A General Synthetic Pathway to Lewis Base-Stabilized, Monomeric Group 13/15 Compounds

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Reactions of an equimolar amount of 4-(dimethylamino)pyridine (dmap) with several Al–E heterocycles $[R_2AlE(SiMe_3)_2]_x$ (E = P, As; R = Me, x = 3; R = Et, x = 2) and Ga–Sb heterocycles $[R_2GaSb(SiMe_3)_2]_x$ (R = Me, x = 3; R = Et, x = 2) in hexane offers a general pathway for the formation of monomeric, Lewis base-stabilized compounds of the type dmap–$(R_2)ME(SiMe_3)_2$ (M = Al, R = Me, E = P **1**, As **2**; R = Et, E = As **3**; M = Ga, E = Sb, R = Me **4**, Et **5**). Compounds **1**, **2**, **3** and **5** have been characterized by single-crystal X-ray diffraction.

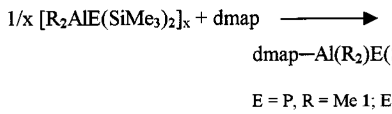
Introduction

Over the last two decades, the synthesis of monomeric group 13/15 compounds of the type $R_2MER'_2$ has received growing interest owing to their fascinating bonding properties.[1] In addition, compounds of the type $[R_2MER'_2]_x$, which may serve as so-called single-source precursors for the preparation of the corresponding semiconducting binary materials, are still in the focus of very intense studies. These compounds are usually obtained in the form of heterocycles (x = 2, 3), heterocubanes (x = 4) or more highly associated cages ($x > 4$), both in solution and in the solid state, as a result of the tendency of the triele atom to utilize its vacant p-valence orbital by increasing its coordination number from 3 to 4. Monomeric group 13/15 compounds $R_2MER'_2$ are only formed with sterically extremely bulky ligands on both M and E, which inhibit the formation of oligomers and lead to the formation of kinetically stabilized monomers.[2] Recently, we demonstrated a synthetic route for the formation of electronically stabilized monomeric compounds. Monomeric, Lewis base-stabilized organoaluminum stibides[3] and bismuthides[4] of the type dmap$-(R_2)AlE(SiMe_3)_2$ (E = Sb, Bi) were obtained by ring-cleavage reactions of the corresponding heterocycles $[R_2AlER'_2]_x$ with 4-(dimethylamino)pyridine (dmap). The triele atom is coordinatively and electronically saturated by interaction with the strong base, while the *lone pair* of the pentele atom is still active for coordination chemistry. Prior to our studies, only a few examples of structurally characterized, Lewis base-stabilized amino-, phosphanyl-, and arsanylalane monomers had been reported. $Me_3N-Al(H_2)NR_2$ and $Me_3N-Al(H_2)As(SiMe_3)_2$ were synthesized by the reaction of $H_3Al-NMe_3$ with sterically bulky secondary amines[5] and $As(SiMe_3)_3$,[6] respectively. Reactions of $H_2AlCl-NMe_3$ with $LiEMes_2$ (E = P, As; Mes = 2,4,6-$Me_3C_6H_2$) led to the formation of $Me_3N-Al(H_2)EMes_2$.[7] Unfortunately, no general pathway for the synthesis of this specific class of compounds has been developed so far. The reactions are limited to Me_3N-stabilized AlH_3 or H_2AlCl as starting compounds. However, the desired monomeric compounds are of particular interest because they may serve as general building blocks for the synthesis of bimetallic complexes of the type dmap$-(R_2)ME(R'_2)-M'L_n$ (M = triele; E = pentele; M′ = transition metal),[8] where the pentele atom bridges a "soft" transition metal and a "hard" main-group metal fragment.[9] Complexes of this type can be considered as transition metal derivatives of an amphoteric main group element ligand.[10] Up to now, $Me_3N-(Me_3SiCH_2)_2$-$AlP(Ph)_2-Cr(CO)_5$ is the only structurally characterized compound of this type, which was prepared in a very special reaction by Beachley et al.[10a,11] However, this specific reaction pathway couldn't be successfully expanded to the synthesis of other comparable bimetallic complexes.

In this paper we wish to present our extended studies on ring-cleavage reactions of Al$-$E heterocycles containing the lighter homologues of group 15, P and As, as well as on Ga$-$Sb heterocycles, demonstrating the general and convenient purpose of this particular reaction type for the synthesis of the desired class of compounds.

