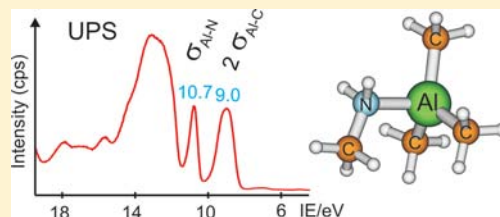


Trimethylaluminum and Borane Complexes of Primary Amines

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Supporting Information

ABSTRACT: Trimethylaluminum (TMA) complexes of methyl-, *n*-propyl-, cyclopropyl-, allyl-, and propargylamine were synthesized and their experimental properties and theoretical characteristics were compared with the respective amine–borane analogues. The amine ligand of an amine–TMA Lewis acid–base complex can be easily changed by another amine through a 2:1 amine–TMA intermediate in pentane at room temperature. The exchange of the same ligands in the case of amine–boranes requires remarkably more time in line with the calculated relative energy of the respective transition state. The ¹H and ¹³C NMR experiments examining the addition of one or more equivalent of amine to the respective Lewis acid–base complex conclude in the fast exchange of the amine ligand in the NMR time scale only in the cases of amine–TMA complexes, which could also be caused by similar 2:1 complexes. However, in gas phase, only 1:1 amine–TMA complexes are present as evidenced by ultraviolet photoelectron spectroscopy (UPS). The observed UP spectra, which are the first recorded photoelectron spectra of primary amine–TMA compounds, indicate that the stabilization effect of the lone electron pair of nitrogen atom in amines during the borane complexation is stronger than that of the TMA complexation. In line with this observation, the destabilization of the $\sigma_{\text{Al-C}}$ orbitals is lower than that of $\sigma_{\text{B-H}}$ orbitals during the formation of amine–TMA and amine–borane complexes, respectively. As showed by theoretical calculations, the CH₄ elimination of the studied amine–TMA complexes is exothermic, indicating the possibility of using these compounds in metal organic chemical vapor deposition techniques (MOCVD). On the other hand, our experimental conditions avoid this methane elimination and constitutes the first procedure employing distillation to isolate primary amine–TMA complexes.



INTRODUCTION

Lewis acid–base complexes might be substantially different if the electron acceptor or the donor atom is changed. Considering the notable effect of the substitution of the donor atom,¹ it is adequate to raise the question: what kind of differences can be observed between the complexes with the change of the acceptor atom from boron to aluminum?

As amine–boranes present a potential as hydrogen storage materials, current theoretical and experimental studies are providing deeper insight of this possibility.² It has been evidenced that the substitution on the nitrogen atom can reduce the exothermicity of the dehydrogenation, therefore the substituent effect in some primary amines may help in understanding reaction pathways in hydrogen release of these Lewis acid–base complexes.³ The potential of the novel cyclic amine–borane, BN–methylcyclopentane, proved that searching new substituents and understanding their behavior may help to find the best hydrogen storage material.⁴ The hydrogen storage possibility of ammonia–alane and related compounds was examined by high level theoretical methods.⁵ It was shown by theoretical calculations that the elimination reaction of the first molecule of hydrogen is about 15 kJ/mol endothermic. However, secondary amine–alanes are supposed to be very unstable compounds because the hydrogen elimination was observed at low temperature.⁶ Therefore, to study experimentally and theoretically

the N–Al bond in Lewis acid–base complexes of primary amines, trimethylaluminum (TMA) was chosen. Analogue to hydrogen elimination from amine–alanes, ammonia–TMA was shown to lose methane at elevated temperature.⁷ Similar alkane elimination of amine–alane derivatives makes these substrates suitable for metal–organic chemical vapor deposition techniques (MOCVD).⁸ While conventional ceramics are produced generally by the direct reaction of Al powder with either nitrogen or ammonia, which requires a high temperature (around 1500 °C), MOCVD techniques using ammonia–TMA can be performed at 400–800 °C to achieve aluminum nitride thin layer.⁹ The AlN semiconductor crystal growth was investigated by quantum chemical methods.¹⁰ It was shown that the ammonia excess reduced the barrier of the alkane elimination while this barrier increased by the change of methyl group on Al atom to ethyl substituent. The *t*-butylamine–TMA complex was found to be an alternative precursor for AlN thin film deposition.¹¹

Another exciting aspect of these Lewis acid–base complexes is the feasible second amine ligand entrance constructing trigonal bipyramidal bonding structure of aluminum atom.¹² Although complexes containing pentacoordinate Al atom are known among organometallic compounds,¹³ (for example

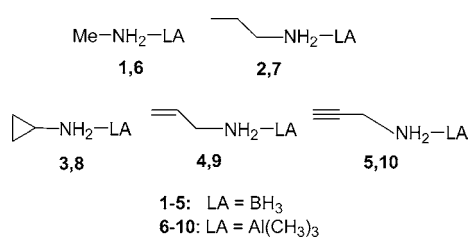
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bis(trimethylamine)–alane has been synthesized),¹⁴ at the best of our knowledge, pentacoordinated derivatives of amine–TMA complex have never been prepared. Recent experimental results reveal the possibility of an N–H···N hydrogen bonded adduct of ammonia–TMA with a second ammonia instead of the creation of trigonal bipyramidal structure.¹⁵ IR measurements of ammonia–TMA were performed at relatively high pressure using hydrogen carrier gas. The pressure of the ammonia was 200–800 times higher than that of the used TMA. While at 66 mbar the results was only a reproduction of a previous experiment resulting in 1:1 adduct formation,¹⁶ at 400 mbar one more NH₃ is attached to the ammonia–TMA complex, producing the hydrogen bonded form.¹⁵ On the other hand, Minh et al. showed by theoretical calculations that this hydrogen bonded 2:1 amine–TMA adduct is 7.9 kJ/mol less stable than that which contains the five coordinated Al atom.¹⁷

In this study, cyclopropyl-, allyl-, and propargylamine were chosen as Lewis bases and TMA or BH₃ as Lewis acids to examine the possible conjugative interactions between the unsaturation (or pseudounsaturation) at the β,γ -position and the dative bond in Lewis acid–base complexes (Chart 1). As a standard, TMA

Chart 1

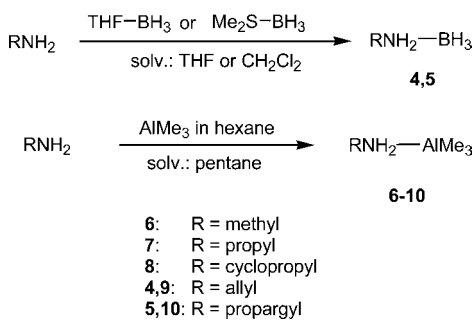


complexes of methylamine and propylamine were also studied because of their simplicity and easy handling. Their preparation and experimentally determined properties are reported here. Characterization of the molecules employing gas phase ultraviolet photoelectron spectroscopy (UPS) provides further valuable information about the structure of these complexes. The results are also accompanied by theoretical calculations, to achieve a profound insight in the comparative properties of amine–boranes and amine–TMA complexes.

