Fast H/D Exchange of $B,B′,B″$-Tribromoborazine in C_6D_6 in the Presence of Aluminum Tribromide: First Evidence for an Electrophilic Substitution Reaction of Borazines in Solution

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S *Supporting Information*

ABSTRACT: A solution of $B,B′,B″$-tribromoborazine $(BrBNH)_3$ in excess C_6D_6 in a sealed NMR tube shows no changes for over 14 months at room temperature but undergoes fast (within minutes) H/D exchange in the presence of $AlBr_3$ as a Lewis acid, as evidenced by ^{1}H, ^{2}H, ^{11}B, and ^{27}Al NMR spectroscopy. The proposed electrophilic exchange mechanism is in agreement with the results of DFT computations. To our knowledge, this is the first example of the electrophilic substitution reaction of borazines in solution.
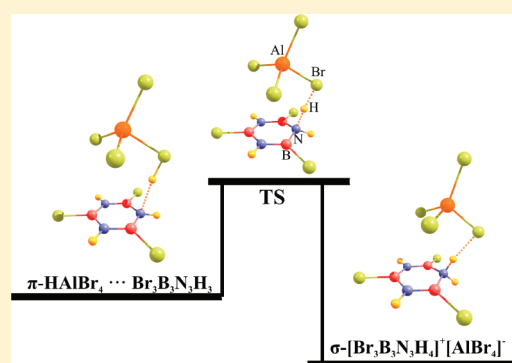
INTRODUCTION

Borazine[1] is isoelectronic to benzene and has similar physical properties but quite different chemical reactivity. While benzene readily undergoes electrophilic substitution reactions, addition reactions are more common for borazine.[2] Dahl and Schaeffer[3] studied exchange reactions between borazine and a series of deuterated compounds. The reaction of borazine with DCl mostly leads to addition products, but the H/D exchange reaction operates in parallel and leads to substitution of only three (all imide) hydrogens to deuterium. In contrast to benzene, no scrambling was observed due to 1,2-shifts, and so the final product of the substitution reaction is $N,N′,N″$-trideuteroborazine. Treatment of borazine with ND_4Cl and DCN results in fast N—H/N—D exchange, while treatment with D_2, B_2D_6, and $NaBD_4$ results in B—H/B—D exchange. Such selectivity was attributed to different exchange mechanisms. It was supposed that N—H/N—D exchange proceeds via an electrophilic substitution reaction, but no evidence for this mechanism was provided.[3] In previous work[4] aluminum trihalides were used to abstract X^- from TiX_4 in the presence of aromatic hydrocarbons, resulting in arene complexes $[TiCl_3\text{-}\eta^6Ar]^+$ (Ar = $C_6Me_xH_{6-x}$, x = 3, 4) undergoing fast H/D exchange with C_6D_6. However, toluene and C_6D_6 do not undergo H/D exchange in the presence of TiX_4 and AlX_3.[4]

Electrophilic substitution reactions for borazines were unknown until 1999 when Chiavarino et al. reported gas-phase alkylation of borazine.[5,6] In the present communication we report on a fast H/D exchange between $(BrBNH)_3$ and deuterobenzene in solution, which is catalyzed by the Lewis acid $AlBr_3$. To our knowledge, this is the first example of the electrophilic substitution reaction for tribromoborazine in solution.

EXPERIMENTAL DETAILS

BBr_3 was synthesized from elements by the standard procedure[7] with 57.6% yield. Bromine impurities were removed by storing over liquid mercury at room temperature for ca. 48 h. The obtained BBr_3 was purified by multiple (no less than two times) slow distillations in sealed wholeglass systems in vacuum at room temperature (saturated vapor pressure ca. 60 Torr).

Synthesis of $(BrBNH)_3$ was carried out by the hot tube method analogously to the synthesis of $(ClBNH)_3$.[8] All operations have been performed in a specially designed wholeglass apparatus. $B,B′,B″$-Tribromoborazine was synthesized by passing gaseous BBr_3 (7.60 g, 0.0303 mol) over solid NH_4Br (4.47 g, 0.0456 mol) at 200−220 °C. Nitrogen was used as a carrier gas. Colorless needle crystals of $(BrBNH)_3$ were formed in the cold zone of the apparatus and purified by multiple (no less than 3 times) sublimations in vacuum at 60−65 °C (saturated vapor pressure ca. 0.2 Torr). Yield: 0.229 g (7.2%).