Results

The reaction of equimolar amounts of 4-(dimethylamino)-pyridine (dmap) with several Al$-$E heterocycles $[R_2AlE(SiMe_3)_2]_2$ (E = P, As; R = Me, Et) in hexane resulted in the formation of the corresponding Lewis base-stabilized monomers **1$-$3** in almost quantitative yield (Scheme 1). Monomers prepared in this way are extremely sensitive to-



$$1/x\ [R_2AlE(SiMe_3)_2]_x + \text{dmap} \longrightarrow \text{dmap}{-}Al(R_2)E(SiMe_3)_2$$

E = P, R = Me **1**; E = As, R = Me **2**, Et **3**

Scheme 1. Synthesis of monomeric, Lewis base-stabilized phosphanyl- and arsanylalanes

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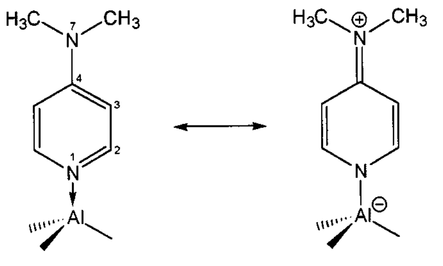
wards air and moisture, particularly in solution. At −30 °C, compounds **1−3** were obtained as crystalline, light yellow solids.

The ^{1}H and ^{13}C NMR spectra of **1−3** show resonances due to the organic ligands bound to the metal centers and the expected resonances of dmap. Integration of the signals due to the organic ligands and dmap indicated a 1:1 stoichiometry of dmap:$R_2AlE(SiMe_3)_2$ (E = P, As; R = Me, Et). The proton resonances of the organic ligands bound to the metal centers appear further downfield (MeAl, EtAl, and Me_3Si resonances) than those of the starting heterocycles, while those of the dmap molecule are shifted upfield. These findings are in agreement with results observed for similar borane adducts,[12] and correspond to a partial rearrangement of the charge distribution within the aromatic ring as shown in Scheme 2.



Scheme 2

Single-crystal X-ray analyses of **1** (Figure 1), **2** (Figure 2), and **3** (Figure 3) clearly show the presence of monomeric $R_2AlE(SiMe_3)_2$ molecules, to which one dmap molecule is coordinated. Compounds **2** and **3** crystallize in the triclinic space group $P\bar{1}$ (no. 2), while **1** crystallizes in the monoclinic space group $P2_1/c$ (no. 14). Both **1** and **2** crystallize with two independent molecules in the asymmetric unit.

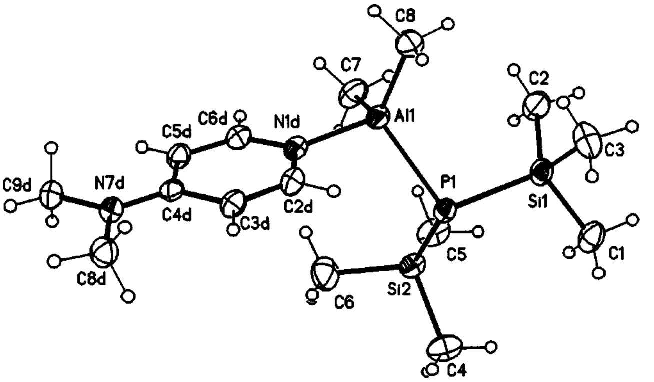


Figure 1. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **1**; for clarity, only one independent molecule of the asymmetric unit is presented; selected bond lengths [pm] and angles [°]: Al1−N1d 198.4(2), Al1−P1 237.9(1), Al1−C7 197.7(2), Al1−C8 197.7(2), P1−Si1 223.6(1), P1−Si2 223.7(1); C7−Al1−C8 115.3(1), Si1−P1−Si2 104.8(1), N1d−Al1−P1 101.0(1), Si1−P1−Al1 102.5(1), Si2−P1−Al1 101.8(1)

