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DFT Modeling of Chemical Vapor Deposition of GaN from Organogallium Precursors. 1. Thermodynamics of Elimination Reactions

Alexey Y. Timoshkin*

*Inorganic Chemistry Group, Department of Chemistry, St. Petersburg State University, University Pr. 2,
Old Peterhof, 198904, Russia*

Holger F. Bettinger[†] **and Henry F. Schaefer, III**[‡]

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

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The thermochemistry of dissociation and elimination reactions of organogallium precursors for the GaN chemical vapor deposition (CVD) is studied at the hybrid Hartree−Fock/density functional level of theory (B3LYP/pVDZ). Geometries, relative energies, vibrational frequencies of $R_xGaNR'_x$ species, and their dissociation products (NR_x, GaR_x, $x = 1-3$; (R, R′ = H, CH_3) are presented. Methane elimination from the source adducts is exothermic at standard conditions, while hydrogen elimination is endothermic. Both for R = H, CH_3 elimination reactions are predicted to be more favorable compared to dissociation into components, in contrast to the halogen containing precursors. The Ga−N bond dissociation enthalpies (kJ mol^{-1}) are the highest for $R_2GaNR'_2$ compounds (313−382), followed by RGaNR′ (196−266); and for donor−acceptor complexes $R_3GaNR'_3$ (56−100) they are the lowest. $(CH_3)_xGaNH_x$ isomers are more than 50 kJ mol^{-1} lower in energy than $H_xGaN(CH_3)_x$ species, but the formation of Ga−H and N−H bonds is the thermodynamically most favorable process. Hence, the replacement of alkyl groups might be viable during the CVD process from trimethylgallium and ammonia.

Introduction

Gallium nitride is a prospective material for high-power high-frequency electronic and optoelectronic devices. Hexagonal GaN is used commercially as a blue-light emitting diode material. The properties of GaN and of suitable precursors have been studied extensively over the past decade. A comprehensive summary of the chemistry of Ga−N compounds can be found in a 1996 special issue of Gmelin's handbook.[1] Many different chemical vapor deposition (CVD) processes have been employed to produce high purity monocrystalline GaN, and a variety of precursors, such as azides, hydrazides, and different types of donor−acceptor adducts have been proposed and examined.[2−11] One of the commercially most important ways to synthesize GaN is via the metal organic vapor phase epitaxy (MOVPE) of trimethylgallium $Ga(CH_3)_3$ (TMG) and ammonia. Petzke and Zehe[12] found that under atmospheric pressure the $Ga(CH_3)_3(g) + NH_3(g) = GaN(s) + 3CH_4(g)$ equilibrium is almost quantitatively moved to the right side at $T > 800$ °C. The thermodynamic analysis of this reaction has been presented by Chegnov et al.[13] One of the major factors affecting the GaN deposition is the donor−acceptor interaction of the TMG and NH_3 components and their adduct formation.[14]

Despite the extensive experimental investigations,[15] the detailed mechanism of the GaN CVD process is still unclear, and the thermodynamic properties of many gas-phase organogallium precursors and possible intermediates are unknown. Thus, we investigate computationally structural and thermodynamic aspects of organogallium compounds, which might form in the gas phase before adsorbing on the hot surface and decomposing into GaN. In the present work, we consider GaH_3, TMG, NH_3, and $N(CH_3)_3$ as starting substances and present their molecular geometries as well as those of donor−acceptor adducts and their dissociation products. We present enthalpies, entropies, and Gibbs energies of the dissociation and elimination processes in the gas phase. Vibrational spectra of all compounds investigated are given in the Supporting Information and may help in the experimental identification of possible intermediates in the GaN CVD process. Structural properties and thermodynamics of association processes will be considered in the following report (see the second part of this series: "Structures of the Oligomers and Thermodynamics of the Association Processes"[80]).

Computational Details

All computations were performed using the Gaussian 94 program package.[16] All geometries were fully optimized using self-consistent-field (SCF) and density functional theory (DFT). The three-parameter exchange functional of Becke[17] with the gradient-corrected correlation functional of Lee, Yang, and Parr[18] (B3LYP) was used for the DFT studies. The polarized valence double-ζ (pVDZ) basis set of Ahlrichs and co-workers[19] was used throughout. These basis sets are contracted in the following way: H (4s, 1p) → [2s, 1p], C (7s, 4p, 1d) → [3s, 2p, 1d], N (7s, 4p, 1d) → [3s, 2p, 1d], Ga (14s, 10p, 6d) → [5s, 4p, 3d]. The effective core potential (ECP) basis set of Hay and Wadt,[20] augmented by d and p polarization functions, (LANL2DZP) was also employed in preliminary computations. All stationary points of the potential energy surface (PES) were

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* Corresponding author. E-mail: alex@dux.ru.

[†] Present address: Department of Chemistry MS 60, P.O. Box 1892, Rice University, Houston, TX 77098-1892.

[‡] E-mail: hfsiii@arches.uga.edu.

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characterized by analytic evaluation of second derivatives, with the exception of structures computed with the LANL2DZP basis set, for which second derivatives were evaluated by finite differences of analytic first derivatives.

Because of the flatness of the PES's with respect to rotation of methyl groups, we encountered several cases (e.g., NMe_2, $GaMe_2$, $GaMe_3$, MeGaNMe) where the structures of highest possible symmetry were incorrectly predicted to be stationary points of higher order if the standard Gaussian energy and geometry convergence criteria and integration grid (75 radial shells with 302 angular points per shell) were employed. As many two-electron integrals and their derivatives are computed by numerical integration, the numerical accuracy of density functional computations depends on the nature of the integration grid. The stationary points turned out to be minima when we used a finer integration grid consisting of 99 radial shells with 590 angular points per shell along with tighter convergence of the self-consistent field iterative procedure (10^{-12} a.u.).

Since many of the compounds studied possess almost freely rotating methyl groups, the computed absolute entropies are expected to be overestimated. However, when the reaction entropy is considered, these errors cancel each other as long as the number of free rotors on both sides of the equation is equal. Therefore, the reaction entropies reported in the present study are expected to be more reliable than the absolute entropies of individual compounds.

Results and Discussion

I. Donor and Acceptor Species: NH_x, GaH_x, $N(CH_3)_x$, $Ga(CH_3)_x$ ($x = 1-3$). The theoretical structural data for all 12 distinct molecules are presented in Figure 1, and vibrational frequencies are available in the Supporting Information. For NH_x species the predicted bond lengths are 0.011−0.015 Å longer, and valence angles are 1.6−2.1° smaller compared to experiment (Figure 1c), but the vibrational frequencies are in good agreement with experimental data.[21] The present structural results for C_{3v} symmetric trimethylamine $N(CH_3)_3$ (Figure 1f) are in agreement with previous theoretical predictions,[22] as well as with experimental data derived from gas-phase electron diffraction.[23] The vibrational spectrum of TMA (given as Supporting Material) also agrees well with experiment.[24]

The recent photoelectron spectroscopy investigation of Chunhua et al.[25] found the $^2B_1$ state of C_{2v} symmetry to be the ground state of the $N(CH_3)_2$ radical. This conclusion was also supported by DFT calculations carried out by those authors. Our B3LYP/pVDZ computations are in agreement with experiment only when the fine integration grid (cf. Computational Details) and tighter convergence criteria are employed. Similarly, the C_{2v} symmetry minimum described in early theoretical studies by Bock and Trachtman[26,27] for the $Ga(CH_3)_2$ radical is only obtained when the two-electron integrals and their derivatives are determined more accurately than by default in Gaussian.

