

Reactions of *cis*-2,3-Dimethylaziridine, 3-Pyrroline and Pyrrolidine with Me₃Al and Me₃Ga: Adducts and Dimeric Amides

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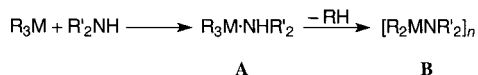
The reactions of Me₃Al and Me₃Ga with *cis*-2,3-dimethylaziridine (**1-H**), 3-pyrroline (**2-H**) and pyrrolidine (**3-H**) have been investigated. At room temperature, monomeric adducts [Me₃M·LH] are obtained (M = Al, Ga; L = **1–3**). [Me₃Al·**1-H**] is the first example of a structurally characterized adduct of an aziridine and a group 13 metal. On heating in mesitylene, all adducts except [Me₃Ga·**2-H**] evolve methane to form the corresponding amides; the Ga complexes require somewhat higher temperatures for this reaction. In contrast to the unsubstituted aziridine derivatives (which are *trimers*), dimethylaziridine amides Me₂M-**1** are *dimers*, as shown by X-

ray crystallography. NMR spectroscopic data suggest the occurrence of a *cis-trans* equilibrium for these dimers in solution. For the pyrroline and pyrrolidine derivatives, the X-ray structures suggested large changes in the C–C and C–N bond lengths on formation of the adducts and amides. However, DFT calculations reveal that these changes are artefacts, and that the real bond length changes are fairly modest.

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Introduction

Compounds containing both a group 13 (Al, Ga) atom and nitrogen are of considerable interest, owing to their potential use as single-source precursors for the fabrication of aluminium/gallium nitrides. Two common types of single-source precursors are trialkylmetal–amine adducts **A** and their alkane elimination products **B**. A drawback of adducts **A** is that they dissociate relatively easily into their trialkylmetal and amine components. Amides **B** do not suffer from this problem, but they are invariably associated (into dimers or higher) and thus have a reduced volatility (Scheme 1).

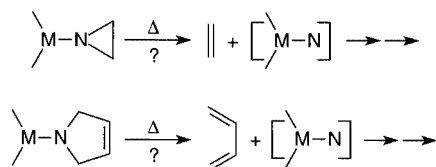


Scheme 1

Despite these disadvantages, both types of compounds have been studied for their potential as MOCVD pre-

cursors. Aluminium amides and imides have been studied extensively,^[1] and several Me₃Al–secondary amine adducts have been reported.^[2] Gallium amides have been synthesized by hydrocarbon or salt elimination reactions^[3] or by other means.^[4] Several metallacyclic aluminium and gallium nitrogen compounds have also been reported.^[5]

We were interested in preparing aluminium/gallium adducts or amides in which the amide could easily lose its hydrocarbon fragment through some kind of elimination reaction, potentially providing lower decomposition temperatures and/or reduced carbon contamination of the nitride formed. We chose the aziridinyl and 3-pyrrolinyl fragments, which should easily eliminate an alkene or a diene, respectively, as represented schematically in Scheme 2.

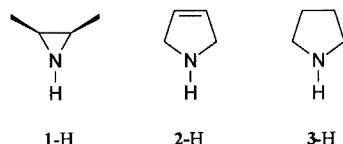


Scheme 2

Amides derived from the parent aziridine and Me₃Al^[5b] and GaH₃^[23] have been reported. These have trimeric structures, however, and hence a vapour pressure too low for convenient MOCVD usage. We have studied the reactions of Me₃Al and Me₃Ga with *cis*-2,3-dimethylaziridine **1-H**, in the hope of obtaining more volatile amides. No Al

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or Ga derivatives of 3-pyrroline (**2-H**) have yet been reported. Derivatives of the (presumably more stable) pyrrolidine (**3-H**) have been included here for comparison. Since **2-H** is expensive and the synthesis of the pure compound is cumbersome, we have also used a commercially available mixture of **2-H** and **3-H** (Scheme 3).



Scheme 3

Results and Discussion

Aziridine Adducts [Me₃M·1-H]

Treatment of Me₃M (M = Al, Ga) with dimethylaziridine in mesitylene at room temperature cleanly afforded the 1:1 Lewis acid-base adducts [Me₃M·1-H]. No further reaction to afford the amides occurred under these conditions. This is somewhat surprising, since Stucky reported that the reaction between Me₃Al and unsubstituted aziridine produced the amide [Me₂AlNC₂H₄]₃ directly, without formation of a detectable adduct ("solvated intermediate").^[5b] Also, Trotter described the formation of [H₂GaNC₂H₄]₃ from GaH₃·NMe₃ and aziridine at room temperature, again without a detectable intermediate.^[23] In our case, considerable heating (95 °C for Al, 155 °C for Ga) was required to induce methane elimination. It may be that the methyl substituents on the aziridine ring reduce its reactivity: in the adduct (see below), the amine proton is *cis* to the aziridine methyls, and is thus shielded by these groups as well as the bulky Me₃Al moiety. Another explanation might be that elimination is slower in the mesitylene solvent we use than in the neat aziridine employed by Stucky and Trotter.

As far as we are aware, [Me₃Al·1-H] is the first structurally characterized adduct of an aziridine with a group 13 metal (Al–Tl). Figure 1 shows the structure of the complex. The Me₃Al group is located *trans* to the aziridine

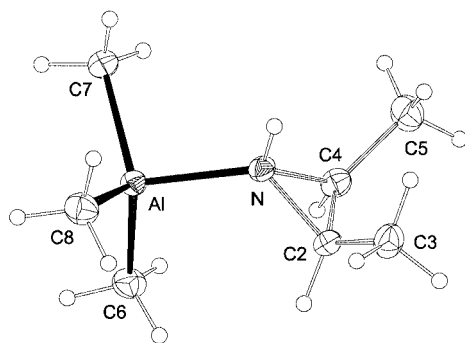


Figure 1. Molecular structure and atom numbering scheme for [Me₃Al·1-H]; selected bond lengths (Å): Al–C6 1.975(2), Al–C7 1.981(2), Al–C8 1.976(2), Al–N 1.977(2), N–C4 1.490(3), N–C2 1.495(2), C2–C4 1.472(3)

methyl groups. The C–N ring bonds [1.493(3) Å av] appear to be slightly elongated with respect to those observed for unsubstituted aziridine [1.467(3) av]^[15] and *cis*-2-methyl-3-phenylaziridine (1.475 av., no errors given),^[16] whereas the differences in C–C bond lengths are small [1.472(2) vs. 1.462(3) and 1.486, respectively]. The most notable changes in the ¹H NMR spectrum on formation of the adduct are a low-field shift of the NH proton ($\Delta\delta$ = 0.33 ppm) and a high-field shift of the aziridine methyl groups ($\Delta\delta$ = –0.64 ppm).