The purity of $(BrBNH)_3$ was confirmed by EI mass spectrometry, ^{1}H and ^{11}B NMR, X-ray crystallography, and vapor pressure measurements (for more details on tensimetry studies, see ref 9). Single crystals of
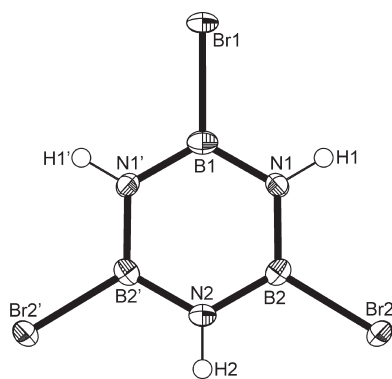
Figure 1. Molecular structure of tribromoborazine in the crystal. Bond lengths [Å] and angles [deg]: Br1−B1 1.951(6), Br2−B2 1.937(4), B1−N1 1.406(4), N1−B2 1.419(5), N2−B2 1.423(5), N1−H1 0.89(4), N2−H2 0.86(6), B1−N1−B2 120.3(3), B2−N2−B2′ 120.6(4), Br1−B1−N1 119.6(2), N1−B1−N1′ 120.7(4), Br2−B2−N2 119.1(3), N1−B2−N2 119.1(3), Br2−B2−N1 121.8(3).

(BrBNH)$_3$ were grown over several days in a glass ampule in vacuum at ca. 45 °C (with a temperature gradient of about 5 °C).

Electron ionization mass spectra were measured using an MX-1321 apparatus with direct probe introduction. MS (EI, 30 eV, 120 °C): (BrBNH)$_3^+$ 100, Br$_2$B$_3$N$_3$H$_3^+$ 84, BrB$_3$N$_3$H$_3^+$ 35, B$_3$N$_3$H$_3^+$ 11. MS (EI, 70 eV, 120 °C): (BrBNH)$_3^+$ 94; Br$_2$B$_3$N$_3$H$_3^+$ 100; (BrBNH)$_3^{2+}$ 21; BrB$_3$N$_3$H$_3^+$ 41; (Br$_2$B$_3$N$_3$H$_3$)$^{2+}$ 16; (BrB$_3$N$_3$H$_3$)$^{2+}$ 14; B$_3$N$_3$H$_3^+$ 22. ^{1}H NMR (C$_6$D$_6$): broad signal at 4.86 ppm. ^{11}B NMR (C$_6$D$_6$) singlet at 27.64 ppm.

Crystal structure analysis was performed on an Oxford Diffraction Gemini R Ultra CCD using molybdenum radiation (λ = 0.71073 Å). An analytical absorption correction from crystal faces was applied. The structure was solved by direct methods with the program SIR-97, and full-matrix least-squares refinement on F^2 in SHELXL-97 was carried out.[10] All hydrogen-atom parameters were refined with isotropic displacements. CSD-423154 contains the supplementary crystallographic data for this paper. This data can be obtained from the Inorganic Crystal Structure Database at Fachinformationszentrum Karlsruhe via http://www.fiz-karlsruhe.de/icsd.html.

NMR Studies. NMR spectra were acquired on a Bruker Avance 400. Sample preparation: C$_6$D$_6$ was degassed by multiple freezing−cooling cycles under vacuum, stored in a sealed glass ampule over molecular sieves (4 Å), and distilled in vacuum before use. Solutions for the NMR studies have been prepared by the following procedure. Solution 1: (BrBNH)$_3$ (0.0402 g, 0.126 mmol) was dissolved in C$_6$D$_6$ (2.33 g, 2.65 mL, 0.0277 mol) in a sealed wholeglass system under vacuum, which contained an NMR ampule, sealed under vacuum. Solution 2: AlBr$_3$ (0.1642 g, 0.6157 mmol) was dissolved in C$_6$D$_6$ (1.87 g, 2.13 mL, 0.0223 mol) in a sealed wholeglass system under vacuum. The solution was divided into two parts and a NMR ampule. Solution 3: 0.64 mL of solution 2 and 0.62 mL of solution 1 were mixed in a sealed wholeglass system under vacuum, and part of it was sealed in a NMR ampule. Further details on systems used for sample preparation can be found in the Supporting Information (Figure 3S).