Monomethyl gallium $GaCH_3$ as well as gallane GaH_3 are known experimentally,[28] and have been thoughtfully studied by electronic structure methods.[26,27,29−31] The present B3LYP/pVDZ results for GaH_3 are in excellent agreement with earlier data.[29] On the other hand, the B3LYP/pVDZ method overestimates the Ga−C distance in C_{3v} symmetric $GaCH_3$ by 0.02 Å, while the Ga−C−H valence angle and vibrational frequencies are in good agreement with CCSD(T)/TZP values.[30]

Trimethylgallium $Ga(CH_3)_3$ (TMG) has been extensively studied both experimentally and theoretically. Gas-phase electron diffraction at −20 °C revealed that a model with static CH_3 groups is unsatisfactory. The following geometric parameters have been obtained: Ga−C 1.967(2), C−H 1.082(3), Ga−C−H 112.1(0.8).[32] Graves and Scuseria[33] found the C_3 structure to be a minimum at SCF/DZ and SCF/DZP levels of theory, but the three hydrogen atoms were lying only 0.07° out of the C−Ga−C plane. In contrast, Trachtman et al.[26,27] found TMG to be C_{3h} symmetric at SCF and MP2 levels of theory with a basis set of DZP quality, in agreement with early assumptions of Edwards and Jones[34] and B3LYP/6-311+G(2d,p) computations.[35] Our optimized C_{3h} structure is a minimum at B3LYP/pVDZ only when the finer integration grid is used. Otherwise it is a second-order stationary point (B3LYP/pVDZ), or a transition state (B3LYP/LANL2DZP). The potential energy surface of TMG is obviously remarkably flat, and rotation of the CH_3 groups is essentially free: Edwards and Jones determined that the energy required for rotation of one CH_3 group is 0.0025 eV.[34] The vibrational spectrum of TMG (see Supporting Information) is in good agreement with gas-phase IR experimental data.[36]

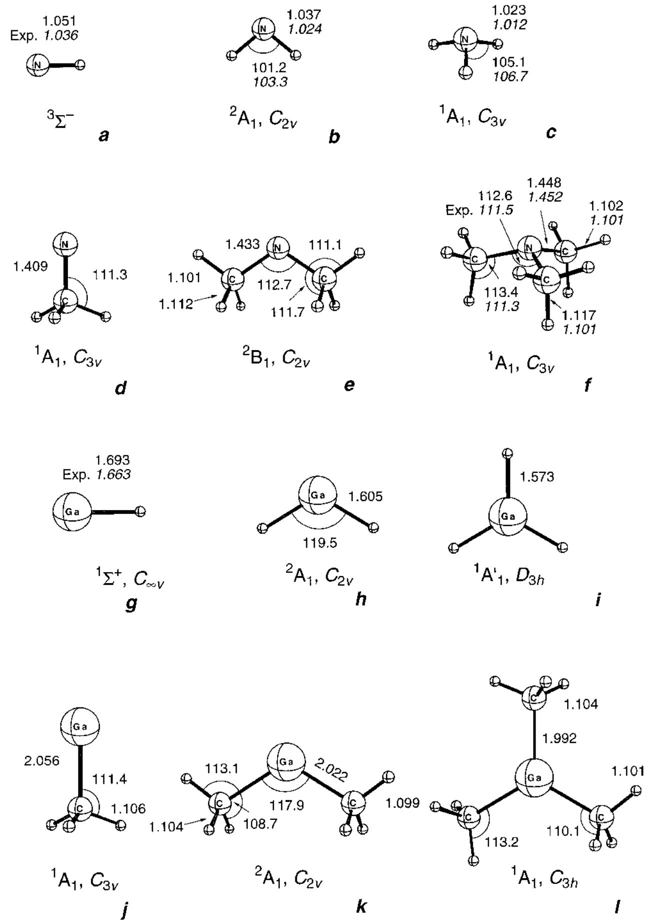

Figure 1. Geometries of donor and acceptor compounds: NH (a), NH_2 (b), NH_3 (c), $N(CH_3)$ (d), $N(CH_3)_2$ (e), $N(CH_3)_3$ (f), GaH (g), GaH_2 (h), GaH_3 (i), $Ga(CH_3)$ (j), $Ga(CH_3)_2$ (k), $Ga(CH_3)_3$ (l) at the B3LYP/pVDZ level of theory. Bond lengths are in Å, bond angles in degrees.

Note that the structural trends predicted for $N(CH_3)_x$ species are quite opposite to those of the other YR_x compounds. With decreasing coordination number x of the central atom, the corresponding bond lengths are increasing in GaH_x, NH_x, and $Ga(CH_3)_x$. In contrast, the N−C bond length is decreasing in $N(CH_3)_x$ when the coordination number is decreasing from $x = 3$ to $x = 1$ (Figure 1).

II. Monomer Compounds with a Ga−N Bond. *A. $R_3GaNR'_3$ (R, R′ = H, CH_3) Adducts with Tetracoordinated Ga and N Centers.* The acceptor molecule (R_3Ga) distorts from planarity,

TABLE 1: Selected Geometric and Thermodynamic Characteristics of Monomer Compounds $R_xGaNR'_x$, Standard Enthalpies $\Delta H^{diss}_{(298)}$, and Entropies $\Delta S^{diss}_{(298)}$ for the Dissociation Process $R_xGaNR'_x = R_xGa + NR'_x$ plus Standard Enthalpies $\Delta H^{elim}_{(298)}$ and Entropies $\Delta S^{elim}_{(298)}$ for the RR′ Elimination Reaction $R_xGaNR'_x = R_{x-1}GaNR'_{x-1} + RR'$: All Results from the B3LYP/pVDZ Level of Theory