RESULTS AND DISCUSSION

Synthesis and NMR Studies of Compounds. Amine–boranes were synthesized using the ligand exchange method, mixing the free amine with freshly distilled borane–tetrahydrofuran (BH₃–THF) or borane–dimethyl sulfide (BH₃–SMe₂) reagents in tetrahydrofuran or dichloromethane solvent (Scheme 1).¹⁸

Scheme 1



These complexes were purified by removal of the low boiling compounds in vacuo and used without further purification. The amine–trimethylaluminum complexes were prepared in pentane by the addition of TMA solution in hexane to the pure amines (Scheme 1). Although the syntheses reported in the literature for some primary amine–TMA adducts suggest that pure complexes can be obtained by removing in vacuo the low boiling reagents in excess and solvent,¹⁹ we employed distillation in vacuo (in case of methylamine–TMA sublimation) to purify the products in very good yields. The first isolation of this series of primary amine–TMA complexes was thus performed.

While amine–boranes are kinetically stable compounds, the unsaturated amine–TMA compounds diluted in benzene have generally half lifetime ($\tau_{1/2}$) around 1–2 days at room temperature. Characterization in benzene-*d*₆ solution was performed by ¹H, ¹³C, ¹⁴N, ¹⁵N, and ¹¹B or ²⁷Al NMR spectroscopy. The ¹H NMR spectra of 4 and 9 with allylamine can be seen in Figure S1 of the Supporting Information (SI), showing the typical changes observed during the complexations. The chemical shifts of the hydrogen atoms of the NH₂ group are both downfield shifted by the complexation ($\Delta\delta$ 3.5 (4) and 0.9 ppm (9)). On the other hand, for the other hydrogen atoms of the allylamine moiety opposite downfield and upfield effects are observed after the complexation with borane and TMA, respectively.

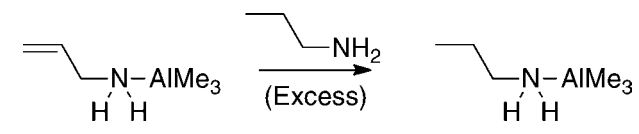
Fascinating concentration dependence is observed in the case of TMA complexation: two small signals augment next to the H signal of the TMA moiety when the concentration increased. Similarly, in the ¹³C NMR spectrum, two small peaks are also observed next to the C signal of the TMA moiety. Methylamine–TMA 6 was examined by COSY 2D NMR technique, which indicated that each of these three signals in the ¹H NMR spectrum belongs only to one of the three signals in the ¹³C NMR spectrum. Moreover, EXSY experiments showed that there is no exchange between these species. No significant change in the ¹H NMR spectrum was observed by cooling 6 diluted in toluene-*d*₈ up to 193 K. Consequently, these peaks are considered as a consequence of a partial association of these compounds in C₆D₆ solution, according to the similar phenomenon, which was reported in the case of Me₃N–AlHMe₂.²⁰

In contrast to the downfield shift observed in the ¹⁴N and ¹⁵N NMR spectra upon borane complexation of amine,¹ both the ¹⁴N and ¹⁵N NMR chemical shifts in the studied primary amine–TMA complexes are upfield shifted respectively to those of the free amines.²¹ The ¹¹B and ²⁷Al NMR chemical shifts are around –20 ppm and around 170 ppm for primary amine–boranes and amine–TMA complexes, respectively. The latter result for ²⁷Al NMR chemical shifts indicates clearly that, in the studied complexes, four-coordinated Al center have been established.²² Attempts to detect five-coordinated aluminum compounds by ²⁷Al NMR spectroscopy were unsuccessful, but the background of spectra renders their detection difficult.²³ To study the mechanism of the complexation and the possibility of the attachment of a second amine molecule on the formed complex, *n*-propyl-, allyl-, and propargylamine were added to TMA until 3 equiv of amine excess were reached (SI Figures S2–S4). By addition of amine to TMA complexes, the ¹H NMR peaks belonging to the amine moiety are shifted continuously while the concentration rises. Differentiated 1:1 and 2:1 adducts and free amine cannot be distinguished, thus the exchange of the amine ligands with the free amine is found to be faster than the NMR time scale. When the sample containing 2 equiv of allylamine with TMA in toluene-*d*₈ was cooled up to 185 K, the exchange

was still observed. In contrast, similar experiments with allylamine and allylamine–borane lead by ^1H and ^{13}C NMR spectroscopy to the observation of separated signals corresponding to the 1:1 adduct and the free amine even at room temperature (SI Figures S5–S6).

Some additional experiments were performed to determine whether the amine ligand can be exchanged: Allylamine–borane **4** or allylamine–TMA **9** and 4 equiv of *n*-propylamine in pentane were stirred at room temperature for 2 h. The products obtained are mainly allylamine–borane **4** and *n*-propylamine–TMA **7**, respectively (Scheme 2). However, after 20 h at room temperature,

Scheme 2



75% of propylamine–borane was observed with compound **4**, indicating that the reaction is similar but the activation barrier seems to be higher. The reversed test in case of TMA complex showed that propylamine ligand could also be changed to allylamine, although in that case the result after 2 h of the reaction was a 1:4 mixture of **7**:**9**.

Computational Studies. Theoretical calculations were carried out using BMK/6-311+G(2df,p) level, which give useful information on the nature of the studied complexes. In the case of cyclopropyl and propargyl derivatives there were two conformers, while in *n*-propyl and allenyl derivatives, five conformers were found as minima on the respective potential energy surface (SI Figure S7). The highest energy difference between the most stable and least stable conformers is less than 16 kJ/mol (SI Table S1). In the studied molecules, the typical N–B and N–Al bonds are about 1.62 Å and 2.08 Å, respectively (SI Table S2). Both borane and TMA complexation cause the N–C bond elongation. The bonding structure of nitrogen becomes more pyramidal during the complexation, and in amine–boranes it is slightly more planar than in amine–boranes. Similarly, the TMA moiety is more planar than the BH_3 , the sum of the angles around the Al atom is about 350° , which is more than 10° higher than that around the boron atom.

