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Donor−Acceptor Complexes of Borazines

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Donor−acceptor complexes of borazine (BZ) and its substituted derivatives with Lewis acids (A = MCl_3, MBr_3; M = B, Al, Ga) and Lewis bases (D = NH_3, Py) have been theoretically studied at the B3LYP/TZVP level of theory. The calculations showed that complexes with Lewis bases only are unstable with respect to dissociation into their components, while complexes with Lewis acids only (such as aluminum and gallium trihalides) are stable. It was shown that formation of ternary $D \rightarrow BZ \rightarrow A$ complexes may be achieved by subsequent introduction of the Lewis acid (acceptor A) and the Lewis base (donor D) to borazine. The nature of substituents in the borazine ring, their number, and position were shown to have only minor influence on the stability of ternary $D \rightarrow BZ \rightarrow A$ complexes due to the compensation effect. Much weaker acceptor properties of borazine are explained in terms of large endothermic pyramidalization energy of the boron center in the borazine ring. In contrast to borazine, binary complexes of the isoelectronic benzene were predicted to be weakly bound even in the case of very strong Lewis acids; ternary DA complexes of benzene were predicted to be unbound. The donor−acceptor complex formation was predicted to significantly reduce both the endothermicity (by 70−95 kJ mol^{-1}) and the activation energy (by 40−70 kJ mol^{-1}) for the borazine hydrogenation. Thus, activation of the borazine ring by Lewis acids may be a facile way for the hydrogenation of borazines and polyborazines.

Introduction

In recent years, boron−nitrogen-based systems, in particularly ammonia borane,[1−3] received much attention as hydrogen-storage materials. Temperature induced and catalytic dehydrogenation of BH_3NH_3 leads to amido $[H_2BNH_2]_n$ and imidoboranes $[HBNH]_n$.[4−6] In particular, borazine $[HBNH]_3$, a six-membered heterocyclic compound with alternating atoms of boron and nitrogen in the ring, and polyborazines were experimentally observed among the reaction products. Reaction pathways of ammonia borane dehydrogenation with formation of borazine have been extensively theoretically studied by Nutt and McKee.[7] Hydrogenation of imidoboranes is endothermic and requires relatively large activation energies, which poses a problem for the ammonia borane regeneration. Low reactivity of borazine and polyborazines is often attributed to the aromatic stabilization.

Despite of the fact that aromaticity has no precise quantitative definition[8] and is not directly measurable experimentally,[9] it is one of the fundamental and important concepts in modern chemistry. There are many approaches to quantify aromaticity based on structural, energetic, magnetic, and reactivity criteria.[8] However, applied to inorganic heterocycles, "all these criteria can diverge quite strongly from each other" as mentioned by Jemmis and Kiran.[10]

Benzene usually serves as classic example of an aromatic compound, and aromaticity of the inorganic heterocycles is often compared to that of benzene. Borazines are often called "inorganic benzenes" for their aromatic behavior. Similar to benzene, borazine features the perfectly planar B_3N_3 ring with equivalent B−N distances. According to the Harmonic oscillator measure of aromaticity (HOMA),[11] benzene and borazine have the same degree of aromaticity.[12] From the energetic point of view, the aromaticity of inorganic heterocycles is usually associated with the aromatic stabilization energy (ASE).[13] There are many definitions of ASE,[14] and the computed ASE of borazine (41.8−46.4 kJ mol^{-1})[16,15] is

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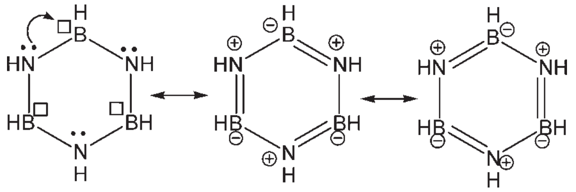
Scheme 1. Resonance Structures of Borazine

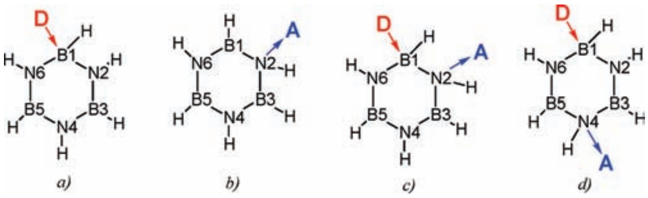


lower than ASE of benzene (92.5−150.6 kJ mol^{-1}).[15−17] Thus, according to this energetic criteria, borazine is less aromatic than benzene. Using the energy decomposition analysis, Fernandes and Frenking[18] concluded that borazine has a small degree of aromaticity, a conclusion supported by Islas et al.[19] on the basis of analysis of electron localization function (ELF). Similar conclusions are reached using magnetic criteria. Schleyer's nucleus independent chemical shifts (NICS)[20] show a relatively small negative value for borazine (−3.2)[16] in comparison with a large negative value for benzene (−10.7)[16] that indicates much lower aromaticity of borazine.

Reactivity criterion is often associated with the energy of electrophilic substitution reaction (for example, protonation and methylation energies).[21,22] Timoshkin and Frenking[23] proposed the enthalpy of self-dimerization of inorganic heterocylce as another reactivity criterion of aromaticity. According to these reactivity criteria,[21−23] aromaticity of borazine is about half of that of benzene. Much lower aromaticity of borazine is attributed to the large electronegativity of nitrogen compared to boron and predominant localization of the electron density in the vicinity of nitrogen atoms.

Resonance structures of borazine (Scheme 1) show the presence of vacant orbitals on B atoms and the lone electron pairs on N atoms, which can be utilized for formation of the conjugated π system in the ring. However, in the presence of Lewis acids and bases, such orbitals can be involved in donor−acceptor σ-bond formation (Scheme 2). The σ-complexes of benzene with such hard Lewis acid as H$^+$ are well-known intermediates in electrophilic substitution reactions (so-called Wheland intermediates),[24] which have been isolated and structurally characterized using the bulky carborane anions.[25] Similar σ-complexes of borazines with H$^+$ (protonated borazines) are also known in the gaseous state,[22] although electrophilic substitution reactions of borazines are rare. In contrast to benzene, addition reactions are much more common for the borazine chemistry.

Scheme 2. Donor−Acceptor Complexes of Borazine, Considered in the Present Work[a]



[a] (a) Complex with Lewis base; (b) complex with Lewis acid A; (c) 1-2 isomer of ternary complex; (d) 1-4 isomer of ternary complex.

In the present report, we for the first time theoretically explore the ability of borazines to donor−acceptor σ-bond complex formation with neutral Lewis acids and bases. To date, only two examples of neutral borazine complexes featuring donor−acceptor (DA) σ-bonds are experimentally known. These are complexes of hexamethylborazine with acceptor molecules $AlBr_3$ and $GaCl_3$, both compounds were synthesized and structurally characterized by the Nöth group in the 1980s.[26,27] More recently, Pinkas and co-workers demonstrated that the heavier group 13 analogue of borazine, the substituted alumazene $[R_3Al_3N_3R'_3]$ (R = Me, R′ = (2,6-$^iPr_2C_6H_3$)),[28] forms a series of σ-complexes with donor molecules such as pyridines and nitriles.[29] Very recently, Fan et al. used donor properties of an amino group in 1,3,4,5,6-pentamethyl-2-aminoborazine to generate borazine-substituted Al_2N_2 rings and borazine-based polymers.[30] It was shown that 1,3,4,5,6-pentamethyl-2-aminoborazine does not form complexes which involve nitrogen atoms of the heterocycle.

In contrast to π-complexes of borazines, which were the subject of both experimental[31,32] and theoretical[33−35] works, the σ-complexes of borazines with neutral donor and acceptor molecules have not been studied theoretically. In the present report, we for the first time systematically address the donor and acceptor properties of borazines. The process of σ-complex formation is in direct concurrence with the electron delocalization in the ring. If σ-complex is formed, the conjugated π-system of the heterocycle will be destroyed. The loss of the aromatic stabilization of heterocycle should enhance its reactivity. To test this hypothesis, hydrogenation reactions of borazine and its DA complexes have also been explored in the present report.

Computational Details

All computations have been carried out using the standard Gaussian 03 program package[36] on the High-Performance Computing cluster of St. Petersburg State University. Density functional theory in the framework of hybrid

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Table 1. Comparison of the Experimental and Theoretical Dissociation Enthalpies (in kJ mol^{-1}) and Entropies (in J mol^{-1} K^{-1}) for the Homogeneous Gas Phase Dissociation of the Aluminum Trichloride−Ammonia Adduct at 739 K: $AlCl_3NH_3 = AlCl_3 + NH_3$

parameter	B3LYP/TZVP	B3LYP/aug-cc-pVTZ	MP2/TZVP	MP2/aug-cc-pVTZ	experiment[a]
$\Delta_{diss}H°_{739}$	139.5	130.0	156.4	154.9	137.2 ± 3.8
$\Delta_{diss}S°_{739}$	118.1	117.0	138.5	126.1	120.5 ± 9.2

[a] Reference 45.