■ RESULTS AND DISCUSSION

Structure of the Solid Compound. The crystal structure of (BrBNH)$_3$ was established for the first time. Molecules (BrBNH)$_3$ are essentially planar. The B−N distances inside the ring are slightly unequal due to pronounced Br···H−N hydrogen bonding in the crystal. Major structural parameters are summarized in Figure 1; experimental details are given in Table 1. Both trifluoro-[11] and

Table 1. Crystallographic Data

empirical formula	B$_3$Br$_3$H$_3$N$_3$
M_r	317.18
cryst size [mm]	0.40 × 0.28 × 0.18
T [K]	123(1)
space group	$Pnma$
cryst syst	orthorhombic
a [Å]	14.1228(8)
b [Å]	13.8457(7)
c [Å]	4.0654(2)
V [Å^3]	794.95(7)
Z	4
ρ_{calcd} [g/cm^3]	2.650
μ [mm^{-1}]	15.136
Θ range [deg]	3.24−30.51
completeness to Θ	0.979
index range	$-20 \leq h \leq 18$
	$-14 \leq k \leq 19$
	$-5 \leq l \leq 5$
data/restrains/params	3825/0/53
unique reflns $I > 2\sigma(I)$ (R_{int})	1233 (0.0367)
GOF in F^2	0.991
R_1/wR_2 ($I > 2\sigma(I)$)	0.0323, 0.0655
R_1/wR_2 (all data)	0.0523, 0.0697
largest diff. [e Å^{-3}]	−1.060, 0.186

trichloroborazine[12] also feature planar structures as well as isoelectronic 1,3,5-tribromobenzene.[13] B−N and B−Br bond distances are in good agreement with previously reported values for substituted bromoborazines (BrBNMe)$_3$ and (BrBNC$_6$F$_5$)$_3$.[14]

H/D Exchange Studies. In the ^{1}H NMR spectra of solution 1 ((BrBNH)$_3$ concentration = 47 mmol/L) a broad signal, attributed to a N−H group, is observed at 4.86 ppm. The ^{11}B NMR spectrum shows a single broad peak at 27.7 ppm. No changes are observed in the ^{1}H NMR spectra after 14 months in a sealed glass system stored in the dark at room temperature (Figure 2a). On the contrary, solution 3, prepared beforehand and stored at the same conditions, does not show any signal in the N−H region of the ^{1}H NMR spectra (Figure 2b) but exhibits a corresponding signal in ^{2}H NMR spectra (Figure 2c), suggesting complete H/D exchange between the N−H group of (BrBNH)$_3$ and the C−D group of deuterobenzene. In order to study the rate of the exchange, a freshly prepared solution of 35 mg of AlBr$_3$ in 0.6 mL of C$_6$D$_6$ was added to an equal amount of solution 1 in a drybox. After 5 min the signal at 4.86 ppm in the ^{1}H spectrum has almost completely disappeared and the corresponding signal in the ^{2}H NMR spectrum is clearly visible, indicating the exchange effectively proceeds within minutes. No changes are observed in ^{11}B and ^{27}Al NMR; a single broad peak at 27.7 ppm in ^{11}B NMR and a single peak at 77.3 ppm in ^{27}Al NMR are observed, which indicates a similar chemical environment of boron and aluminum atoms, which agrees with the presence of fully deuterated tribromoborazine and aluminum tribromide.

Formation of fully deuterated (BrBND)$_3$ was confirmed by an MS study of the solid residue after vaporization of the solvent from solution 3 (see Figure 2S in the Supporting Information).