Aziridine Amides [Me₂M·1]₂

On heating in solution, the Al and Ga adducts both eliminate methane to give [Me₂Al·1]₂ and [Me₂Ga·1]₂, respectively. The amides, which are isostructural, crystallize as centrosymmetric dimers with a planar M₂N₂ ring; the aziridinyl and MMe₂ planes are nearly perpendicular to the M₂N₂ plane. Figure 2 shows the structure of the Al derivative. The bond lengths within the aziridinyl groups are virtually indistinguishable from those of adduct [Me₃Al·1-H]. These dimeric structures should be contrasted with the *trimeric* structures of the unsubstituted aziridinyl derivatives reported by Stucky,^[5b] Trotter^[23] and Müller,^[5c] in which the six-membered M₃N₃ rings are markedly twisted. It seems likely that the added bulk of the methyl substituents in **1** is responsible for the lower degree of association, as it would result in steric hindrance between these methyl groups and the MMe₂ unit *cis* to it in any trimeric ring structure. Indeed, increased steric hindrance at aluminium instead of at the aziridine also results in the formation of dimers, as illustrated by the structure of [(BH₄)₂AlNC₂H₄]₂.^[17]

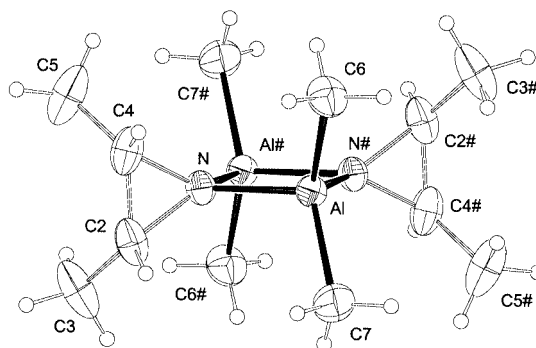
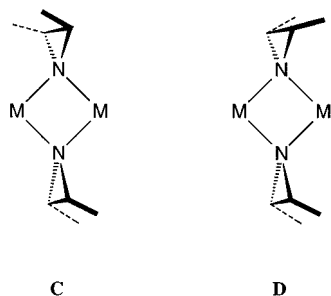


Figure 2. Molecular structure and atom numbering scheme for [Me₂Al·1]₂; selected bond lengths (Å): Al–C6 1.951(2), Al–C7 1.951(2), Al–N 1.938(2), Al–N# 1.929(2), N1–C4 1.489(2), N–C2 1.493(3), C2–C4 1.467(4); for the isostructural Ga complex: Ga–C6 1.955(8), Ga–C7 1.953(7), Ga–N 1.986(6), Ga–N# 2.000(5), N–C2 1.48(1), N–C4 1.49(1), C2–C4 1.47(1); # indicates symmetry-related atoms (–x, 1–y, 1–z)

In the solid state, both amides have a *trans* arrangement of the aziridine moieties (structure C). In solution, we see two sets of signals for the aziridine CH and CH₃ groups in a roughly 1:1 ratio; this is particularly clear in the ¹³C spectra [the CH₃(M) signals are broad and do not show a clear splitting]. This might indicate a dimer–trimer equilibrium, but in view of the concentration independence of this phe-

nomenon a more logical explanation would be a *cis-trans* equilibrium (e.g. **C** \rightleftharpoons **D**), apparently slow on the NMR timescale (Scheme 4).



Scheme 4

Pyrroline and Pyrrolidine Adducts, $[\text{Me}_3\text{M}\cdot\mathbf{2}\text{-H}]$ and $[\text{Me}_3\text{M}\cdot\mathbf{3}\text{-H}]$

Treatment of Me_3M with **2-H** and **3-H** at room temperature in toluene afforded the 1:1 Lewis acid-base adducts $[\text{Me}_3\text{M}\cdot\mathbf{2}\text{-H}]$ and $[\text{Me}_3\text{M}\cdot\mathbf{3}\text{-H}]$. No further reaction to afford the amides occurred under these conditions. A peak due to the NH group was observed in each ^1H NMR spectrum. Compared with those of free **2-H** and Me_3Al , the most notable changes in the ^1H NMR spectrum on formation of the adduct are a low-field shift of the NH proton ($\Delta\delta = 0.90$ ppm) and a high-field shift of the methyl groups of Me_3Al ($\Delta\delta = -0.17$ ppm). If a 2:1 mixture of **2-H** and **3-H** is used, the two adducts co-crystallize in approximately the same ratio as was present in solution. The crystal structures both of pure $[\text{Me}_3\text{Al}\cdot\mathbf{2}\text{-H}]$ and of the $[\text{Me}_3\text{Al}\cdot\mathbf{2}\text{-H}]/[\text{Me}_3\text{Al}\cdot\mathbf{3}\text{-H}]$ mixture were determined, and show only minor differences in bond lengths. Remarkably, pure $[\text{Me}_3\text{Al}\cdot\mathbf{3}\text{-H}]$ and $[\text{Me}_3\text{Ga}\cdot\mathbf{3}\text{-H}]$ crystallize in space groups different from those found for $[\text{Me}_3\text{Al}\cdot\mathbf{2}\text{-H}]$ and the co-crystal. However, the molecular conformations are fairly similar for all these compounds. Figure 3 shows the structures of $[\text{Me}_3\text{Al}\cdot\mathbf{2}\text{-H}]$ and $[\text{Me}_3\text{Al}\cdot\mathbf{3}\text{-H}]$. $[\text{Me}_3\text{Al}\cdot\mathbf{3}\text{-H}]$ has been prepared before, by Krannich.^[2a]

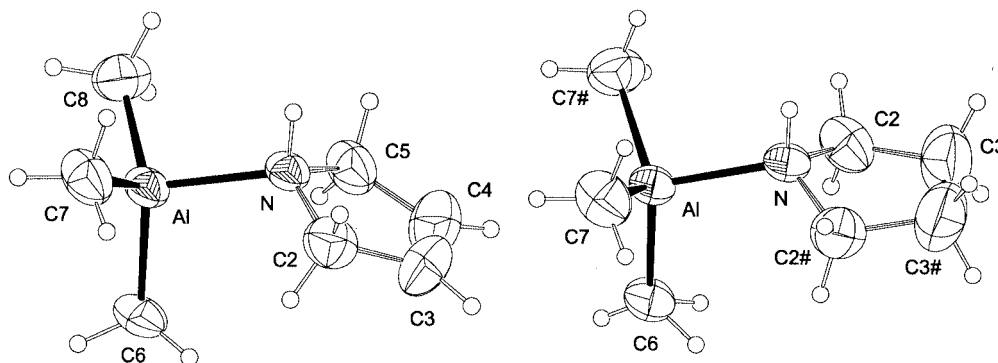


Figure 3. Structures of $[\text{Me}_3\text{Al}\cdot\mathbf{2}\text{-H}]$ (left) and $[\text{Me}_3\text{Al}\cdot\mathbf{3}\text{-H}]$ (right); selected bond lengths (\AA) for $[\text{Me}_3\text{Al}\cdot\mathbf{2}\text{-H}]$: Al–C6 1.984(3), Al–C7 1.966(5), Al–C8 1.963(4), Al–N 1.999(3), N–C2 1.485(5), N–C5 1.495(5), C3–C4 1.264(8); for $[\text{Me}_3\text{Al}\cdot\mathbf{3}\text{-H}]$: Al–C6 1.977(4), Al–C7 1.967(3), Al–N 1.997(3), N–C2 1.468(4), C3–C3# 1.48(1) where # indicates symmetry-related atoms ($x, 1/2-y, z$); for $[\text{Me}_3\text{Ga}\cdot\mathbf{3}\text{-H}]$ (refined in $P2_1$, i.e. not isostructural with $[\text{Me}_3\text{Al}\cdot\mathbf{3}\text{-H}]$): Ga–C6 2.00(1), Ga–C7 2.07(4), Ga–C8 1.91(4), Ga–N 2.11(1), N–C2 1.57(5), N–C5 1.38(5), C3–C4 1.53(3)