Table 2. Comparison of the uncorrected complex dissociation energies $\Delta_{diss}E$,[a] BSSE correction E_{BSSE}, and BSSE-corrected dissociation energies $\Delta_{diss}E_{corr}$[b] at B3LYP and MP2 levels of theory. All values in kJ mol^{-1}

	B3LYP/TZVP (B3LYP/aug-cc-pVTZ)			MP2/TZVP (MP2/aug-cc-pVTZ)		
complex	$\Delta_{diss}E$	E_{BSSE}	$\Delta_{diss}E_{corr.}$	$\Delta_{diss}E$	E_{BSSE}	$\Delta_{diss}E_{corr.}$
BCl_3−BZ	−43.3 (−48.0)	7.9 (2.2)	−51.2 (−50.2)	15.5 (20.6)	50.8 (18.4)	−35.3 (2.2)
$AlCl_3$−BZ	50.2 (44.7)	7.1 (3.1)	43.1 (41.6)	93.3 (94.5)	33.1 (13.0)	60.2 (81.5)
1-NH_3,2-BCl_3−BZ	−6.0 (−39.5)	15.0 (3.2)	−21.0 (−42.7)	85.7	77.8	7.9
1-NH_3,2-$AlCl_3$−BZ	80.0 (48.1)	14.0 (4.2)	66.0 (43.9)	153.5	58.8	94.7
1-Py,2-BCl_3−BZ	8.0 (−0.8)	12.0 (3.8)	−4.0 (−4.6)	122.2	82.6	39.6
1-Py,2-$AlCl_3$−BZ	91.9	11.2	80.7	187.4	63.5	123.9

[a] $\Delta_{diss}E$: energy of the complex dissociation into components. For binary complexes: MCl_3−BZ = MCl_3 + BZ; for ternary complexes: 1-D,2-MCl_3−BZ = D + MCl_3 + BZ (M = B, Al; D = NH_3, Py). [b] $\Delta_{diss}E_{corr} = \Delta_{diss}E + E_{BSSE}$.

three-parameter exchange functional of Becke[37] with the gradient corrected correlation functional of Lee, Yang, and Parr[38] (B3LYP) with all electron TZVP basic set[39] was used throughout. The basis sets are (311/1) for H; (62111/411/1) for B, C, N, and F; (73211/6111/1) for Al and Cl; (842111/63111/511) for Ga and Br. For selected compounds, an augmented correlation-consistent aug-cc-pVTZ basis set[40] was used. All structures have been fully optimized and verified to be minima or transition states (TS) by subsequent vibrational analysis. Intrinsic reaction coordinate scans confirmed that obtained TS are connecting reactant and products. Basis set superposition error (BSSE) was estimated by the counterpoise method[41,42] realized in Gaussian03. The B3LYP method provides adequate description of thermodynamic properties of 13−15 DA complexes,[43] as well as 13−15 heterocycles.[23] Errors in the standard formation enthalpy for benzene and borazine are 6 and 51 kJ mol^{-1}, respectively. Note that B3LYP/TZVP error in the standard formation enthalpy of borazine of 51 kJ mol^{-1} is 25−37 kJ mol^{-1} larger than the error for the high level ab initio method CCSD(T)/CBS.[44] Predicted standard entropies correlate very accurately with the experimental data for both borazine and benzene.[23]

Performance of the chosen theoretical method was tested on the example of the donor−acceptor $AlCl_3NH_3$ complex, for which experimental dissociation enthalpy and entropy at 739 K were obtained by the tensimetry method, as reported in a recent review.[45] A comparison of the performance of B3LYP and MP2[46] methods with TZVP and aug-cc-pVTZ basis sets is presented in Table 1. The B3LYP/TZVP level of theory provides better agreement with experimental values. Use of the expanded aug-cc-pVTZ basis set leads to an underestimated value of dissociation enthalpy. Dissociation enthalpies of $AlCl_3NH_3$ obtained at MP2/TZVP and MP2/aug-cc-pVTZ level of theory are overestimated by 19 and 18 kJ mol^{-1}, respectively. Note that underestimated values for the dissociation enthalpies at B3LYP/6-311++G(d,p) level of theory were reported by Gilbert[47] for BR_3 (R = H, CH_3) adducts with ammonia and methylamines and by Ogava and Fujimoto[48] for $GaCl_3NH_3$ adduct. Apparently, the B3LYP method with medium sized TZVP basis sets yield better agreement with the experimental results than with the expanded aug-cc-pVTZ basis set due to the partial cancellation of errors between the basis set deficiency and the medium-range electron correlation treatment.[49]

We also tested performance of different computational methods to the selected complexes studied in the present work. Results are summarized in Table 2 and will be briefly discussed here. Predicted at the MP2/TZVP level, dissociation energies of the complexes are significantly (by 43−114 kJ mol^{-1}) larger compared to results obtained at the B3LYP/TZVP level of theory. Large differences are also found for the BSSE values. The BSSE correction at the B3LYP/TZVP level of theory is relatively small: it ranges from 7 to 15 kJ mol^{-1} for the binary borazine (BZ)→A and ternary D→BZ→A adducts, respectively. In contrast, at the MP2/TZVP level of theory, BSSE increases significantly (up to 33−83 kJ mol^{-1}). Use of the expanded aug-cc-pVTZ basis set reduces BSSE at the B3LYP level of theory to 2−4 kJ mol^{-1}, while at the MP2/aug-cc-pVTZ level BSSE values are much larger: 13−18 kJ mol^{-1}.

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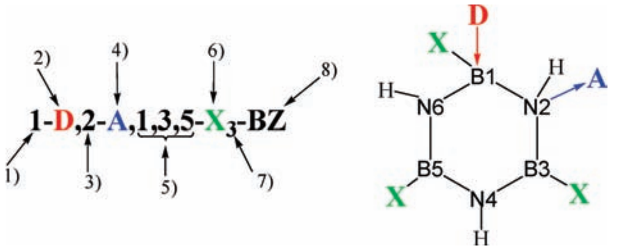
Scheme 3. Labeling of the Donor−Acceptor Complexes of Borazines Used in the Present Report[a]



[a] (1) The coordination position of donor molecule (Lewis base) D; (2) the nature of Lewis base D; (3) coordination position of Lewis acid A; (4) the nature of Lewis acid A; (5) coordination positions of substituents X in heterocycle; (6) the nature of the substituent X; (7) the number of substitutes X in heterocycle; (8) the nature of heterocycle (BZ indicates borazine).

Large BSSE values at the MP2 level of theory have been recently reported by Gilbert[50] for $B(C_6F_5)_3$ complexes.

Complex dissociation energies, which are corrected for BSSE, are 16−52 kJ mol^{-1} larger at the MP2 level of theory compared to B3LYP, both with TZVP and aug-cc-pVTZ basis sets. Thus, results obtained at the B3LYP/TZVP level provide the lower limit of the complex stability. Since BSSE values at the B3LYP/TZVP level of theory are relatively small (about 7 kJ mol^{-1} per donor−acceptor bond) and given the fact that the counterpoise method generally overestimates BSSE,[51] in the following discussion, only results obtained at the B3LYP/TZVP level of theory and uncorrected for BSSE will be considered.

Our attempts to evaluate NICS[20] values for the donor−acceptor complexes of borazines at the B3LYP/aug-cc-pVTZ level of theory provided no definitive conclusions (Figures 1S and 2S in Supporting Information). Since borazine loses planarity upon complex formation, the choice of points in space for the NICS computation becomes arbitrary. Our results indicate that the NICS values are very sensitive to the chosen point in space, which is attributed to the large effect of peripheral atoms of the donor and acceptor molecules. A possible solution would be construction of the 3D grid network for NICS evaluation,[9] but this lies out of scope of the present work. Therefore, NICS values will not be discussed in the present report.

Results and Discussion

For the labeling of complexes, we will use the notation shown in Scheme 3.

Borazine Complexes with Lewis Bases. Optimization attempts (without a symmetry constraint) of the complex between borazine and ammonia (Figure 1) resulted in van der Waals bound fragments. Since the B3LYP/TZVP method is not suitable for studying van der Waals interactions, these weakly bound species will not be considered in the present report. The relaxed scan of the potential energy surface (PES) for the 1-NH_3−BZ system with respect to B−NH_3 donor−acceptor bond distance revealed only a shallow minimum (Figure 2) which lies above the energy of separated BZ and NH_3 fragments. Addition of electron-withdrawing (F and Cl) substituents to the boron atom of borazine slightly lowers the endothermic interaction energy and (in the case of Cl−borazine) makes the shallow minimum slightly more pronounced. The absence of explicit minima and the endothermic interaction energies indicate the instability of σ-bonded borazine−ammonia complexes. Apparently, the donor strength of the single NH_3 molecule is not sufficient to disrupt the conjugated π-system of borazine and enforce it into the σ-complex formation.

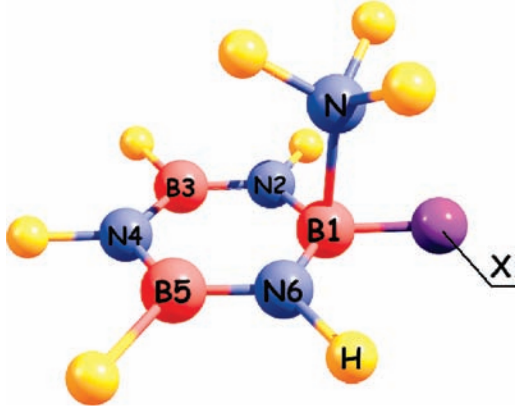


Figure 1. Starting geometry for the geometry optimizations and relaxed PES scans of borazine−ammonia complexes 1-NH_3,1-X−BZ (X = H, F, Cl).