In addition, toluene, present in the source C$_6$D$_6$ as an impurity (estimated toluene content is about 0.02%), also undergoes complete H/D exchange of aromatic protons upon addition of
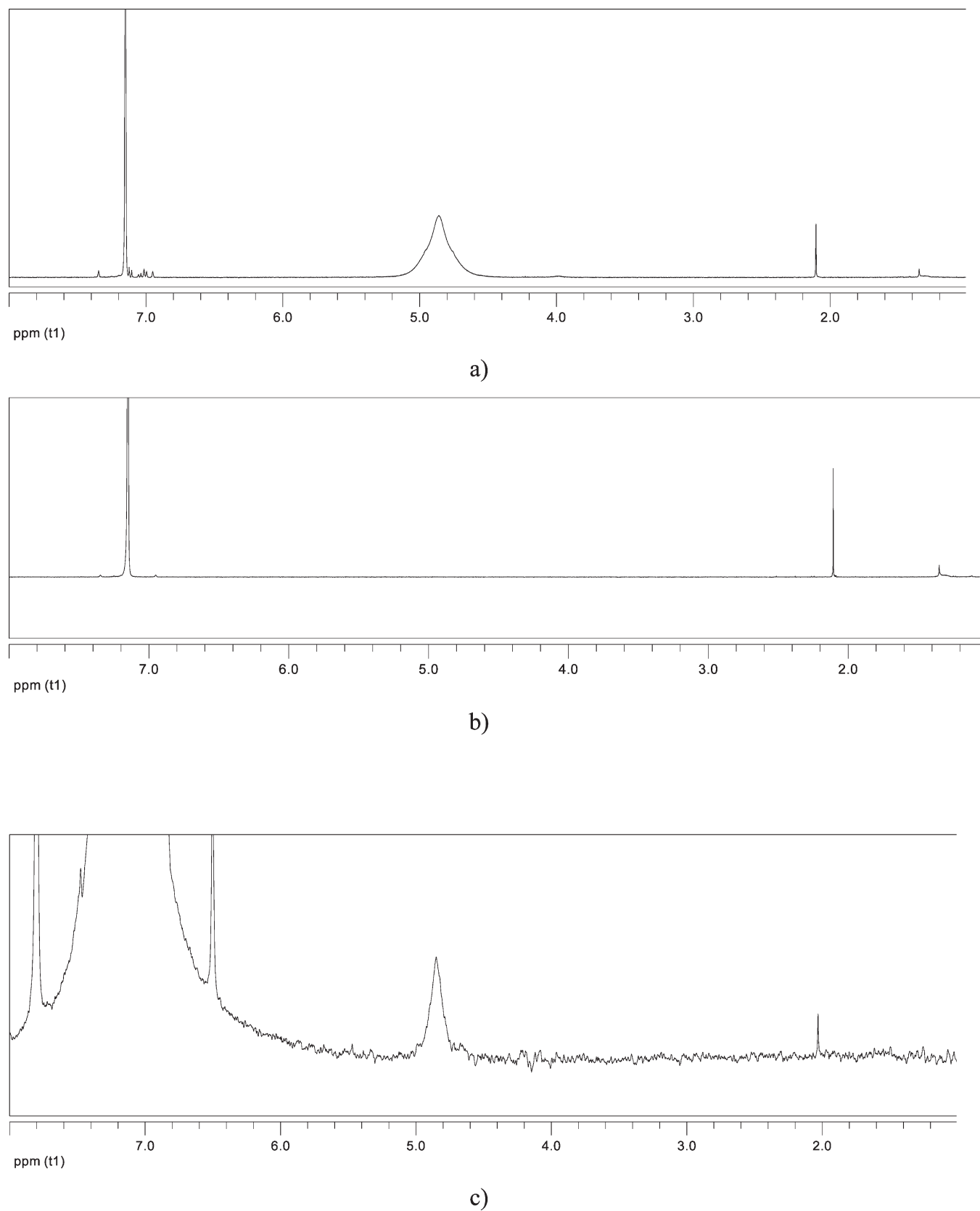
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Figure 2. NMR spectra in deuterobenzene: (a) ^{1}H NMR of (BrBNH)$_3$, (b) ^{1}H NMR of the solution of (BrBNH)$_3$ after addition of AlBr$_3$, and (c) ^{2}H NMR of the solution of (BrBNH)$_3$ after addition of AlBr$_3$.

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Scheme 1. Proposed H/D Exchange via Electrophilic Substitution Reactions
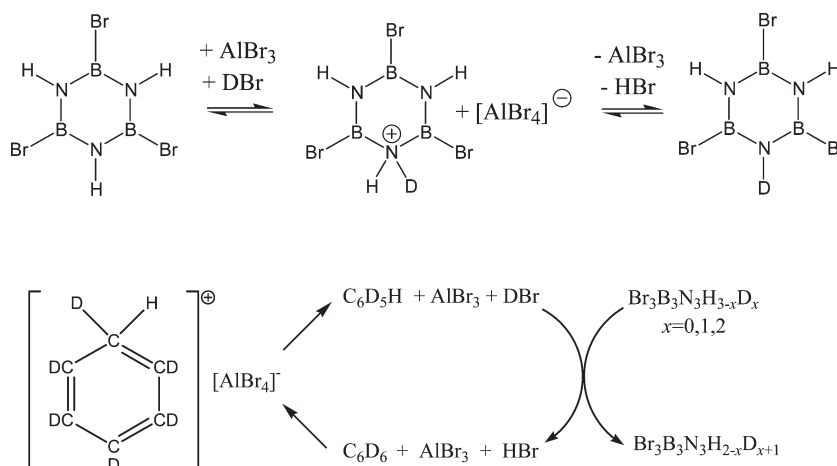
AlBr$_3$. Signals at 7.02–7.13 ppm corresponding to protons of the aromatic ring completely disappear after AlBr$_3$ addition, while the singlet at 2.10 ppm corresponding to protons of the aliphatic CH$_3$ group of toluene is observed after 14 months after addition of AlBr$_3$. According to ^{2}H NMR spectra, the presence of small amounts of CH$_2$D groups is detected both in the source solvent and in the sample after addition of AlBr$_3$. Although we cannot completely rule out H/D exchange in CH$_3$ groups of toluene, its rate is much slower compared to the fast exchange of aromatic protons. In our opinion, this indicates a fast electrophilic substitution of the aromatic protons between C$_6$D$_6$ and toluene.