Pyrroline and Pyrrolidine Amides, $[\text{Me}_2\text{M}\cdot\mathbf{2}]_2$ and $[\text{Me}_2\text{M}\cdot\mathbf{3}]_2$

On heating in solution, the pyrroline and pyrrolidine adducts eliminate methane to give dimeric amides. Pyrroline appears to be a bit more reactive, and the Ga compounds require heating to higher temperatures than the Al compounds. Complex $[\text{Me}_2\text{Ga}\cdot\mathbf{2}]_2$ could not be prepared in this way, because disproportionation of the 3-pyrroline (to pyrrole, pyrrolidine and possibly 2-pyrroline) occurred at the temperature required for reaction. The other amides crystallize as dimers with planar or near-planar M_2N_2 rings, as shown in Figure 4 for $[\text{Me}_2\text{Al}\cdot\mathbf{2}]_2$ and in Figure 5 for $[\text{Me}_2\text{Ga}\cdot\mathbf{3}]_2$.

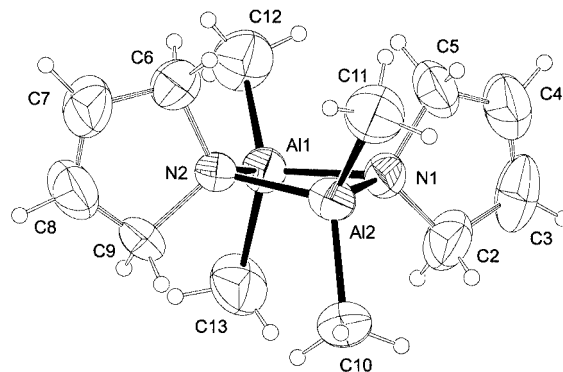


Figure 4. Structure of $[\text{Me}_2\text{Al}\cdot\mathbf{2}]_2$; selected bond lengths (\AA): Al1–C12 1.94(2), Al1–C13 2.00(1), Al1–N1 1.98(1), Al1–N2 1.92(1), Al2–C10 1.93(1), Al2–C11 1.98(2), Al2–N1 1.94(1), Al2–N2 1.94(1), N1–C2 1.46(2), N1–C5 1.51(2), C3–C4 1.33(2), N2–C6 1.50(1), N2–C9 1.52(1), C7–C8 1.27(2)

Bond Length Changes Associated with Adduct and Amide Formation

The availability of several X-ray structures of adducts and amides makes it tempting to evaluate the bond length changes accompanying formation of these adducts and amides. One should, however, be careful in doing this for two reasons:

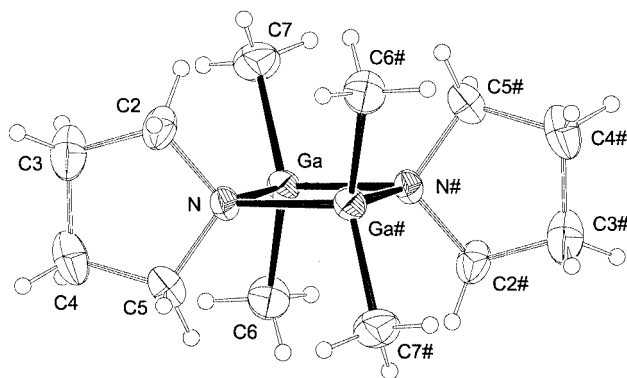


Figure 5. Structure of [Me₂Ga-3]₂; selected bond lengths (Å): Ga–C7 1.969(6), Ga–C6 1.978(7), Ga–N# 2.017(5), Ga–N 2.028(5), N–C5 1.468(8), N–C2 1.482(7), C3–C4 1.512(12)

1. Bond length changes would be expected to be of the order of a few hundredths of an Å (i.e., not much larger than the error margins of X-ray structure determinations).
2. Many structures probably suffer from nonresolvable disorder problems, as we show further on. We find that the C–C and C–N bond lengths both of pyrrolines and of pyrrolidines often refine to unrealistically small values (see below). It is not clear a priori how strongly

the other bond lengths in the molecule will be affected by such disorder problems.

To address these issues, we carried out geometry optimizations at the B3LYP/6-31G* level for all relevant Al species. The advantage of such theoretical results is that the *random* errors in bond lengths are much smaller (typically ≈ 0.001 Å) than found in X-ray structures. There are still significant *systematic* errors, but these should not strongly affect the bond length *changes* we are interested in. We first discuss the theoretical results (Table 1) and then compare them to the X-ray data (Table 2, Table 3).

For pyrrolidines and pyrrolines, complexation to AlMe₃ results in an elongation of the C–N bonds by about 0.02–0.03 Å. The adjacent C–C bonds are shortened by a much smaller amount (ca. 0.01 Å), and the distal C–C bond is not affected significantly. The same effects can be observed in the dimeric amides, and are even more pronounced there. For aziridine and dimethylaziridine, we find much smaller changes in the C–N and C–C bond lengths (≈ 0.01 Å at most). We tentatively interpret this as follows. The changes in C–N bond lengths for pyrrolidine and pyrroline derivatives are due to the changes in hybridization of the nitrogen atom, which becomes closer to sp³ and hence uses a larger *p*-contribution for the C–N bonds. For the aziridines, however, the composition of the N hybrids used for forming the C–N bonds is nearly “fixed” by the small

Table 1. Calculated bond length changes (Å; B3LYP/6-31G*) on formation of Al adducts and amides

L	Al–C	[Me ₃ Al·LH]			Al–C	[Me ₂ AlL] ₂		
		C–N	C1–C2	C2–C3		C–N	C1–C2	C2–C3
Aziridine	+0.022	+0.008	–0.003	n/a	+0.005	+0.002	–0.003	n/a
1	+0.024	+0.010	–0.001	+0.002	(<i>trans</i>) +0.009	+0.005	–0.004	0
					(<i>cis</i>) +0.009	+0.006	–0.004	0
2	+0.023	+0.027	0	–0.001	+0.008	+0.045	–0.011	–0.025
3	+0.024	+0.022	–0.005	0	+0.010	+0.020	–0.007	–0.001

Table 2. Reference bond lengths (Å) for ligands **1-H**–**3-H** (Calculated for free Me₃Al: Al–C = 1.975 Å.)

