EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Reactions and Mechansims of B-Substituted Amine Boranes with THF·BH3

Authors: Yu Guo, Xinghua Wang, Nana Ma, Yilin Cao, Sajjad Hussain, Jie Zhang, Donghui Wei, and Xuenian Chen

To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201900847

Link to VoR: http://dx.doi.org/10.1002/ejic.201900847

WILEY-VCH

10.1002/ejic.201900847

WILEY-VCH

Reactions and Mechanisms of B-Substituted Amine Boranes with THF·BH_3

Yu Guo,[a] Xinghua Wang,[b] Nana Ma,[a] Yilin Cao,[a] Sajjad Hussain,[a] Jie Zhang,*[a] Donghui Wei,*[b] and Xuenian Chen*[a,b]

Abstract: The reactions of NH_3BH_2R (R = Me, Ph and Cl) with $THFBH_3$ have been investigated and it was found that different substituents on the B atom help to proceed the reactions in different ways. The expected doubly-bridged B-substituted aminodiborane products, similaring to aminodiborane (ADB, $BH_2(\mu\text{-}H)(\mu\text{-}NH_2)BH_2$) *via* the reaction of ammonia borane (AB, NH_3BH_3) and tetrahydrofuran borane ($THFBH_3$), are not obtained. Two competitive reactions occurred with the change of R = Me or Ph. When R is a Me group, an "open" version of B-substituted *μ*-aminodiborane, $THFBH(Me)(\mu\text{-}NH_2)BH_3$, is formed as a major product; when R is a Ph group, AB and $THFBH_2Ph$ are formed as mian products *via* the intermolecular NH_3-THF exchange reaction. However, if R is Cl, then NH_3BH_2Cl reacts with $THFBH_3$ through reversible intermolecular Cl-H exchange mechanism. Furthermore, DFT calculations are performed to elucidate the formation mechanism of $THFBH(Me)(\mu\text{-}NH_2)BH_3$ *via* the reaction of NH_3BH_2Me and $THFBH_3$ as well as the exchange mechanism of Cl-H in the reaction of NH_3BH_2Cl and $THFBH_3$.

Introduction

Aminodiborane (ADB, $BH_2(\mu\text{-}H)(\mu\text{-}NH_2)BH_2$, Figure 1) was first formed serendipitously in 1938 and then prepared through a tedious procedure with a low yield.[1,2] During the last following few decades, although its structure was established unambiguously,[3-5] intensive studies on this compound were not carried out extensively perhaps due to its instability and inaccessibility. In 2010, a facile method for the synthesis of ADB was developed by reacting ammonia borane (AB, NH_3BH_3) with tetrahydrofuran borane ($THFBH_3$),[6] which is also considered as a general method for the preparation of N-substituted *μ*-aminodiborane.[7] The new synthetic method benefited from the study of the dihydrogen bond[8] and the nucleophilicity of the B-H bonding pair electrons that leads to the formation of the B-N bond.[9] Previous methods for the synthesis of N-substituted ADB[10,11] are not suitable for the synthesis of unsubstituted ADB. In 2015, it was demonstrated that the formation rates and conversions of N-methyl aminodiboranes decrease with the increase of methyl substitution.[12] It is evident that N-substitution has significant effect on the properties of the resultant ADB derivatives.

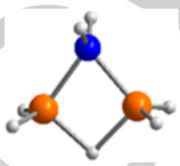
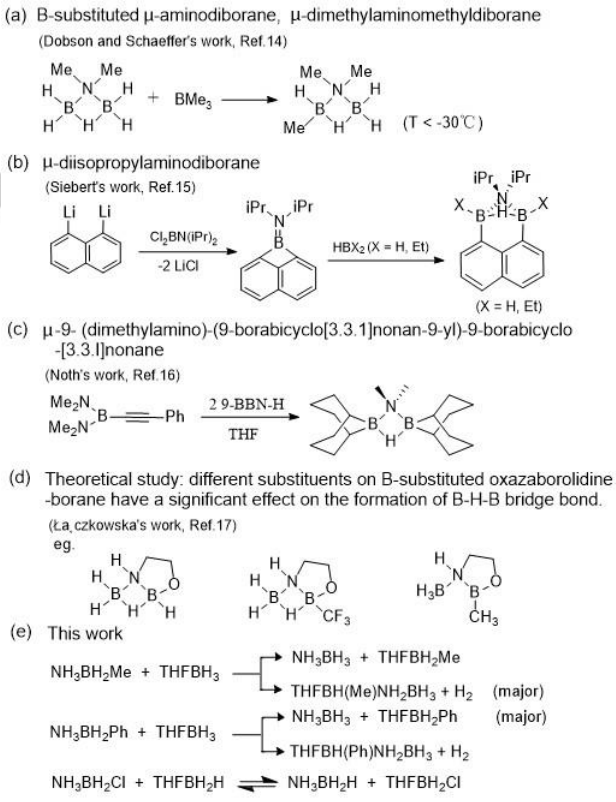


Figure 1. Structure of $BH_2(\mu\text{-}H)(\mu\text{-}NH_2)BH_2$. N, blue; B, orange; H, light-gray.