The proposed mechanism (Scheme 1) includes [Br$_3$B$_3$N$_3$H$_3$D]$^+$ ions which are analogous to Wheland intermediates.[15] Such "arenium" ions as C$_6$H$_7$$^+$ were experimentally isolated with bulky counterions and structurally characterized by Reed et al.[16] Recently, borazinium ions [R$_3$B$_3$N$_3$H$_4$]$^+$ were obtained via reaction of donor–acceptor complexes R$_3$B$_3$N$_3$H$_3$·AlBr$_3$ with HBr and structurally characterized by the Nöth group as tetrabromoaluminate salts.[17]

In order to start a series of electrophilic substitution reactions, generation of active HBr or DBr species is needed and may be achieved in two ways.

(1) Reaction of AlBr$_3$ with traces of water (for example, from the used solvent C$_6$D$_6$), which is unlikely due to careful experimental procedures.

(2) HBr abstraction from reaction of (BrBNH)$_3$ or C$_6$D$_6$ with AlBr$_3$ due to either intra- or intermolecular HBr/DBr elimination. In the latter case formation of AlBr$_2$C$_6$D$_5$ intermediate could not be ruled out, analogously to possible formation of AlCl$_2$C$_6$H$_5$ discussed by Olah et al.[18]

In both cases formation of HBr/DBr in the presence of excess AlBr$_3$ starts the classical catalytic cycle generating arenium ions C$_6$D$_6$H$^+$. Subsequent H/D scrambling leads to DBr, which in turn will react with (BrBNH)$_3$ to form borazinium ion (BrB-NH)$_3$D$^+$ and eventually to the fully deuterated (BrBND)$_3$, since the tribromoborazine to deuterobenzene ratio is 1:446.

Computational Studies. To shed more light into the mechanism of H/D exchange, quantum chemical computations were performed for gaseous AlBr$_3$–HBr–(BrBNH)$_3$ and AlBr$_3$–HBr–(HBNH)$_3$ systems without taking into account solvation effects. All computations were carried out using the

standard Gaussian 03 program package[19] on the High-Performance Computing cluster of St. Petersburg State University. Density functional theory in the framework of the hybrid three-parameter exchange functional of Becke[20] with the gradient-corrected correlation functional of Lee, Yang, and Parr[21] (B3LYP) with an all-electron TZVP basic set[22] was used throughout. The basis sets are (311/1) for H, (62111/411/1) for B and N, (73211/6111/1) for Al, and (842111/63111/511) for Br. All structures have been fully optimized and verified to be minima or transition states (TS) by subsequent vibrational analysis. Intrinsic reaction coordinate (IRC) scans confirmed that obtained TS are connecting reactant and products. Such level of theory has been previously used by us to study borazine complexes.[23]

The relative energies of the (B$_3$N$_3$H$_7$)$^+$ ions suggest that the nitrogen-protonated isomer is by 133 kJ mol^{-1} more stable than the boron-protonated one. Thus, in acidic media, hydrogen exchange is expected to occur only at the nitrogen center.

The optimized structures of the compounds involved in hydrogen exchange and the reaction profile for tribromoborazine and borazine are given in Figure 3. Predicted structural parameters for gaseous borazinium tetrabromoaluminates [Br$_3$B$_3$N$_3$H$_4$]$^+$[AlBr$_4$]$^-$ and [B$_3$N$_3$H$_7$]$^+$[AlBr$_4$]$^-$ agree well with those experimentally found in solid borazinium salts [Et$_3$B$_3$N$_3$H$_4$]$^+$[AlBr$_4$]$^-$ and [(t-Bu)$_3$B$_3$N$_3$H$_4$]$^+$ [AlBr$_4$]$^-$[17] (see Table 2S, Supporting Information, for details).