The natural population analysis (NPA)²⁴ charge of N atom becomes more positive by 0.17 charge units along the borane complexation, while in amine–TMA complexes it is comparable with the charge of the N atom in the respective amines (SI Table S3). In the complexes, the NPA charge of the B and Al atom is less positive than that in the Lewis acid monomers with ca. 0.54 and 0.15 charge units, respectively. This is in line with the NBO analysis, which shows that in the studied N–B and N–Al dative bonds the participation of the N atom is about 81% and 92%, respectively (SI Table S4). In the BH_3 moiety of the amine–boranes, the H atoms are negatively charged, while in the BH_3 monomer they have a positive partial atomic charge. The sum of the partial atomic charge changes in BH_3 group upon complexation by ca. -1.07 charge units. The C atoms attached to the Al have smaller negative charge, while the sum of the charges in the methyl groups is slightly more negative in the complexes than in the TMA monomer. On average, the AlMe_3 moiety becomes more negative, with 0.18 charge units.

The differences between the complexation reactions of methylamine with diborane and methylamine with TMA dimer were

studied because TMA dimerizes in the experimental conditions of the complexation reaction (Figure 1).²⁵ In the studied

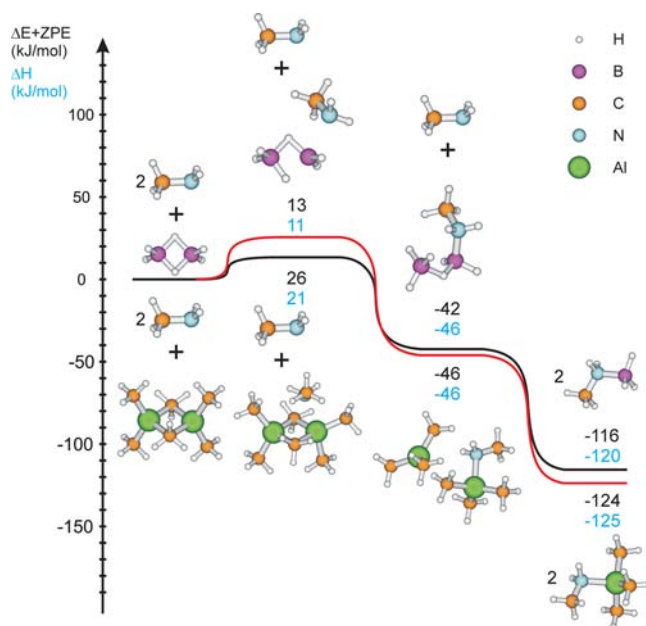


Figure 1. Energy profile for the complexation of B_2H_6 (black) and Al_2Me_6 (red) with two methylamine molecules at the BMK/6-311+G(2df,p) level. ZPE corrected energy values are in black, and enthalpy values are in blue.

reaction, the presence of a second equivalent of amine is taken into account, this latter being involved in a second step, establishing the second Lewis acid–base complex of the reaction. The energy differences between the reaction paths of TMA dimer and diborane with methylamines are less than 14 kJ/mol in all steps. In the studied complexation reaction, only one transition state was found, which belongs to the first amine addition to the dimer. The second amine reacts with the uncomplexed Lewis acid moiety without barrier (similarly to the reaction of aziridine or cyclopropylamine with BH_3).¹ The analogue reaction path to the formation of diammoniate of diborane²⁶ was not investigated because these structures were not observed in the studied cases by ^{11}B NMR spectroscopy. Note that in comparing the calculated reaction path of diborane and methylamine to the similar reaction of ammonia and diborane, the methyl group slightly stabilizes all the products and the transition state (Figure 1).²⁷

The dimerization energy of borane is 97 kJ/mol higher than that of TMA (calculated at the BMK/6-311+G(2df,p) level), therefore the complexation energies of Lewis acid monomers and dimers are different (Table 1). The calculated complexation energy slightly varies for different amine conformers (SI Table S5), therefore the energy differences between the conformers are also changed by the complexation. Neither the H_2 nor the CH_4 elimination is affected by increasing the alkyl chain, although the unsaturation slightly enhances the exothermicity of the elimination reaction. In the case of H_2 elimination, this tendency is opposite to the demand that the reaction needs to be close to thermoneutral in attendance to the recycling of the possible hydrogen storage material. On the other hand, while H_2 elimination of ammonia–alane is calculated to be endothermic,⁵ the methane elimination of the amine–TMA studied above is exothermic. A similar effect upon the change of the substituent was observed in case of H_3GaNH_3 and

Table 1. Complexation Enthalpies and Reaction Enthalpies of the H₂ and CH₄ Release Reactions of the Studied Molecules^a

no.		R-NH ₂ + LA → RNH ₂ -LA ^b		2R-NH ₂ +(LA) ₂ → 2 RNH ₂ -LA		elimination ^c	
BH ₃	AlMe ₃	-BH ₃	AlMe ₃	-BH ₃	AlMe ₃	-BH ₃	AlMe ₃
1	6	-139	-94	-120	-125	-20	-4
2	7	-140	-95	-121	-126	-20	-4
3	8	-126	-78	-95	-93	-26	-12
4	9	-135	-90	-113	-117	-22	-9
5	10	-131	-85	-103	-107	-19	-9

^aEnthalpy values are in kJ/mol, calculations performed at BMK/6-311+G(2df,p) level. In the case of amines containing three carbons, results of conformer "I" are collected in the table. See SI Figure S7 for the structure of the conformers. ^bCounterpoise correction was used. ^cThe most stable conformers were chosen to calculate the H₂ or CH₄ elimination in the following reactions: R-NH₂-BH₃ → R-NH=BH₂ + H₂ or R-NH₂-Al(CH₃)₃ → R-NH=Al(CH₃)₂ + CH₄.

Me₃GaNH₃.²⁹ As well as the *t*-butylamine-TMA,¹¹ Me₃GaNH₃ is also demonstrated as a suitable MOCVD precursor.³⁰

As mentioned in the Introduction, using amine excess, the formation of two kinds of 2:1 adducts is possible (Figure 2).

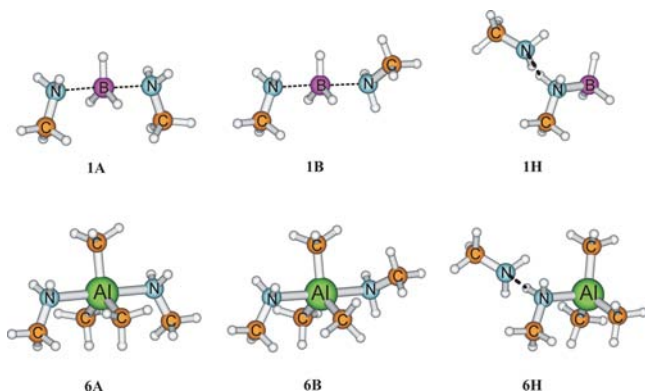


Figure 2. Two different conformers of bis(methylamine)-borane and bis(methylamine)-TMA complexes and the H-bonded 2:1 adduct of 1 and 6 with one additional methylamine.