Ligand	C _α –N	C _α –C _β	C _β –C _β
Aziridine ^[15]	1.463(2), 1.464(2), 1.469(2), 1.470(2), 1.465(2), 1.468(2)	1.463(2), 1.465(2), 1.459(1)	
Av:	1.467	1.462	
Calcd. (aziridine):	1.473	1.485	
	1.477 ^[15]	1.487 ^[15]	
Calcd. (1-H):	1.480	1.491	
Pyrrolines ^[16]	1.470, 1.477, 1.462, 1.469	1.498, 1.534, 1.505, 1.509	1.279, 1.313
Av:	1.470	1.512	1.296
Calcd. (2-H):	1.483	1.515	1.333
Pyrrolidines ^[17]	1.494, 1.513	1.480, 1.523	1.448
Av:	1.504	1.502	1.448
Calcd. (3-H):	1.466	1.544	1.558

Table 3. Observed and calculated bond lengths (Å) for adducts and amides

Ligand	Complex	M–C	M–N	N–C _α	C _α –C _β	C _β –C _β
Aziridine	[Me ₃ Al·1-H] X-ray	1.975(2), 1.981(2), 1.976(2)	1.977(2)	1.490(3), 1.495(2)	1.472(3)	
	[Me ₃ Al·1-H] calcd.	1.997–2.001	2.081	1.490	1.490	
	[Me ₃ AlAz] ₃ [5b]	1.96(2), 1.98(2),	1.91(2), 1.94(1),	1.41(2), 1.48(2),	1.46(3), 1.46(3)	
		1.94(2)	1.88(2)	1.52(2)		
	[H ₂ GaAz] ₃ [23]	n/a	1.93(1), 1.99(2),	1.49(3), 1.50(3),	1.51(4), 1.60(5)	
Pyrroline			1.99(2)	1.53(4), 1.67(4)		
	[Me ₂ Al·1] ₂ X-ray	1.951(2)	1.938(2)	1.489(2), 1.493(3)	1.467(4)	
	[Me ₂ Ga·1] ₂ X-ray	1.955(8), 1.953(7)	1.986(6)	1.48(1), 1.49(1)	1.47(1)	
	[Me ₂ Al·1] ₂ calcd. (<i>trans</i>)	1.983–1.984	1.974–1.988	1.485	1.487	
	[Me ₃ Al·2-H] X-ray	1.984(3), 1.966(5), 1.963(4)	1.999(3)	1.485(5), 1.495(5)	1.441(8), 1.489(8)	1.264(8)
Pyrrolidine	[Me ₃ Al·2-H] calcd.	1.997–1.998	2.107	1.505	1.510	1.333
	[Me ₂ Al·2] ₂ X-ray	1.94(2), 2.00(1),	1.98(1), 1.92(1),	1.46(2), 1.50(1),	1.37(2), 1.38(2),	1.27(2), 1.33(2)
		1.93(1), 1.98(2)	1.94(1), 1.94(1)	1.51(2), 1.52(1)	1.40(2), 1.42(2)	
	[Me ₂ Al·2] ₂ calcd.	1.983	2.001–2.008	1.503	1.508	1.332
	[Me ₃ Al·3-H] X-ray	1.977(4), 1.967(3)	1.997(3)	1.468(4)	1.512(6)	1.48(1)
Pyrrolidine	Me ₃ Ga·3-H X-ray	2.00(1), 2.07(4), 1.91(4)	2.11(1)	1.38(5), 1.57(5)	1.47(6), 1.52(5)	1.53(3)
	[Me ₃ Al·3-H] calcd.	1.998–1.999	2.106	1.493	1.544	1.557
	[Me ₂ Ga·3] ₂ X-ray	1.969(6), 1.978(7)	2.017(5), 2.028(5)	1.468(8), 1.482(7)	1.50(1), 1.52(1)	1.51(1)
	[3 ₂ -Al·3] ₂ X-ray [24]	n/a	1.958(2), 1.967(2)	1.494(3), 1.500(3)	1.528(4), 1.531(4)	1.526(4)
	[Me ₂ Al·3] ₂ calcd.	1.984–1.986	2.002–2.004	1.505, 1.507, 1.515, 1.515	1.529, 1.530, 1.538, 1.541	1.533, 1.533

CNC angle, so adduct or amide formation have little effect there. In agreement with this interpretation, the Al–C bonds of Me₃Al become longer on adduct formation by about 0.023 Å, independent of the nature of the amine.

To compare experimentally determined and calculated bond length changes, we need accurate reference bond lengths for our ligands. The structure of aziridine has been determined accurately.^[18] For pyrroline, however, the only crystallographic data available is for two derivatives containing π -acceptor substituents at nitrogen.^[19] The only available “non-disordered” X-ray structure for pyrrolidine available to date concerns a molecule intercalated in an aluminophosphate.^[20] Relevant data are collected in Table 2. For pyrroline and in particular for pyrrolidine, the reported C β –C β bond lengths are too short. This indicates that these reference structures are already affected by some kind of disorder, which – in particular for the pyrrolidine intercalate – is unsurprising. Therefore, use of these reference bond lengths to assess bond length changes expected to be only a few hundredth of an Å is probably useless.

If we now compare the calculated and observed bond lengths for the adducts and amides (Table 3), we see that observed ring bond lengths are in general shorter, and in several cases – in particular for pyrrolidines and pyrrolines – much shorter. Several differences exceed the X-ray error limits, are larger than expected for any systematic errors in the B3LYP/6-31G* results, and are large enough to indicate unrealistic “observed” bond lengths (i.e., more than about 0.05 Å too short). A large in-plane libration amplitude for the whole ring might contribute for free pyrrolidine, but probably not for the adducts and amides. It thus seems likely that there are unresolved disorder problems in several of the structures.

Pyrrolidine rings are invariably puckered. The calculated puckering amplitudes^[21] (Table 4) are consistently larger than the observed ones. This suggests the presence of dis-

order in the *orientation* of the puckering: any such disorder would result in a more nearly planar ring^[22] as well as too short C–C and/or C–N bonds.

Table 4. Ring-puckering amplitudes for pyrroline and pyrrolidine rings

Compound	Ring puckering amplitude
C ₄ H ₆ N-NO X-ray ^[19a]	≈ 0
C ₄ H ₆ N-SSCTe(I)(C ₄ H ₈) X-ray ^[19b]	≈ 0
2-H calcd.	0.156
[Me ₃ Al·2-H] X-ray	0.086
[Me ₃ Al·2-H] calcd.	0.198
[Me ₂ Al·2] ₂ X-ray	≈ 0/0.133
[Me ₂ Al·2] ₂ calcd.	0.226
3-H X-ray ^[17]	0.290
3-H calcd.	0.429
[Me ₃ Al·3-H] X-ray	0.292
Me ₃ Ga·3-H X-ray	0.329
[Me ₃ Al·3-H] calcd.	0.367
[Me ₂ Ga·3] ₂ X-ray	0.398
[3 ₂ Al] ₃ X-ray ^[24]	0.374/0.384
[Me ₂ Al·3] ₂ calcd.	0.421

Pyrroline rings have a near-planar CH₂CH=CHCH₂ fragment, but the ring may be folded somewhat along the CH₂–CH₂ line to produce an envelope-type conformation. Calculations predict that this happens both in free pyrroline and in its adduct and amide. Folding in the X-ray structure of adduct [Me₃Al·2-H] is smaller than predicted by calculations; the X-ray structure of amide [Me₂Al·2]₂ has two inequivalent rings, one of which is planar, while the other is distinctly folded. It seems likely that the potential for folding the ring is very flat, so that the actual structures are to a large degree determined by packing forces. Therefore, disordered structures can also be expected for pyrroline derivatives.

Clearly, in the presence of such disorder problems, little meaning can be attached even to those C–C and C–N bond lengths that look “reasonable”. We thus conclude that a comparison of bond length changes on the basis of X-ray structures would be meaningless.

Decomposition Studies

All amides were tested under a variety of flow rates and substrate (Si) temperatures (up to 800 °C) in various configurations of a simplified MOCVD set-up. In several cases, dark-coloured deposits were observed. However, X-ray analysis of these deposits never gave any evidence for the formation of crystalline nitrides. We therefore decided to study the stability of the amides by DSC measurements.