x	R,R′	R(Ga−N), Å	∠RGaN, deg	∠GaNR′, deg	$S^0_{(298)}$, J mol^{-1} K^{-1}	μ, D	$\Delta H^{diss}_{(298)}$, kJ mol^{-1}	$\Delta S^{diss}_{(298)}$, J mol^{-1} K^{-1}	$\Delta H^{elim}_{(298)}$, kJ mol^{-1}	$\Delta S^{elim}_{(298)}$, J mol^{-1} K^{-1}
3	H,H	2.180	98.2	111.4	284.9	5.27	100.2	126.0	52.1	109.0
	H,CH_3	2.193	98.7	111.1	372.7	4.80	88	133.8	−24.1	137.5
	CH_3,H	2.222	98.5	111.4	422.8	4.64	75.6	166.0	−7.3	127.4
	CH_3,CH_3	2.270	100.9	108.7	504.1	4.17	56.3	180.2	−19.2	156.5
	mean	2.216	99.1	110.7	396.1	4.72	80	151.5	0.4	132.6
2	H,H	1.820	116.6	124.3	263.3	1.29	381.6	156.7	237.3	118.5
	H,CH_3	1.837	116.5	123.4	323.9	0.92	321.0	184.4	151.4	159.4
	CH_3,H	1.831	117.0	124.5	363.9	0.56	377.8	166.4	189.2	132.2
	CH_3,CH_3	1.851	118.2	123.8	433.0	0.01	312.9	185.6	169.5	158.1
	mean	1.835	117.1	124.0	347.7	0.69	348	173.3	187	142.0
1	H,H	1.694	161.5	126.0	251.1	2.45	265.5	129.7	249.4	114.3
	H,CH_3	1.676	158.1	151.7	297.0	1.61	199.9	132.3	166.4	124.0
	CH_3,H	1.701	161.7	123.9	309.8	3.36	264.4	122.8	219.0	111.2
	CH_3,CH_3	1.682	158.3	149.6	360.0	2.69	195.5	121.2	199.7	102.3
	mean	1.688	159.9	137.8	305.3	2.53	231	126.5	209	113.0

thereby lowering the effective D_{3h} symmetry, during the formation of the $R_3GaNR'_3$ adduct. The structural changes of the donor molecule are less pronounced.[37,38] Usually, the adducts formed from simple inorganic acceptor molecules (R = halogen, H) have C_{3v} symmetry. However, in the case of R = CH_3 the point group symmetry of the whole adduct remains unclear. Laboy and Ault investigated matrix-isolated complexes of $Al(CH_3)_3$ with PH_3, PMe_3, OMe_2, or SMe_2 by IR spectroscopy,[39] and found that the degeneracy of the E vibrational modes of $Al(CH_3)_3$ group is lifted under adduct formation due to lowering of the symmetry from effective D_{3h} to C_s. However, this also can be attributed to intermolecular forces (host−guest interactions) in the argon matrix.[40] Other experimentalists assume C_{3v} or C_3 symmetry of adducts as a model to fit the gas-phase electron diffraction[37] or microwave spectroscopy data.[38] In computational studies C_{3v} symmetry is usually used.

Selected geometric parameters for the adducts are given in Figure 2, and vibrational spectra are summarized in the Supporting Information section (Table 1s). In general, the expected bond lengthening of the terminal bonds is observed under complex formation. The N−C, Ga−H, and Ga−C distances are increased by 0.027, 0.014, and 0.02 Å, respectively, with respect to free donor and acceptor molecules. In contrast, N−H bond lengths in Me_3GaNH_3 and H_3GaNH_3 adducts are 0.001 Å shorter than that in free NH_3, possibly due to the overestimation of the N−H bond length in NH_3 at the B3LYP/pVDZ level of theory (Figure 1c). Major structural and thermodynamic properties of adducts are summarized in Table 1.

H_3GaNH_3. This donor−acceptor molecular complex has not been isolated. In contrast to the known H_3GaPH_3, an attempt to produce H_3GaNH_3 by direct reaction of digallane Ga_2H_6 with an excess of ammonia at −78 °C results in the formation of the involatile solid $[H_2Ga(NH_3)_4]^+[GaH_4]^-$;[41] H_2 elimination is not observed under these conditions. Our geometric parameters (Figure 2a) and vibrational frequencies for H_3GaNH_3 are in good agreement with previous theoretical assessments.[34,42] Cramer and Gladfelter computed a exothermicity for the H_3GaNH_3 dimerization of about 45 kJ mol^{-1} with almost no difference between the MP2 and B3LYP levels of theory.[43] This indicates that dimerization should be possible to a moderate degree in the gas phase, facilitating H_2 evolution and $[H_2GaNH_2]_3$ trimer formation.

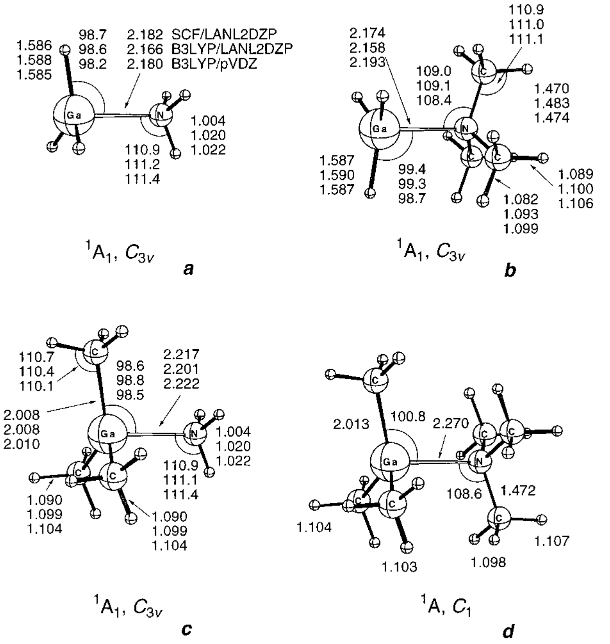

Figure 2. Geometries of adduct compounds: H_3GaNH_3 (a), $H_3GaN(CH_3)_3$ (b), $(CH_3)_3GaNH_3$ (c), and $(CH_3)_3GaN(CH_3)_3$ (d) at the SCF/LANL2DZP, B3LYP/LANL2DZP, and B3LYP/pVDZ (a−c) and B3LYP/pVDZ (d) levels of theory. Bond lengths are in Å, bond angles in degrees.

$(CH_3)_3GaNH_3$. This white crystalline product with melting point of 31 °C was the first adduct of TMG described in the literature.[44] The IR and Raman spectra in the solid state at 77 K, obtained by Durig and co-workers[45] and computed by Edwards and Jones,[34] have been assigned on the basis of C_{3v} symmetry. Our optimized geometric parameters of $(CH_3)_3GaNH_3$ are presented in Figure 2b. The gas-phase Ga−N stretching vibration is predicted by B3LYP/pVDZ to be at 285 cm^{-1}; this is lower than the experimental value of 357 cm^{-1} found in solid state,[45] but consistent with the early data of 289 cm^{-1} obtained by Edwards and Jones at the SCF/Huz43/1* level of theory.[34]

Comparing the ^1H NMR relative shift of the CH_3 protons of $(CH_3)_3GaNH_3$ with literature data for other adducts, Lieb et al.[46] estimated a dissociation enthalpy of 77.4 kJ mol^{-1} for $(CH_3)_3GaNH_3$. Our B3LYP/pVDZ result of 75.5 kJ mol^{-1} is in good agreement with Lieb's estimate. $(CH_3)_3GaNH_3$ begins to evolve CH_4 at 70 °C, and at 120 °C it decomposes to give

$[Me_2GaNH_2]_3$.[3] On further heating to 140 °C and above, more CH_4 is evolved and a white polymeric material, probably $(-Ga(CH_3)\text{-}NH-)_n$, is formed.[47] Thermal decomposition of both TMG and $TMGNH_3$ obey first-order kinetics, while thermal decomposition of ammonia is a second-order kinetic process.[48]