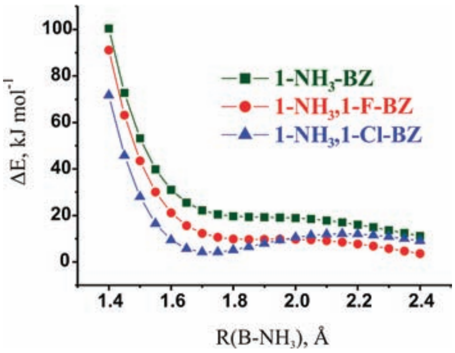


Figure 2. Relaxed PES scan for borazine−ammonia complexes. Relative energy (Δ*E*, kJ mol^{-1}) of 1-NH_3−BZ, 1-NH_3,1-F−BZ, and 1-NH_3,1-Cl−BZ complexes with respect to the energies of free fragments versus the boron−ammonia distance R(B−NH_3), Å. B3LYP/TZVP level of theory.

Borazine Complexes with Lewis Acids. Optimized structures of borazine complexes with BCl_3 and $AlCl_3$ are presented in Figure 3; structures of other complexes are given in the Supporting Information. All structures are true minima on PES. Upon D−A bond formation, the borazine ring loses planarity. This fact, in our opinion, indicates the destruction of the conjugated π-system of borazine. As a consequence, the bond distances in the ring become nonequivalent. B3−N4 and B1−N6 bonds shorten with respect to uncomplexed borazine (they stream toward value of a double B=N bond of 1.36 Å[52]), while the remaining B−N distances are elongated toward the characteristic value of 1.56 Å for the single B−N bond.[53] Predicted donor−acceptor distances are 1.694 and 2.114 Å for N−BCl_3 and N−$AlCl_3$, respectively. These values are slightly larger compared to B−N and Al−N donor−acceptor bond distances in molecular complexes.[54]

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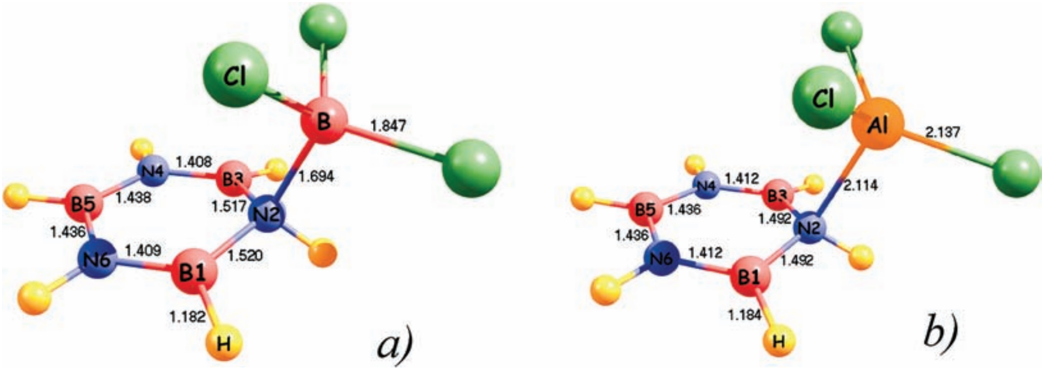

Figure 3. Optimized structures: (a) 2-BCl_3−BZ; (b) 2-$AlCl_3$−BZ. B3LYP/TZVP level of theory. All distances are in angstroms.

Table 3. Predicted Structural and Thermodynamic Characteristics for Gaseous Binary Complexes of Borazines with MX_3 (B3LYP/TZVP Level of Theory)

complex	R(N−MX_3), Å	q_{CT} (MX_3)	$\Delta_{diss}H°_{298}$, kJ mol^{-1}	$\Delta_{diss}S°_{298}$, kJ mol^{-1} K^{-1}	$\Delta_{diss}G°_{298}$, kJ mol^{-1}
BCl_3−BZ	1.694	−0.283	−48	147	−92
$AlCl_3$−BZ	2.114	−0.160	44	143	2
$AlBr_3$−BZ	2.130	−0.141	33	140	−9
$GaCl_3$−BZ	2.248	−0.155	24	137	−17

Energetic characteristics for the BZ→A complex formation are summarized in Table 3. Note the dramatic difference between complexes of borazine with BCl_3 and $AlCl_3$. The dissociation enthalpy for BCl_3−BZ is exothermic by 48 kJ mol^{-1}, while for $AlCl_3$−BZ it is endothermic by 44 kJ mol^{-1}. The relaxed PES scans with respect to DA bond distance R(N−MCl_3) revealed the clearly expressed minima both for M = B and M = Al (Figure 4). Thus, borazine complexes with BCl_3 are only kinetically stable, their exothermic dissociation is protected by the relatively small barriers of about 10 kJ mol^{-1}. In contrast, borazine complex with ACl_3 is energetically stable with respect to dissociation and is by about 90 kJ mol^{-1} more stable than complex with BCl_3. Note, however, that the value of the charge transfer, the amount of charge accepted by BCl_3 (0.28$\bar{e}$), is larger than that in case of $AlCl_3$ (0.16$\bar{e}$). This indicates somewhat stronger donor−acceptor interaction with BCl_3 despite the endothermic complex formation energy. The large difference in the complex formation energy between BCl_3 and $AlCl_3$ is mainly due to the large difference in reorganization energy (the energy required for the transformation of MCl_3 from planar geometry in the ground state to pyramidal geometry in the DA complex). Large reorganization energies of acceptor molecule, which seriously affect the complex stability, were theoretically predicted for the complexes of silicon halides[55] and boron halides.[56] Reorganization energies of BCl_3 and $AlCl_3$ are 119 and 36 kJ mol^{-1} for the BCl_3−BZ and $AlCl_3$−BZ complexes, respectively. Taking into account these reorganization energies, B−N and Al−N donor−acceptor bond energies are comparable to each other (134 and 119 kJ mol^{-1}, respectively) and in accord with charge transfer values of 0.28 and 0.16$\bar{e}$.

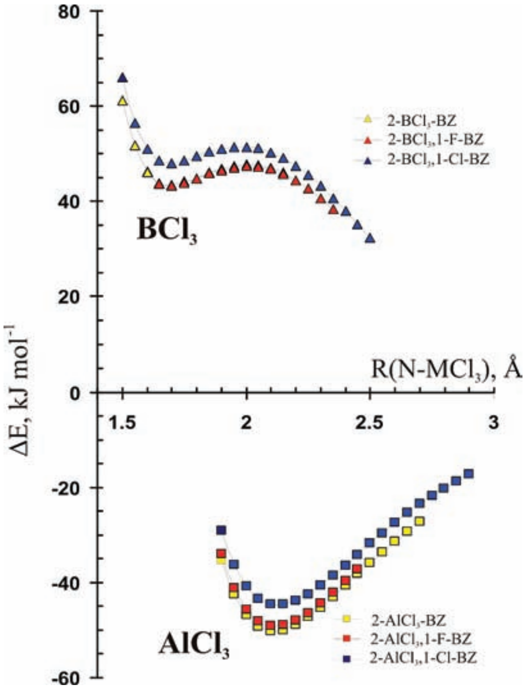

Figure 4. Relaxed PES scans for borazine complexes with Lewis acids MCl_3. Relative energy (Δ*E*, kJ mol^{-1}) of complexes with respect to the energies of isolated free fragments versus the nitrogen−MCl_3 distance R(N−MCl_3). B3LYP/TZVP level of theory.

Substitution of $AlCl_3$ by other group 13 halides results in the lowering of complex dissociation energy in the order $AlCl_3 > AlBr_3 > GaCl_3 \gg BCl_3$ (Table 3). The influence of substituents in the heterocycle in BZ→A series is the same for the all studied acceptor molecules, and it will be illustrated here only on the example of the strongly bound complexes with $AlCl_3$ (Table 4). Introduction of electron-withdrawing (halogen) substituents into the borazine ring expectedly lowers the dissociation energy of the complex. For example, the addition of three fluorine substituents to boron atoms results in lowering the dissociation energy by 10 kJ mol^{-1} and addition of

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Table 4. Predicted Structural and Thermodynamic Characteristics for Gaseous Binary Complexes of Substituted Borazines with $AlCl_3$ (B3LYP/TZVP Level of Theory)

heterocycle	R(N−$AlCl_3$), Å	q_{CT} ($AlCl_3$)	$\Delta_{diss}H°_{298}$, J mol^{-1}	$\Delta_{diss}S°_{298}$, kJ mol^{-1} K^{-1}	$\Delta_{diss}G°_{298}$, kJ mol^{-1}
BZ	2.114	−0.160	44	143	2
1-F−BZ	2.116	−0.153	43	146	−0.2
1-Cl−BZ	2.125	−0.145	39	144	−4
1,3,5-F_3−BZ	2.137	−0.130	34	150	−10
1,3,5-Br_3−BZ	2.186	−0.092	11	151	−34
1,3,5-Me_3−BZ	2.085	−0.170	63	173	11
2,4,6-Me_3−BZ	2.115	−0.104	34	177	−19
Me_6−BZ	2.107	−0.075	48	173	−3
1,3,5-F_3, 2,4,6-Me_3BZ	2.148	−0.084	27	172	−24