The enthalpy of the complexation for the 1:1 adduct to produce five-coordinated aluminum complex was found to be less than 18 kJ/mol exothermic for the studied molecules (Table 2). This is in line with the NPA charge changes, in sight of the partial atomic charge of N, which becomes slightly less negative in the structures containing a pentacoordinated Al atom than what was observed in the 1:1 complexes (SI Tables S3 and S6). On the other hand, the stabilization of hydrogen bonded complexes is between 18 and 26 kJ/mol. Thus, it is supposed that the hydrogen bonded 2:1 adducts of amine-TMA complexes are the majority in NMR solvent and these complexes are obtained mostly during the above-mentioned addition reaction. It is possible that the ¹H and ¹³C NMR chemical shift exchange (observed during the addition of amine in excess) takes place through amine-TMA 2:1 complexes containing pentacoordinated aluminum atoms. This phenomenon is supported by our calculations, as it was found no energy barrier in the reaction between the 1:1 complex of methylamine-TMA 6 and the free methylamine to form 6A, 6B, or 6H.

Table 2. Complexation Enthalpies of the Studied 2:1 Adducts and Difference of the Complexation Enthalpies of the Studied 1:1 and 2:1 Adducts^a

no.		$\Delta H_{2:1 \text{ adduct}}^{\text{complexation}}$		$\Delta \Delta H^{\text{complexation}}$	
BH ₃	AlMe ₃	BH ₃	AlMe ₃	BH ₃	AlMe ₃
1A	6A	-64	-111	76	-17
1B	6B	-64	-109	75	-15
1H	6H	-164	-115	-25	-21
2A	7A	-62	-110	78	-16
2B	7B	-62	-108	78	-13
2H	7H	-165	-116	-25	-21
3A	8A	-50	-77	76	1
3B	8B	-50	-77	77	1
3H	8H	-147	-103	-21	-26
4A	9A	-57	-102	78	-13
4B	9B	-56	-100	79	-10
4H	9H	-156	-106	-21	-16
5A	10A	-59	-102	71	-17
5B	10B	-59	-99	71	-14
5H	10H	-154	-103	-23	-18

^aEnthalpy values are in kJ/mol, calculations performed at BMK/6-311+G(2df,p) level, counterpoise correction was used.²⁸ In the case of amines containing three carbons, results of conformer "I" are collected in the table. See Figure 2 and SI Figure S7 for the structure of the conformers.

Similarly, the second amine can connect to the amine-borane complex through H-bond in a reaction with comparable enthalpy change as it is calculated in the case of amine-TMA complexes (Table 2). The optimized structures of the 2:1 amine-borane adducts containing pentacoordinated B atom are first-order saddle points on the respective potential energy surfaces possessing high relative energy to the found H-bonded minima (about 100 kJ/mol). This energy difference can be responsible of the observed separate ¹H and ¹³C NMR signals of the free amine and the complex upon the addition of allylamine to allylamine-borane.³¹ According to the NBO analysis, the involvement of B and Al atoms of the dative bonds in the trigonal bipyramidal structures are about 5% (SI Table S7).

To rationalize the difference between the reactions of allylamine-borane 4 or allylamine-TMA 9 with *n*-propylamine, and *n*-propylamine-borane 2 or *n*-propylamine-TMA 7 with allylamine, the mechanisms we proposed were calculated (Figure 3). In line with 2:1 amine-TMA adducts, the complex containing Al atom with trigonal bipyramidal bonding structure is found to be an intermediate of the reaction. On the other hand, when two amines are attached to BH₃, the 2:1 adduct is a transition state, as it was found in the cases of the above-mentioned structures including pentacoordinated B atom. The 67 kJ/mol energy barrier in the case of the reaction of allylamine-borane 4 with *n*-propylamine is in line with the observation that the reaction occurred slowly at room temperature. The experimentally observed preference of *n*-propylamine to allylamine in the case of TMA complexation is reflected in a slight energy difference of the two complexes.

Photoelectron Spectroscopy. The photoelectron spectra of 4–10 were recorded, and the assignment based on OVG calculations are compiled in Table 3. In the case of amine-boranes 4 and 5, the first calculated IEs are slightly different from the observed values, but it is supposed that the split of the two $\sigma_{\text{B-H}}$ orbitals is underestimated. Lloyd and Lyaugh indicated that the $\sigma_{\text{B-H}}$ orbitals are strongly localized on the BH₃

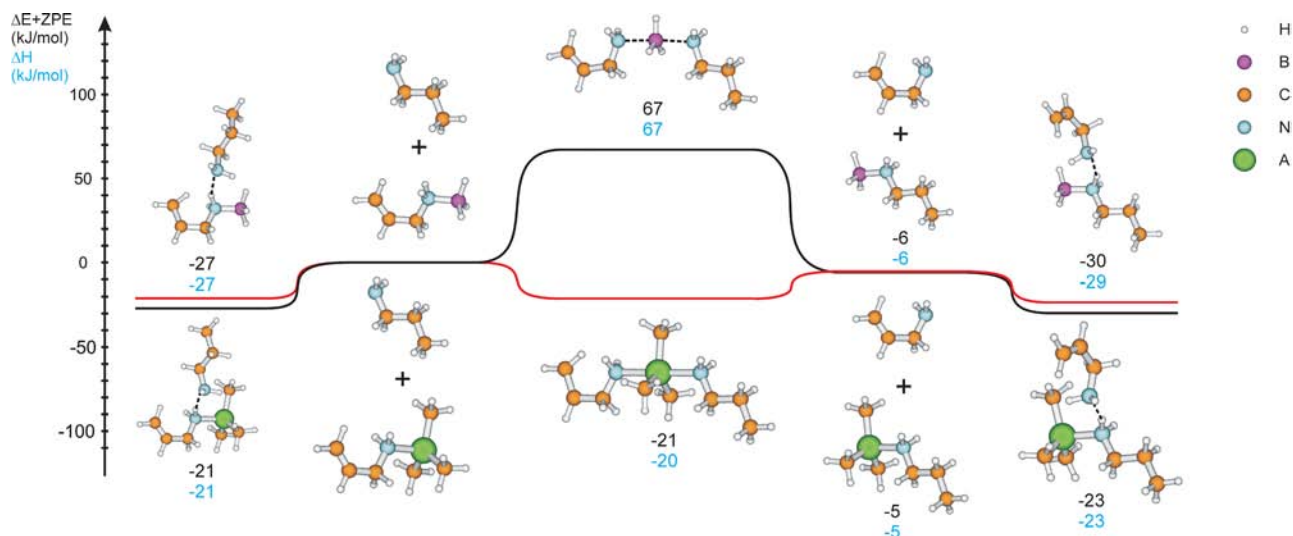


Figure 3. Energy profile for the reaction of allylamine–borane **4I** (black) and allylamine–TMA **9I** (red) with propylamine at BMK/6-311+G(2df,p) level of the theory. The ZPE corrected energy values are in black, and enthalpy values are in blue. Counterpoise correction was used.²⁸

group, so the effective local symmetry is still C_{3v} , although the molecular symmetry is lower.³² A Jahn–Teller split of these orbitals cannot be predicted well by OVGf calculations. Nevertheless, except for the result of σ_{B-H} orbitals, the calculated IEs of the 1:1 complex of allylamine– and propargylamine–borane fit well with the measurement and indicate that there is no interaction between the dative bond and the π -systems.

