crystallographically derived molecular structures of **2** and **3a**; thermal ellipsoids drawn at the 50% probability level. For clarity, hydrogen atoms, solvent molecules, and some carbon ellipsoids have been removed. Selected distances [Å] and angles [°] for **2**: B–C1 1.410(3), B–C2 1.535(3), B–C3 1.586(3), C1–N1 1.266(5), C2–N2 1.147(2), N1–Al 1.89(4), avg. Al–Cl 2.109(1); Al-N1-C1 113.8(3), C11-N1-C1 121.2(4), N1-C1-B 171.6(3), C1-B-C2 113.18(16), B-C2-N2 175.54(19), C2-N2-C21 179.4(2), $\Sigma(\measuredangle_B)$ 359.88, $\Sigma(\measuredangle_{N1})$ 359.91, $\Sigma(\measuredangle_{ClAlCl})$ 338.27, $\measuredangle$(plane C11-N1-Al)/(plane C3-B-C2) 87.06. Selected distances [Å] and angles [°] for **3c**: B–C1 1.57(1), B–C2 1.55(1), B–C3 1.59(2), C1–N1 1.15(1), C2–N2 1.15(1), B–Ga 2.179(9), avg. Ga–I 2.581(1); C11-N1-C1 172.1(8), N1-C1-B 177.8(8), C1-B-C2 99.3(6), B-C2-N2 167.3(8), C2-N2-C21 173.6(7), $\Sigma(\measuredangle_{CBC})$ 336.21, $\Sigma(\measuredangle_{Ga})$ 321.70.

two isonitrile units to become markedly different: one straightens to become an essentially linear, conventional isonitrile "ligand" (angles at C2 and N2 $>175°$), while the other bends at N1 at a near-perfect sp^2 angle and forms a 1-aza-3-boraallene unit. The distinction between the isonitrile and azaboraalene moieties is underlined by the significant differences in the B–C(N) and (B)C–N distances (B–C1 1.410(3), B–C2 1.535(3) Å; C1–N1 1.266(5), C2–N2 1.147(2) Å), as well as the near right-angle between the C11-N1-Al and C3-B-C2 planes (87.06°), analogous to the well-known orthogonal geometry of the substituents in conventional organic allenes. While its accuracy is affected by the disorder in the molecule, the measured N–Al distance in **2** (1.89(4) Å), is clearly within the normal range for dative N(sp^2)–$AlCl_3$ bonds.[20] Based on these data, compound **2** can be described as a 1,3-azaboraallene stabilized by both a Lewis acid and a Lewis base.

The only other Group 13 Lewis acids that we found to undergo selective reactions with **1** to form stable products

were the trihalogallanes GaX_3 (X = Cl, Br, I). Addition of these acids to solutions of **1** provided mixtures generating only one ^{11}B NMR resonance at higher field relative to that of the starting material (X = Cl, **3a**, $\delta = -31.2$; X = Br, **3b**, $\delta = -28.0$; X = I, **3c**, $\delta = -27.1$). However, all attempts to isolate compounds **3a** and **3b** as solids led only to impure brown oils whose NMR data indicated the presence of the starting materials as well as some decomposition. Nevertheless, we were able to obtain reliable ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of **3a** and **3b** from their reaction solutions as long as the solvent was not removed. Only in the case of **3c** were we able to isolate a pure solid sample of the adduct, in this case as yellow crystals in moderate yield. The NMR data of **3a–c** indicated that the CNDipp units are symmetrical, with one signal for the iPr CH units and two for the CH_3 units in both the ^1H and $^{13}C\{^1H\}$ NMR spectra. The shift of the ^{11}B NMR resonances to higher field and the symmetry of the CNDipp units together provided good evidence for the binding of the Lewis acid to the boron atom.