The aziridine amides [Me₂Al-1]₂ and [Me₂Ga-1]₂ show an endothermic effect at their melting points (≈ 100 °C), a broad exotherm at 330–430 °C (Al) or 390–450 °C (Ga), and a very sharp endotherm at 450 °C (Al) or 470 °C (Ga). [Me₂Al-2]₂ shows an endotherm at the melting point (≈ 64 °C) and a weak exotherm at 240–260 °C, followed by a sharp and large endotherm at 275 °C. Neither [Me₂Al-3]₂ nor [Me₂Ga-3]₂ show any such sharp endotherms up to the maximum temperature investigated (640 °C); weak effects were seen around 230 °C (ex), 300 °C (ex) and 330 °C (end) for Al, and around 300 °C (ex/end) for Ga. It thus appears that derivatives of **1** and **2** indeed undergo some kind of decomposition at a significantly lower temperature than those of saturated analogue **3**. However, we have not yet ascertained the nature of this decomposition.

Conclusions

The introduction of methyl substituents on aziridine has significant implications for its reaction behaviour with Me₃Al and Me₃Ga. In the first place, amide formation was slowed down so much that the amine *adducts* could be isolated and (for M = Al) crystallized. Secondly, the degree of association of the amides is reduced from 3 to 2, which might increase their volatility enough to allow their usage as MOCVD single-source precursors, although we have not yet been able to grow crystalline nitrides from them. Finally, the presence of the methyl groups allows observation of what are probably the *cis* and *trans* isomers of the amide dimer.

Adducts and amides for pyrroline and pyrrolidine could also be isolated. Comparison of calculated and observed bond lengths in the heterocyclic rings shows that the changes associated with complexation and amide formation are quite modest, and are completely swamped by random errors and hidden disorder in the X-ray structures.

Experimental Section

General Procedures: All manipulations of air- and moisture-sensitive compounds were performed under dry nitrogen by standard

glove box and Schlenk techniques. Mesitylene, toluene and hexane were distilled over sodium/benzophenone under an atmosphere of nitrogen prior to use. *cis*-2,3-Dimethylaziridine (**1-H**) was prepared by the published procedure^[6] and dried over KOH and distilled prior to use. 3-Pyrroline (**2-H**, 97% pure), pyrrolidine (**3-H**) and a 2:1 **2-H**/**3-H** mixture were purchased from Aldrich. Yields of crude adducts and amides (i.e. after evaporation of the solvent, as described below) were essentially quantitative (>95%) except for that of [Me₂Ga-2]₂. Yields after crystallization were much lower (typically 10–25%) due to the high solubility of most complexes in the solvents used. ¹H and ¹³C NMR spectroscopic data were collected for about 0.3 M C₆D₆ solutions at room temperature on Bruker DPX 200 and DPX 300 spectrometers. Elemental analyses were performed by the Analytical Laboratory of the Industriepark Kaiserau (Haus Heidbruch), 51789 Lindlar, Germany. Melting points were obtained with a Büchi B-545 melting point apparatus in silicon grease-sealed capillaries and are uncorrected. DSC measurements were performed on a Perkin–Elmer DSC7. In a glove box, samples (approximately 1.5 mg) were encapsulated in a 30 μL sample vessel. This copper vessel fits closely into a stainless steel holder capable of withstanding 150 bar. DSC measurements covered the range of 30 °C to 650 °C, with a scanning rate of 20 °C/min.

Synthesis

[Me₃Al-1-H]: Compound **1-H** (3.5 mmol) was added slowly (0.5 h) at room temperature to a stirred solution of Me₃Al (0.25 g, 3.5 mmol) in mesitylene (4 mL) in a glove-box. After the reaction was complete, the Schlenk tube was taken out of the glove-box and the solvent was removed in vacuo at about 45 °C. The product, a white solid powder, was crystallized from toluene/hexane at about –20 °C. M.p. 75.7 °C. ¹H NMR: δ = –0.47 (s, 9 H, CH₃Al), 0.33 (d, 6 H, CH₃C), 0.87 (s, 1 H, NH), 1.81 (m, 2 H, CH) ppm. ¹³C NMR: δ = –9.1 (br, CH₃Al), 11.1 (CH₃C), 34.7 (CH) ppm. C₇H₁₈NAl (143.21): calcd. C 58.77, H 12.58, N 9.79, Al 18.86 found C 59.00, H 12.88, N 9.56, Al 18.56.

[Me₃Ga-1-H]: This compound was obtained in the same way as [Me₃Al-1-H], with Me₃Ga instead of Me₃Al. However, we did not succeed in crystallizing it. M.p. 45.7 °C. ¹H NMR: δ = –0.17 (s, 9 H, CH₃Ga), 0.40 (d, 6 H, CH₃C), 0.84 (s, 1 H, NH), 1.68 (m, 2 H, CH) ppm. ¹³C NMR: δ = –6.3 (br, CH₃Ga), 11.5 (CH₃C), 33.4 (CH) ppm. C₇H₁₈NGa (185.95): calcd. C 45.22, H 9.76, N 7.53, Ga 37.49; found C 44.98, H 9.52, N 7.48, Ga 37.26.

[Me₂Al-1]₂: *cis*-2,3-Dimethylaziridine (13.1 mmol) was added slowly (0.5 h) at room temperature to a stirred solution of Me₃Al (0.94 g, 13.1 mmol) in mesitylene (6 mL) in a glove-box. During the mixing, the solution warmed spontaneously. After it had cooled down to room temperature, the Schlenk tube was taken out of the glove-box. The solution was heated to 95 °C for 1 h, during which period evolution of gas (methane) was visible. After the solution had cooled, volatiles were removed in vacuo at 60 °C. The product, a white solid powder, was crystallized from toluene/hexane at about –20 °C. M.p. 94.7 °C. ¹H NMR: δ = –0.58 (s, 12 H, CH₃Al), 0.93–0.97 (m, 12 H, CH₃C), 2.04–2.09 (m, 4 H, CH) ppm. ¹³C NMR: δ = –9.5 (br, CH₃Al), 14.2, 14.3 (CH₃C), 36.0, 36.4 (CH) ppm. C₁₂H₂₄N₂Al₂ (254.33): calcd. C 56.72, H 11.02, N 11.02, Al 21.24; found C 56.40, H 10.99, N 10.77, Al 21.47.

[Me₂Ga-1]₂: This compound was obtained in the same way as [Me₂Al-1]₂ (with Me₃Ga instead of Me₃Al), except that the solution was heated to 155 °C instead of 95 °C. The light-yellow product was crystallized from toluene/hexane at about –20 °C. M.p. 101.5 °C. ¹H NMR: δ = –0.22 (s, 12 H, CH₃Ga), 0.94–0.95 (m,

12 H, CH_3C), 1.89–1.95 (m, 4 H, CH) ppm. ^{13}C NMR: δ = –7.1 (CH_3Ga), 14.7, 14.8 (CH_3C), 34.3, 34.9 (CH) ppm. $\text{C}_{12}\text{H}_{24}\text{N}_2\text{Ga}_2$ (339.81): calcd. C 42.44, H 8.25, N 8.25, Ga 41.06; found C 42.30, H 8.23, N 8.27, Ga 40.92.