The photoelectron spectra of the studied amine–TMA complexes provide some general information. First of all, they indicate that amine–TMA complexes form 1:1 adducts in gas phase because their calculated IEs fit well with the measured values (Table 3). The first photoelectron band in the spectra of amine–TMA complexes can be ordered to the σ_{Al-C} orbitals, which are destabilized by about 0.8 eV comparing to the TMA monomer (9.85 eV).³³ On the spectrum of methylamine– and propylamine–TMA, the second band at 10.7 and 10.6 eV respectively belongs to σ_{N-Al} . They are about 0.8 eV higher than σ_{P-Al} bond in trimethylphosphine–TMA (9.87 eV).³⁴ By comparing the studied allyl and propargyl derivatives, it can be seen that amine moiety is more stabilized in amine–boranes (Figure 4) than in the corresponding aluminum derivatives. On the other hand the destabilization of σ_{Al-C} orbitals is smaller than that of σ_{B-H} in amine–boranes. Although, the borane complexation of amines containing double or triple bond at β,γ -position leads to the separation of the π orbitals and the lone electron pairs of N atom in both cases, a weak interaction was noticed in propargylamine–TMA **10** between the dative bond and one π orbital. The changes of orbital interactions in cyclopropylamine upon borane complexation have been discussed in our previous paper in detail.¹ In the case of **8**, similar interactions were found, which are in line with the calculated relative energy change in the conformers of cyclopropylamine upon borane and TMA complexation (SI Table S1).

CONCLUSIONS

Primary amine–TMA complexes have been synthesized and characterized by NMR and photoelectron spectroscopy. Both spectra of compounds show that the vaporization of the complexes during their purification provides only 1:1 adduct. Although the first mole of methane elimination of 1:1 amine–TMA complexes is calculated to be exothermic, and methane

elimination was observed in the case of several secondary amine–TMA complexes upon heating,³⁸ this decomposition has been avoided in our procedure.

The reaction pathways we found for diborane or TMA dimer with two methylamines are similar; the calculated enthalpy difference during the reaction steps is always less than 10 kJ/mol. On the other hand, the calculated complexation enthalpy of the studied amines with borane is systematically about 45 kJ/mol higher than with TMA, which could be originated from the dimerization enthalpies of borane and TMA. The experimentally observed differences between the propensity to change the amine ligand of the two Lewis acids is rationalized by theoretical calculations. It is shown that on both BH_3 and TMA centers the Lewis bases can be changed by a reaction including a trigonal bipyramidal structure with two amine ligands. However, this structure is a transition state in the case of amine–borane with a relative energy of 67 kJ/mol, while it is an intermediate lying 21 kJ/mol lower than the separated reactants for amine–TMA. The investigation on the 2:1 adducts including pentacoordinated B and Al atoms indicates that trigonal bipyramidal structures of 2:1 amine–TMA complexes are supposed to support the continuous ligand exchange in case of amine excess observed by 1H and ^{13}C NMR spectroscopy.

Analyzing the calculated geometrical parameters the most striking difference between amine–boranes and amine–TMA complexes is that the BH_3 center is more pyramidalized. The phenomenon that NPA charge of N atoms increases upon borane complexation while in amine–TMA complexes it remains similar to the N atom in the corresponding free amines can be explained by two reasons: one is the lower electronegativity of the Al atom than B atom and the second is that the methyl group is a better electron donor than hydrogen. It is in accord with the observation that the charge of Al atom in TMA decreases about 0.4 charge unit less than the charge of B atom in borane during the complexation with an amine. According to the NBO analysis, the participation of the N atom in the dative bond of the 1:1 complexes is 11% higher in amine–boranes than in amine–TMA. It is in line with the observed photoelectron spectra, in which the stabilization of the amine moiety is higher in the case of borane complexation than during the formation of TMA complex. In accord with this observation, the destabilization of

Table 3. Experimental and Calculated Ionization Energies (in eV)^a

no.	calculated		measured	assign	no.	calculated		measured	assign						
	1:1	2:1				1:1	2:1								
est distr	0	100			est distr	18	82								
4	10.52	8.80	9.88	10.1	σ_{B-H}	7	8.88	8.55	8.74	8.8–9.0	2 σ_{Al-C}				
	10.60	9.76	10.12	10.7	π		8.89	8.59	8.74	10.6		σ_{N-Al}			
	10.66	9.86	10.23		σ_{B-H}	10.64	8.98	9.83							
	12.22	10.52	10.27	12.2–12.5	σ_{N-B}		10.60	10.60	10.38						
	13.56	10.72	10.31	13.3	σ_{C-H}	est distr		2	98						
	14.32	10.82	11.82	14.1	σ_{C-H}		8	8.90	8.56		8.77		8.9–9.1	2 σ_{Al-C}	
	15.05	12.68	12.91	15.0	σ_{C-C}	8.91		8.62	8.81		10.39		8.92		9.70
		12.92	13.27			11.38	9.93	10.18	11.4					2 σ_{cyc}	
		13.27	13.58			11.61	10.78	10.81							
		13.51	13.83				10.83	11.05							
		13.80	14.10				11.00	11.36							
		14.15	14.66				12.00	11.78							
		14.99	15.24												
		15.24													
est distr	0	100			est distr	24	76								
5	10.67	9.07	10.23	10.4	σ_{B-H}	9	8.94	8.66	8.82	9.0–9.2	2 σ_{Al-C}				
	10.68	10.39	10.42		σ_{B-H}		8.94	8.69	8.83	10.5		$\sigma_{N-Al}(\sigma_{cyc})$			
	11.21	10.41	10.46	11.2–11.6	π_1	10.63	9.32	10.08							
	11.34	10.46	10.51		π_2		10.83	10.06	10.21		11.0		2 σ_{cyc}		
	12.77	10.54	10.82	12.7	σ_{N-B}	est distr		43	57						
	15.23	11.04	10.85	14.9–15.1	σ_{C-H} , σ_{C-N-H}		10	9.04	8.82		8.85		9.0–9.2	2 σ_{Al-C}	
	15.68	11.05	11.00	15.4–15.7	σ_{N-C}	9.04		8.84	8.88		10.88		9.47		10.49
		11.15	12.36			11.15	10.73	10.71	11.1					π_2	
		14.17	14.47			11.33	10.75	10.78	11.6		$\sigma_{N-Al}+\pi_1$				
		14.19	14.86				10.78	10.89							
		14.89	15.19				10.85	10.95							
		15.06	15.28				11.67	11.15							
	est distr	26	74			est distr	43	57							
	6	8.96	8.63	8.80	9.0	2 σ_{Al-H}	9.04	8.82	8.85	9.0–9.2	2 σ_{Al-C}				
8.96		8.66	8.82			9.04	8.84	8.88							
10.83		9.16	10.19	10.7	σ_{N-Al}	10.88	9.47	10.49	10.7	$\sigma_{N-Al}-\pi_1$					
		11.06	10.63			11.15	10.73	10.71	11.1	π_2					

