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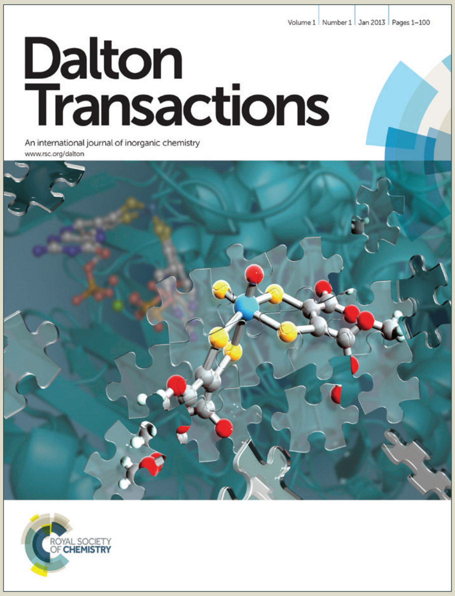

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Hydrometallation of amino-trialkynylsilanes - intramolecular M-N interactions (M = Al, Ga) and potential activation of Si-N bonds[†]

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Received

Hydrometallation of a pyrrolidyl functionalised trialkynylsilane, H_8C_4-Si(C≡C-CMe_3)$_3$, with equimolar quantities of H-M(CMe_3)$_2$ (M = Al, Ga) resulted in the formation of mixed alkenyl-dialkynylsilanes (**3a**, **3b**) which have a Lewis-acidic Al or Ga atom in geminal position to the Si atom and form four-membered M-N-Si-C heterocycles by a strong interaction of the amine N atoms with the Lewis-acidic metal atoms. This interaction results in a concomitant lengthening and weakening of the Si-N bonds. Dual hydrometallation afforded alkynyl-dialkenylsilanes (**4a**, **4b**) with two Lewis-acidic metal atoms. Al-N and Ga-N interactions to one of the Lewis-acidic centers led again to the formation of M-N-Si-C heterocycles. The second Al atom of **4a** interacted with C-H bonds of the vinylic *tert*-butyl group, while the Ga atom of **4b** was coordinated to the α-C atom of the remaining alkynyl substituent. Dual hydrometallation of the corresponding pyrrolyl-trialkynylsilane resulted in compounds with different structures (**5a**, **5b**) due to the delocalisation of the lone pair of electrons at nitrogen in the aromatic ring.

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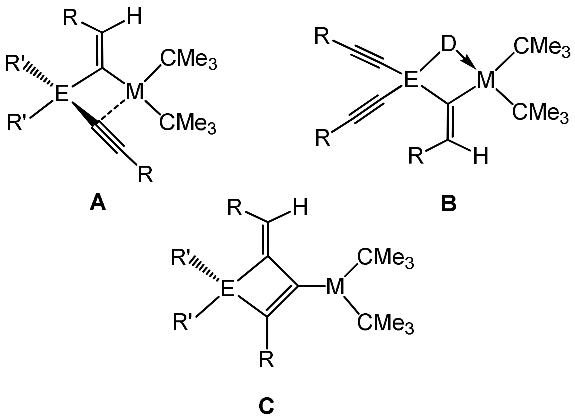
One metal atom is coordinated to the α-C atom of the alkynyl group, the other has a close contact to a C-H bond of the pyrrole ring. The synthesis of **4b** gave an unprecedented bicyclic by-product (**6**) which has a Ga-H-Ga 3c-2e bond. It was formally formed by hydrogallation of the trialkyne with the sesquihydride $[H_2Ga\text{-}CMe_3]_2[H\text{-}Ga(CMe_3)_2]_2$ and was also obtained by the selective reaction with this starting material.