[Me₃Al-2-H]: Compound 2-H (4 mmol) was added slowly (0.5 h) at room temperature to a stirred solution of Me₃Al (289 mg, 4 mmol) in toluene (1.0 mL) in a glove-box. After the reaction was complete, the Schlenk tube was taken out of the glove-box and put it in a refrigerator at about –20 °C for crystallization to take place. The formed crystals were transparent and light yellow. M.p. 65.5 °C. ^1H NMR: δ = –0.54 (s, 9 H, CH_3Al), 1.86, (s, 1 H, NH), 3.51, (br. s, 4 H, CH_2), 5.44, (br. s, 2 H, CH) ppm. ^{13}C NMR: δ = –11.2 (CH_3Al), 55.4 (CH_2), 128.9 (CH) ppm. $\text{C}_7\text{H}_{16}\text{NAl}$ (141.19): calcd. C 59.60, H 11.34, N 9.93, Al 19.13; found C 59.80, H 11.20, N 10.11, Al 19.32.

[Me₂Al-2]₂: Compound 2-H (10 mmol) was added slowly (0.5 h) at room temperature to a stirred solution of Me₃Al (0.72 g, 10 mmol) in mesitylene (5 mL) in a glove-box. During the mixing, the solution warmed spontaneously. After it had cooled down to room temperature, the Schlenk tube was taken out of the glove-box. The solution was heated to 90 °C for 30 min, during which period evolution of gas (methane) was visible. After cooling the solution, volatiles were removed in vacuo at 40 °C. The transparent white product was crystallized from toluene/hexane at about –20 °C. M.p. 64.1 °C. ^1H NMR: δ = –0.53 (s, 12 H, CH_3Al), 3.51, (br. s, 8 H, CH_2), 5.43, (br. s, 4 H, CH) ppm. ^{13}C NMR: δ = –11.4 (CH_3Al), 55.4 (CH_2), 128.8 (CH) ppm. $\text{C}_{12}\text{H}_{24}\text{N}_2\text{Al}_2$ (250.30): calcd. C 57.63, H 9.60, N 11.20, Al 21.58; found C 57.33, H 9.58, N 10.98, Al 21.53.

[Me₃Al-3-H]: This compound was obtained in the same way as [Me₃Al-2-H], with use of 3-H instead of 2-H. The formed crystal was transparent and light yellow. M.p. 70.1 °C. ^1H NMR: δ = –0.52 (s, 9 H, CH_3Al), 0.89–0.96, (m, 4 H, $\beta\text{-CH}_2$), 1.42, (s, 1 H, NH), 2.16–2.19 (m, 4 H, $\alpha\text{-CH}_2$) ppm. ^{13}C NMR: δ = –9.6 (br, CH_3Al), 24.7 ($\beta\text{-CH}_2$), 46.4 ($\alpha\text{-CH}_2$) ppm. $\text{C}_7\text{H}_{18}\text{NAl}$ (143.21): calcd. C 58.77, H 12.58, N 9.79, Al 18.86; found C 58.44, H 12.42, N 9.67, Al 19.08.

[Me₂Al-3]₂: This compound was obtained in the same way as [Me₂Al-2]₂ (with use of 3-H instead of 2-H), except that the solution was heated at 125 °C for 1.5 h instead of at 90 °C for 30 min. The product was a light-white powder. However, we did not succeed in crystallizing it. M.p. 59.3 °C. ^1H NMR: δ = –0.59 (s, 12 H, CH_3Al), 1.29–1.35, (m, 8 H, $\beta\text{-CH}_2$), 2.57–2.63 (m, 8 H, $\alpha\text{-CH}_2$) ppm. ^{13}C NMR: δ = –11.9 (br, CH_3Al), 25.1 ($\beta\text{-CH}_2$), 49.7 ($\alpha\text{-CH}_2$) ppm. $\text{C}_{12}\text{H}_{28}\text{N}_2\text{Al}_2$ (254.33): calcd. C 56.72, H 11.02, N 11.02, Al 21.24; found C 56.54, H 10.86, N 10.99, Al 20.98

Mixture (Cocrystal) of [Me₃Al-2-H] and [Me₃Al-3-H]: This compound was obtained in the same way as [Me₃Al-2-H], with the use of a 2:1 mixture of 2-H/3-H. The product, a light-white solid powder, was crystallized from toluene/hexane at about –20 °C. M.p. 59.1 °C. ^1H and ^{13}C NMR spectra corresponded to a 2:1 mixture of [Me₃Al-2-H] and [Me₃Al-3-H] (see data given above). An NMR spectrum of a fragment of a large single crystal showed the same ratio of 2-H/3-H as in the bulk mixture, demonstrating that the two compounds cocrystallize. Anal; found C 59.46, H 11.36, N 10.09, Al 19.31.

Mixture (Cocrystal) of [Me₂Al-2]₂ and [Me₂Al-3]₂: This compound was obtained in the same way as [Me₂Al-2]₂ (with the use of a 2:1 mixture of 2-H/3-H), except that the solution was heated at 130 °C for 3 h instead of at 90 °C for 30 min. The product, a transparent

light-white powder, was crystallized from toluene/hexane at about –20 °C. M.p. 65.8 °C. The ^1H and ^{13}C NMR spectra recorded at room temperature corresponded to a 2:1 mixture of [Me₂Al-2]₂ and [Me₂Al-3]₂ (see data given above) and did not show separate peaks for a mixed dimer. We do not know whether this means that the mixed dimer does not form or that exchange is rapid on the NMR timescale. Anal; found C 57.40, H 9.61, N 10.97, Al 21.72.

[Me₃Ga-2-H]: This compound was obtained in the same way as [Me₃Al-2-H], with the use of Me₃Ga instead of Me₃Al. The formed crystals were transparent light white. M.p. 35.5 °C. ^1H NMR: δ = –0.23 (s, 9 H, CH_3Ga), 1.51, (s, 1 H, NH), 2.96, (br. s, 4 H, CH_2), 5.05, (br. s, 2 H, CH) ppm. ^{13}C NMR: δ = –6.8 (CH_3Ga), 53.6 (CH_2), 126.8 (CH) ppm. $\text{C}_7\text{H}_{16}\text{NGa}$ (183.93): calcd. C 45.71, H 8.77, N 7.62, Ga 37.91; found C 45.61, H 8.82, N 7.79, Ga 38.07.

Attempted Synthesis of [Me₂Ga-2]₂: Treatment of Me₃Ga with 2-H to form [Me₂Ga-2]₂ was carried out similarly to that of Me₃Al with 2-H. Heating to 155 °C was required for reaction. After evaporation of the solvent, a yellow-brown powder was left. ^1H NMR did not show any peaks attributable to the (protonated or deprotonated) pyrrolinyl group in the δ = 4 to 6 ppm range. Instead, broad singlets at δ = 6.29 and 6.85 ppm and several multiplets in the 0.9–2.8 ppm range were observed, which suggested that disproportionation to pyrrole and pyrrolidine and possibly isomerization to 2-pyrroline had occurred. No further attempts were made to separate or purify the products.