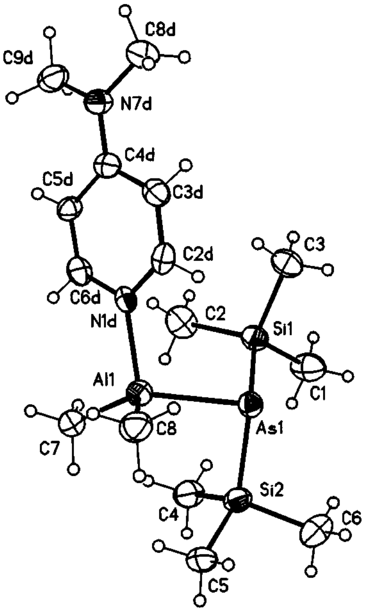


Figure 2. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **2**; for clarity, only one molecule of the asymmetric unit is presented; selected bond lengths [pm] and angles [°]: Al1−N1d 197.5(4), Al1−As1 247.2(2), Al1−C7 196.5(4), Al1−C8 197.3(4), As1−Si1 233.7(2), As1−Si2 233.8(2); C7−Al1−C8 114.7(2), Si1−As1−Si2 101.1(1), N1d−Al1−As1 104.5(2), Si1−As1−Al1 105.0(1), Si2−As1−Al1 98.0(1)

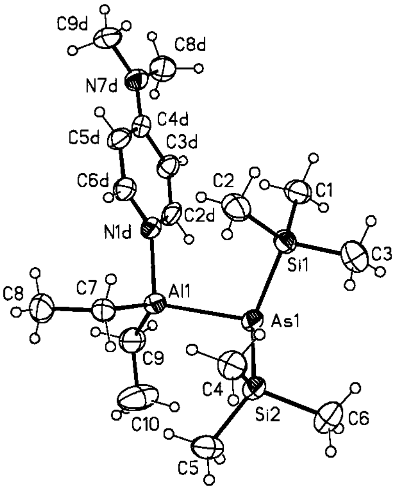


Figure 3. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **3**; selected bond lengths [pm] and angles [°]: Al1−N1d 198.8(3), Al1−As1 247.3(1), Al1−C7 196.5(4), Al1−C9 198.9(3), As1−Si1 233.4(1), As1−Si2 234.1(1); C7−Al1−C9 115.3(2), Si1−As1−Si2 101.3(1), N1d−Al1−As1 105.0(1), Si1−As1−Al1 103.5(1), Si2−As1−Al1 101.8(1)

As found in the corresponding monomers of the higher homologues dmap−$Al(R_2)E(SiMe_3)_2$ (R = Me, Et, E = Sb, Bi),[3,4] the substituents bonded to Al and the particular pentele atom adopt a staggered conformation relative to one another. The average Al−C bond lengths (**1**: 197.7, 197.5; **2**: 196.9, 196.6; **3**: 197.7 pm) and C−Al−C bond angles [**1**: 115.3(1), 114.6(1)°; **2**: 114.7(2), 115.7(2)°; **3**: 115.3(2)°] are within the expected ranges, while the E−Si bond lengths (**1**: 223.7, 222.9; **2**: 233.8, 233.9; **3**: 233.8 pm) are at the lower end of typical E−Si bond lengths.[13] They are only slightly shorter than in the starting compounds {average E−Si distances found in $[Me_2AlP(SiMe_3)_2]_2$: 225.9

pm; [$Me_2AlAs(SiMe_3)_2]_2$: 234.5 pm; [$Et_2AlAs(SiMe_3)_2]_2$: 234.9 pm}.

The Al−N bond lengths [**1**: 198.4(2), 197.7(2); **2**: 197.5(4), 198.9(4); **3**: 198.8(3) pm] are almost the same as those observed in the corresponding monomeric compounds of the heavier group 15 elements dmap−$(R_2)AlE(SiMe_3)_2$ (R = Me, Et, E = Sb, Bi), indicating the strong donor capacity of dmap. In addition, the almost equal Al−N distances demonstrate that the particular pentele atom does not have a significant electronic influence on the Lewis acidity of the Al fragment. Typical Al−N distances of adducts with tricoordinated N centers are comparable [e.g. 2-methylpyridine−$AlCl_3$: 194.2(2) pm, stronger Lewis acid],[14] while adducts with tetracoordinated N centers show significantly longer Al−N distances [e.g. $Me_3Al{-}NMe_3$: 210(1) pm; $H_3Al{-}NMe_3$: 206.3(8) pm (gas phase); $Me_3Al{-}NH_3$: 200.4(5) pm (powder diffraction); H_3Al-tmp (tmp = 2,2,6,6-tetramethylpiperidine): 204(1) pm].[15] However, compounds containing stronger Lewis acids [e.g. $Cl_3Al{-}NMe_3$: 196(1) pm (single-crystal analysis)[16]; 194.5(35) pm (electron diffraction)[17]] show comparable Al−N distances. Compared to analogous Lewis base-stabilized monomers of the type $Me_3N{\rightarrow}Al(R_2)ER'_2$, the dmap adducts show the shortest Al−N distances [Al−N (in pm): $Me_3N{\rightarrow}Al(H_2)N(tmp)_2$ 205.8(2);[5a] $Me_3N{\rightarrow}Al(H)(Cl)N(SiMe_3)_2$ 201.6(5);[5b] $Me_3N{\rightarrow}Al(H_2)As(SiMe_3)_2$ 199.8(7);[6] $Me_3N{\rightarrow}Al(H_2)PMes_2$ 200.9(8)[7]].