$H_3GaN(CH_3)_3$. Geometric parameters for this extensively studied adduct are presented in Figure 2c. IR and Raman spectroscopy of a $Ga_2H_6-N(CH_3)_3$ mixture at 77 K revealed the formation of 2 products: $GaH_3\cdot 2NMe_3$ and H_3GaNMe_3.[41] Gallane derivatives with bifunctional donors have been studied by O'Hare et al.[49] For the solid $(GaH_3)_2$tmea (tmea = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) they found a Ga−N distance of 2.085(3) Å and Ga−H distances ranging from 1.32(7) Å up to 1.54(6) Å. The Ga−N stretching mode has been assigned at 488 cm^{-1} in the gas phase,[50] and 508 cm^{-1} in solid phase.[51] Our B3LYP/pVDZ (unscaled) result is 474 cm^{-1}. X-ray diffraction analysis of single crystals of $H_3GaN(CH_3)_3$ revealed a rhombohedral lattice with $z = 1$. The Ga−N bond length of 1.97(9) Å was reported to have a large uncertainty, while the hydrogen atoms could not be located.[52] The microwave spectroscopic gas-phase Ga−N distance is 2.111(2) Å,[51] and 2.124 Å according to gas-phase electron diffraction.[53] It should be noted that our computed Ga−H distance of 1.587 Å is in agreement with the 1.59 derived from the microwave data,[51] but significantly longer than the Ga−H bond length of 1.498 Å determined by gas-phase electron diffraction.[53] This disagreement is probably caused by bond shrinkage during the gas-phase electron diffraction experiment[54] and by the large uncertainty of the experimental data due to possible complex dissociation under the experimental conditions.

Recently the molecular structure of H_3GaNMe_3 has been revisited by Downs and co-workers[55] on the basis of gas-phase electron diffraction, X-ray diffraction and ab initio studies. According to their findings, both Ga−N (2.139 Å) and Ga−H (1.522 Å) bonds are longer than obtained previously from experiment,[51−53] but shorter than our B3LYP/pVDZ results. The Ga−N bond in Me_3GaNH_3 (2.22 Å) is 0.03 Å longer than in H_3GaNMe_3 (2.19 Å) according to our computations; the same trend is observed experimentally: 2.17 Å for Me_3GaNH_3[56] and 2.14 Å for H_3GaNMe_3.[55]

The dissociation energy of H_3GaNMe_3 was computed by Downs and co-workers at the MP2/6-31G(d) and MP2/6-311G-(d,p) levels of theory to be 164 and 167 kJ mol^{-1}, respectively.[55] This value seems to be too high; for the Al analogue Marsh and Schaefer predicted a dissociation energy of 130 kJ mol^{-1} at the CCSD/DZP level of theory,[22] but according to trends established for the group 13−15 complexes,[57] the dissociation enthalpy should be *lower* for the Ga than for the Al species. Under complex formation with NMe_3 the GaH_3 fragment is less distorted from planarity than AlH_3 (the HGaN angle is 99.3°, and the HAlN angle is 104.3°), which also indicates weaker bonding in the case of GaH_3. The HGaN bond angles, predicted both by MP2[55] and B3LYP (present work) methods are in good agreement with experimental findings.[55]

Our predicted B3LYP/pVDZ dissociation ($H_3GaNMe_3 \rightarrow H_3Ga + NMe_3$) enthalpy of 88 kJ mol^{-1} is about 80 kJ mol^{-1} lower than at MP2,[55] and the B3LYP result agrees well with the trends discussed above.[57] Such a significant difference between DFT and MP2 may be caused by the frozen core approximation used by Downs and co-workers.

$(CH_3)_3GaN(CH_3)_3$. Although this adduct is not formed during the CVD process from TMG and ammonia, it can be used for GaN deposition in ammonia atmosphere at 850−1000 °C.[79] The $(CH_3)_3GaN(CH_3)_3$ complex has been studied extensively experimentally.[58,59] The structure with staggered methyl groups was optimized here in C_{3v} symmetry, and has one imaginary frequency (A_2 symmetry, value of $5i$ cm^{-1}) corresponding to the rotation around the Ga−N bond. A saddle point is also obtained with the finer integration grid. Since our goal in this case was to test experimental and computed bond dissociation energies, we did not perform any further steps to locate the minimum with highest point group symmetry on the PES. Optimization in C_1 symmetry leads to a structure (Figure 2d) which has a low 12 cm^{-1} frequency mode. As has been shown previously, the rotational barriers in adducts are quite small[57] and will not significantly change the bond dissociation energy. The calculated Ga−N and Ga−C bond lengths (2.27 and 2.01 Å) in the asymmetric C_1 $(CH_3)_3GaN(CH_3)_3$ structure are somewhat larger than the experimental values of 2.20[58a] (2.09[58b]) and 1.998[58a] (1.989[58b]) Å, and at the same time the predicted N−C distance of 1.472 Å is slightly shorter compared to the experimental value of 1.484 Å. The C−Ga−C (116.6°) and C−N−C (110.4°) bond angles are in excellent agreement with experiment (116.7° and 109.6°, respectively).

There are some discrepancies in the literature concerning experimental values of the dissociation enthalpy and entropy for $(CH_3)_3GaN(CH_3)_3$. The values of 72 kJ mol^{-1} and 145 J mol^{-1} K^{-1}, for ΔH and ΔS, respectively, published in the review by Goldshtein and co-workers[60] and reproduced in Gmelin's handbook[61] originate from the early work of Stevens, Park, and Oliver,[62] and in fact correspond to the dissociation enthalpy and entropy of $(C_2H_5)_3GaN(CH_3)_3$, but not $(CH_3)_3GaN(CH_3)_3$. The latter authors, however, as well as Lieb et al.[46] provide a value of 88 kJ mol^{-1} for the dissociation enthalpy of $(CH_3)_3GaN(CH_3)_3$, reportedly to be taken from the early studies of Coates.[47,63] But there is no dissociation enthalpy of $(CH_3)_3GaN(CH_3)_3$ reported in the cited Coates papers;[47,63] the estimated 88 kJ mol^{-1} value comes from the book by Coates.[64] Our predicted gas-phase value of 56 kJ mol^{-1} is somewhat lower than this 88 kJ mol^{-1} experimental estimate. The difference may be caused by additional stabilization of the complex in solution. The order of the dissociation enthalpies (in kJ mol^{-1}) for $GaMe_3$ as obtained from experiment [$NH_3(77) < NMe_3$ (88)], is opposite to the B3LYP/pVDZ prediction: NH_3 (76) > NMe_3 (56). However, the latter order is in qualitative agreement with the order found experimentally for the $GaEt_3$ acceptor: NH_3 (80) > NMe_3 (71).[46]

B. $R_2GaNR'_2$ ($R, R' = H, CH_3$) Compounds with Tricoordinated Ga and N Centers. The facile methane loss from the $R_3GaNR'_3$ adducts discussed above leads formally to the formation of tricoordinated monomer compounds. Properties of these yet unknown species are presented in this section. Geometric parameters are given in Figure 3, and thermodynamic properties are summarized in Table 1. H_2GaNH_2 is found to be planar and to have C_{2v} symmetry (Figure 3a), in agreement with the aluminum analogue studied by Davy et al.[65] H_2GaNMe_2 and Me_2GaNH_2 with tricoordinated Ga and N centers do not exist in monomeric form as they undergo fast dimerization and trimerization to yield the well-known $[H_2GaNMe_2]_2$[66] and $[Me_2GaNH_2]_3$.[3] However, in 1996 Müller reported IR data for the matrix-isolated aluminum analogue Me_2AlNH_2 along with results from ab initio computations.[67] Our optimized Me_2GaNH_2 structure of C_{2v} symmetry (Figure 3c) agrees well with that obtained by Müller for Me_2AlNH_2. Me_2GaNMe_2 is asymmetric, in contrast to hydrogen analogues, probably because of intramolecular interactions of the methyl groups. The same symmetry lowering was observed for the Me_3GaNMe_3 compound studied in the present work.