^aCalculations are performed by OVGF/6-311+G(d,p) method except for 2:1 amine–TMA adducts where scaled OVGF/6-31+G(d) method was employed. The weighted average of the estimated IEs was calculated by employing the Boltzmann distribution determined by the calculated relative energies of the conformers. In the case of 2:1 complexes, pentacoordinated and H-bonded conformers were grouped and their distribution in gas phase was also estimated (est distr). For further details, see SI.

σ_{B-H} is also higher along the complexation than what was obtained in the case of σ_{Al-C} orbitals in amine–TMA complexes.

The calculated enthalpies of the H₂ elimination reactions are close to the previously studied primary amine–boranes, but regarding the enthalpy change of dehydrogenation, the advantage of the studied amine–boranes is not remarkable.¹ The mechanism of the methane elimination of the amine–TMA is supposed to be a complex procedure, nevertheless it is calculated to be exothermic in the case of the studied molecules. Moreover, these complexes can be evaporated, which supports that primary amine–TMA complexes are promising materials for MOCVD purposes.

EXPERIMENTAL SECTION

1. Materials. Methylamine, cyclopropylamine, propylamine, allylamine, propargylamine, THF-BH₃, Me₂S-BH₃, and AlMe₃ in hexane were purchased from the Aldrich Company and used without further

purification. Amine–boranes have been prepared as previously reported.^{1,18}

2. General. ¹H (400.13 MHz), ¹³C (100.62 MHz), ¹¹B (128.4 MHz), ¹⁴N (28.91 MHz), ¹⁵N (40.55 MHz), and ²⁷Al (104.26 MHz) NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer equipped by a 5 mm BBOF probe. For the ¹⁵N NMR experiments, INEPT pulse sequence with decoupling was employed and CPD sequence from the Bruker Library was used for the ¹³C, ¹¹B, and ¹⁴N. Chemical shifts are given in ppm (δ) relative to external BF₃–Et₂O (¹¹B NMR), external CH₃NO₂ (¹⁴N, ¹⁵N NMR) and external AlCl₃ (²⁷Al NMR). The ¹H and ¹³C chemical shifts were calculated referred to the solvent (in C₆D₆ δ 7.16 ppm and δ 128.06 ppm for ¹H and ¹³C, respectively, and in CDCl₃ δ 7.27 and δ 77.0 ppm for ¹H and ¹³C, respectively). Spectra were recorded at 297 K unless indicated.

The instrument used for the UPS measurements has been described earlier,³⁹ and it is completed with a new, 19 cm long heatable inlet. During the experiments the temperature of the inlet was around 100 °C to avoid the condensation of the vaporized sample prior to entering the reaction chamber. The samples were heated to around

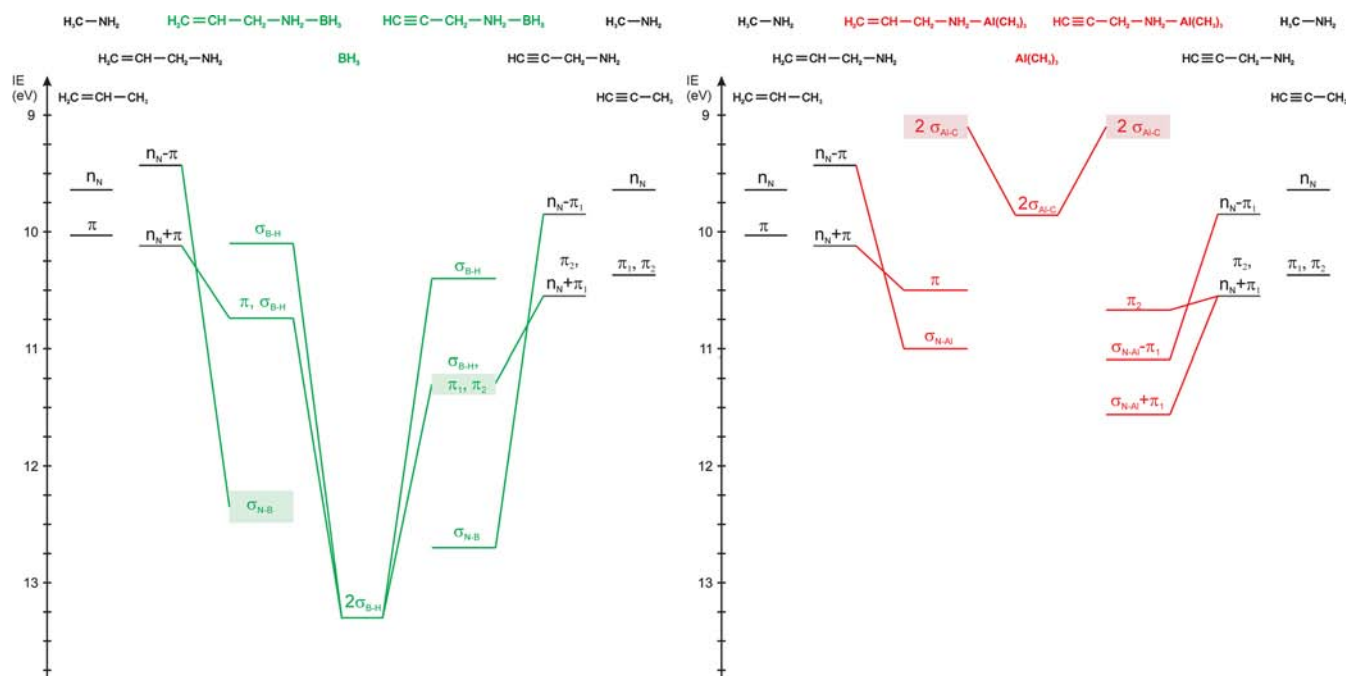


Figure 4. Correlation between the measured ionization energies of allyl and propargyl derivatives. The IEs (except of the complexes) are taken from refs 35–37. Note that assignment of the plotted IEs of propargylamine is based on our OVGf calculations.