B-substituted amine boranes are also well known.[13] However, very few examples of B-substituted *μ*-aminodiborane have been documented (Scheme 1). In 1970 Dobson and Schaeffer reported the first example of B-substituted *μ*-aminodiborane, *μ*-dimethylaminomethyldiborane.[14] After that, *μ*-diisopropylamino-diborane was obtained by the reaction of boron bridged naphthalene with diborane and diethylborane (X = H, Et).[15] *μ*-9-(dimethylamino)-(9-borabicyclo[3.3.1]nonan-9-yl)-9-borabicyclo-[3.3.1] nonane was also synthesized by the reaction of



Scheme 1. The preparative reactions of the B-substituted aminodiborane derivatives.

[a] *Y. Guo, Drs. N. Ma and S. Hussain, Profs. Drs. Y. Cao, J. Zhang, and X. Chen, Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007 (China) E-mail: xnchen@htu.edu.cn, jie.zhang@htu.edu.cn*

[b] *X. Wang, Prof. Dr. D. Wei and X. Chen, College of Chemistry and Molecular Engineering, Zhengzhou UniversityZhengzhou, Henan 450001 (China). donghuiwei@zzu.edu.cn*

Supporting information and the ORCID identification numbers for the authors of this article can be found under https://

bis(dimethylamino)(phenylethynyl)-borane with 9-BBN-H in 1995.[16] It was found that different substituents on B-substituted oxazaborolidine-borane impact significantly on the formation of the B-H-B bridge bond in this type of complex.[17] To the best of our knowledge, no previous report is available for an ADB derivative with substitued B atom andnon-substitued N atom.

Herein we report the reactions between NH_3BH_2R (R = Me, Ph, and Cl) and $THFBH_3$ that lead to three different results: the formation of $THFBH(Me)(\mu\text{-}NH_2)BH_3$ (R = Me) and $THFBH_2Ph$ (R = Ph) as major products. An interesting reversible intermolecular chloride-hydride exchange between NH_3BH_2Cl and $THFBH_3$ was also observed.

Results and Discussion

In B-substituted amine boranes, the substituents on the boron atom not only affect the hydridicity of the H on B atom, but also have significant inference on the stability of the corresponding amine boranes. For example, NH_3BH_2Me and NH_3BH_2Ph are stable in THF after 170 hours at 20 ℃,[18,19] but NH_3BH_2Cl decomposes immediately in THF at 30 ℃.[20] The B-substituted amine boranes are generally less stable as compared with AB and N-substituted AB. In order to explore the influence of B-substituents on the reactions, we chose amine boranes bearing a different electronic effect substituent on boron such as NH_3BH_2Me, NH_3BH_2Ph, and NH_3BH_2Cl, and allow them to react individually with $THFBH_3$.

Reaction of NH_3BH_2Me with $THFBH_3$

When NH_3BH_2Me was treated with 1 equiv of $THFBH_3$ in THF at 0 ℃ for 0.5 h, the ^{11}B NMR spectrum shows the formation of an "open" version of B-methyl-substituted μ-aminodiborane, $THFBH(Me)(\mu\text{-}NH_2)BH_3$, NH_3BH_3, BH_4^- and $(NHBMe)_3$ (Figure 2, bottom). After 3 hours, NH_3BH_2Me disappeared almost and $THFBH_2Me$ appeared along with an unknown species (signal "i" in Figure 2). Base on the products and unreacted reactants detected in ^{11}B NMR (Figure 2), it is believed that the reaction between NH_3BH_2Me and $THFBH_3$ is complicated and several

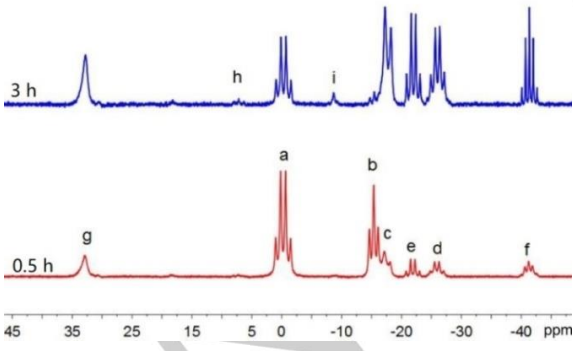


Figure 2. ^{11}B NMR spectra of the reaction NH_3BH_2Me with 1 equiv of $THFBH_3$ in THF at 0 ℃. a, $THFBH_3$; b, NH_3BH_2Me; c, and d, $THFBH(Me)(\mu\text{-}NH_2)BH_3$; e, NH_3BH_3; f, BH_4^-; g, $(NHBMe)_3$; h, $THFBH_2Me$; i, unknown species.