TABLE 2: Structural and Thermodynamic Trends for $R_xGaNR'_x$ Compounds[a] from the B3LYP/pVDZ Level of Theory

x	R,R′	$\Delta r_{(Ga-R)}$, Å (%)	$\Delta r_{(N-R')}$, Å (%)	$\Delta r_{(Ga-N)}$, Å (%)	$\Delta\alpha_{(RGaN)}$, deg (%)	$\Delta\alpha_{(GaNR')}$, deg (%)	$\Delta\Delta H^{diss}$, kJ mol^{-1}
3	H,H	0.019 (1.2)	0.007 (0.7)	0.360 (16.5)	18.4 (18.7)	12.9 (11.6)	−281.4
	H,CH_3	0.021 (1.4)	0.025 (1.7)	0.356 (16.3)	17.8 (18.0)	12.3 (11.1)	−233.0
	CH_3,H	0.027 (1.4)	0.007 (0.7)	0.391 (17.6)	18.5 (18.8)	13.1 (11.8)	−302.2
	CH_3,CH_3	0.028 (1.4)	0.024 (1.6)	0.418 (18.4)	17.3 (17.1)	15 (13.8)	−254.2
2	H,H	0.032 (2.0)	−0.005 (0.5)	0.126 (6.9)	44.9 (38.5)	1.7 (1.4)	116.1
	H,CH_3	0.040 (2.6)	0.029 (2.0)	0.161 (8.8)	41.6 (35.7)	28.3 (22.9)	121.1
	CH_3,H	0.033 (1.6)	−0.006 (0.6)	0.130 (7.1)	44.7 (38.2)	−0.6 (0.5)	113.4
	CH_3,CH_3	0.037 (1.9)	0.025 (1.7)	0.169 (9.1)	40.1 (33.9)	25.9 (20.9)	117.5

[a] $\Delta r_{(Ga-R)}$, $\Delta r_{(N-R')}$, $\Delta r_{(Ga-N)}$ denotes the corresponding bond length difference between $R_xGaNR'_x$ and $R_{x-1}GaNR'_{x-1}$ compounds. $\Delta\alpha_{(RGaN)}$ and $\Delta\alpha_{(GaNR')}$ denotes the corresponding bond angle difference between $R_{x-1}GaNR'_{x-1}$ and $R_xGaNR'_x$ compounds. $\Delta\Delta H^{diss}$ denotes difference between the standard dissociation enthalpy of $R_xGaNR'_x$ and $R_{x-1}GaNR'_{x-1}$ compounds: $\Delta\Delta H^{diss} = \Delta H^{diss}_{298}(R_xGaNR'_x) - \Delta H^{diss}_{298}(R_{x-1}GaNR'_{x-1})$.

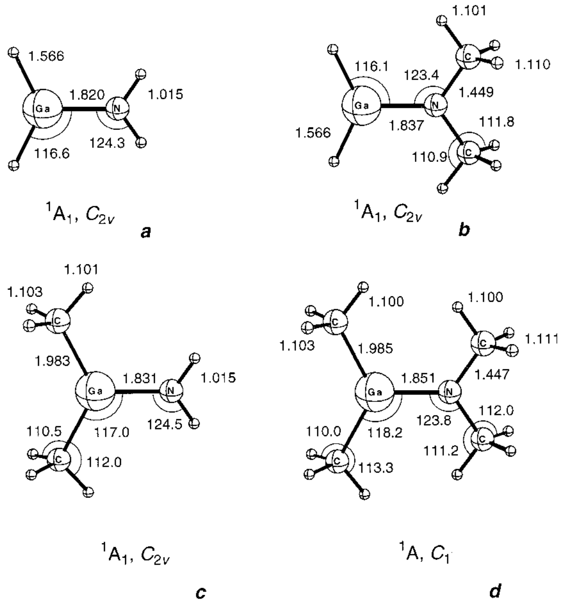

Figure 3. Geometries of $R_2GaNR'_2$ monomer compounds: H_2GaNH_2 (a), $H_2GaN(CH_3)_2$ (b), $(CH_3)_2GaNH_2$ (c), and $(CH_3)_2GaN(CH_3)_2$ (d) at the B3LYP/pVDZ level of theory. Bond lengths are in Å, bond angles in degrees.

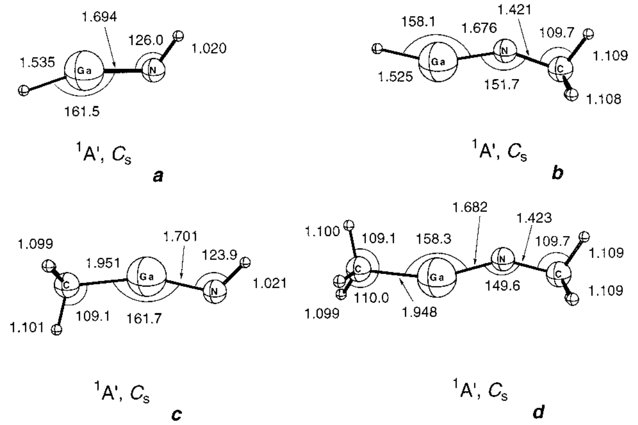

Figure 4. Geometries of RGaNR′ monomer compounds: HGaNH (a), $HGaN(CH_3)$ (b), $(CH_3)GaNH$ (c), and $(CH_3)GaN(CH_3)$ (d) at the B3LYP/pVDZ level of theory. Bond lengths are in Å, bond angles in degrees..

Several monomeric gallium monoamides with bulky substituents (R = *t*-Bu; trip = 2,4,6-*i*-$Pr_3C_6H_2$; R′ = *t*-Bu, $SiPh_3$, 1-Ad, Ph, dipp = 2,4-*i*-PrC_6H_3) have been synthesized and structurally characterized by Power and co-workers in 1993.[68] In agreement with our results, $trip_2GaNPh_2$ has a planar C_2GaNC_2 core. All other compounds have nonequivalent substituents on the nitrogen atom and are distorted from planarity, as much as 88.7° in *t*-Bu_2GaN(*t*-Bu)$SiPh_3$. The computed Ga−N distances are shorter compared to experimental findings; this may be due to steric repulsion of the highly strained substituents.