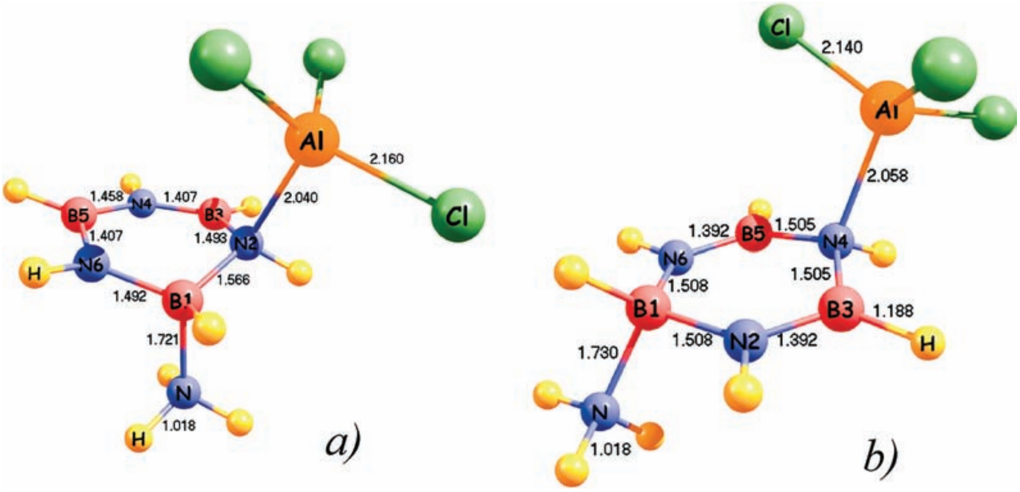

Figure 5. Optimized structures: (a) 1-NH_3,2-$AlCl_3$−BZ; (b) 1-NH_3,4-$AlCl_3$−BZ. B3LYP/TZVP level of theory. All distance in angstroms.

three bromine substituents by 30 kJ mol^{-1}. It is expected that introduction of the electron-donating substituents should result in the increase of complex dissociation energy. In contrast, introduction of three methyl substituents to nitrogen atoms of *B*,*B*′,*B*″-trifluoroborazine unexpectedly lowers the dissociation energy by additional 7 kJ mol^{-1}. Thus, methyl substituents located on nitrogen atoms have a destabilizing effect on the complex stability. This effect may be compared to the well-known difference in reactivity of meta- versus ortho- and para-benzenes.

Since the σ-complexes of hexamethylborazine with group 13 Lewis acids are known experimentally,[26,27] the influence of methyl substituents on the complex stability was considered further. Addition of three methyl groups to boron atoms expectedly increases complex dissociation energy of *B*,*B*′,*B*″-trimethylborazine (by 19 kJ mol^{-1} with respect to the unsubstituted borazine, Table 3). In contrast, addition of three methyl groups to nitrogen atoms results in lowering of the complex dissociation energy of *N*,*N*′,*N*″-trimethylborazine by 10 kJ mol^{-1}. Full methylation only slightly affects the donor properties of heterocycle; the difference between dissociation energies of hexamethylborazine and borazine complexes amounts to only 4 kJ mol^{-1}. The donor−acceptor bond distance in $AlCl_3$−hexamethylborazine decreases slightly (by 0.007 Å) compared to the $AlCl_3$−borazine complex, but the charge transfer value lowers by half.

We conclude that $AlCl_3$ forms the most stable σ-complex with *B*,*B*′,*B*″-trimethylborazine (with sizable dissociation enthalpy of 63 kJ mol^{-1}), while its complex with *B*,*B*′,*B*″-tribromborazine is very weakly bound (standard dissociation enthalpy of only 11 kJ mol^{-1}). The latter value is much smaller than dissociation energies of the dimeric M_2X_6 molecules, and therefore, molecular complexes of *B*,*B*′,*B*″-tribromborazine with group 13 Lewis acids are predicted to be unstable.

Since PES scans of borazine complexes with donor molecule (NH_3) revealed no minima and PES scans of borazine complexes with acceptor molecules showed well-defined minima (Figure 2), it can be concluded that the donor properties of borazine are significantly stronger than its acceptor properties.

Ternary Borazine Complexes with Both Lewis Acids and Lewis Bases. Upon complexation with MX_3, the borazine ring loses planarity. The conjugated π-system is destroyed, and partially unfilled orbitals of boron atoms become available for the interaction with the lone pair of the donor molecule. Thus, despite the fact that structure optimization for binary borazine complexes with neutral Lewis base (ammonia; Scheme 2a) resulted in van der Waals bound fragments, it is expected that introduction of a Lewis base to the "preactivated" BZ→A complex (Scheme 2b) may lead to the stable ternary complexes of the D→BZ→A type. Two structural isomers, which differ by the position of donor and acceptor moieties, are theoretically feasible and will be denoted as 1-2 and 1-4 isomers (Scheme 2c,d, respectively). In accord with these expectations, the geometry optimizations indeed resulted in minima structures both for 1-2 and 1-4 isomers. The optimized structures of ternary complexes between borazine, $AlCl_3$, and ammonia are given in Figure 5, and those for other ternary complexes can be found in the Supporting Information.

Structural and thermodynamic properties for the selected isomers are summarized in Table 5. The DA bond lengths in 1-2 isomers are 0.018 Å shorter than in 1-4 isomers, which

Table 5. Structural and Thermodynamic Characteristics of 1-2 and 1-4 Isomers of Ternary Complexes[a]

acceptor	BCl_3				$AlCl_3$			
donor	$D = NH_3$		$D = Py$		$D = NH_3$		$D = Py$	
parameter	1-2 isomer	1-4 isomer	1-2 isomer	1-4 isomer	1-2 isomer	1-4 isomer	1-2 isomer	1-4 isomer
R(B−D), Å	1.713	1.727	1.683	1.699	1.721	1.730	1.686	1.703
R(N−A), Å	1.650	1.669	1.634	1.661	2.040	2.058	2.017	2.048
q_{CT} (D)	0.394	0.356	0.372	0.350	0.392	0.354	0.124	0.065
q_{CT} (A)	−0.344	−0.347	−0.344	−0.360	−0.235	−0.227	−0.146	−0.140
q_{CT} (in the ring)	−0.050	−0.009	−0.028	0.010	−0.156	−0.127	0.022	0.075
$\Delta_{diss}H°_{298}$, kJ mol^{-1}	−23	−41	−6	−31	63	47	78	57
$\Delta_{diss}S°_{298}$, J mol^{-1} K^{-1}	303	301	331	318	287	290	318	307
$\Delta_{diss}G°_{298}$, kJ mol^{-1}	−113	−131	−105	−125	−22	−40	−16	−34

[a] R(B−D) is the length of DA bond with Lewis base (donor D); R(N−A) is the length of DA bond with Lewis acid A; q_{CT} is the charge transfer on the fragments. B3LYP/TZVP level of theory.

is consistent with energetic favorability of 1-2 isomers (by 16−25 kJ mol^{-1}).

In line with our findings for binary borazine complexes with Lewis acids, formation of ternary D→BZ→A complex leads to alternating bond lengths in the heterocycle. Compared to the B−N distance of 1.431 Å in free borazine, B3−N4 and B5−N6 distances in 1-NH_3,2-$AlCl_3$−BZ complex are shortened to 1.407 Å, while remaining B−N distances are lengthened to 1.458−1.566 Å. The similar bond length alternation is also observed for 1-4 isomer.

Mulliken population analysis reveals that the ring system (heterocycle) in ternary D−BZ−A complexes serves as a conductor of electron density from the donor (NH_3) to the acceptor ($AlCl_3$) fragment. The amount of charge transfer q_{CT} is 0.35−0.4$\bar{e}$ (Table 4). Note that the electron density donated by ammonia is always larger than that accepted by $AlCl_3$; the small portion of the electron density is accepted by the borazine ring. This may be related to the larger electronegativity of boron atoms in the heterocycle as compared to Al and Ga atoms in the acceptor molecules $AlCl_3$ and $GaCl_3$. Note that, in accord with the electronegativity trend, in terms of charge transfer BCl_3 is a much stronger acceptor than $AlCl_3$ ($q_{CT}(BCl_3) = -0.34\,\bar{e}$ while $q_{CT}(AlCl_3) = -0.24\,\bar{e}$).

Replacement of ammonia by pyridine leads to somewhat stronger ternary complexes. Standard dissociation enthalpies of 1-Py,2-MX_3−BZ complexes are by about 15 kJ mol^{-1} larger than that of 1-NH_3,2-MX_3−BZ (Table 5).

Influence of Substituents in the Heterocycle on the Stability of Ternary Complexes. Our theoretical results predict that the binary complexes of borazine BZ→A with such Lewis acids as group 13 metal halides can potentially interact with Lewis bases with formation of yet unknown ternary D→BZ→A complexes. It is of interest, if such ternary D→BZ→A complexes can be further stabilized by varying substituents in the heterocycle (introduction of electron donating or electron withdrawing groups). To investigate this issue, several ternary complexes of monosubstituted borazines 5-X−BZ (X = CH_3, H, F, Cl, CF_3) have been considered (Figure 6). Results show that the net influence of the substituents on the energetics of the complex formation is small: dissociation enthalpies differ by less than 5 kJ mol^{-1} (Table 6). However, with the increase of the electron-withdrawing ability in the series $CH_3 < H < F < Cl < CF_3$, the length of the B−NH_3 bond expectedly decreases, while the length of the N−BCl_3 bond increases. This compensation effect may be responsible for the fact that the overall stability of the ternary complex with respect to dissociation into components is only slightly affected by the nature of substituent.

The number of substituents and their position in the ring have very minor influence on the stability of D−A complexes with mono-, bis- and tris-fluorine-substitutied borazines. The difference in complex formation enthalpies is only about 5−10 kJ mol^{-1}. (Table 3S, Supporting Information).