competitive reactions may occur in this process at 0 ℃. An NH_3-THF exchange reaction results in the formation of NH_3BH_3 and $THFBH_2Me$ as shown in equation 1. It is worthy to note that NH_3BH_3 and $THFBH_2Me$ should be formed in a stoichiometric ratio of 1:1 on the basis of equation 1, but only trace amount of $THFBH_2Me$ and an unknown species (signal "i") are observed in ^{11}B NMR after 3 hours. This result indicates that $THFBH_2Me$ may be an active species that is consumed in other reactions and the Me group redistribution may occur as described in the literature[18] but the mechanisms are not clear. The asymmetric peak "c" in Figure 2 may also be related to the Me group redistribution. During the reaction process, NH_3BH_3 is formed (equation 1) but does not further react with $THFBH_3$ to produce ADB because the reaction was carried out at 0 ℃, which is consistent with the previous experimental results.[6,12] $THFBH(Me)(\mu\text{-}NH_2)BH_3$ was detected as a major product (Figure 2) and H_2 was also determined by ^1H NMR spectrum during the experiment as shown in the Supporting Information (Figure S1a). This observation indicates that the formation mechanism of $THFBH(Me)(\mu\text{-}NH_2)BH_3$ by equation 2 may be similar to the formation of ADB in the reaction of AB and $THFBH_3$. In this reaction, $NH_3BH(Me)(\mu\text{-}H)BH_3$ (**1**) is first formed as an intermediate (equation 3), from which the BH_4^- anion and $[NH_3BHMeTHF]^+$ cation are formed when the bridge hydrogen moves to BH_3 group (equation 4). The BH_4^- anion was detected but the $[NH_3BHMeTHF]^+$ cation could not be observed in ^{11} B NMR spectrum. As this type of larger species usually shows broad ^{11}B NMR peaks, which may lead to the broadening beneath its ^{11}B resonances. On the other hand, a large amount of $THFBH_3$, compared with NH_3BH_2Me, remains unreacted after 3 hours (Figure 1, top), which may be caused by the dehydrogenation of NH_3BH_2Me to $(NHBMe)_3$ under the current reaction conditions (equation 5). However, when $THFBH_3$ is present in excess in the reaction, the amount of $(NHBMe)_3$ based on ^{11}B NMR is obviously decreased in comparison with the forming $(NHBMe)_3$ by the reaction at 1:1 ratio (Figures S1c and S1g). These results seem to be inconsistent with theoretical results of the borane-catalyzed dehydrogenation of the NH_3BH_3 to $(NHBH)_3$ reported by Dixon group in 2007[21]. An attempt to purify $THFBH(Me)(\mu\text{-}NH_2)BH_3$ was not successful, borazine was mixed with the product after fraction distillation as shown in Figure S1h.

$$NH_3BH_2Me + THFBH_3 \rightarrow NH_3BH_3 + THFBH_2Me \quad (1)$$
$$NH_3BH_2Me + THFBH_3 \rightarrow THFBH(Me)(\mu\text{-}NH_2)BH_3 + H_2 \quad (2)$$
$$NH_3BH_2Me + THFBH_3 \rightarrow NH_3BH(Me)(\mu\text{-}H)BH_3 + H_2 \quad (3)$$
$$NH_3BH(Me)(\mu\text{-}H)BH_3 + THF \rightarrow [NH_3BHMeTHF]^+[BH_4]^- \quad (4)$$
$$3\ NH_3BH_2Me \rightarrow (NHBMe)_3 + 2\ H_2 \quad (5)$$

In order to understand the above reaction process, we treated NH_3BH_2Me with an excess amount of $THFBH_3$ in THF at -40 ℃ and the reaction temperature was gradually increased to 30 ℃ in 5 hours. The reaction was monitored by ^{11}B NMR. Two signals at δ -13.29 (doublet) and δ -24.99 (quartet) are observed when the temperature was at -20 ℃ (Figure S1c). In comparison with our previous work in which ammonia diborane ($NH_3BH_2(\mu\text{-}H)BH_3$, AaDB) is a key intermediate for the formation of ADB in the

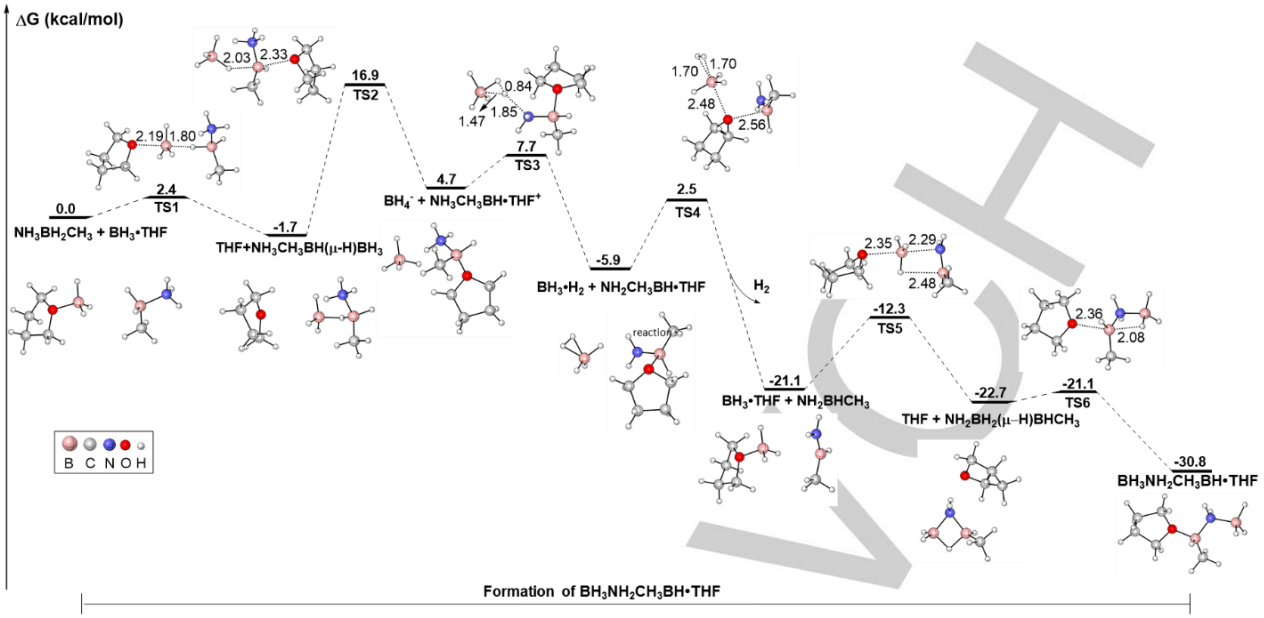


Figure 3. Energy profile for the reaction of NH_3BH_2Me with $THFBH_3$ calculated at the DLPNO-CCSD(T)/def2-TZVP//M06-2X/6-311++G(d, p)/SMD_{THF} level.