50 °C to reach the sufficient pressure in the ionization chamber. The average pressure measured next to the ionization chamber was about $2\text{--}3 \times 10^{-4}$ mbar. The electron counts were collected for 100 ms in each accumulation point of one scan of the spectrum, and about 30 scans were collected to provide one spectrum. The bands were calibrated to He, N_2 , and MeI, while fwhm (full width at half-maximum) was 0.06 eV at the $\text{N}_2 \Sigma_g^+$ peak (15.60 eV).

3. Synthesis of Amine–Trimethylaluminum Complexes.

Caution! $\text{Al}(\text{CH}_3)_3$ is highly pyrophoric and should be used under a nitrogen atmosphere or under vacuum in a well-ventilated hood.

Synthesis of Methylamine–Trimethylaluminum. Trimethylaluminum in hexane (1 mL of 2 M soln, 2 mmol) and pentane (5 mL) were introduced in a 500 mL three-necked flask, and the flask was immersed in a liquid nitrogen bath. Excess of dry methylamine gas (about 0.5 g, 16 mmol) was introduced into the flask. The flask was closed by stopcocks, and the mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was evacuated through a trap immersed in an ice bath, while the glassware was slightly heated with a hot gun. The complex was selectively condensed in the trap and residual solvent was removed at 0 °C for 15 min. White crystals were obtained and used for further analysis. To prepare an NMR sample, the pure product was condensed on the coldfinger with the NMR solvent (C_6D_6) and then collected in an NMR tube at room temperature under nitrogen.

General Procedure for Propylamine-, Cyclopropylamine-, Allylamine-, and Propargylamine–Trimethylaluminum. The amine (3 mmol) and pentane solvent (5 mL) were introduced in the three-necked flask under nitrogen. The TMA solution in hexane (0.5 mL of 2 M soln, 1 mmol) was slowly inserted in the last step by syringe through a septum. After about 45 min of stirring at room temperature, the purification was performed as in case of methylamine–TMA. Propargylamine–TMA was distilled into the trap without any heating because some unidentified impurities were observed otherwise. Colorless liquids were obtained.

Methylamine–Trimethylaluminum (6). Yield 88% (based on trimethylaluminum); $t_{1/2} \approx 9.5$ days in C_6D_6 2 M at room temperature. The $^1J_{\text{CH}}$ for TMA moiety is given for the largest peak. ^1H NMR (C_6D_6): δ –0.74, –0.68, –0.57 (s, s, s, 9H, $\text{Al}(\text{CH}_3)_3$), 1.16 (brd-s, 2H, NH_2), 1.64 (s, 3H, CH_3NH_2). ^{13}C NMR (C_6D_6): δ –10.2, –9.2, –7.0 (brd, $^1J_{\text{CH}} = 110.3$ Hz (q), $\text{Al}(\text{CH}_3)_3$), 26.8 ($^1J_{\text{CH}} = 138.7$ Hz (q),

CH_3NH_2). ^{14}N NMR (C_6D_6): δ –410.9 (brd). ^{15}N NMR (C_6D_6): δ –365.0. ^{27}Al NMR (C_6D_6): δ 172.8 (brd).

Propylamine–Trimethylaluminum (7). Yield 97% (based on trimethylaluminum); $t_{1/2} \approx 16$ days in C_6D_6 2 M at room temperature. ^1H NMR (C_6D_6): δ –0.57, –0.53, –0.43 (s, s, s, 9H, $\text{Al}(\text{CH}_3)_3$), 0.50 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H, CH_2CH_3), 0.88 (tq, $^3J_{\text{HH}} = 7.3$ Hz, 2H, CH_2CH_3), 1.47 (brd-s, 2H, NH_2), 2.13 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H, NH_2CH_2). ^{13}C NMR (C_6D_6): δ –9.6, –8.5, –6.8 (brd, $^1J_{\text{CH}} = 106.7$ Hz (q), $\text{Al}(\text{CH}_3)_3$), 10.9 ($^1J_{\text{CH}} = 125.5$ Hz (q), CH_2CH_2), 24.8 ($^1J_{\text{CH}} = 125.8$ Hz (t), CH_3CH_2), 43.1 ($^1J_{\text{CH}} = 137.6$ Hz (t), CH_2NH_2). ^{14}N NMR (C_6D_6): δ –393.6 (brd). ^{15}N NMR (C_6D_6): δ –347.6. ^{27}Al NMR (C_6D_6): δ 172.1 (brd).

Cyclopropylamine–Trimethylaluminum (8). Yield 88% (based on trimethylaluminum); $t_{1/2} \approx 2.5$ days in C_6D_6 2 M at room temperature. ^1H NMR (C_6D_6): δ –0.77, –0.68, –0.66 (s, s, s, 9H, $\text{Al}(\text{CH}_3)_3$), –0.12 (m, 2H, cyclopropyl), 0.21 (m, 2H, cyclopropyl), 1.46 (brd-s, 2H, NH_2), 1.76 (m, 1H, NH_2CH). ^{13}C NMR (C_6D_6): δ –9.3, –8.3, –6.8 (brd, $^1J_{\text{CH}} = 110.7$ Hz (q), $\text{Al}(\text{CH}_3)_3$), 6.4 ($^1J_{\text{CH}} = 162.6$ Hz (t), CH_2 , cyclopropyl), 24.3 ($^1J_{\text{CH}} = 178.8$ Hz (d), NH_2CH). ^{14}N NMR (C_6D_6): δ –385.1. ^{15}N NMR (C_6D_6): δ –340.1. ^{27}Al NMR (C_6D_6): δ 172.2 (brd).

Allylamine–Trimethylaluminum (9). Yield 77% (based on trimethylaluminum); $t_{1/2} \approx 38.5$ h in C_6D_6 2 M at room temperature. ^1H NMR (C_6D_6): δ –0.67, –0.62, –0.54 (s, s, s, 9H, $\text{Al}(\text{CH}_3)_3$), 1.52 (brd-s, 2H, NH_2), 2.72 (d, $^3J_{\text{HH}} = 6.1$ Hz, 2H, CH_2NH_2), 4.70 (dm, $^3J_{\text{HH}} = 10.3$ Hz, $^2J_{\text{HH}} = 0.9$ Hz, 1H, CH_2CH), 4.83 (dm, $^3J_{\text{HH}} = 17.1$ Hz, $^2J_{\text{HH}} = 0.9$ Hz, 1H, CH_2CH), 5.20–5.30 (m, 1H, CH_2CH). ^{13}C NMR (C_6D_6): δ –9.6, –8.5, –6.8 ($^1J_{\text{CH}} = 109.3$ Hz (q), $\text{Al}(\text{CH}_3)_3$), 43.5 ($^1J_{\text{CH}} = 139.4$ Hz (t), CH_2CH), 117.5 ($^1J_{\text{CH}} = 157.0$ Hz (t), CH_2NH_2), 134.6 ($^1J_{\text{CH}} = 155.8$ Hz (d), CH). ^{14}N NMR (C_6D_6): δ –392.6. ^{15}N NMR (C_6D_6): δ –346.2. ^{27}Al NMR (C_6D_6): δ 172.9 (brd).