General Notes on Complex Stability. Complexes with Py are 15 kJ mol^{-1} more stable than ammonia complexes. Note that an increase of the dissociation enthalpy by changing ammonia to pyridine is accompanied by shortening the donor−acceptor bond lengths (both with Lewis acid and with Lewis base; Table 7).

Table 8 presents energetic changes which accompany complex formation. It is interesting that reorganization energy of BCl_3 is significant (129−140 kJ mol^{-1}) which leads to negative dissociation energies despite quite a strong bond energy. Large reorganization energy of BCl_3 was predicted for the BCl_3F^- complex (158.2 and 171.1 at the B3LYP/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels of theory).[56] In contrast, $AlCl_3$ has small reorganization energy (36−54 kJ mol^{-1}). Reorganization energy of the heterocycle is small for BZ−A complex formation (34−58 kJ mol^{-1}) but increases dramatically for ternary complexes (125−180 kJ mol^{-1}). We attribute this to unfavorable pyramidalization of boron center compared to favorable pyramidalization of nitrogen center. In fact, pyramidalization of NH_3 from planar to pyramidal is exothermic by 18 kJ mol^{-1} (experimental[57] inversion barrier of NH_3 is 24.3 kJ mol^{-1}) while pyramidalization of BH_3 from planar to tetrahedral is endothermic by 93 kJ mol^{-1}.

Overall, DA bond energies, evaluated taking into account reorganization energies, are quite large (120−320 kJ mol^{-1}) and show that borazine is potentially a strong complex agent, but its ability to form ternary complexes is shadowed by large unfavorable reorganization energy of the ring.

Analyzing the stability of complexes (Table 7), one notes that the complex formation is always disfavorable by entropy. For complexes with BCl_3, the process of complex formation is endothermic and the existence of such complexes in the gas phase is prohibited thermodynamically. Even in the case of the exothermic complex

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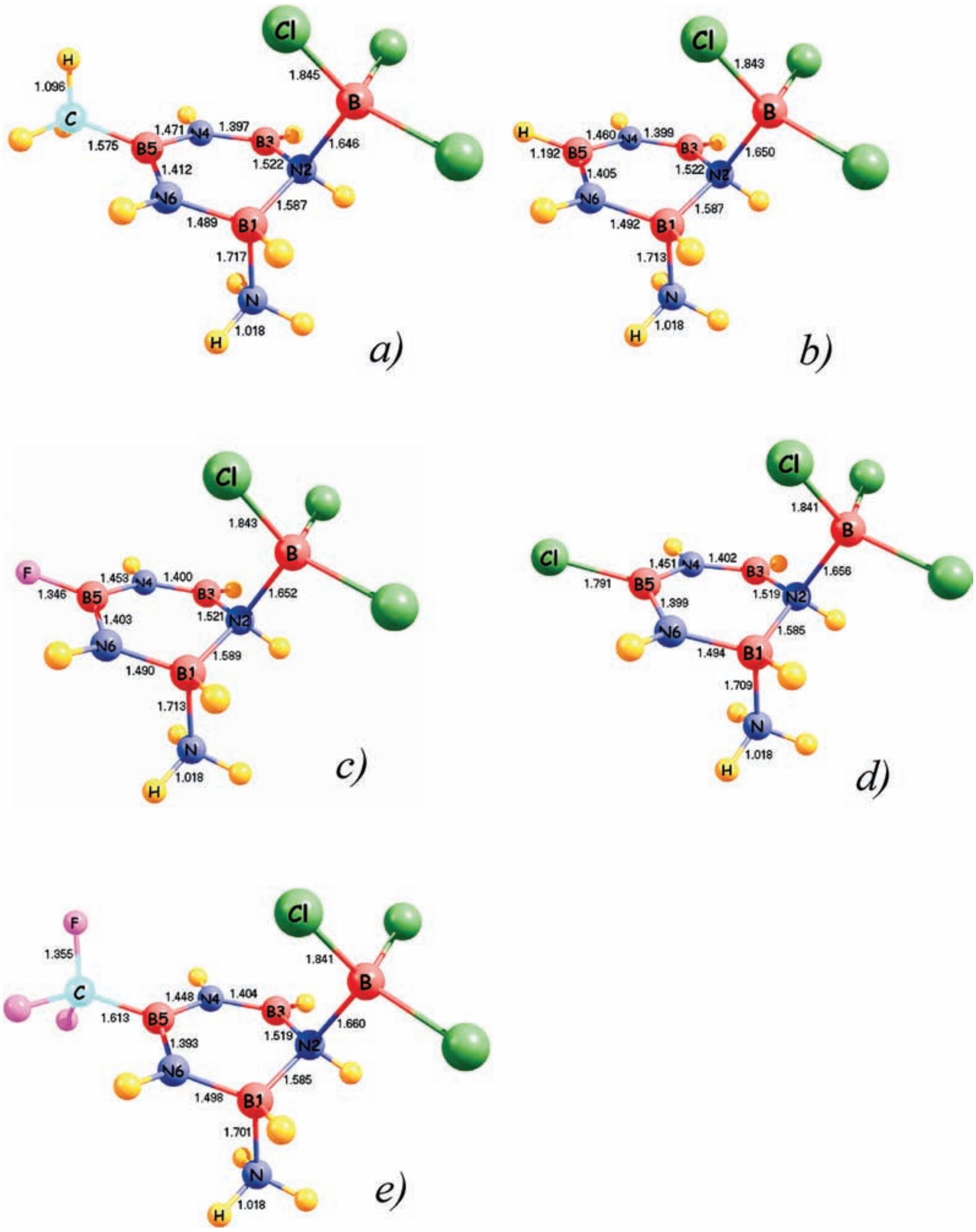

Figure 6. Optimized structures: (a) 1-NH_3,2-BCl_3,5-CH_3−BZ; (b) 1-NH_3,2-BCl_3−BZ; (c) 1-NH_3,2-BCl_3,5-F−BZ; (d) 1-NH_3,2-BCl_3,5-Cl−BZ; (e) 1-NH_3,2-BCl_3,5-CF_3−BZ. B3LYP/TZVP level of theory. All distances are in angstroms.

Table 6. Predicted Structural and Thermodynamic Characteristics for Gaseous Ternary 1-NH_3,2-BCl_3,5-X-BZ (X = CH_3, H, F, Cl, CF_3) Complexes of Substituted Borazines (B3LYP/TZVP Level of Theory)

parameter	CH_3	H	F	Cl	CF_3
R(B−NH_3), Å	1.717	1.713	1.713	1.709	1.701
R(N−BCl_3), Å	1.646	1.650	1.652	1.656	1.660
q_{CT} (NH_3)	0.386	0.394	0.387	0.400	0.405
q_{CT} (BCl_3)	−0.348	−0.344	−0.334	−0.330	−0.318
q_{CT} (ring)	−0.038	−0.050	−0.053	−0.070	−0.087
$\Delta_{diss}H°_{298}$, kJ mol^{-1}	−20	−23	−22	−23	−25
$\Delta_{diss}S°_{298}$, J mol^{-1} K^{-1}	314	303	304	305	325
$\Delta_{diss}G°_{298}$, kJ mol^{-1}	−113	−113	−113	−114	−121

formation with $AlCl_3$, the Gibbs free energy $\Delta G°_{298}$ of complex dissociation in the gas phase is close to zero or even negative due to the unfavorable entropy factor. However, such complexes may be stabilized in the condensed phase (in nonpolar solvents or in the crystal state). To address this issue, we estimated Gibbs free energy values for the complex formation in solution.

Estimation of the Thermodynamic Characteristics of Complex Formation in the Condensed Phase. To estimate the thermodynamic characteristics of complex formation

Table 7. Influence of Acceptor Nature on the Main Structural and Thermodynamic Properties of 1-D,2-A-BZ Complexes (B3LYP/TZVP Level of Theory)

acceptor	BCl_3			$AlCl_3$		
parameter\donor		NH_3	Py		NH_3	Py
R(B−D), Å		1.713	1.683		1.721	1.686
R(N−A), Å	1.694	1.650	1.634	2.114	2.040	2.017
q_{CT} (D)		0.394	0.372		0.392	0.397
q_{CT} (A)	−0.283	−0.344	−0.344	−0.160	−0.344	−0.229
q_{CT} (ring)	0.283	−0.050	−0.028	0.160	−0.028	−0.168
$\Delta_{diss}H°_{298}$, kJ mol^{-1}	−48	−23	−6	44	63	78
$\Delta_{diss}S°_{298}$, J mol^{-1} K^{-1}	147	303	331	143	287	318
$\Delta_{diss}G°_{298}$, kJ mol^{-1}	−92	−113	−105	2	−22	−16

Table 8. Dissociation ΔE_{diss}, Reorganization ΔE_{reorg}[a] and Sum of Bond Energies $E_{D\text{-}BZ} + E_{A\text{-}BZ}$ (in kJ mol^{-1}) for Selected Borazine Complexes with Lewis Acids and Bases (B3LYP/TZVP Level of Theory)

compound	ΔE_{diss}	ΔE_{reorg} (cycle)	ΔE_{reorg} (D)	ΔE_{reorg} (A)	$E_{D\text{-}BZ} + E_{A\text{-}BZ}$
2-BCl_3−BZ	−43	58		119	134
1-NH_3,2-BCl_3−BZ	−6	148	0.3	133	276
1-NH_3,4-BCl_3−BZ	−26	159	0.2	127	261
1-Py,2-BCl_3−BZ	8	170	3.0	140	321
1-Py,4-BCl_3−BZ	−18	180	2.4	129	294
2-$AlCl_3$−BZ	50	34		36	119
1-NH_3,2-$AlCl_3$−BZ	80	125	0.3	50	255
1-NH_3,4-$AlCl_3$−BZ	62	134	0.3	45	242
1-Py,2-$AlCl_3$−BZ	92	147	2.9	54	296
1-Py,4-$AlCl_3$−BZ	70	155	2.4	47	275