reaction of AB with $THFBH_3$,[22] the two resonances observed in the present ^{11}B NMR study are in good agreement with $NH_3BH(Me)(\mu\text{-}H)BH_3$ (**1**), a counterpart of AaDB. The doublet and quartet can be assigned to *B*HMe and *B*H_3, respectively, in the molecule of **1** (see Figure S1c in the Supporting Information). It should be noted that intermediate **1** was not observed at higher temperatures. When NH_3BH_2Me was treated with 1 equiv of $THFBH_3$ in THF at -40 ℃ and the temperature was gradually increased to room temperature, similar signals were observed in ^{11}B NMR spectroscopy (Figure S1f).

Based on the information described above, we proposed a possible mechanism for the reaction of NH_3BH_2Me and $THFBH_3$ to produce $THFBH(Me)(\mu\text{-}NH_2)BH_3$. This mechanism is further confirmed by theoretical study. We performed DFT and DLPNO-CCSD(T)[23] calculations using Gaussian 09[24] and ORCA[25] programs. The energy profile for the reaction of NH_3BH_2Me with $THFBH_3$ is provided in Figure 3. As shown in Figure 3, the B-H bond in NH_3BH_2Me attacks the B atom in $THFBH_3$ to form $NH_3BH(Me)(\mu\text{-}H)BH_3$ *via* a S_N2-type transition state TS1, then BH_4^- is dissociated through transition state TS2. Subsequently, a molecule of H_2 is desorbed *via* the transition states TS3 and TS4. After the transition state TS5, transformed into a four-memberedring intermediate $BH_2(\mu\text{-}H)(\mu\text{-}NH_2)BHMe$. Finally, THF attacks on the B atom in BH_2Me group to form the final product *via* transition state TS6. The energy barriers of TS1-6 are 2.4, 18.6, 3.0, 8.4, 8.8, and 1.6 kcal/mol, respectively, which indicates that the reactions can occur smoothly at room temperature and even at low temperatures.

Reaction of NH_3BH_2Ph and $THFBH_3$

The reactivity of NH_3BH_2Ph against $THFBH_3$ is quite similar to the reactivity of NH_3BH_2Me that also comprises two processes: the intermolecular NH_3-THF exchange (equation 6) and the formation of $THFBH(Ph)(\mu\text{-}NH_2)BH_3$ (equation 7). Because the reaction of NH_3BH_2Ph and $THFBH_3$ proceeds very slowly at 0 ˚C, in order to explore the reaction process, we adjust the reaction to room temperature. Under this reaction condition, the coexisting NH_3BH_3 and $THFBH_3$ react to form ADB (equation 8). Moreover, in addition to the formation of ADB, the intermolecular NH_3-THF exchange between $THFBH_3$ and NH_3BH_2Ph proved to be a dominant process on the basis of the integration value in $^{11}B\{^1H\}$ NMR spectra (Figure. S2). This is perhaps due to the weaker electron donating ability of the phenyl group as compared with methyl group, as a result, the nucleophilicity of B-H bond on the NH_3BH_2Ph is lowered that reduced the ability of reaction of NH_3BH_2Ph with $THFBH_3$ to form $THFBH(Ph)(\mu\text{-}NH_2)BH_3$.

$$NH_3BH_2Ph + THFBH_3 \rightarrow NH_3BH_3 + THFBH_2Ph \quad (6)$$
$$NH_3BH_2Ph + THFBH_3 \rightarrow THFBH(Ph)NH_2BH_3 + H_2 \quad (7)$$
$$NH_3BH_3 + THFBH_3 \rightarrow BH_2(\mu\text{-}NH_2)(\mu\text{-}H)BH_2 + H_2 \quad (8)$$

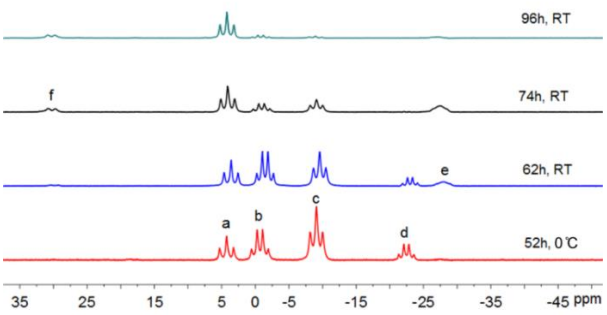


Figure 4. ^{11}B NMR spectra of the reaction mixture of NH_3BH_2Cl and $THFBH_3$ in THF. a, $THF{\cdot}BH_2Cl$; b, $THF{\cdot}BH_3$; c, NH_3BH_2Cl; d, NH_3BH_3; e, $NH_2B_2H_5$; f, $(NHBH)_3$.