[Me₃Ga-3-H]: This compound was obtained in the same way as [Me₃Al-3-H] (with the use of Me₃Ga instead of Me₃Al). The formed crystal was cloudy and colourless. M.p. 48.3 °C (ref.^[5e] 47 °C). ^1H NMR: δ = –0.18 (s, 9 H, CH_3Ga), 0.90–0.97, (m, 4 H, $\beta\text{-CH}_2$), 1.15, (s, 1 H, NH), 2.12–2.15 (m, 4 H, $\alpha\text{-CH}_2$) ppm. ^{13}C NMR: δ = –6.8 (br, CH_3Ga), 24.84 (s, $\beta\text{-CH}_2$), 46.7 ($\alpha\text{-CH}_2$) ppm. $\text{C}_7\text{H}_{18}\text{NGa}$ (185.95): calcd. C 45.25, H 9.69, N 7.54, Ga 37.53; found C 45.11, H 9.60, N 7.69, Ga 37.27.

[Me₂Ga-3]₂: This compound was obtained in the same way as [Me₂Al-3]₂ (with the use of Me₃Ga instead of Me₃Al), except that the solution was heated at 170 °C for 2.5 h instead of at 125 °C for 1.5 h. The product, a white solid, was crystallized from toluene at about –20 °C. M.p. 65.8 °C (ref.^[5d], 74–75 °C; 64–67 °C^[5a]). ^1H NMR: δ = –0.28 (s, 12 H, CH_3Ga), 1.29–1.36, (m, 8 H, $\beta\text{-CH}_2$), 2.59–2.65 (m, 8 H, $\alpha\text{-CH}_2$) ppm. ^{13}C NMR: δ = –10.2 (CH-Ga), 24.9 ($\beta\text{-CH}_2$), 51.6 ($\alpha\text{-CH}_2$) ppm. $\text{C}_{12}\text{H}_{28}\text{N}_2\text{Ga}_2$ (339.81): calcd. C 42.44, H 8.25, N 8.25, Ga 41.06; found C 42.27, H 8.06, N 8.34, Ga 40.87.

X-ray Crystal Structure Determinations

General: Crystals of these Al and Ga complexes were generally found to be soft. The crystal fragments sampled were cut from larger crystals, resulting in irregular shapes. Both factors may have contributed to the generally poor quality of the X-ray structure determinations (see below). Crystals were mounted in thin-walled glass capillaries under Ar. Data were collected on an Enraf–Nonius CAD4 diffractometer by use of graphite-monochromated Mo- K_α radiation (0.71073 Å). Details of all structure determinations are collected in Table 5 and Table 6. Since the glass capillaries prevented accurate description of the crystal shape, semi-empirical absorption corrections from ψ -scans^[7] were applied. Structures were solved by use of the PATTY option^[8] of the DIRDIF program system.^[9] Refinements were carried out with the SHELXL-97 package.^[10] All refinements were full-matrix, least-squares on F^2 . All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed at cal-

culated positions, and refined isotropically in riding mode, unless noted otherwise (see below). Geometrical calculations^[11] revealed neither unusual geometric features, nor unusual short intermolecular contacts. The calculations revealed no higher symmetry and no solvent-accessible areas. The structure drawings in Figure 1–5 show 30% thermal ellipsoids. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-187355 to -187364. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Notes on Individual Structures

[Me₃Al-1-H]: 1-H was refined freely.

[Me₃Al-2-H]: All hydrogen atoms refined freely.

[Me₃Al-2-H]/[Me₃Al-3-H] Cocrystal: 1-H was refined freely. The crystal structure determination was hampered by the poor crystal quality and more than average decay (up to 15%). No reliable data could be collected above 22° (resolution 0.95 Å).

[Me₃Al-3-H]: To test the presence of the mirror plane, a full least-squares refinement was performed in space group *P*2₁. Although the

R factor was lower (0.0589), the standard deviations in bond angles and distances were significantly higher. Moreover, a statistical analysis of the intensities favours a centrosymmetric space group.

[Me₃Ga-3-H]: The crystal structure determination was hampered by the very poor crystal quality. No reliable data could be collected above 22° (resolution 0.95 Å). Because the semiempirical absorption correction by itself was not adequate, presumably due to the poor quality of the data and hence of the ψ -scans, an additional absorption correction was applied by use of the DIFABS procedure.^[12] Even then it was necessary to use the ISOR option for N1 in the least-squares refinement to provide physically acceptable anisotropic thermal displacement parameters.

[Me₂Al-2]: The crystal structure determination was hampered by the extremely poor crystal quality. No reliable data could be collected above 21° (resolution 0.99 Å).

[Me₂Al-2]₂/[Me₂Al-3]₂ Cocrystal: The crystal structure determination was hampered by the very poor crystal quality. No reliable data could be collected above 23° (resolution 0.91 Å).

Calculations

All calculations were carried out with the GAMESS-UK package^[13] by use of the B3LYP hybrid density functional^[14] and the

Table 5. Details of crystal structure determinations for [Me₃Al-1-H], [Me₂Al-1]₂, [Me₂Ga-1]₂, [Me₃Al-2-H] and [Me₂Al-2]₂/[Me₂Al-3]₂