The Al−P [237.9(1), 237.4(1) pm **(1)**] and Al−As bond lengths [247.2(2), 247.0(2) **(2)**, 247.3(1) pm **(3)**] are also relatively short. Comparable Al−P distances in phosphanylalanes were found in the monomeric compounds $Trip_2AlP(Ada)(SiPh_3)$ [234.2(2) pm][18] (Trip = 2,4,6-$i\mathrm{Pr}_3C_6H_2$) and Tmp_2AlPPh_2 [237.7(1) pm],[2a] while the Lewis base-stabilized monomer $Me_3N{\rightarrow}Al(H_2)PMes_2$ shows a slightly longer distance [240.9(3) pm].[7] The Al−As distances in **2** and **3** [247.2(2), 247.0(2); 247.3(1) pm] are almost the same as those in monomeric $Tmp_2AlAsPh_2$ [248.5(2) pm][2a] but slightly longer than those in $Me_3N{\rightarrow}Al(H_2)As(SiMe_3)_2$ [243.8(2) pm][6] and $Me_3N{-}Al(H)AsSi(i\mathrm{Pr})_3]_2$.[19] The shortest Al−As distances were found in the borazine analogue $[Mes^*AlAsPh]_3{\cdot}Et_2O$ (Mes* = 2,4,6-$t\mathrm{Bu}_3C_6H_2$), which, however, only has tricoordinated Al centers.[20] The comparable Lewis base-stabilized monomer $Me_3N{-}Al(H_2)As(SiMe_3)_2$ is sterically less hindered than **2** and **3** and contains a slightly stronger Lewis acidic Al center due to the weaker +I effect of the H- relative to the Me-substituents. The Al−P and Al−As distances agree very well with the sum of the covalent radii of the corresponding central atoms (Al−P: 235 pm; Al−As: 246 pm).[21] Interestingly, the starting heterocycles show significantly longer Al−E distances. The average Al−E distances found in $[Me_2AlP(SiMe_3)_2]_2$ (245.7 pm), $[Me_2AlAs(SiMe_3)_2]_2$ (253.6 pm) and $[Et_2AlAs(SiMe_3)_2]_2$ (253.5 pm) are elongated by 8 (Al−P) and 6 pm (Al−As), respectively. In contrast, the Al−E distances of the corresponding monomeric stibides [dmap−$(Me_2)AlSb(SiMe_3)_2$: 269.1(1) pm; dmap−$(Et_2)AlSb(SiMe_3)_2$: 267.9(1) pm][3] and bismuthide [dmap−$(Me_2)AlBi(SiMe_3)_2$: 275.5(2) pm][4] are on average less shortened (Al−Sb: 3−5 pm; Al−Bi: 2 pm) compared to those of the starting heterocycles {$[Me_2AlSb(SiMe_3)_2]_3$: 271.9 pm;[22] $[Et_2AlSb(SiMe_3)_2]_2$: 273.5 pm;[23] $[Me_2AlBi(SiMe_3)_2]_3$: 277.4 pm[24]}. Obviously, intramolecular steric repulsion between the ligands is less intense within the heterocycles of the heavier homologues of group 15 owing to the increasing atomic radii of the penteles from P to Bi.