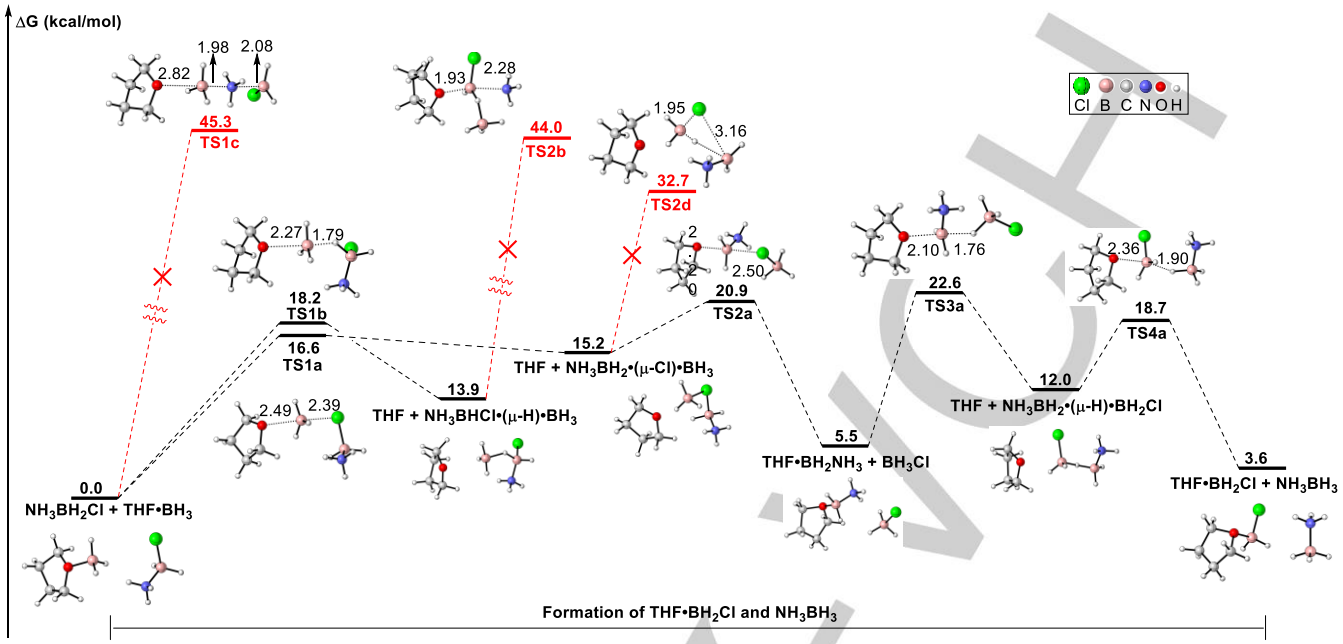


Figure 5. Energy profiles for the reaction of NH_3BH_2Cl with $THFBH_3$ calculated at the M06-2X/6-311++G(d, p)/SMD_{THF} level and 273.15 K.

It is also worthy to note that the temperature of the reaction of NH_3BH_2R with $THFBH_3$ should be kept below 0 ℃. Since NH_3BH_3 and $THFBH_3$ coexist in the system during the reaction, not only the corresponding aminodiborane but some boron-containing compounds such as borazine are also produced at elevated temperatures.

Reaction of NH_3BH_2Cl and $THFBH_3$

The reaction of NH_3BH_2Cl and $THFBH_3$ is completely different from the reaction of NH_3BH_2R (R = Me and Ph) and $THFBH_3$. The expected "open" version of B-substituted ADB derivative is not observed. When NH_3BH_2Cl was treated with 1 equiv of $THFBH_3$ at 0 ℃, AB and $THFBH_2Cl$ were detected. The reaction is proved to be a reversible process (equation 9) and reached its equilibrium after 52 h at 0 ℃ (see Figure S3a). This reaction was repeated with different NH_3BH_2Cl to $THFBH_3$ ratios (1:1, 1:2 and 1:3) for three times and an average value of the equilibrium constant (0.11) was calculated based on the ^{11}B NMR integration data, which is consistent with the calculation results at 0 ℃ (see Figure 5 and Table S1 in the Supporting Information).

$$NH_3BH_2Cl + THFBH_3 \rightleftharpoons NH_3BH_3 + THFBH_2Cl \quad (9)$$

The above equilibrium can only maintain at a temperature below 0 ℃. Once the temperature is raised to room temperature, the original equilibrium is destroyed. This is due to the reaction of NH_3BH_3 and $THFBH_3$ to form ADB and then converted into borazine at room temperature. Figure 4 shows the ^{11}B NMR spectra of the mixture of NH_3BH_2Cl and $THFBH_3$ at 0 ℃ and at room temperature.