Introduction

The activation of σ-bonds in catalytic or stoichiometric reactions is in the focus of current research interests. In recent groundbreaking investigations it was shown that frustrated Lewis-pairs (FLPs) based on main-group elements are extraordinarily suitable for an application in such processes.[1] They unite Lewis-basic and –acidic centers in single molecules or bimolecular systems and are extremely valuable for the dipolar activation or coordination of small molecules. However, frustration is not a necessary prerequisite of this outstanding reactivity and active Lewis-pairs have been reported in which inter- or intramolecular adduct formation does not significantly influence specific secondary reactions.[1] More recently, aluminium was introduced as a new and very effective Lewis-acid which due to its inherently high polarising capability does not require activation by electron withdrawing substituents.[2] The applicability of Al-based FLPs in various secondary reactions has been impressively demonstrated independently by several research groups.[3,4] One aspect was the intramolecular σ-bond activation in highly functionalised compounds which had donor groups attached to Si or Ge atoms and coordinatively unsaturated Lewis-acidic Al or Ga atoms in the same molecule. These compounds were easily synthesised by hydrometallation[5] of silyl- or germylalkynes $R'_nE(C\equiv C\text{-}R)_{4-n}$ (E = Si, Ge; R = alkyl, aryl; R' = alkyl, NR_2, Cl) with Group 13 element hydrides HMR_2 (M = Al, Ga) and had the Si or Ge atoms in a geminal arrangement to the three-coordinate Al or Ga atoms. Alkenyl or mixed alkenyl-alkynyl silanes[6-10] and germanes[10-14] were formed of which the latter were found to be of particular interest. The high polarity of the E-C_α(alkynyl) bond and the resulting large partial negative charge of the C_α atom leads to a close intramolecular contact between C_α and the neighbouring electropositive, Lewis acidic metal atom (**A**, Scheme 1) while the presence of electron donor atoms such as N or Cl (D) resulted in strong intramolecular M-D contacts (D = N, Cl) with the formation of four-membered E-C-M-D heterocycles (**B**). The described interactions result in an activation of the E-C and E-D bonds as evident from a lengthening of these bonds and supported by quantum chemical calculations[14]. Synthetic applications were the synthesis of sila-[7,9] and germacyclobutenes[12] (**C**) starting with **A** *via* thermally induced 1,1-carbometallation, a spontaneous *tert*-butyl-chlorine exchange (**B**, D = Cl),[9] the facile insertion of isocyanates and –thiocyanates into activated E-N bonds[14] and the formation of a new Ge-C≡C-Ph moiety by C-H bond activation and a unique exchange of an alkynyl against a NR_2 group.[14] These results demonstrate impressively the highly promising properties of these functionalised compounds which may find wide application in secondary reactions: (i) They form fascinating structures with diverse, interesting and unique structural motifs which verify intramolecular σ-bond activation by M-X interactions. (ii) The activated compounds may undergo rearrangement reactions which lead to the formation of heterocycles[7,9,12] or unusual exchange products.[9,14] (iii) The intramolecular Lewis-acid-base interactions give access to compounds that feature strained rings. Cleavage of the M-X bonds in these rings results in a situation with free Lewis-acidic and –basic centers which is similar to that of FLPs and may allow the application of these compounds for the activation or coordination of e.g. heterocumulenes or terminal alkynes.[14] (iv) The weakening of the E-X bonds facilitates insertion reactions.[14] (v) Further weakening and finally breaking of the E-X bonds with the migration of X to the Lewis-acidic center may result in the formation of silyl or germyl cations.[15] In this article we report on the syntheses of aminotrialkynylsilanes and their hydrometallation reactions with H-M(CMe_3)$_2$ (M = Al, Ga). The expected products are promising candidates for studying the above stated possible reactivity patterns.

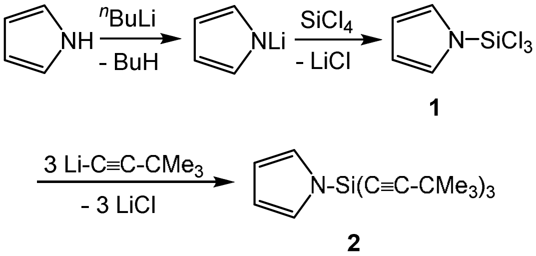


Scheme 1 (E = Si, Ge; M = Al, Ga)

Results and Discussion

Pyrrolyl-trialkynylsilane, C_4H_4N-Si(C≡C-CMe_3)$_3$ (**2**), was obtained in high yield from the amine C_4H_4NH, $SiCl_4$ and *in situ* generated LiC≡C-CMe_3 (Scheme 2) following a procedure developed previously for the synthesis of the pyrrolidyl analogue C_4H_8N-

$Si(C{\equiv}C\text{-}CMe_3)_3$.[9] The trichloride intermediate **1** was isolated as an extremely water sensitive and corrosive, colourless liquid, while the trialkynylsilane **2** is a moderately air-sensitive, colourless solid. The molecular structure of compound **2** is shown in Figure 1. The Si atom is coordinated by the pyrrolyl group and three ethynyl substituents in a tetrahedral fashion. The ethynyl groups have C≡C bond lengths in the characteristic range of about 120 pm. Compared to standard values of around 177 pm in compounds with $N\text{-}Si[C(sp^3)]_3$ groups[16] the Si-N bond length of 174.4(2) pm is relatively short which may be caused by the bonding of the Si atom to three hard sp-hybridised C atoms. An even shorter Si-N distance has been observed in the pyrrolidyl compound $C_4H_8N\text{-}Si(C{\equiv}C\text{-}CMe_3)_3$ (169.6(2) pm)[9] in which a saturated N-heterocycle is attached to silicon. In the latter case the lone pair of electrons at nitrogen may interact with the Si atom by hyperconjugation and hereby strengthen the Si-N bond. There is no comparable effect in compound **2** because the lone pair is delocalised in the aromatic ring. The N atoms of both compounds have a planar coordination with a sum of all angles of 360°. The most acute of these angles in **2** (105.9(2)°) expectedly includes the C atoms of the aromatic ring. The ethynyl groups of **2** showed characteristic resonances in the ^{13}C NMR spectrum at $\delta = 112.6$ (β-C) and 76.8 (α-C) and two absorptions in the IR spectrum at 2207 and 2160 cm^{-1}.