Besides the structural similarity of **1**, **2**, **3**, and the higher homologues dmap−$(R_2)AlE(SiMe_3)_2$ (R = Me, Et, E = Sb, Bi)[3,4] in almost every structural feature, the compounds show one remarkable difference: The Si−E−Si and Si−E−Al bond angles decrease significantly with increasing atomic number of the group 15 element. While the Si−P−Si angles in **1** are 104.8(1) and 102.9(1)°, the corresponding Si−As−Si angles in **2** [101.1(1) and 101.9(1)°] and **3** [101.3(1)°] are smaller. The corresponding stibides dmap−$Al(R_2)Sb(SiMe_3)_2$ [R = Me 97.6(2)°; Et 99.1(1)°] and bismuthides dmap−$Al(R_2)Bi(SiMe_3)_2$ [R = Me 95.7(1)°; Et 97.4(1)°] again show significantly reduced angles. These findings are in agreement with the well-known tendency within group 15 trihydrides H_3E, which show constantly decreasing H−E−H angles from 106.8° (NH_3)[25] to 91.3° (SbH_3),[26] as well as in triphenyl [C−E−C angles decrease from 102.8° (PPh_3), 100.1° ($AsPh_3$), 97.8° ($SbPh_3$) to 93.9° ($BiPh_3$)][27] and trimethyl derivatives Me_3E [C−E−C angles decrease from 110.6° (NMe_3)[28] to 94.2° ($SbMe_3$)].[29] Only $BiMe_3$ shows a slightly bigger C−Bi−C angle of 96.7°.[30] The smaller bond angles of the stibides and bismuthides relative to the amides result both from the decreased steric repulsion between the $SiMe_3$ groups owing to the increased E−Si bond length and from the increased s-character of the *lone pair* and the increased p-character of the bonding electron pairs due to relativistic effects and the lanthanide-contraction (inert-pair effect).[31]

In an attempt to prove the generality of the described reaction pathway for the synthesis of group 13/15 monomers, we also investigated reactions of Ga−Sb heterocycles $[R_2GaSb(SiMe_3)_2]_x$ (R = Me, x = 3; R = Et, x = 2) with dmap. Again, the monomeric compounds dmap−$Ga(R_2)Sb(SiMe_3)_2$ (R = Me **4**, Et **5**, Scheme 3) were obtained in almost quantitative yield. However, they are more temperature labile than the Al derivatives and start to decompose significantly at room temperature both in solution and in the solid state. Therefore, the reaction has to be performed between −10 and 0 °C and the resulting monomers have to be stored at −30 °C.

$$1/x\ [R_2GaSb(SiMe_3)_2]_x + \mathrm{dmap} \longrightarrow \mathrm{dmap}{-}Ga(R_2)Sb(SiMe_3)_2$$

R = Me **4**, Et **5**

Scheme 3. Synthesis of monomeric, Lewis base-stabilized stibinogallanes

Single crystals of **5** were obtained from a solution in hexane at −30 °C. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ (no. 2). **5** (Figure 4) is isostructural to the corresponding Al derivative dmap−$Al(Et_2)Sb(SiMe_3)_2$[3] and shows comparable Ga−C (199.4 pm) and Sb−Si distances

(255.0 pm) as well as C−Ga−C [117.2(2) °] and Si−Sb−Si bond angles [99.3(1) °].

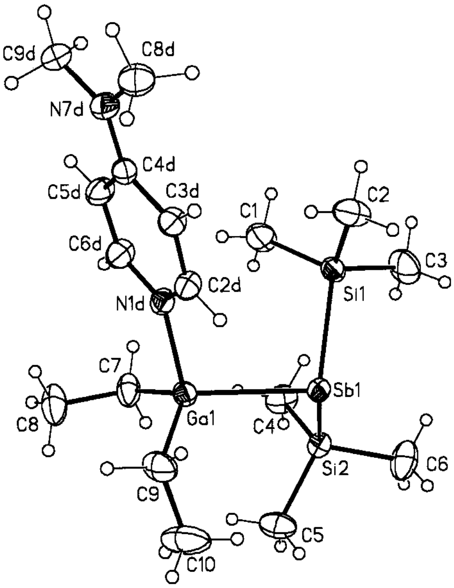


Figure 4. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **5**; selected bond lengths [pm] and angles [°]: Ga1−N1d 206.6(2), Ga1−Sb1 264.8(1), Ga1−C7 198.5(2), Ga1−C9 200.3(2), Sb1−Si1 254.8(1), Sb1−Si2 255.3(1); C7−Ga1−C9 117.2(2), Si1−Sb1−Si2 99.3(1), N1d−Ga1−Sb1 103.6(1), Si1−Sb1−Ga1 100.6(1), Si2−Sb1−Ga1 99.3(1)