Two possible pathways of intermolecular NH_3-THF exchange or Cl-H exchange are considered in reaction 9. In order to figure out the mechanism, we performed a DFT calculations at the M06-2X/6-311++G(d, p)/SMD_{THF} level and 273.15 K. The energy profiles for the possible reaction pathways of NH_3BH_2Cl with $THFBH_3$ are provided in Figure 5. As shown in Figure 5, the B-Cl bond in NH_3BH_2Cl attacks the B atom in $THFBH_3$ to form a B-Cl-B bridge bond through TS1a in the most energetically favorable pathway. The free energy barrier of the transition state TS1a is computed to be 16.6 kcal/mol. Then, THF attacks the B atom in BH_2(μ-Cl) moiety and the B-Cl-B bridge bond breaks to form $[THFBH_2NH_3]^+[BH_3Cl]^-$ through TS2a. This process only requires an energy of 5.7 kcal/mol. The B-H bond in the $[BH_3Cl]^-$ anion interacts with the B atom in the $[THFBH_2NH_3]^+$ cation to form a B-H-B bridge bond (TS3a), which needs to overcome the highest energy barrier of 17.1 kcal/mol. Finally, THF is coordinated with the B atom of BH_2Cl in NH_3BH_2(μ-H)BH_2Cl, which makes the B-H-B bridge bond broken to form the final products of $THFBH_2Cl$ and NH_3BH_3 with the energy barrier of 6.7 kcal/mol (TS4a). Related to the NH_3-THF exchange, the free energy barriers of the other possible pathways associated with TS1-2b, TS1c, and TS2d are too high to overcome for the reaction. Furthermore, when NH_3BH_2Cl was dissolved in THF solution at room temperature, the $THFBH_2Cl$ failed to be detected after days. This observation indicates that THF cannot replace NH_3 from NH_3BH_2Cl to form $THFBH_2Cl$ in THF solution. Therefore, both the experimental observation and theoretical analysis support the mechanism of the intermolecular H-Cl exchange rather than the NH_3-THF exchange in the reaction of NH_3BH_2Cl with $THFBH_3$.

Conclusions

We have investigated the reactions between B-substituted amine boranes (NH_3BH_2R) and $THFBH_3$. It was found that when R is Me, an electron-donating group, the major product of the reaction is $THFBH(Me)(\mu\text{-}NH_2)BH_3$. When R is Ph, a weak electron-donating group, the reaction mainly tends to undergo the intermolecular NH_3-THF exchange to produce AB and $THFBH_2Ph$. The reversible intermolecular Cl-H exchange reaction occurs when the R group is Cl, an electron-withdrawing group. The R group on the B atom affects the nucleophilicity of the B-H bond. The strong electron-donating ability of the R group reinforces the hydricity of H on the B atom and increases the nucleophilicity of the B-H bond, which probably are the reasons for the different reactions of NH_3BH_2R (R = Me, Ph, and Cl) and $THFBH_3$.

Experimental Section

General remarks

All manipulations were carried out on a Schlenk line or in a glove box filled with high-purity nitrogen. The ^{11}B NMR spectra were obtained at 128 MHz or 193 MHz and externally referenced to $BF_3 \cdot OEt_2$ in C_6D_6 (δ = 0.00 ppm).

Reaction of NH_3BH_2Me with $THFBH_3$ at low temperature

NH_3BH_2Me (0.031 g, 0.68 mmol) was put into a 10 mL flask which was connected to a Schlenk line and then 5 mL of THF was added. The flask was cooled in an ice-water bath and $THFBH_3$ (0.68 mL, 1 mol/L) was added into the reaction mixture dropwise. The reaction mixture was stirred for 3 h at this temperature and monitored by ^{11}B NMR spectroscopy. After NH_3BH_2Me disappeared completely, the reaction mixture was condensed to another flask. The collected liquid was subjected to fractional distillation to remove the excess $THFBH_3$ to further purify the products. The ^{11}B NMR spectra of the final product are provided in the Supporting Information (Figure S1h).

Reaction of NH_3BH_2Ph with $THFBH_3$

At room temperature, NH_3BH_2Ph (0.104 g, 0.97 mmol) was placed in a 10 mL flask which was connected to a Schlenk line. Then 2 mL of THF and 4 mL of $THFBH_3$ solution (1 mol/L) were added. The mixture was stirred for 42 h and monitored by ^{11}B NMR spectroscopy. After NH_3BH_2Ph disappeared completely, the reaction mixture was condensed to another flask.

Reaction of NH_3BH_2Cl with $THFBH_3$

NH_3BH_2Cl (0.065 g, 1 mmol) was put into a 10 mL flask which was connected to a Schlenk line and then 2 mL of THF was added. After the flask was cooled in an ice-water bath, 1 mL of $THFBH_3$ solution (1 mol/L) was added. The reaction mixture was stirred at this temperature and monitored by ^{11}B NMR spectroscopy until the equilibrium was reached (52 h). The ^{11}B NMR spectra are provided in the supporting Information (Figure S3a and b). The reaction was repeated with the NH_3BH_2Cl to $THFBH_3$ ratios of 1:2 and 1:3 using the same procedure.

Density Functional Theory (DFT) Calculation

All DFT calculations were carried out by using Gaussian 09.[23] The M06-2X functional was used with a standard 6-311++G(d,p) basis set and SMD model in THF solvent to optimize the geometries of all the structures. The frequency calculations were performed for all stationary points to confirm the local minima or transition state (TS) structures and to derive Gibbs free energies ($\triangle$G, $kcalmol^{-1}$ at 298K). The natural population analysis (NPA) was based on the geometry from the single crystal X-ray diffraction analysis of ADB and ADB-Me.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Numbers, 21771057, U1804253, 21773214, and 21571052).

Keywords: B-substituted aminodiborane • B-substituted amine boranes •$THF{\cdot}BH_3$ • mechanism

[1] H. I. Schlesinger, D. M. Ritter, A. B. Burg, *J. Am. Chem. Soc*. **1938**, *60*, 1296-1330.