As was shown by Barry and Richeson in 1996,[69a] monomer amidocomplexes can be stabilized by introducing oxygen or nitrogen-containing Lewis donors. In fact, these authors spectroscopically identified formation of *n*-Bu_2GaNH(*t*-Bu)·THF and $Bu_2GaNH(2,6\text{-}C_6H_3Me_2)\cdot Py$, but there are no structural data available. Without a donor molecule the formation of the dimeric species [*t*-Bu_2GaNH(*t*-Bu)]$_2$ was observed. It is assumed that the THF and Py donor molecules are coordinated to the Ga center thereby blocking oligomerization processes. Very recently, quinuclidine-stabilized monomeric monoamidogallane $H_2GaN(SiMe_3)_2$-quin has been structurally characterized by Gladfelter and co-workers.[69b] It was found that quinuclidine coordinates to the Ga center, which adopts a distorted tetrahedral geometry. These results indicate that during the CVD process using an excess of ammonia, additional coordination of NH_3 to the tricoordinated Ga center should be possible.

Since the coordination number on the Ga and N centers decreases from four in $R_3GaNR'_3$ to three in $R_2GaNR'_2$, all bond lengths are shortened, and the RGaN and GaNR′ angles are widened. Ga−N bond lengths change considerably (by 0.35−0.42 Å, Table 2). This significant bond shrinkage agrees well with the increase of the GaN dissociation enthalpy (by 230−300 kJ mol^{-1}). For the terminal bonds this trend is less pronounced: bond shortening for Ga−C, Ga−H, N−C, N−H bonds is about 0.7−1.7% compared to 16−18% for the Ga−N bond.

C. RGaNR′ (R, R′ = H, CH_3) Compounds with Dicoordinated Ga and N Centers. These compounds have the formal composition $GaNH_2$ and $GaCNH_4$, and for them many different isomers are possible. The RGaNR′ ligand arrangement is not expected to be energetically the most favorable one, since Davy and Jaffrey[65] pointed out that for the aluminum analogue the HAl−NH structure lies 41 kcal mol^{-1} higher in energy than the Al−NH_2 minimum. We report here the structures (Figure 4) and thermodynamic properties (Table 1) of RGa−NR′ isomers only as these are monomer building blocks for larger associated species, which will be discussed in the following report (see the second part of this series: “Structures of Oligomers and Thermodynamics Association Processes”[80]). Since it was shown for ClAlNH that the triplet state lies 100 kJ mol^{-1} above the singlet at B3LYP/DZP,[70] only singlet states are considered here. Our bend C_s symmetric structure for HGaNH agrees well with the one obtained by Davy for HAl−NH at the CCSD/TZ2P level of theory.[65] The Ga−N distance in RGaNR′ compounds is further decreased compared to tricoordinated species $R_2GaNR'_2$

(by 7−9%), but the Ga−N bond dissociation enthalpy is 110−120 kJ mol^{-1} lower than its value for $R_2GaNR'_2$ (Table 2). This difference in dissociation enthalpies may be attributed to the high instability of the R_2Ga and NR'_2 radicals which leads to extremely high dissociation enthalpies for $R_2GaNR'_2$. Compared to $R_2GaNR'_2$, all RGaN angles are further increased by more than 40°, the GaNC angles are increased by 25−30°, but GaNH angles stay essentially the same.

D. General Remarks on Monomer Compounds. The Ga−N bond distance is strongly influenced by the coordination number of the Ga and N centers. This effect is 10 times smaller (Table 2) for the Ga−R and N−R′ terminal bonds, and the C−H bond distances in the methyl groups are hardly influenced by complex formation. All Ga−R and N−R bond lengths increase due to complex formation of tetracoordinated $R_3GaNR'_3$ donor−acceptor adducts. In contrast, additional bond formation stabilizes N−H, Ga−H, and Ga−C bonds in tri- and dicoordinated compounds, since their bond length in the complexes is shorter by 0.03, 0.11, and 0.17 Å compared to free molecules. The notable exception is the N−C bond in $N(CH_3)_x$ which lengthens under complex formation by 0.011−0.026 Å regardless of the coordination number.

The influence of the methyl group rotation in the complexes is studied at the SCF/LANL2DZP level of theory. A structure of $H_3GaN(CH_3)_3$ with three methyl groups rotated (Hessian index 3) lies 66 kJ mol^{-1} higher in energy than the minimum (Figure 2b), in good agreement with the 64 kJ mol^{-1} (SCF/DZP) difference obtained for the aluminum system $H_3AlN(CH_3)_3$ by Marsh and Schaefer.[22] Methyl group rotation causes an increase of the Ga−N bond length by 0.023 Å (from 2.174 to 2.197 Å). Rotation of three methyl groups is energetically less demanding for the $(CH_3)_3GaNH_3$ compound: the rotated structure (Hessian index three) lies only 9 kJ mol^{-1} higher in energy than the minimum (Figure 2c). Also the increase of the Ga−N distance is smaller: only 0.013 Å (from 2.217 to 2.230 Å). These results suggest that the smaller nitrogen center has higher sensitivity toward the steric effects of the methyl groups than the gallium center.

$(CH_3)_xGaNH_x$ compounds are 55, 97, and 117 kJ mol^{-1} more stable thermodynamically than their $H_xGaN(CH_3)_x$ isomers ($x = 1, 2, 3$, respectively). However, the relative isomer stability and the Ga−N bond dissociation enthalpies do not correlate, i.e., the lower total energy of $(CH_3)_xGaNH_x$ is not necessarily due to a stronger Ga−N bond. In fact, the less stable $H_3GaN(CH_3)_3$ isomer has an even larger Ga−N dissociation enthalpy (88 kJ mol^{-1}), than the more favorable isomer $(CH_3)_3GaNH_3$ (76 kJ mol^{-1}).

The Ga−N bond dissociation enthalpies (given in kJ mol^{-1}) are the highest for $R_2GaNR'_2$ compounds (313−382), followed by RGaNR′ (196−266); and for donor−acceptor complexes $R_3GaNR'_3$ (56−100) they are the lowest. The high value of the Ga−N bond dissociation enthalpy for unsaturated $R_2GaNR'_2$ and RGaNR′ compounds may facilitate polymerization of these species, thereby preserving the Ga−N bond in the gas phase. We will discuss structural and thermodynamic properties of oligomer compounds in our following report (ref 80).

III. Preferable Distribution of Terminal Groups R and R′ (R, R′ = H, CH_3). Different distribution of substituents R, R′ = H, CH_3 is possible in the investigated GaN precursor species $R_xGaNR'_x$. Although the $(CH_3)_xGaNH_x$ species are more stable than their $H_xGaN(CH_3)_x$ isomers, the possibility of ligand exchange reactions (where CH_3 is replaced by H) has to be taken into account, especially as the CVD is often carried out in an excess of ammonia. Therefore, knowledge of the N−H, N−C, Ga−C, and Ga−H bond energies is essential. Bond energies are defined by Pauling “in such a way that their sum over all bonds of a molecule which can be satisfactorily represented by a single valence-bond structure is equal to the enthalpy of formation of the molecule from its constituent atoms in their normal states.”[71] The bond-dissociation energy of a bond in a molecule, on the other hand, is defined as “the energy required to break that bond alone, that is, to split the molecule into the two parts that were previously connected by the bond under consideration.”[71]

It is well-known from experiment that the N−H bond is stronger than the N−C bond by 105 kJ mol^{-1}.[72] Indeed, the total energies of all (Me, H) oligomer compounds studied are more than 100 kJ mol^{-1} lower than those of the (H, Me) isomers. Here and later on in this paper the notation (H, Me) indicates that the first substituent (H) is attached to the Ga center, and the second one (Me) to the nitrogen center, i.e., H_2GaNMe_2.