Single-crystal X-ray diffraction of **3c** revealed the clear and unsupported connection of the GaI_3 unit to boron, which itself is significantly pyramidalized ($\Sigma(\measuredangle_{CBC})$ 336.21°). Interestingly, the B–Ga distance in **3c** (2.179(9) Å) is within the range of dative boron–gallium bonds of the opposite polarity (i.e. Ga→B, 2.11–2.19 Å[12,13]), and is clearly longer than known covalent Ga–B bonds (2.04–2.10 Å.[7] However, the GaI_3 unit in **3c** is strongly pyramidalized as measured by the sum of the I-Ga-I angles (321°), and is more pyramidalized than all other known adducts of GaI_3 with Lewis bases of Groups 15 or 16, which are in the range 328–345°.[20] This phenomenon is perhaps a result of the sterically encumbered environment surrounding the Lewis acid unit. The isonitrile C-N-C angle, a reliable indicator of the degree of π acceptance of the CNR unit, is much more linear in **3c** ($\measuredangle$C-*N*-C 172.1(8), 173.6(7)°) than in the precursor **1** ($\measuredangle$C-N-C 149.9(2), 145.2(2)°), but slightly less linear than the non-aluminum-bound nitrogen atom of **2** (179.4(2)°). Unfortunately, the disorder in the structure provides considerable uncertainty to the measured B–C and C–N distances, making comparisons of these parameters with other structures impractical.

In order to better understand the nature of the bonds between the B^I compound and the EX_3 Lewis acids, density functional theory calculations at the OLYP/TZP level of theory (see the Supporting Information for more details) were carried out on the experimentally observed adducts **2**, **3a**, and **3c**, and their non-observed alternative isomers **2′** (B→Al), **3a′** (N→Ga), and **3c′** (N→Ga). Calculations of the total electronic energy showed that N→$AlCl_3$ adduct **2** was more stable than its hypothetical B→$AlCl_3$ isomer **2′** by 10.0 kcal mol^{-1}. In contrast, only small total energy differences were observed between the B→Ga and (hypothetical) N→Ga adducts **3a**/**3a′** and **3c**/**3c′** when the acid unit is kept constant: N→$GaCl_3$ bonding is favored over B→$GaCl_3$ by 0.69 kcal mol^{-1} while B→GaI_3 bonding is favored over N→GaI_3 by 0.33 kcal mol^{-1}.

The fragment approach is based on the methods of Morokuma[21] and Ziegler and Rauk[22] and consists of decomposing the interaction energy between two or more purposeful molecular entities ("fragments"), which, when put together, form the molecule of interest. The B/N→E interactions are decomposed into their different energetic contributions in Table 1. In all cases, the B→E interaction results in a more negative interaction energy than the N→E interaction; however, the difference is notably larger in the Ga adducts, again suggesting that the B→Ga interaction is more favorable than the B→Al one. This is despite the significantly higher E_{Pauli} values in the B→Ga adducts. These relatively strong destabilizing Pauli interactions between the soft atoms B and Ga are compensated by the larger attractive electrostatic and orbital interactions between them, the latter presumably due to the better orbital overlap between the two soft atoms.

Table 1: Interaction energy decomposition (kcal mol^{-1}) for the B/N→E bonds in the calculated adduct models **2/2′**, **3a/3a′**, and **3c/3c′**.

	2′ B→$AlCl_3$	**2** N→$AlCl_3$	**3a** B→$GaCl_3$	**3a′** N→$GaCl_3$	**3c** B→GaI_3	**3c′** N→GaI_3
E_{el}	−50.60	−54.71	−65.52	−51.81	−62.99	−45.48
E_{orb}	−61.54	−50.50	−78.22	−47.95	−76.62	−44.83
E_{Pauli}	70.84	71.25	95.47	73.13	97.45	71.54
E_{int}[a]	−41.30	−33.95	−48.27	−26.64	−42.15	−18.77

[a] E_{int} = total interaction energy = $E_{el} + E_{orb} + E_{Pauli}$.

In line with the experimental observation of gallium's preference for binding boron, the B→Ga bonds in **3a** (WBI: 0.496) and **3c** (WBI: 0.467) were calculated to be stronger than the B→Al bond in **2′** (WBI: 0.398), even though the B–Ga distance in **3c** is somewhat overestimated theoretically (ca. 7% longer than the crystallographically determined distance; see Figures S1 and S2 for calculated metrics of the model structures). Interestingly, the boron atoms in the B→E adduct models **2′**, **3a**, and **3c** retain significant negative charge (−0.320, −0.268, and −0.201, respectively) despite the donation of electron density to the attached Lewis acid. The frontier orbitals of **2**/**2′**, **3a**/**3a′**, and **3c**/**3c′** are presented in the Supporting Information (Figures S3 and S4). The HOMOs of the B→E adduct models **2′**, **3a**, and **3c** all contain a major contribution from the B→Al/Ga dative bond (σ donation). Either the HOMO or HOMO−1 levels of the N→EX_3 adduct models **2**, **3a′**, and **3c′** comprise the N→E dative bond, which originates from an antibonding N–C π* orbital (which is also bonding between B and C).