We optimized TS connecting HAlBr$_4$···Br$_3$B$_3$N$_3$H$_3$ and [Br$_3$B$_3$N$_3$H$_4$]$^+$[AlBr$_4$]$^-$ (by analogy with benzene, called π and σ complexes, respectively). Two conformers (which are different in the location of the AlBr$_3$ moiety around the heterocycle) have been considered for both σ and π complexes (Figure 3a). IRC scan confirmed that the obtained TS is connecting isomer 1 of π-HAlBr$_4$···Br$_3$B$_3$N$_3$H$_3$ and isomer 1 of σ-[Br$_3$B$_3$N$_3$H$_4$]$^+$[AlBr$_4$]$^-$.

Analogous computations have been made for the borazine system (Figure 3b). In this case upon optimization isomer 2 of π-HAlBr$_4$···B$_3$N$_3$H$_6$ converged to σ-[B$_3$N$_3$H$_7$]$^+$[AlBr$_4$]$^-$ (isomer 2). We also obtained the TS connecting π-HAlBr$_4$···B$_3$N$_3$H$_6$ and isomer 1 of σ-[B$_3$N$_3$H$_7$]$^+$[AlBr$_4$]$^-$, as confirmed by IRC scan.

In both systems, σ complexes are more stable than π complexes (by 11 and 41 kJ mol^{-1} for tribromoborazine and borazine, respectively). Note that for (BrBNH)$_3$ the TS lies only 25 kJ mol^{-1} higher than the most stable σ complex and 14 kJ mol^{-1} higher than the most stable π complex. The small activation energy indicates
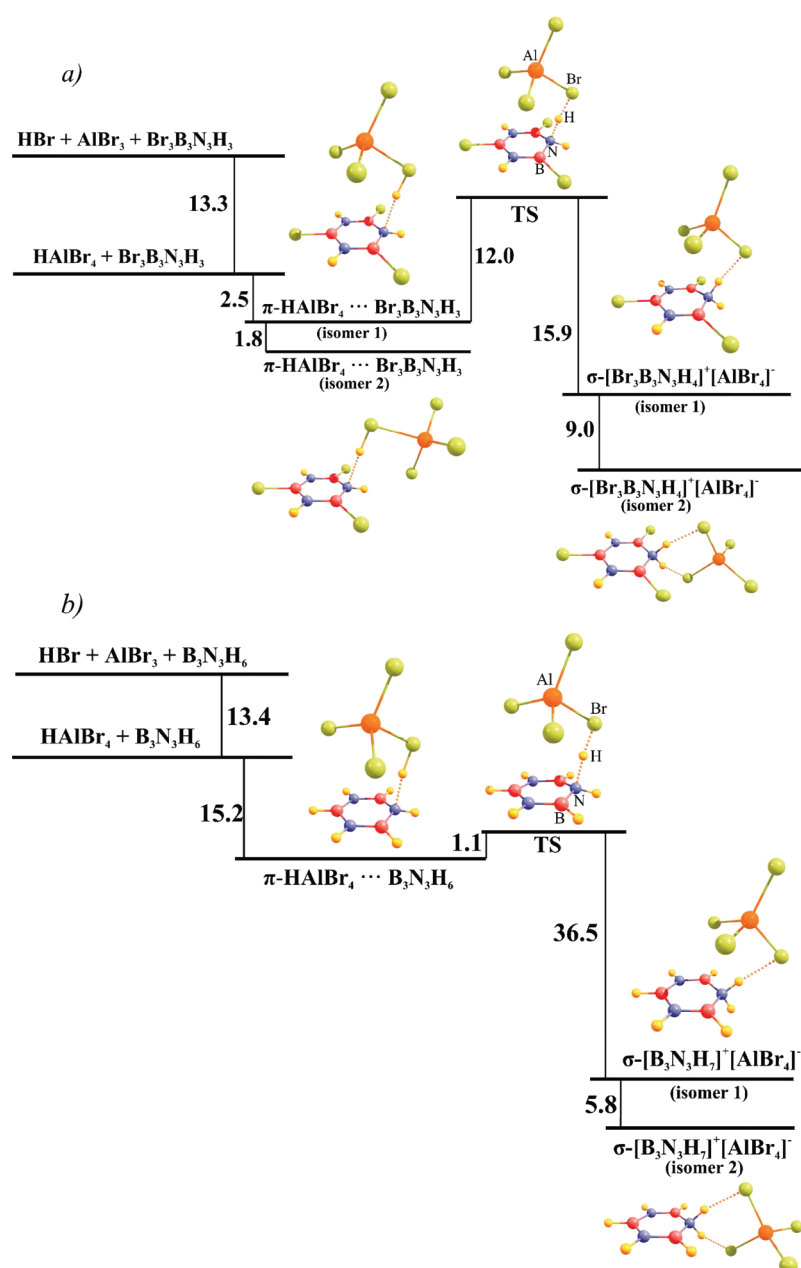
Figure 3. Energetic profiles for the AlBr$_3$-catalyzed hydrogen exchange for (a) tribromoborazine and (b) borazine. Relative energies are in kJ mol^{-1}. B3LYP/TZVP level of theory.