The corresponding data for bonds involving gallium are not well documented, since GaH_3 itself does not exist as a stable compound in the gas phase. Theoretical values for the Ga−H bond energy in GaH_3 are 260 kJ mol^{-1} (CASSCF/ECP),[31] 263 kJ mol^{-1} (QCISD/TZP),[73] and 271 kJ mol^{-1} (BLYP/DZP//LSDA/DZP).[74] The bond-dissociation energy of the first Ga−H bond in GaH_3 is 338.7 kJ mol^{-1}.[31] The Ga−C bond energy, 237 ± 17 kJ mol^{-1} according to Gmelin’s handbook,[61] was revised to 253.4 ± 10.9 kJ mol^{-1} by Bock and Trachtman[27] in 1994. The bond-dissociation energy of the first Ga−C bond in $GaMe_3$ is estimated as 322.2 kJ mol^{-1} at the MP2(full)/HUZSP-(2d,p) level of theory.[27]

Hence, previous data suggests that the bond energies and the bond-dissociation energies of Ga−H are slightly larger than that of Ga−C bonds. However, one should be careful when comparing these data directly since they were produced by different experimental techniques or predicted at different levels of theory. Therefore, we find it desirable to estimate the difference of the Ga−C and Ga−H bond energies based on data obtained at a uniform level of theory, but not via the direct computation of atomization energies of GaH_3 and $Ga(CH_3)_3$ as this would not be very reliable using DFT.

A. Estimation of Ga−H Bond Energy. The difference of the Ga−H and Ga−C bond energies can be estimated from the dissociation energies and total energies obtained in the present study. Recently Yang and co-workers[74] successfully utilized known bond energies to estimate unknown M−Y bond energies for a large group of inorganic ring compounds $[H_2MYH_2]_2$ and $[H_2MX]_2$, where M = Al, Ga, In; Y = P, As; X = Cl, Br. The necessary M−H and Y−H bond energies were derived from the atomization energies of MH_3 and YH_3. Because the definition of the bond energy is molecule specific, the question arises whether the M−H and Y−H bond energies of MH_3 and YH_3 can be transferred to the $[H_2MYH_2]_2$ and $[H_2MX]_2$ systems. Yang et al. used the change of the length of the bond under consideration as a criterion for transferability and concluded that bond energies are transferable if the change in bond length is less than 0.01 Å. Employing a fitting procedure, Yang and co-workers[74] found bond energies for all compounds by two different methods and concluded that the close agreement of the data obtained strongly supports the assumption of the transferability of the bond energies and the validity of the bond energy model employed.

Of course, bond energies cannot be transferred to other systems generally.[75] Following Yang et al.[74] we use the change in bond length as a criterion to judge whether bond energies may be transferred. For all investigated compounds, the C−H bond is longer than in free CH_4, but the maximum difference is only 0.01 Å (in the case of trimethylamine), which is only a 0.9% change in bond length. Only the Ga−N bond length differs significantly among the compounds investigated, ranging from 2.27 Å in Me_3GaNMe_3 to 1.68 Å in HGaNMe (Table 1). Such significant changes cannot be neglected, and therefore it is necessary to choose such reactions for deriving the bond energy, which do not include species with significantly different Ga−N bond lengths. To estimate the Ga−H bond energy, the dissociation processes of the (Me, H) and (H, Me) isomers of $R_3GaNR'_3$ have been considered, and additional information on the Ga−N bond dissociation energies for the isomers was used.

For example, let us consider dissociation processes for H_3GaNMe_3 (**1**) and Me_3GaNH_3 (**2**) isomers, eqs 1 and 2.

$$H_3GaNMe_3 = H_3Ga + NMe_3,\ \Delta H^{diss}{}_1 = 88.0\ \text{kJ mol}^{-1} \quad (1)$$

$$Me_3GaNH_3 = Me_3Ga + NH_3,\ \Delta H^{diss}{}_2 = 75.6\ \text{kJ mol}^{-1} \quad (2)$$

In terms of bond energies, the dissociation enthalpy can be presented as the sum of Ga−N bond energy and reorganization energy of free components:

$$\Delta H^{diss}{}_1 = E_{Ga-N1} + E_{reor1},\ \text{ and } \Delta H^{diss}{}_2 = E_{Ga-N2} + E_{reor2}$$

The difference of Ga−N bond energies between (**1**) and (**2**) may be presented as

$$E_{Ga-N1} - E_{Ga-N2} = \Delta H^{diss}{}_1 - \Delta H^{diss}{}_2 + (E_{reor2} - E_{reor1}) = 12.4 + (E_{reor2} - E_{reor1})\ (\text{kJ mol}^{-1})$$

The value of the reorganization energies E_{reor1} and E_{reor2} is first of all associated with the distortion of the acceptor fragment from planarity, since the structural changes of donor fragments are less pronounced.[37] This energy was found not to exceed 30 kJ mol^{-1} for metal halide systems, where structural changes are the largest. For example, the distortion energies are 28 kJ mol^{-1} for $AlCl_3$ (distortion angle 10.8°, B3LYP/DZP) and 30 kJ mol^{-1} for $GaCl_3$ (distortion angle 10.9°, SCF/HUZSP*[76]) but only 0.2 kJ mol^{-1} (B3LYP/DZP) for the almost unperturbed NH_3 fragment. The distortion angles are much smaller for R_3GaNR_3' adducts (8.5° for TMG and 8.2° for GaH_3) and therefore the difference of reorganization energies of the two isomers is close to zero:

$$E_{reor2} - E_{reor1} \approx 0,\ \text{ and } E_{Ga-N1} - E_{Ga-N2} \approx 12.4\ (\text{kJ mol}^{-1})$$

All errors associated with the reorganization energies of the fragments are accumulated in this value ($E_{reor2} - E_{reor1}$) and may approximately cancel each other, since the changes in bond lengths and bond angles are in the same order for both isomers.