In contrast, the Ga−N distance is much longer [206.6(2) pm], demonstrating the reduced Lewis acidity of the Et_2Ga-relative to the Et_2Al-fragment, but almost the same as in 2-(methyl)pyridine−$Ga(Me_2)Cl$ [206.6(3) pm].[32] However, 4-(methyl)pyridine−$Ga(Mes_2)SeMes$, which also contains a tricoordinated N base, shows a slightly longer Ga−N distance [209.5(3) pm],[33] while in the methylene-bridged compound $Me_3N-Ga(CH_2CMe_2)CH_2P(Ph_2)-Cr(CO)_5$, which contains a tetracoordinated N center, the Ga−N distance is significantly increased [223.5(3) pm].[10c] Very recently, Gladfelter et al. described the synthesis of several quinuclidine-stabilized amido- and azidogallanes by the reaction of quinuclidine-stabilized dichlorogallane quin−$Ga(H)Cl_2$ with Li amides and azides. The X-ray structures of four compounds showed dative Ga−N distances between 206 and 210 pm,[34] which are comparable to that found in Me_3N-GaH_3 [208.1(4) pm].[35] The Ga−Sb distance of 264.8(1) pm found in **5** is the shortest Ga−Sb bond length ever observed. It is also shorter than the Al−Sb distances found in the Lewis base-stabilized Al−Sb monomers (267−270 pm).[3] An analogous tendency was observed for the Al−Sb and Ga−Sb heterocycles {e.g. $[Me_2MSb(SiMe_3)_2]_3$: 270.2(1)−273.8(1) pm (M = Al),[22] 267.7(1)−271.4(1) pm (M = Ga)[36]; $[Et_2MSb(SiMe_3)_2]_2$: 272.3(1), 272.9(1) pm (M = Al),[23] 271.8(1), 272.9(1) pm (M = Ga)[37]}. Although the covalent radii of Al and Ga are almost the same (Al 125 pm; Ga 126 pm), the Ga−Sb heterocycles tend to have slightly shorter inter-metallic bond lengths than the Al−Sb compounds.

Conclusions

Four- and six-membered group 13/15 heterocycles can be cleaved by reaction with the strong Lewis base 4-(dimethylamino)pyridine (dmap). Previous reports on Al−Sb and Al−Bi heterocycles are extended in these studies to the corresponding Al−P and Al−As heterocycles as well as to Ga−Sb compounds. In all cases, Lewis base stabilized monomers of the type dmap−$M(R_2)E(SiMe_3)_2$ were formed in almost quantitative yield. This convenient reaction type seems to be a general, useful synthetic pathway for the synthesis of the desired class of compounds, allowing access to a wide variety of monomeric group 13/15 compounds. The coordination chemistry of the resulting monomers is currently under investigation.

Experimental Section

General Considerations: All manipulations were performed in a glovebox under a Ar-atmosphere or by standard Schlenk techniques. $[Me_2GaSb(SiMe_3)_2]_3$ [36] and $[Et_2GaSb(SiMe_3)_2]_2$ [37] were prepared by literature methods. Although the synthesis of $[Me_2AlP(SiMe_3)_2]_2$,[38] $[Me_2AlAs(SiMe_3)_2]_2$,[39] and $[Et_2AlAs(SiMe_3)_2]_2$ [40] is described in the literature, these compounds were prepared by the dehydrosilylation reaction between the corresponding alane R_2AlH and $E(SiMe_3)_3$ according to a procedure described previously.[22,23] − ^1H and $^{13}C\{^1H\}$ spectra were recorded using a Bruker AMX 300 spectrometer, using C_6D_5H as internal reference (δ^1H = 7.154; $\delta^{13}C$ = 128.0). − Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Bonn.