The charge flow upon combination of **1** with the Lewis acids $AlCl_3$, $GaCl_3$, and GaI_3 can thus be visualized using the ETC-NOCV technique,[23,24] and deformation electron density maps of **2**/**2′**, **3a**/**3a′**, and **3c**/**3c′** are shown in Figure 4. In all six cases, electron density is shown to flow from the Lewis basic unit **1** to the central atom of the Lewis acid unit EX_3. Interestingly, the maps also clearly indicate that when E is bound to nitrogen, the donated electron density comes from the nitrogen atom itself, with little density originating from the contiguous π system. In contrast, when E is bound to boron, the donated electron density originates from the entire NCBCN π system, which is in line with the delocalization in this moiety previously ascribed to $RB(CNR)_2$ compounds.[19]

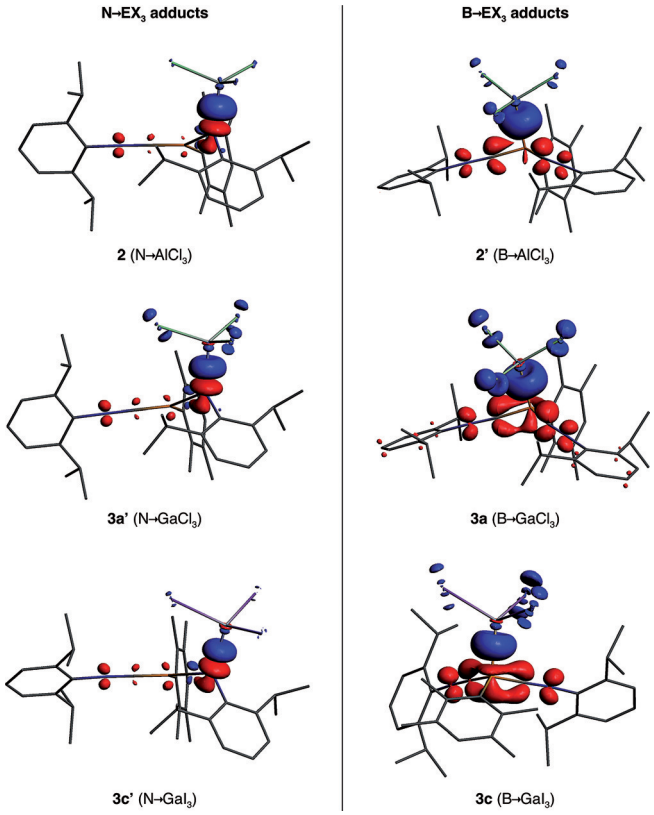

Figure 4. ETS-NOCV deformation maps of **2**/**2′**, **3a**/**3a′**, and **3c**/**3c′** showing the flow of electron density upon combination of the Lewis acidic and basic fragments (electron density flows from red to blue upon fragment combination).

This work has revealed the ditopic Lewis basic nature of the borylene bis(isonitrile) compound **1**, in addition to presenting the first main-group Lewis adducts constructed using a boron-centered Lewis base. The ditopicity of **1** with Lewis acids provides clear information about the nature of the donor sites in terms of the hard–soft acid–base (HSAB) concept. The hard Lewis acid $AlCl_3$ binds the hard nitrogen donor site, while the softer acids GaX_3 preferentially bind to the electron-rich boron atom. This finding provides further evidence of the softness of monovalent boron Lewis bases, which was earlier suggested by Kinjo's coordination of an RBL_2 species to the soft metal gold (and less stable binding with copper). Thus we have demonstrated that monovalent boron species can act as effective—and soft—Lewis donors to main-group Lewis acids, potentially allowing us to control the reactivity of similar species by altering the soft/hard nature of the acid used.

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