[2] H. I. Schlesinger, D. M. Ritter, A. B. Burg, *J. Am. Chem. Soc*. **1938**, *60*, 2297-2300.

[3] S. H. Bauer, *J. Am. Chem. Soc.* **1938**, *60*, 524–530.

[4] K. Hedberg, A. J. Stosick, *J. Am. Chem. Soc.* **1952**, *74*, 954–958.

[5] K. K. Lau, A. B. Burg, R. A. Beaudet, *Inorg. Chem.* **1974**, *13*, 2787–2791.

[6] X. Chen, J. C. Zhao, S. G. Shore, *J. Am. Chem. Soc*. **2010**, *132*, 10658−10659.

[7] a) B. Wrackmeyer, E. Molla, P. Thoma, E. V. Klimkina, O. L. Tok, T. Bauer, R. Kempe, Z. *Anorg. Allg. Chem*. **2011**, *637*, 401−405; b) A. C. Malcolm, K. J. Sabourin, R. McDonald, M. J. Ferguson, E. Rivard, *Inorg. Chem*. **2012**, *51*, 12905−12916; c) H. Helten, A. P. M. Robertson, A. Staubitz, J. R. Vance, M. F. Haddow, I. Manners, *Chem. Eur. J*. **2012**, *18*, 4665−4680.

[8] a) R. H. Crabtree, *Science*. **1998**, *282*, 2000-2001; b) R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, *Acc. Chem. Res*. **1996**, *29*, 348-354; c) R. Custelcean, J. E. Jackson, *Chem. Rev*. **2001**, *101*, 1963-1980; d) I. Alkorrta, I. Rozas, J. Elguero, *Chem. Soc. Rev*. **1998**, *27*, 163-170; e) W. T. Klooster, T. F. Koetzle, P. E. M. Siegbahn, T. B. Richardson, R. H. Crabtree, *J. Am. Chem. Soc*. **1999**, *121*, 6337-6343; f) T. B. Richardson, S. D. Gala, R. H. Crabtree, *J. Am. Chem. Soc*. **1995**, *117*, 12875-12876; g) A. J. Lough, S. Park, R. Ramachandran, R. H. Morris, *J. Am. Chem. Soc*. **1994**, *116*, 8356-8357; h) X. Chen, J. C. Zhao, S. G. Shore, *Acc. Chem. Res.* **2013**, *46*, 2666-2675; i) V. I. Bakhmutov, Dihydrogen Bonding: Principles, Experiments, and Applications; Wiley: Hoboken, NJ, **2007**.

[9] a) Q. Zhao, R. D. Dewhurst, H. Braunschweig, X. Chen, *Angew. Chem. Int. Ed.* **2019**, *58*, 3268-3278; b) X. -M. Chen, H. Li, Q. -Y. Yang, R. -R. Wang, E. J. M. Hamilton, J. Zhang, X. Chen, *Eur. J. Inorg. Chem.* **2017**, 4541-4545; c) X. -M. Chen, N. Ma, Q.-F. Zhang, J. Wang, X. Feng, C. Wei, L. -S. Wang,J. Zhang, X. Chen, *J. Am. Chem. Soc.* **2018**, *140*, 6718–6726. d) X. -M. Chen, N. Ma, X. -R. Liu, C. Wei, C. Cui, B. -L. Cao, Y. Guo, L. -S. Wang, Q. Gu, X. Chen, *Angew. Chem. Int. Ed*. **2019**, *58*, 2720-2724. e) X. -M. Chen, S. -C. Liu, C. -Q. Xu, Y. Jing, D. Wei, J. Li, X. Chen, *Chem. Commun*. **2019**, *55*, 12239-12242; f) J. C., Jr. Lee, E. Peris, A. L. Rheingold, R. H. Crabtree, *J. Am. Chem.Soc.* **1994**, *116*, 11014-11019; g) M. E. Sloan, A. Staubitz, T. J. Clark, C. A. Russell, G. C. Lloyd-Jones, I. Manners, *J. Am. Chem. Soc.* **2010**, *132*, 3831-3842; h) C. A. Jaska, K. Temole, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424-9434; i) Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa, H. Ogino, *J. Am. Chem. Soc.* **2009**, *131*, 14946-14957; j) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2009**, *131*, 15440-15456; k) J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, N. K. Szymczak, *J. Am. Chem. Soc.* **2007**, *129*, 11936-11949; l) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey, J. C. Linehan, *Inorg. Chem.* **2008**, *47*, 8583-8585; m) A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem.,*

Int. Ed. **2008**, *47*, 6212-6215; n) X.-M. Chen, J. Wang, S.-C. Liu, J. Zhang, D. Wei, X. Chen, *Dalton Trans*, **2019**, *48*, 14984–14988.

[10] a) A. B. Burg, C. L. Randolph, *J. Am. Chem. Soc*. **1949**, *71*, 3451−3455; b) A. B. Burg, *J. Am. Chem. Soc*. **1952**, *74*, 1340−1341; c) J. R. Spielman, *J. Chem. Educ*. **1970**, *47*, 225−226.