General Preparation of dmap −$Al(R_2)E(SiMe_3)_2$: 4-(Dimethylamino)pyridine (2.00 mmol) was added to a solution of the respective Al−E heterocycle (1.00 mmol) in hexane and the resulting suspension was heated at reflux for 30 min. The resulting clear, slightly yellow solution was stored at −30 °C. After 10 h, compounds **1−3** were obtained as colorless or light yellow solids.

dmap −$Al(Me_2)P(SiMe_3)_2$ (1): Yield 0.66 g (1.85 mmol, 93%). − ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.02 (d, $^3J_{P-H}$ = 1.6 Hz, 6 H, AlMe), 0.56 (d, $^3J_{P-H}$ = 3.9 Hz, 18 H, $SiMe_3$), 2.00 (s, 6 H, NMe_2), 5.71 [d, $^3J_{H-H}$ = 6.4 Hz, 2 H, C(3)-H], 8.26 [dd, $^{3,4}J_{H-H}$ = 5.6 / 1.5 Hz (AA′XX′), 2 H, C(2)-H]. − $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): δ = −4.4 [AlMe (d, $^2J_{C\text{-}P}$ = 12.5 Hz)], 6.1 [$SiMe_3$ (d, $^2J_{C\text{-}P}$ = 10.4 Hz)], 38.6 (NMe_2), 106.9 [C(3)-H], 148.0 [C(2)-H], 155.3 [C(4)]. − $C_{15}H_{34}AlN_2PSi_2$ (356.57): calcd. C 50.50, H 9.64; found C 50.71, H 9.88.

dmap −$Al(Me_2)As(SiMe_3)_2$ (2): Yield 0.75 g (1.88 mmol, 94%). − ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.03 (s, 6 H, AlMe), 0.61 (s, 18 H, $SiMe_3$), 1.92 (s, 6 H, NMe_2), 5.58 (d, $^3J_{H-H}$ = 6.6 Hz, 2 H, C(3)-H), 8.18 (dd, $^{3,4}J_{H-H}$ = 5.8 / 1.5 Hz, 2 H, C(2)-H). − $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): δ = −4.1 (AlMe), 6.3 ($SiMe_3$), 38.6 (NMe_2), 106.8 [C(3)-H], 147.3 [C(2)-H], 155.5 [C(4)]. − $C_{15}H_{34}AlAsN_2Si_2$ (400.52): calcd. C 45.14, H 8.60; found C 45.28, H 8.71.

dmap −$Al(Et_2)As(SiMe_3)_2$ (3): Yield 0.74 g (1.72 mmol, 86%). − ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.60 (s, 18 H, $SiMe_3$), 0.86 (q, $^3J_{H-H}$ = 8.1 Hz, 4 H, Et-CH_2), 1.51 (t, $^3J_{H-H}$ = 8.1 Hz, 6 H, Et-CH_3), 1.91 (s, 6 H, NMe_2), 5.58 [d, $^3J_{H-H}$ = 7.3 Hz, 2 H, C(3)-H], 8.20 [dd, $^{3,4}J_{H-H}$ = 5.9 / 1.4 Hz, 2 H, C(2)-H]. − $^{13}C\{^1H\}$

Table 1. Crystallographic data and measurements for dmap−Al(Me$_2$)P(SiMe$_3$)$_2$ (**1**), dmap−Al(Me$_2$)As(SiMe$_3$)$_2$ (**2**), dmap−Al(Et$_2$)As(SiMe$_3$)$_2$ (**3**), and dmap−Ga(Et$_2$)Sb(SiMe$_3$)$_2$ (**5**)

	1	2	3	5
Empirical formula	$C_{15}H_{34}AlN_2PSi_2$	$C_{15}H_{34}AlAsN_2Si_2$	$C_{17}H_{38}AlAsN_2Si_2$	$C_{17}H_{38}GaN_2SbSi_2$
M [g mol^{-1}]	356.57	400.52	428.57	518.14
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P1$(bar) (No. 2)	$P1$(bar) (No. 2)	$P1$(bar) (No. 2)
a [Å]	14.3849(3)	9.4486(6)	9.4839(6)	9.5773(3)
b [Å]	13.1337(3)	16.1715(13)	9.9883(8)	10.3393(4)
c [Å]	24.2830(6)	16.4331(14)	14.0512(11)	14.1058(5)
α [deg]		69.504(4)	78.462(4)	77.594(2)
β [deg]	102.011(2)	73.748)4)	77.301(5)	76.594(2)
γ [deg]		87.298(4)	70.398(4)	69.676(2)
V [Å^3]	4487.28(18)	2254.4(3)	1211.63(16)	1260.26(8)
Z	8	4	2	2
Radiation (wavelength, Å)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
μ [mm^{-1}]	0.266	1.650	1.540	2.237
temp. [K]	123(2)	123(2)	123(2)	123(2)
D_{calcd} [g cm^{-3}]	1.056	1.180	1.175	1.365
Crystal dim. [mm]	0.35 × 0.30 × 0.15	0.20 × 0.10 × 0.05	0.30 × 0.25 × 0.05	0.35 × 0.15 × 0.10
$2\theta_{max}$ [deg]	56.6	50.0	50.0	56.6
No. of rflns. rec.	46610	31736	15304	21830
No. of nonequiv. rflns. rec.	10622	7916	4252	5999
R_{merg}	0.047	0.132	0.083	0.062
No. of parameters refined	383	383	210	210
$R1$[a]; $wR2$[b]	0.032, 0.092	0.051, 0.082	0.042, 0.095	0.027, 0.067
Goodness of fit[c]	1.034	0.868	0.964	1.040
Final max, min Δρ [e Å^{-3}]	0.288, −0.252	0.434, −0.602	0.754, −0.508	0.661, −1.511