[a] ΔE_{reorg}(fragment) = E(fragment in complex geometry) − E(fragment in optimized ground state geometry).

in solution, let us consider the difference between two homogeneous reactions: (1) complex formation in the gas phase; (2) complex formation in the inert solvent media.

$$A_{(g)} + D_{(g)} + BZ_{(g)} = 1\text{-D,2-A}-BZ_{(g)} \qquad \Delta_{(1)}H°_{298}(g), \Delta_{(1)}S°_{298}(g) \qquad (1)$$

$$A_{(solv)} + D_{(solv)} + BZ_{(solv)} = 1\text{-D,2-A}-BZ_{(solv)} \qquad \Delta_{(2)}H°_{298}(solv), \Delta_{(2)}S°_{298}(solv) \qquad (2)$$

According to Kondrat'ev,[58] the enthalpies of complex formation of group 13 metal trihalides with nitrogen and oxygen-containing donors in the inert solvent are equal or even slightly more exothermic than the respective values for the gaseous complexes. Therefore, the theoretically predicted gas phase complex formation enthalpies may serve as an upper limit of the complex formation enthalpy in the inert solvent media: $\Delta_{(2)}H°_{298}(solv) \approx \Delta_{(1)}H°_{298}(g)$. Please note that the process of ternary complex formation in the solid state will be energetically even more favorable due to the exothermic crystallization energy of the complex.

To estimate the entropy difference between reactions 1 and 2, values of solvation entropies of all compounds are needed. The simplest way to estimate the solvation entropy is to take a value of so-called "self solvation", solvation of vapor molecules in their own melt. Thus, "self-solvation" entropy may be estimated as vaporization entropy of the nonpolar liquid at its boiling point (Trouton's constant, about 90 J mol^{-1}K^{-1}).[59] This approximation may be justified in a sense that translational degrees of freedom are lost both in the devaporization and solvation process. Thus, we can estimate the entropy of the solvation of one gaseous mole in the inert solvent as 90 J mol^{-1} K^{-1}. Taking into account that the number of gaseous moles in reaction 1 decreases by two, the entropy difference between reactions in the gas phase and in solution $\Delta_{(1)}S°_{298}(g) - \Delta_{(2)}S°_{298}(solv)$ may be estimated as −180 J mol^{-1} K^{-1}. This ensures that the reaction in the inert solvent is less disfavored by entropy compared to the gas phase reaction. As a consequence, the standard Gibbs energies for the ternary complex formation in the inert solvent $\Delta_{(2)}G°_{298}(solv)$ become about 54 kJ mol^{-1} more negative than for the same reaction in the gas phase.

The estimated Gibbs energy values for selected ternary complexes are summarized in Table 9. On the basis of these estimations, ternary D→BZ→A complexes will be thermodynamically stable with respect to dissociation into free D, A, and BZ both in the inert solvent medium and in the solid state at low temperatures.

Similar estimations, based on the solution-gas phase reaction entropy difference of 90 J mol^{-1} K^{-1}, were performed for the binary BZ→A complexes (Table 9); the standard Gibbs energies for the complex formation in the inert solvent become about 27 kJ mol^{-1} more negative. We must state that reported thermodynamic values in inert solvent media are based on crude approximations and absolute values may have considerable errors. However, our estimated negative Gibbs energy values for the complex formation between hexamethylborazine and Lewis acids $AlBr_3$ and $GaCl_3$ agree well with the experimental observation of such complexes both in the solid state and in solution.[26,27] Both $AlBr_3$−hexamethylborazine

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Table 9. Values for Standard Enthalpies $\Delta H°_{298}$, Gibbs Energies $\Delta G°_{298}$ (in kJ mol^{-1}), Standard Entropies $\Delta S°_{298}$ (in J mol^{-1} K^{-1}), and Equilibrium Constants K_{298} of Processes of Complex Formation in the Gas Phase (B3LYP/TZVP Level of Theory) and Estimated Values in the Inert Solvent Media

process	$\Delta H°_{298}$	$\Delta S°_{298}$ (gas)	$\Delta G°_{298}$ (gas)	K_{298} (gas)	$\Delta S°_{298}$ (solv)	$\Delta G°_{298}$ (solv)	K_{298} (solv)
$AlCl_3 + BZ = AlCl_3{-}BZ$	−44.5	−143.4	−1.7	2.0	−53.4	−28.5	9.8×10^4
$AlCl_3$ + 1,3,5-$F_3{-}BZ$ = 2-$AlBr_3$-1,3,5-$F_3{-}BZ$	−34.5	−150.0	10.2	1.6×10^{-2}	−60.0	−16.6	810
$AlCl_3$ + 1,3,5-$Br_3{-}BZ$ = 2-$AlBr_3$-1,3,5-$Br_3{-}BZ$	−10.5	−151.0	34.4	9.4×10^{-7}	−61.0	7.6	0.05
$AlCl_3$ + 1,3,5-$Me_3{-}BZ$ = 2-$AlCl_3$-1,3,5-$Me_3{-}BZ$	−62.6	−173.5	−10.9	81	−83.5	−37.8	4.2×10^6
$AlCl_3$ + 2,4,6-$Me_3{-}BZ$ = 2-$AlCl_3$-2,4,6-$Me_3{-}BZ$	−33.7	−177.4	19.1	4.5×10^{-4}	−87.4	−7.7	22
$AlCl_3 + Me_6{-}BZ$ = 2-$AlCl_3$-$Me_6{-}BZ$	−48.4	−173.3	3.3	0.26	−83.3	−23.5	1.3×10^4
$AlBr_3 + Me_6{-}BZ$ = 2-$AlBr_3$-$Me_6{-}BZ$[a]	−32.9	−177.9	20.2	2.9×10^{-4}	−87.9	−6.7	15[a]
$GaCl_3 + Me_6{-}BZ$ = 2-$GaCl_3$-$Me_6{-}BZ$[a]	−30.1	−171.3	20.9	2.2×10^{-4}	−81.3	−5.9	11[a]
$NH_3 + AlCl_3 + BZ$ = 1-NH_3,2-$AlCl_3{-}BZ$	−63.5	−287.2	22.1	1.3×10^{-4}	−107.2	−31.5	3.3×10^5
$Py + AlCl_3 + BZ$ = 1-Py,2-$AlCl_3{-}BZ$	−78.3	−317.6	16.4	1.3×10^{-3}	−137.6	−37.3	3.4×10^6
$AlCl_3{-}BZ + NH_3$ = 1-NH_3,2-$AlCl_3{-}BZ$	−19.0	−143.8	23.8	6.8×10^{-5}	−53.8	−3.0	3.3
$AlCl_3{-}BZ + NH_3 = AlCl_3{\cdot}NH_3 + BZ$	−99.2	17.5	−104.4	2.0×10^{18}	17.5	−104.4	2.0×10^{18}
$AlCl_3{-}BZ + Py$ = 1-Py,2-$AlCl_3{-}BZ$	−33.8	−174.2	18.1	6.7×10^{-4}	−84.2	−8.7	33
$AlCl_3{-}BZ + Py = AlCl_3{\cdot}Py + BZ$	−102.9	16.1	−107.8	7.4×10^{18}	16.1	−107.7	7.4×10^{18}

[a] Complexes have been experimentally observed in the solid state and in benzene/toluene solution. See refs 26 and 27 for details.

and $GaCl_3$−hexamethylborazine complexes show fluxional behavior in toluene solution above 276 and 220 K, respectively.[26,27] This observation is in qualitative agreement with very small negative Gibbs energy values of the complex formation, predicted in the present work. Thus, estimated equilibrium constants for complex formation in solution at 298 K are 15 and 11 for hexamethylborazine complexes with $AlBr_3$ and $GaCl_3$, respectively.

Synthetic Pathway to the Ternary D−BZ−A Complexes. The obtained theoretical results allow us to propose a viable synthetic pathway toward yet unknown ternary D→BZ→A complexes (Scheme 4). The synthesis can be carried out in inert solvent and should include two steps. In the first step, borazine reacts with Lewis acid to form binary compound BZ→A. In the second step, the resulting complex BZ→A reacts with a donor molecule to form the desired product D→BZ→A (Scheme 4, path a). The opposite reaction order is inappropriate since borazine complexes with donor molecules D→BZ are predicted to be unstable. The major drawback of the proposed synthetic path is a possibility of the direct complex formation between the donor and acceptor molecules to yield molecular complex AD in the step 2 (Scheme 4, path b). The process (b) is much more favorable thermodynamically compared to (a) since very strong adduct AD is formed in process (b) and aromaticity of borazine is restored. However, process (b) may be kinetically hindered due to the activation energy required to break the BZ→A bond. By analogy with group 13 metal halide complexes with ammonia,[60,61] activation energies should be equal or greater than the dissociation enthalpies of BZ→A complexes (~50 kJ mol^{-1}). In contrast, process (a) involves the direct interaction of donor's lone pair with a partially "pre-organized" boron center in the BZ→A complex. Thus, process (a) may be favored due to kinetics reasons, while process (b) is clearly favored thermodynamically. Indeed, Nöth noted that dissolution of $AlBr_3$-$Me_3B_3N_3Me_3$ in tetrahydrofuran (THF) results in liberation of free $Me_3B_3N_3Me_3$,[26] which undoubtedly indicates operation of pathway (b). Note, however, that in solution estimated Gibbs energies for the synthesis of 1-NH_3,2-$AlCl_3$−BZ and 1-Py,2-$AlCl_3$−BZ starting from 2-$AlCl_3$−BZ complex are slightly negative, which makes this pathway thermodynamically allowed. However, if formed, ternary complexes are expected to easily dissociate in solution but may be stable in the solid state. The low temperature conditions may be beneficial for the formation of ternary D→BZ→A complexes by preventing their dissociation into BZ and AD.