Furthermore, we can represent the atomization enthalpies ΔH^{at} of isomers (**1**) and (**2**) in terms of bond energies:

$$\Delta H^{at}{}_1 = 3E_{Ga-H} + E_{Ga-N1} + 3E_{N-C} + 9E_{C-H}$$

$$\Delta H^{at}{}_2 = 3E_{Ga-C} + E_{Ga-N2} + 3E_{N-H} + 9E_{C-H}$$

therefore,

$$\Delta H^{at}{}_1 - \Delta H^{at}{}_2 = 3(E_{Ga-H} - E_{Ga-C}) + E_{Ga-N1} - E_{Ga-N2} + 3(E_{N-C} - E_{N-H})$$

The total energy difference of the two isomers is equal to the difference of their atomization enthalpies, taken with opposite sign:

$$E^{tot}{}_1 - E^{tot}{}_2 = -(\Delta H^{at}{}_1 - \Delta H^{at}{}_2) = 107.2\ \text{kJ mol}^{-1}$$

Assuming that the bond energies given in the literature[72] (E_{N-H} = 391 kJ mol^{-1}, and E_{N-C} = 286 kJ mol^{-1}) can be transferred to our systems, and using the $E_{Ga-N1} - E_{Ga-N2}$ value calculated above, we obtain

$$(E_{Ga-H} - E_{Ga-C}) = 65.1\ \text{kJ mol}^{-1}$$

This value agrees with the ones found for the neighbor elements: for example, the difference of Ge−H and Ge−C bond energies is about 40 kJ mol^{-1}.[72]

Combining this E_{Ga-H} − E_{Ga-C} value with the experimental Ga−C bond energy of 237 ± 17 kJ mol^{-1},[61] we obtain a bond energy for the Ga−H bond of 301 ± 23 kJ mol^{-1}. This value is close to the 271.3 kJ mol^{-1} predicted by Yang and co-workers at the BLYP/DZP//LSDA/DZP level of theory.[74] We conclude that the Ga−H bond is stronger than the Ga−C bond by more than 60 kJ mol^{-1} according to our approximate method (this is much higher than the literature values of about 10 kJ mol^{-1}).

B. Ligand Exchange. Since both Ga−CH_3 and N−CH_3 bonds are weaker than their hydrogen counterparts, formation of Ga−H and N−H bonds might occur under MOCVD conditions, especially when ammonia or hydrogen are used as carrier gases. Although this conclusion is solely based on our thermodynamical analysis, several experimental observations indicate that alkyl vs. hydrogen exchange might be viable. Müller and co-workers found an example for such a reaction using the intramolecularly coordinated alanes $Me_2N(CH_2)_3AlX_2$ (X = Cl, Br),[78] and gallanes $Me_2N(CH_2)_3GaMe_2$[28c] which have H atoms in β-position to the metal. At high temperatures the formation of $HAlX_2$ (X = Cl, Br) (temperature 1000 °C) and Me_2GaH, $MeGaH_2$ and GaH_3 (starting from 600 °C) is observed as identified from matrix-isolation IR spectroscopy. For the CVD of GaN from single molecule organogallium azide compounds, Miehr et al. concluded that "the azide group is probably not playing the dominant role as N-source for GaN growth, as previously has been suggested."[77]

There are also more general indications for such an alkyl vs hydrogen exchange. Ammonia and hydrogen as carrier gases significantly reduce carbon contamination and improve the yield of GaN from the CVD of organogallium systems.[2] But very high temperatures are needed during the final stages of the production of high-purity GaN. This might be due to the high thermal stability of Ga−H and N−H bonds, which were formed from NH_3 and H_2 in the earlier stages of the reaction. A reluctance toward dissociation of terminal bonds is observed for H_3GaNH_3: elimination of H_2 is endothermic (52 kJ mol^{-1}), while methane elimination is exothermic by −24.1 and −7.3 kJ mol^{-1} for H_3GaNMe_3 and Me_3GaNH_3 adducts, respectively, and ethane elimination is also exothermic by −19 kJ mol^{-1} for Me_3GaNMe_3 (Table 3). Also, the morphology of the produced GaN is strongly dependent on the H_2 gas flow,[9a] and if the reaction of TMG with NH_3 is precluded by using a separate flow reactor a better quality of GaN epitaxial layers is obtained.[9b]

Note that even in excess ammonia and at high reactor temperatures, carbon contamination in GaN persists (0.2% at 1300 K).[1] This leads us to the hypothesis that carbon is incorporated into the GaN lattice and therefore is bound more strongly, whereas hydrogen, which cannot be bound chemically in the films, is eliminated at elevated temperatures. Since the

TABLE 3: Dissociation and Elimination Enthalpies (kJ mol^{-1}) for Some Complexes at the B3LYP/pVDZ Level of Theory

	R,R′				
process	Me,Me	Me,H	H,Me	H,H	Cl_3AlNH_3[a]
dissociation: $R_3GaNR'_3 = R_3Ga + NR'_3$	56	76	88	100	149
elimination: $R_3GaNR'_3 = R_2GaNR'_2 + RR'$	−19	−7	−24	52	196

[a] Reference 70, B3LYP/DZP level of theory.

process of carbon incorporation into the GaN lattice may require several steps, several different intermediates with Ga−N and Ga−C bonds may be formed. It should be noted that a Ga−C bond can be more favorable than a Ga−N bond. For example, the bonding to CN groups via carbon is more than 70 kJ mol^{-1} more favorable for $Ga(CN)_3$ than bonding via nitrogen in $Ga(NC)_3$.[79] The possible formation of oligomeric compounds with Ga−C−N skeletons under CVD conditions is an intriguing question, but lies out of the scope of this paper.

Conclusions

The thermodynamic characteristics of dissociation and elimination processes of the source adducts are summarized in Table 3. Unlike the $AlCl_3NH_3$ adduct, where HCl elimination reactions are favorable only if oligomeric species are formed,[70] dihydrogen or methane eliminations from H_3GaNH_3, Me_3GaNH_3, and H_3GaNMe_3 adducts are much more favorable than dissociation into gaseous components, even in the case of formation of monomer species with tricoordinated Ga and N centers (Table 3). This is in part due to the lower stability of the organogallium complexes ($\Delta H^{\rm diss}$ = 60−100 kJ mol^{-1}) compared to the strongly bonded aluminum chloride−ammonia complex (149 kJ mol^{-1}). Therefore, no H_3GaNH_3, Me_3GaNH_3, nor H_3GaNMe_3 complexes exist in the gas phase at elevated temperatures, and as the temperature increases, dihydrogen or methane loss is favorable, in agreement with experimental observations. The Ga−N bond dissociation enthalpies (given in kJ mol^{-1}) are the highest for $R_2GaNR'_2$ compounds (313−382), followed by RGaNR′ (196−266); and for donor−acceptor complexes $R_3GaNR'_3$ (56−100) they are the lowest. The high value of Ga−N bond dissociation enthalpy for unsaturated $R_2GaNR'_2$ and RGaNR′ compounds may facilitate polymerization of these species, thereby preserving the Ga−N bond in the gas phase. $(CH_3)_xGaNH_x$ compounds are 55, 97, and 117 kJ mol^{-1} more stable thermodynamically than their $H_xGaN(CH_3)_x$ isomers (x = 1, 2, 3, respectively). All estimates suggest that the $E_{\rm Ga-H} - E_{\rm Ga-C}$ energy difference (65 kJ mol^{-1}) is lower than the $E_{\rm N-H} - E_{\rm N-C}$ difference (105 kJ mol^{-1}), which energetically makes Ga−H, N−H the best possible ligand arrangement. From these data it is important to conclude that the chemistry of a gallium hydride species might be important for the CVD process even if organogallium precursors are used.

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Supporting Information Available: Harmonic vibrational frequencies and IR intensities for investigated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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