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ [for $I > 2\sigma(I)$]. − [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. − [c] Goodness of fit $= \{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

NMR (50 MHz, C$_6$D$_6$, 25 °C): δ = 4.3 (Et-CH$_2$), 6.1 (SiMe$_3$), 10.6 (Et-CH$_3$), 38.1 (NMe$_2$), 106.4 [C(3)-H], 147.0 [C(2)-H], 155.1 [C(4)]. − $C_{17}H_{38}AlAsN_2Si_2$ (428.57): calcd. C 47.63, H 8.91; found C 47.46, H 8.67.

General Preparation of dmap −Ga(R$_2$)Sb(SiMe$_3$)$_2$: 4-(Dimethylamino)pyridine (2.00 mmol) was added to a solution of the respective Ga−Sb heterocycle (1.00 mmol of the dimer, 0.67 mmol of the trimer) in hexane at −10 °C. The resulting suspension was stirred at this temperature for 1 h, slowly warmed to 0 °C over 2 h, filtered, and stored at −30 °C. After 10 h, compounds **4** and **5** were obtained as colorless or light yellow solids, which are thermolabile. They decompose significantly in solution at 25 °C within 30 min. ^{13}C NMR spectra could therefore not be obtained.

dmap −Ga(Me$_2$)Sb(SiMe$_3$)$_2$ (4): Yield 0.66 g (1.34 mmol, 67%). − ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 0.39 (s, 4.4 H, GaMe$_2$), 0.65 (s, 14 H, SiMe$_3$), 2.05 (s, 6 H, NMe$_2$), 5.69 [d, $^3J_{H-H}$ = 6.9 Hz, 2 H, C(3)-H], 8.10 [d, $^3J_{H-H}$ = 5.7 Hz, 2 H, C(2)-H]. − $C_{15}H_{34}GaN_2SbSi_2$ (489.45): calcd. C 36.73, H 6.95; found C 35.81, H 6.78.

dmap −Ga(Et$_2$)Sb(SiMe$_3$)$_2$ (5): Yield 0.67 g (1.29 mmol, 60%). − ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 0.67 (s, 18 H, SiMe$_3$), 1.03 (q, $^3J_{H-H}$ = 7.9 Hz, 4 H, Et-CH$_2$), 1.52 (t, $^3J_{H-H}$ = 8.0 Hz, 6 H, Et-CH$_3$), 1.99 (s, 6 H, NMe$_2$), 5.67 [d, $^3J_{H-H}$ = 5.7 Hz, 2 H, C(3)-H], 8.13 [d, $^3J_{H-H}$ = 6.0 Hz, 2 H, C(2)-H]. − $C_{17}H_{38}GaN_2SbSi_2$ (518.14): calcd. C 39.43, H 7.41; found C 39.11, H 7.02.

X-ray Structure Solution and Refinement: Crystallographic data of **1**, **2**, **3**, and **5** are summarized in Table 1. Figure 1−4 show the ORTEP diagrams of the solid-state structures of **1**, **2**, **3**, and **5**. Data were collected on a Nonius Kappa-CCD diffractometer. The structures of **1**, **2**, **3**, and **5** were solved by Patterson methods (SHELXS-97)[41] and refined by full-matrix least-squares on F^2 (SHELXL-97).[42] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. Empirical absorption corrections were applied (**2**, **3**, and **5**). The crystallographic data of **1**, **2**, **3**, and **5** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144769 (**1**), CCDC-144768 (**2**), CCDC-144767 (**3**), and CCDC-144770 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ [Fax: (Internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam-ak.uk].

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