Propargylamine–Trimethylaluminum (10). Yield 88% (based on trimethylaluminum); $t_{1/2} \approx 15.5$ h in C_6D_6 2 M at room temperature. ^1H NMR (C_6D_6): δ –0.74, –0.67, –0.56 (s, s, s, 9H, $\text{Al}(\text{CH}_3)_3$), 1.68 (brd-s, 2H, NH_2), 1.87 (t, $^4J_{\text{HH}} = 2.4$ Hz, 1H, CH), 2.77 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2H, CH_2). ^{13}C NMR (C_6D_6): δ –9.8, –8.9, –6.9 ($^1J_{\text{CH}} = 109.3$ Hz (q), $\text{Al}(\text{CH}_3)_3$), 30.2 ($^1J_{\text{CH}} = 143.1$ Hz (t) $^4J_{\text{CH}} = 3.7$ Hz (d), CH_2), 73.6 ($^1J_{\text{CH}} = 250.2$ Hz (d), $^3J_{\text{CH}} = 3.7$ Hz (t) CH), 80.2 ($^2J_{\text{CH}} = 49.9$ Hz (d), $^2J_{\text{CH}} = 8.1$ Hz (t), C). ^{14}N NMR (C_6D_6): δ –388.2. ^{15}N NMR (C_6D_6): δ –349.4. ^{27}Al NMR (C_6D_6): δ 171.2 (brd).

Table 4. Experimental and Calculated Complexation Enthalpies of Ammonia–Borane, Ammonia–TMA, Methylamine–Borane, and Methylamine–TMA

method	ΔH (in kJ/mol)				
	$\text{NH}_3\text{-BH}_3$	$\text{NH}_3\text{-TMA}$	1	6	ref
measured in hexane		115.3 ± 1.0		125.6 ± 1.4	41
measured in benzene		93 ± 5			42
gas			146.4 ± 3.3		22 (43)
estimated	130.1 ± 4.2				22
G3	87.6	102.5	97.7	115.2	
BMK ^a	117.6	83.5	139.1	93.6	

^aBMK/6-311+G(2df,p)//BMK/6-311+G(2df,p) method was used for electron energy calculation and BMK/6-31+G(d,p)//BMK/6-31+G(d,p) level of the theory for enthalpy correction scaled by 0.9728.⁴⁰

4. Computational Details. Although some experimental values are available for the complexation enthalpies of ammonia and methylamine with borane and TMA, as a benchmark we carried out calculation with the highly precise G3 method for these systems (Table 4). To determine the method for amine–trimethylaluminum complexes, different DFT functionals were tested for ammonia–TMA and methylamine–TMA 6 (Table S16 in SI). BSSE correction²⁸ and the respective scaling factors for enthalpy correction⁴⁰ were employed in all the complexation enthalpy calculations. All the calculations including thermal corrections are referred to 298.15 K, 1 atm pressure.

The experimental result of the complexation enthalpy of ammonia–TMA in hexane is 12.8 kJ/mol higher, while in benzene is 9.5 kJ/mol lower than the calculated G3 results. It can be seen that the complexation enthalpy obtained by DFT calculations is generally 25–30 kJ/mol lower than the G3 calculations (Table S16 in SI). Because the difference using 6-31G* or 6-311+G(2df,p) basis is generally less than 3 kJ/mol in the complexation enthalpy, it can be concluded that the calculated complexation enthalpies are only weakly affected by the basis set. It was found that although the BMK method predicts the complexation enthalpy with a 20 kJ/mol error, it can well predict the difference between the complexation enthalpies of ammonia– and methylamine–TMA. The difference in the complexation enthalpies between ammonia– and methylamine–borane was found experimentally to be 16.3 kJ/mol and estimated for 10.1 and 21.5 kJ/mol by G3 and BMK method, respectively (Table 4). The same between ammonia– and methylamine–TMA was obtained experimentally to be 10.3 kJ/mol and calculated as 12.7 and 10.1 kJ/mol, respectively. Therefore, based on the amine–TMA results, BMK/6-311+G(2df,p) method was selected for geometry optimization and electron energy calculation. The existence of only one imaginary frequency was checked for the transition states. IRC calculations were carried out for all the reaction paths at the BMK/6-31+G(d,p) level to confirm the reaction coordinates from the transition states to stable products. It is interesting to note that the transition state geometry of methylamine with TMA dimer is found only at the BMK/6-31+G(d,p) level. Thermal corrections for the studied systems were obtained at BMK/6-31+G(d,f) level of the theory, and 0.9773 and 0.9728 scaling factors were employed for the ZPE and ΔH corrections, respectively.⁴⁰ The stationary points were characterized by second derivative calculations employing the BMK method associated by 6-31+G(d,p) basis set. NPA and NBO calculations were also carried out at BMK/6-311+G(2df,p) level to determine atomic charges in the studied molecules.²⁴

The ionization energies were predicted by OVGf method at 6-311+G(d,p)//BMK/6-311+G(2df,p) or 6-31+G(d)//BMK/6-311+G(2df,p) basis sets (latter was used for 2:1 TMA adducts), which were found to provide good agreement with the measurements (SI Table S17). The equation $\text{IP}(\text{eV}) = 0.9771 * \text{IP}^{6-31+G(d)} + 0.4977$ was used for 2:1 amine–TMA adducts (SI Figure S8). The assignment of the ionization bands was supported by HF molecular orbital calculations employing 6-311+G(2df,p) basis set. All calculations were carried out by Gaussian 03 program package.⁴⁴

■ ASSOCIATED CONTENT

● Supporting Information

Figures from ¹H NMR chemical shift changes of allylamine upon borane and TMA complexation, ¹H, ¹³C, and ²⁷Al chemical shift changes during the addition of allylamine to TMA, ¹H, and ¹³C chemical shift changes upon addition of allylamine to allylamine–borane. Calculated geometric parameters, Cartesian coordinates, relative energies, complexation enthalpies, NPA changes, NBO analysis of the dative bonds, and ionization energies of calculated molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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