that the hydrogen/deuterium exchange should not be kinetically hindered even at room temperature. These theoretical predictions are in good agreement with the observed experimental data on H/D exchange.

In the case of $(HBNH)_3$ the barrier from the σ complex is much higher (42 kJ mol^{-1}) than that from the π complex (1 kJ mol^{-1}), suggesting a π-type transition state. However, the value of 42 kJ mol^{-1} is also not prohibitingly high to disallow H/D exchange in the case of borazine, suggesting that such electrophilic substitution reactions in solution are characteristic for borazine chemistry in general. These barriers are quite small, so the exchange reaction is expected to be operational even at room temperature.

Theoretical activation energies obtained in the present work are comparable with those predicted for the $C_6H_6-HCl-AlCl_3$

electrophilic exchange by Volkov et al. (45−55 kJ mol^{-1}).[24,25] Their quantum chemical computations indicate that the dimeric form of the aluminum trihalide is more likely to serve as a catalytic species for the hydrogen exchange between HCl and C_6H_6. The activation energies for HCl/C_6H_6 dimer-catalyzed exchange predicted at the MP2/LANL2DZ(d)+ level of theory are only 20 and 29 kJ mol^{-1} (for Al$_2$Cl$_6$ and Ga$_2$Cl$_6$, respectively).[24,25] Barriers for the monomer-catalyzed exchange (by AlCl$_3$ and GaCl$_3$) are by about 25 kJ mol^{-1} higher. According to a recent theoretical study, even higher oligomeric ions $M_3X_{10}^-$ and $M_4X_{13}^-$ are expected to be formed in excess of group 13 metal trihalides in solution.[26] It is expected that in borazine systems barriers would also be smaller if higher oligomeric forms of AlBr$_3$ were involved.

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As pointed out by one of the reviewers "ref 3 may be considered to indicate electrophilic substitution upon reaction with DCl as it demonstrates that (a) the product $B_3N_3H_6 \cdot 3DCl$ does not decompose to borazine and (b) once formed it does not exchange with borazine. This leaves little room for other interpretations than an electrophilic substitution by DCl". Indeed, observations of Dahl and Schaeffer allow one to exclude an addition—elimination mechanism for the exchange but do not provide a direct hint to the electrophilic substitution pathway. In our experiment, however, fast H/D exchange with deuterobenzene was simultaneously observed for both $(BrBNH)_3$ and aromatic protons of toluene. Taking into account that electrophilic substitution pathway is well established for aromatic hydrocarbons, our observations provide a direct hint to the operation of the electrophilic substitution pathway, which is supported by computational studies.

■ CONCLUSIONS

In this report we demonstrated a fast H/D exchange between B,B',B''-tribromoborazine and deuterobenzene catalyzed by the Lewis acid $AlBr_3$. Theoretical studies support the hypothesis that the exchange proceeds via an electrophilic substitution mechanism, which should be operational for the parent borazine as well. Our observations on the catalytic role of $AlBr_3$ open wide perspectives for studying electrophilic exchange reactions of borazines in solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Optimized structures, xyz coordinates, total energies, standard enthalpies and standard entropies for all considered compounds, description of the glass system used for sample preparation for NMR studies, mass spectra for the product obtained after solvent evaporation, comparison of the theoretically predicted and experimental bond distances in borazinium salts (10 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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