Another important aspect, which should be taken into account upon discussing the possible synthetic approaches, is the dimerization of acceptor MX_3 molecules. Heavier group 13 metal halides readily form dimers both in the condensed phase and in the inert solvents.[62] Dimerization enthalpies of $AlCl_3$, $AlBr_3$, and $GaCl_3$ are 61.1, 60.7, and 43.7 kJ mol^{-1}, per mol of monomer, respectively.[63] If the dimerization to yield M_2X_6 will be more favorable than the complex formation, complexes will be very thermodynamically unstable with respect to dissociation. The better way to avoid the dimerization of MX_3 is to use Lewis acids which are monomeric, such as group 13 perfluoroaryls.[64] As was shown by Timoshkin and Frenking,[65] $B(C_6F_5)_3$ and especially $Al(C_6F_5)_3$ are much stronger Lewis acids due to their monomeric nature in the gas phase and in solution. Thus, group 13 perfluoroaryls are expected to be excellent candidates for the formation of ternary D→BZ→A complexes. Other strong perfluorinated group 13 acceptors have been theoretically examined by Gilbert.[50]

Donor−Acceptor Complexes with Benzene. Our ideas can be generalized to the σ-complexes of other 13−15 heterocycles, as well as for benzene. In fact, σ-complexes of benzene with strong Lewis acids H^+ and R^+ are widely accepted intermediates in the electrophilic substitution reactions (arenium ions or Wheland intermediates).[24] They have been isolated as stable salts using the bulky carborane anions.[25]

Benzene has a principal possibility of σ-bond complex formation with neutral donor and acceptor molecules

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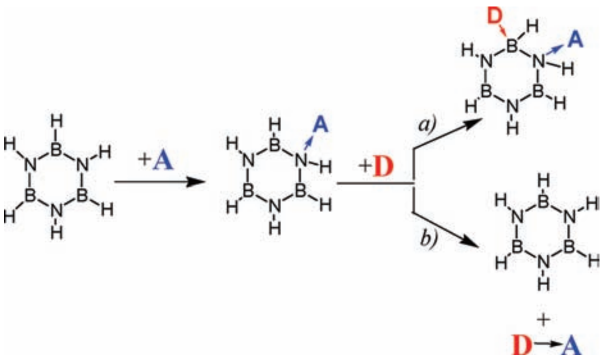
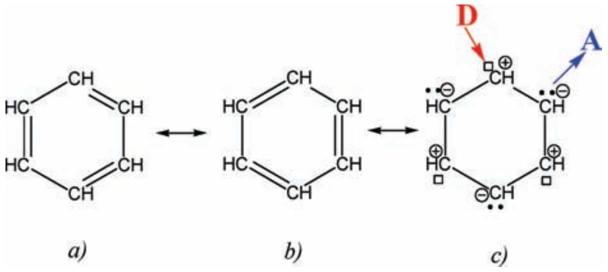
Scheme 4. Proposed Reaction Pathway for the Generation of the Donor−Acceptor Complexes of Borazines (a) and Possible Side Reaction (b)



Scheme 5. Resonance Structures of Benzene and Possible σ-Interaction with Donor and Acceptor Molecules for Structure (c)



(resonance structure c in Scheme 5,c). By analogy with borazine, pyramidalization energy of the benzene ring should play a major role in the possibility of complex formation. Pyramidalization energies of isoelectronic NH_3 and CH_3^- are exothermic (experimental[57] inversion barrier of NH_3 is 24.3 kJ mol^{-1} and computed[66] inversion barrier of CH_3^- is 8.6 kJ mol^{-1} at CCSD(T)/aug-cc-pVTZ level of theory). In contrast, pyramidalization of isoelectronic CH_3^+ and BH_3 is endothermic (121 and 93 kJ mol^{-1}, respectively). On the basis of these values, one can expect larger deformation energy of the benzene ring compared to that of isoelectronic borazine. As a consequence, σ-bonded benzene complexes are expected to be less stable compared to borazine.

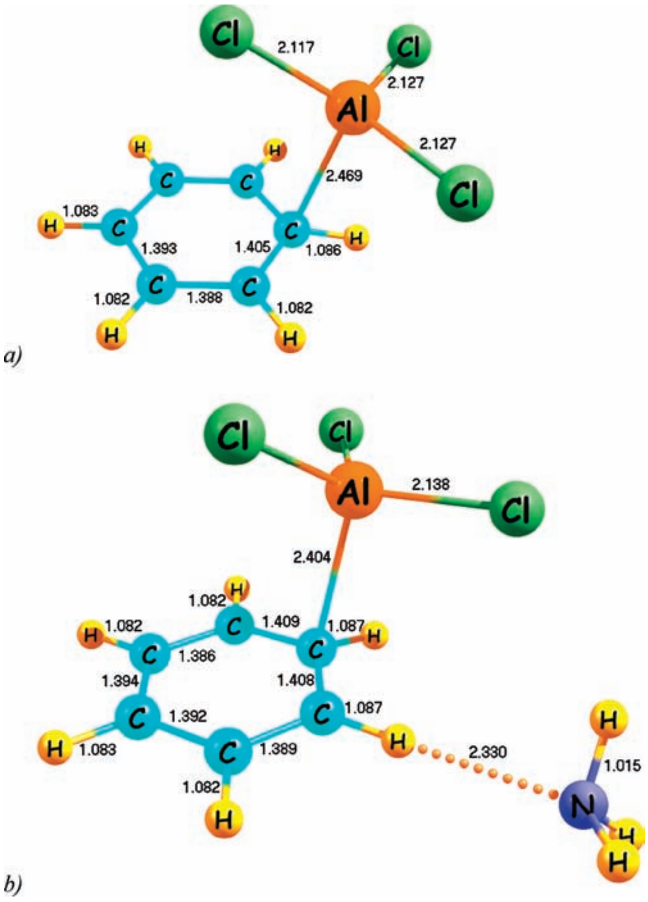


Figure 7. Optimized structures of (a) $AlCl_3$−benzene complex; (b) van der Waals bound ammonia to the $AlCl_3$−benzene complex. B3LYP/TZVP level of theory. All distances are in angstroms.

In agreement with this expectation, geometry optimization for the ternary NH_3−C_6H_6−$AlCl_3$ complex resulted in Van der-Waals bound NH_3 to the binary C_6H_6−$AlCl_3$ complex (Figure 7b). Note that the individual binary $AlCl_3$−C_6H_6 complex (Figure 7a) is a true minimum on PES with relatively weak dissociation energy of only 24.6 kJ mol^{-1} and very long C···Al distance of 2.469 Å. Stronger acceptor molecules, in particular $Al(C_6F_5)_3$, are expected to form stronger DA complexes with benzene. It is worth noting that weak $Al(C_6F_5)_3$−benzene and $Al(C_6F_5)_3$−toluene complexes (predicted at the RI-BP86/def2-TZVPP level of theory; gas phase dissociation energy of 14 kJ mol^{-1})[65] were structurally characterized in the solid state and possess C···Al bond distances of 2.342 and 2.366 Å, respectively.[67] Upon complexation with $AlCl_3$, the benzene ring is only slightly perturbed. Nevertheless, the C−C distances in the ring become nonequivalent. C1−C2 and C3−C4 bond lengths increase up to 1.405 and 1.393 Å, respectively, while the C2−C3 bond decreases to 1.388 Å as compared to 1.392 Å in free benzene. Note, however, that the benzene ring is only marginally distorted from planarity (dihedral angle 2.7) as compared to the clearly pronounced borazine distortion upon complexation with $AlCl_3$.

If one would use the complex formation enthalpy as an aromaticity criterion (the better the complex formation ability, the worse the aromaticity), one concludes that borazine forms much stronger complexes than benzene, and therefore, borazine is less aromatic. However, the larger electronegativity of nitrogen as compared to carbon may significantly contribute to the complex stabilization which is not directly related to the aromaticity.