[11] a) L. D. Schwartz, P. C. Keller, *J. Am. Chem. Soc*. **1972**, *94*, 3015−3018; b) G. E. Schaeffer, L. J. Basile, *J. Am. Chem. Soc*. **1955**, *77*, 331−332; c) D. L. Denton, A. D., II. Johnson, C. W., Jr. Hickam, R. K. Bunting, S. G. Shore, *J. Inorg. Nucl. Chem.* **1975**, *37*, 1037-1038; d) K. W. Böddeker, S. G. Shore, R. K. Bunting, *J. Am. Chem. Soc*. **1966**, *88*, 4396−4401; e) P. C. Keller, *J. Am. Chem. Soc*. **1969**, *91*, 1231; f) P. C. Keller, *Synth. React. Inorg. Met. -Org. Chem.* **1973**, *3*, 307−312.

[12] H. Li, N. Ma, W. Meng, J. Gallucci, Y. Qiu, S. Li, Q. Zhao, J. Zhang, J.-C. Zhao, X. Chen, *J. Am. Chem. Soc*. **2015**, *137*, 12406–12414.

[13] a) A. Kumar, I. K. Priest, T. N. Hooper, A. S. Weller, *Dalton Trans*. **2016**, *45*, 6183-6195; b) A. Kumar, J. S. A. Ishibashi, T. N. Hooper, T. C. Mikulas, D. A. Dixon, S. Y. Liu, A. S. Weller, *Chem. Eur. J*. **2016**, *22*, 310-322; c) P. G. Campbell, J. S. A. Ishibashi, L. N. Zakharov, S. Y. Liu, *Aust. J. Chem*. **2014**, *67*, 521-524; d) P. G. Campbell, A. J. V. Marwitz, S. Y. Liu, *Angew. Chem. Int. Ed*. **2012**, *51*, 6074-6092; e) A. P. M. Robertson, M. F. Haddow, I. Manners, *Inorg. Chem.* **2012**, *51*, 8254-8264; f) A. P. M. Robertson, G. R. Whittell, A. Staubitz, K. Lee, A. J. Lough, I. Manners, *Eur. J. Inorg. Chem.* **2011**, 5279-5287; g) S. K. Kim, W. S. Han, T. J. Kim, T. Y. Kim, S. W. Nam, M. Mitoraj, Ł. Piekos´, A. Michalak, S. J. Hwang, S. O. Kang, *J. Am. Chem. Soc.* **2010**, *132*, 9954-9955.

[14] J. Dobson, R. Schaeffer, *Inorg. Chem.* **1970***, 9,* 2183-2184.

[15] A. Hergel, H. Pritzkow, W. Siebert,*Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1247-1248.

[16] N. Metzler, H. Noth, *Chem. Ber*. **1995**, *128*, 711-717.

[17] K. Z. Łączkowski, Ż. Czyżnikowska, R. Zaleśny, A. B. Łączkowska, *Struct Chem*. **2013**, *24*, 1485–1492.

[18] N. E. Stubbs, André Schäfer, A. P. M. Robertson, E. M. Leitao, T. Jurca, H. A. Sparkes, C. H. Woodall, M. F. Haddow, I. Manners, *Inorg. Chem.* **2015**, *54*, 10878−10889.

[19] D. A. Resendiz-Lara, N. E. Stubbs, M. I. Arz, N. E. Pridmore, H. A. Sparkes, I. Manners, *Chem. Commun*. **2017**, *53*, 11701–11704.

[20] H. K. Lingam, W. Cong, J. C. Gallucci, X. Chen, S. G. Shore, *Inorg. Chem*. **2012**, *51*, 13430−13436.

[21] M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar, D. A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 679-690.

[22] X. Chen, X. Bao, J. C. Zhao, S. G. Shore, *J. Am. Chem. Soc*. **2011**, *133*, 14172–14175.

[23] a) C. Riplinger, P. Pinski, U. Becker, E. F.Valeev, F. Neese, *J. Chem. Phys.* **2016**, *144*, 024109; b) D. G.Liakos, F. Neese, *J. Phys. Chem. A* **2012**, *116*, 4801; c) C. Riplinger, F. Neese, *J. Chem. Phys.* **2013**, *138*, 034106.

[24] Gaussian 09, Revision D.01., M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J . Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford, CT, **2009**.

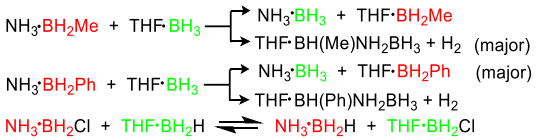
[25] a) F. Neese, F. Wennmohs, ORCA(4.0.1)-An ab initio, DFT and semiempirical SCF-MO package, Max-Planck-Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mulheim a. d. Ruhr, Germany; b) F. Neese, Wiley Interdiscip. Rev.: *Comput. Mol. Sci.* **2012**, *2*, 73–78.

10.1002/ejic.201900847

WILEY-VCH

Entry for the Table of Contents

FULL PAPER



Different substituents on the B atom make NH_3BH_2R react with $THFBH_3$ in different ways. With R = Me or Ph, intermolecular NH_3 and THF exchange occurs and B-substituted *μ*-aminodiborane forms. With R = Cl, a reversible intermolecular chloride-hydride exchange takes place.

B-Substituted Amine Boranes

Yu Guo, Xinghua Wang, Nana Ma, Yilin Cao, Sajjad Hussain, Jie Zhang, Donghui Wei,*and Xuenian Chen**

Page No. – Page No.

Reactions and Mechanisms of B-Substituted Amine Boranes with THF·BH_3