Compound	[Me ₃ Al-1-H]	[Me ₂ Al-1] ₂	[Me ₂ Ga-1] ₂	[Me ₃ Al-2-H]	[Me ₂ Al-2] ₂ /[Me ₂ Al-3] ₂
Crystal colour	transparent cloudy white	transparent cloudy colourless	transparent cloudy white	transparent light yellow	transparent colourless
Crystal shape	rough fragment	rough fragment	rough platelet	rough fragment	very large, very irregular fragment
Crystal size, mm	0.25 × 0.23 × 0.10	0.33 × 0.21 × 0.18	0.31 × 0.29 × 0.08	0.54 × 0.36 × 0.28	1.20 × 0.70 × 0.36
Empirical formula	C ₇ H ₁₈ AlN	C ₁₂ H ₂₈ Al ₂ N ₂	C ₁₂ H ₂₈ Ga ₂ N ₂	C ₇ H ₁₆ AlN	C ₁₂ H ₂₄ Al ₂ N ₂
Molecular mass	143.20	254.32	339.80	141.19	250.29
Temperature, K	148(2)	293(2)	293(2)	293(2)	293(2)
Crystal system,	orthorhombic,	triclinic,	triclinic,	monoclinic,	monoclinic,
Space group	<i>Pcab</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>m</i>
Unit cell det. #,	10982,	25,	25,	22,	23,
θ range	2.100–25.290	10.293–14.897	10.235–14.595	10.273–13.602	10.437–13.217
<i>a</i> , Å	8.3271(2)	7.2341(5)	7.2343(10)	6.2786(5)	14.049(3)
<i>b</i> , Å	19.4095(6)	7.7648(7)	7.7407(9)	9.3098(17)	9.069(4)
<i>c</i> , Å	12.5463(4)	8.7149(11)	8.710(2)	17.0244(18)	7.2797(17)
α , °	90	71.784(8)	71.684(16)	90	90
β , °	90	73.353(10)	73.488(19)	92.354(10)	120.56(2)
γ , °	90	65.969(7)	66.410(11)	90	90
Volume, Å ³	2027.79(10)	417.48(7)	417.26(14)	994.3(2)	798.8(4)
<i>Z</i> , <i>d</i> _{calc.} (g·cm ^{−3})	8, 0.938	1, 1.012	1, 1.352	4, 0.943	2, 1.041
Abs. coeff., mm ^{−1}	0.134	0.156	3.210	0.136	0.163
Scan	area det. ϕ , ω	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	ω
<i>F</i> (000)	640	140	176	312	272
θ range, °	2.10–25.29	2.95–27.47	3.12–27.47	2.39–27.48	4.49–23.00
Index ranges	−9 ≤ <i>h</i> ≤ 10 −23 ≤ <i>k</i> ≤ 23 −14 ≤ <i>l</i> ≤ 15	−9 ≤ <i>h</i> ≤ 9 −10 ≤ <i>k</i> ≤ 10 −11 ≤ <i>l</i> ≤ 11	−9 ≤ <i>h</i> ≤ 0 −10 ≤ <i>k</i> ≤ 9 −11 ≤ <i>l</i> ≤ 10	0 ≤ <i>h</i> ≤ 8 −12 ≤ <i>k</i> ≤ 0 −22 ≤ <i>l</i> ≤ 22	−13 ≤ <i>h</i> ≤ 15 −9 ≤ <i>k</i> ≤ 9 −8 ≤ <i>l</i> ≤ 0
Collected/unique	10982/1839	3834/1917	2068/1918	2481/2276	1197/592
[<i>R</i> _{int.}]	[0.0631]	[0.0383]	[0.0558]	[0.1073]	[0.1396]
Observed [<i>I</i> _o > 2σ(<i>I</i> _o)]	1276	1454	1092	1200	327
DIFABS?, abs. struct. par.	no	no	no	no	no
Relat. transm. fact.		1.057–0.953	1.547–0.841	1.657–0.820	1.244–0.841
Data/restraints/pars.	1839/0/91	1917/0/77	1918/0/77	2276/0/85	592/0/46
Goodness-of-fit on <i>F</i> ²	1.047	1.050	1.050	1.079	1.109
SHELXL-97 wt. pars.	0.0507, 0.5441	0.0661, 0.0509	0.0592, 0.5977	0.1341, 0.1512	0.1348, 0.0000
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0421, 0.1004	0.0444, 0.1154	0.0696, 0.1235	0.0860, 0.2217	0.0915, 0.2277
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0737, 0.1121	0.0650, 0.1255	0.1516, 0.1492	0.1511, 0.2619	0.1441, 0.2668
Diff. peak, hole (e [−] Å ^{−3})	0.195, −0.179	0.305, −0.118	0.677, −0.697	0.470, −0.310	0.241, −0.238

Table 6. Details of crystal structure determinations for [Me₃Al·2-H]/[Me₃Al·3-H], [Me₃Al·3-H], [Me₃Ga·3-H], and [Me₂Al·2]₂[Me₂Ga·3]₂

Compound	[Me ₃ Al·2-H] / [Me ₃ Al·3-H]	[Me ₃ Al·3-H]	Me ₃ Ga·3-H]	[Me ₂ Al·2] ₂	[Me ₂ Ga·3] ₂
Crystal colour	transparent yellow	transparent cloudy light yellow	transparent cloudy colourless	transparent cloudy colourless	transparent colourless
Crystal shape	rough platelet	irregular fragment	rough fragment	large irregular fragment	rough fragment
Crystal size, mm	0.50 × 0.28 × 0.10	0.53 × 0.42 × 0.35	0.46 × 0.33 × 0.23	0.90 × 0.59 × 0.40	0.46 × 0.35 × 0.25
Empirical formula	C ₇ H ₁₆ AlN	C ₇ H ₁₈ AlN	C ₇ H ₁₈ GaN	C ₁ 2-H ₂₄ Al ₂ N ₂	C ₁ 2-H ₂₈ Ga ₂ N ₂
Molecular weight	141.19	143.20	185.94	250.29	339.80
Temperature, K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system,	monoclinic,	monoclinic,	monoclinic,	monoclinic,	monoclinic,
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell det. #,	25,	23,	24,	25,	25,
θ range	9.366–11.407	10.216–11.722	10.311–13.707	10.260–13.630	10.252–14.419
<i>a</i> , Å	6.2765(9)	6.3054(6)	6.3484(8)	8.4774(12)	7.6440(7)
<i>b</i> , Å	9.3588(16)	11.0728(10)	11.0264(16)	8.4981(12)	8.5036(7)
<i>c</i> , Å	16.982(3)	7.6501(15)	7.6364(19)	22.453(3)	12.8894(11)
α, °	90	90	90	90	90
β, °	92.411(19)	107.423(9)	107.838(15)	100.035(14)	106.773(12)
γ, °	90	90	90	90	90
Volume, Å ³	996.6(3)	509.61(12)	508.86(16)	1592.8(4)	802.19(13)
<i>Z</i> , <i>d</i> _{calcd.} (g·cm ^{−3})	4, 0.941	2, 0.933	2, 1.214	4, 1.044	2, 1.407
Abs. coeff., mm ^{−1}	0.136	0.134	2.638	0.163	3.340
Scan	ω/2θ	ω/2θ	ω	ω/2θ	ω
<i>F</i> (000)	312	160	196	544	352
θ range, °	3.24–22.00	2.79–27.46	4.11–21.95	2.57–20.99	3.62–27.44
Index ranges	−6 ≤ <i>h</i> ≤ 6 0 ≤ <i>k</i> ≤ 9 −17 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 8 0 ≤ <i>k</i> ≤ 14 −9 ≤ <i>l</i> ≤ 9	−6 ≤ <i>h</i> ≤ 6 −11 ≤ <i>k</i> ≤ 0 −8 ≤ <i>l</i> ≤ 0	−8 ≤ <i>h</i> ≤ 8 −8 ≤ <i>k</i> ≤ 0 −22 ≤ <i>l</i> ≤ 0	−9 ≤ <i>h</i> ≤ 0 −11 ≤ <i>k</i> ≤ 0 −16 ≤ <i>l</i> ≤ 16
Collected/unique	1266/1217	1334/1228	710/655	1747/1693	1951/1820
[<i>R</i> _{int.}]	[0.0668]	[0.0481]	[0.0555]	[0.1036]	[0.0336]
Observed [<i>I</i> _o > 2σ(<i>I</i> _o)]	547	650	447	822	1125
DIFABS?, abs. struct. par.	no	no	yes, −0.15(16)	no	no
Relat. Transm. fact.	1.164–0.883	1.089–0.923	1.192–0.878	1.527–0.854	1.298–0.803
Data/restraints/pars.	1217/0/89	1228/0/52	655/7/85	1693/0/149	1820/0/75
Goodness-of-fit on <i>F</i> ²	1.013	1.032	1.126	1.072	1.091
SHELXL-97 wt. pars.	0.0774, 0.0000	0.1010, 0.0192	0.0409, 0.6351	0.1657, 5.7380	0.0925, 0.0517
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0706, 0.1417	0.0630, 0.1626	0.0514, 0.0978	0.1064, 0.2917	0.0617, 0.1425
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1840, 0.1799	0.1230, 0.1937	0.1018, 0.1174	0.1955, 0.3624	0.1167, 0.1657
Diff. Peak, hole (e [−] Å ^{−3})	0.204, −0.211	0.263, −0.160	0.300, −0.351	0.292, −0.304	1.198, −0.731

6-31G* basis set.^[15] All structures were fully optimized without symmetry constraints.

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