Reactivity of Borazine Complexes. It is well-known that donor−acceptor complex formation significantly affects reactivity of compounds.[68] Interestingly, as shown by Stephens et al., addition of such Lewis acids as $B(C_6F_5)_3$ activates hydrogen release from ammonia borane BH_3NH_3.[69] Group 13 hydrides also have a catalytic effect on ammonia borane and alane dehydrogenation.[70−72] Since DA complexes of borazines are predicted to be

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Table 10. Standard Enthalpies $\Delta H°_{298}$, Gibbs Energies $\Delta G°_{298}$ (in kJ mol^{-1}), and Standard Entropies $\Delta S°_{298}$ (in J mol^{-1} K^{-1}) of Thermodynamic Processes for the Hydrogenation of Borazine and Its Donor–Acceptor Complexes in the Gas Phase (B3LYP/TZVP Level of Theory)

process	$\Delta H°_{298}$	$\Delta S°_{298}$	$\Delta G°_{298}$
$B_3N_3H_6 + H_2 = B_3N_3H_8$	127.6; 128.4[a]; 116.7[b]	−109.1; −100.8[b]	160.1; 146.9[b]
$AlCl_3 \cdot B_3N_3H_6 + H_2 = AlCl_3 \cdot B_3N_3H_8$	57.6	−126.3	95.3
$AlCl_3 \cdot B_3N_3H_6 \cdot NH_3 + H_2 = AlCl_3 \cdot B_3N_3H_8 \cdot NH_3$	33.1	−140.1	74.8
$B_3N_3H_8 + H_2 = B_3N_3H_{10}$	18.6; 11.7[a]; 8.8[b]	−118.6; −119.0[b]	54.0; 44.4[b]
$AlCl_3 \cdot B_3N_3H_8 + H_2 = AlCl_3 \cdot B_3N_3H_{10}$	5.2	−139.9	46.9
$AlCl_3 \cdot B_3N_3H_8 \cdot NH_3 + H_2 = AlCl_3 \cdot B_3N_3H_{10} \cdot NH_3$	−12.8	−138.1	28.3

[a] B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory, reference 7. [b] CCSD(T)/CBS level of theory for $\Delta H°_{298}$ and MP2/cc-pVTZ level of theory for $\Delta S°_{298}$, reference 44.

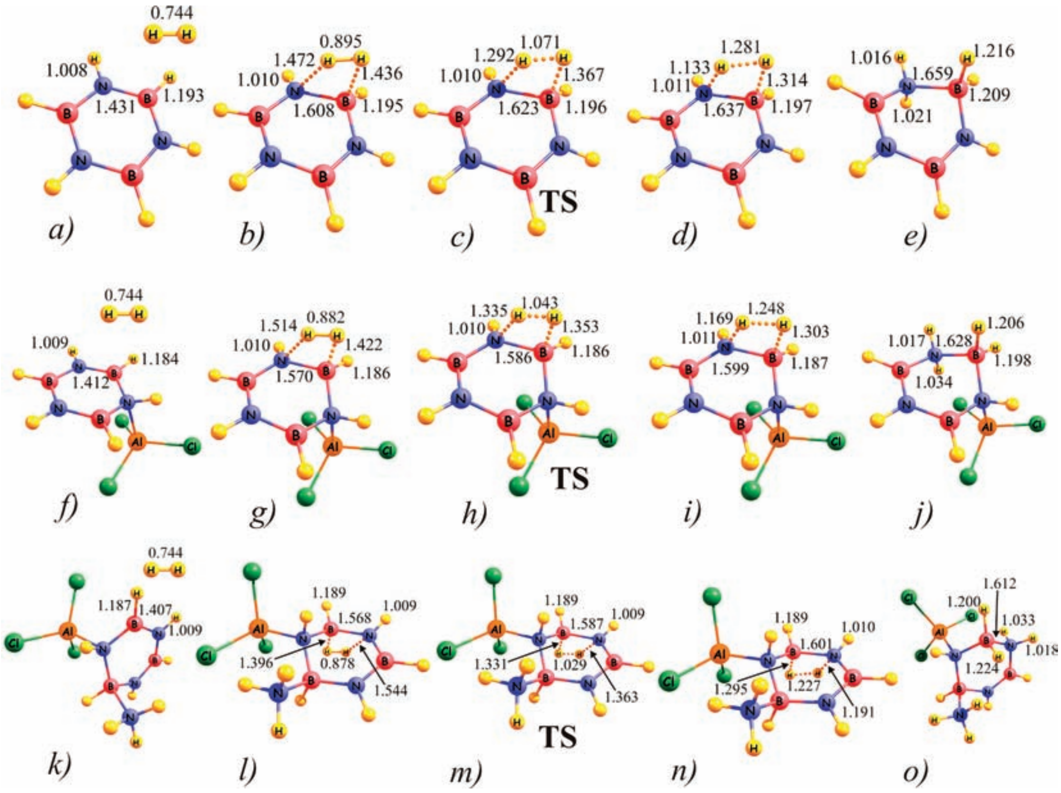

Figure 8. Optimized structures for the hydrogenation of borazine (a–e), 2-$AlCl_3$–BZ complex (f–j), and 1-NH_3,2-$AlCl_3$–BZ complex (k–o). Structures of reactants (a, f, k), products (e, j, o), transition states (c, h, m), and points on IRC scan in forward (d, i, n) and reverse (b, g, l) directions. All distances in angstroms. B3LYP/TZVP level of theory.

viable synthetic targets, it is of interest how the complex formation affects reactivity of borazines and polyborazines. To this end, we considered subsequent hydrogenation reactions of borazine and its DA complexes. Dehydrogenation reactions leading from ammonia borane to borazine have been studied in detail by Nutt and McKee at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory.[7] Initial pathways from ammonia borane to cyclotriborazane were considered by Zimmerman et al.[73] Accurate thermochemistry values for the borazine hydrogenation were reported by Matus et al.[44] However, hydrogenation of σ-complexes of borazine has not been studied before. Several possible isomers for the hydrogenation process have been considered (see Supporting Information). Results obtained for the most stable isomers are presented in Table 10. As can be seen, complex formation significantly reduces the endothermicity of the hydrogenation process. Especially noteworthy is that, in case of the ternary complex, the endothermicity of the hydrogenation process is reduced from 128 to only 33 kJ mol^{-1} for the first step, and it becomes exothermic by 13 kJ mol^{-1} for the second step. Thus, the overall enthalpy for the two steps of hydrogenation is reduced from 146 for the uncomplexed borazine to 63 and 20 kJ mol^{-1} for its binary and ternary complexes, respectively.

Although detailed analysis of the mechanisms of hydrogenation reactions lies out of scope of the present report, we have also investigated a reaction pathway for the first, the most energetically unfavorable, step of the hydrogenation. Transition states have been obtained for the hydrogenation of BZ and its binary and ternary DA complexes with $AlCl_3$ and ammonia. Following the intrinsic reaction coordinate (IRC) confirmed that obtained TS structures connect reactants and products.

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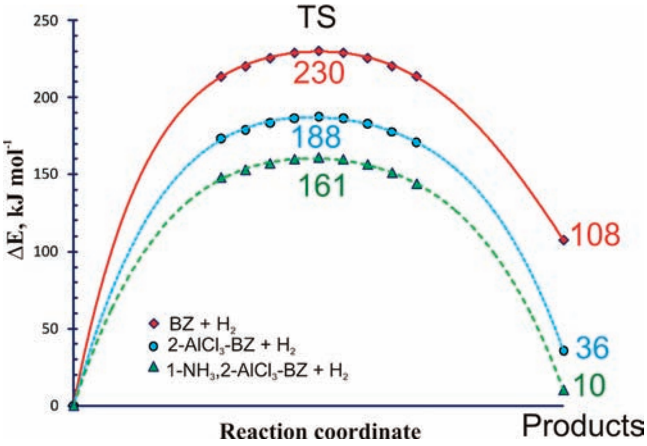

Figure 9. Reaction profiles for hydrogenation of borazine, 2-$AlCl_3$−BZ complex, and 1-NH_3,2-$AlCl_3$−BZ complex. Relative energies with respect to free reactants in kJ mol^{-1}.

Optimized geometries for the most favorable pathways are presented in Figure 8. H···H distance in TS slightly shortens when going from borazine to its binary and ternary complex: from 1.071 to 1.043 and 1.029 Å. Activation energy of the first hydrogenation step lowers from 230 kJ mol^{-1} for borazine to 188 and 161 kJ mol^{-1} for its binary and ternary complexes, respectively (Figure 9).

We conclude that the σ-complex formation significantly enhances reactivity of borazines with respect to hydrogenation (both thermodynamically and kinetically). We assume that complexation of Lewis acids with polyborazines will also enhance their reactivity. Thus, Lewis acid catalysis appears to be an interesting approach for the hydrogenation of borazines and polyborazines.

Conclusions

Latent Lewis acid−base reactivity of borazines toward neutral donor and acceptor molecules has been theoretically explored at B3LYP/TZVP and MP2/TZVP levels of theory. The B3LYP method provides the lower limit for the dissociation energy of the complex.

Acceptor properties of borazines are significantly weaker compared to their donor properties. A strong endothermic pyramidalization energy of boron center and exothermic pyramidalization energy of nitrogen center energetically favor binary complexes with Lewis acids and disfavor binary complexes with Lewis bases. However, the formation of weak ternary complexes, featuring both a Lewis acid and a Lewis base, is feasible in principle. A synthetic pathway to the ternary complexes has been proposed. It includes stepwise interaction with acceptor and then with donor molecules.

In contrast to borazine, the isoelectronic benzene forms much weaker σ-complexes, which may be due to larger pyramidalization energy and larger electron delocalization in the benzene ring. Complexation of borazine significantly reduces both the hydrogenation enthalpies (by 70−95 kJ mol^{-1}) and the activation energies (by 43−69 kJ mol^{-1}). Thus, complex formation with Lewis acids appears to be a perspective way to promote hydrogenation of borazines and polyborazines. Further theoretical and experimental efforts in this direction are expected to be very promising.

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Supporting Information Available: Total energies, standard entropies and enthalpies, optimized structures and *xyz* coordinates for all studied compounds obtained at B3LYP/TZVP level of theory, total energies for selected compounds at MP2/TZVP level of theory. NICS values for borazine and its donor−acceptor complexes computed at B3LYP/aug-cc-pVTZ level of theory (50 pages). This material is available free of charge via the Internet at http://pubs.acs.org.