Scheme 2.

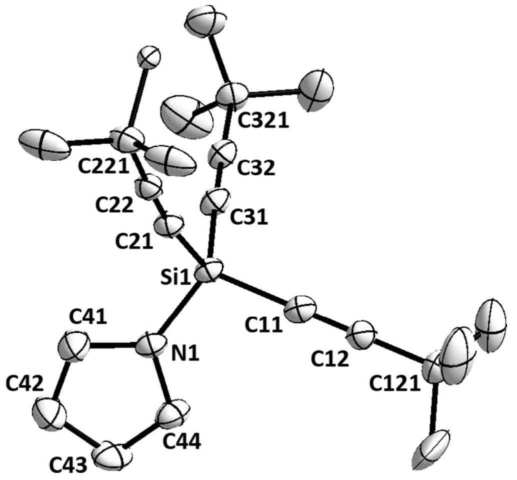
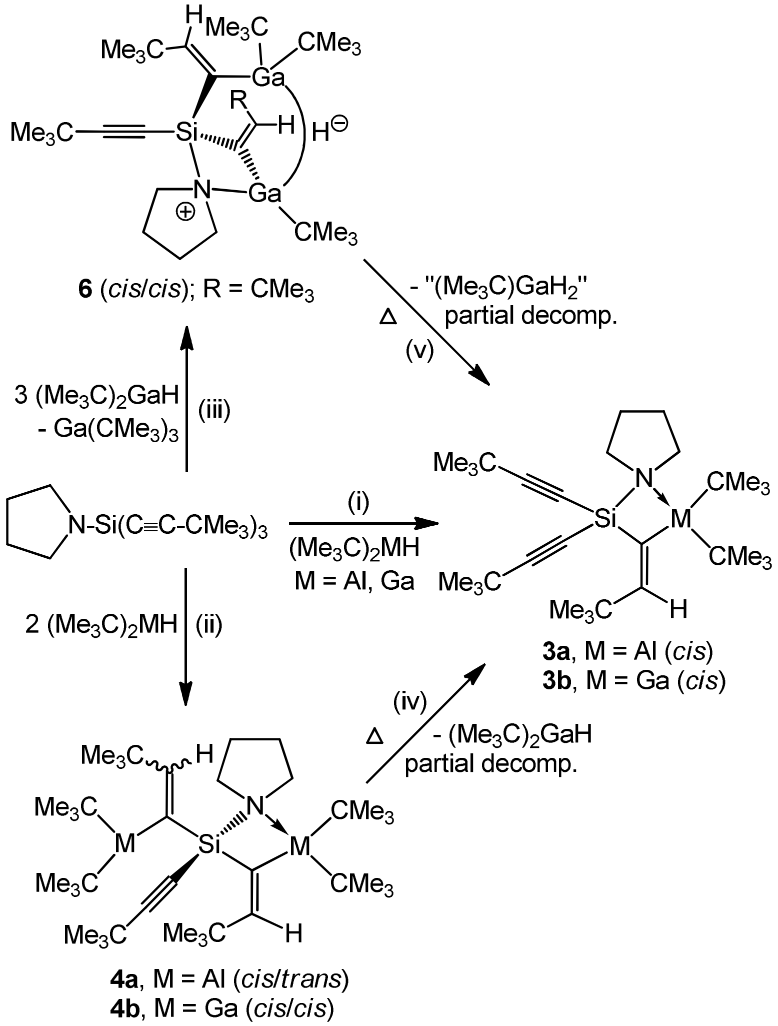


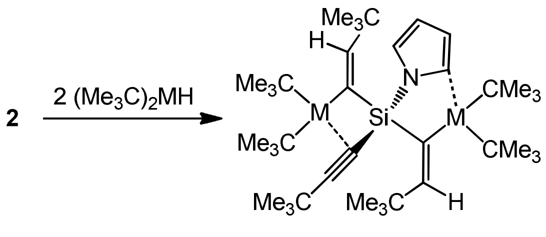
Figure 1. Molecular structure and atomic numbering Scheme of compound **2**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm): Si(1)–N(1) 174.4(2), Si(1)–C(11) 180.6(2), Si(1)–C(21) 181.0(2), Si(1)–C(31) 181.2(2), C(11)–C(12) 119.8(3), C(21)–C(22) 120.1(2), C(31)–C(32) 119.8(3).

Hydrometallation of $C_4H_8N\text{-}Si(C{\equiv}C\text{-}CMe_3)_3$ with one equivalent of $H\text{-}M(CMe_3)_2$ (M = Al, Ga) in toluene afforded the *cis*-addition products **3** (**3a**, M = Al; **3b**, M = Ga) in high yields of approximately 80% ((i) in Scheme 3, *cis* refers to the positions of Al or Ga and H atoms across the C=C bond). The reactions were regiospecific with the electropositive metal atoms bound to the C atom connected to the Si atom (partial negative charge at C caused by the electronegativity difference between C and Si) and stereospecific (*cis*) as a result of the concerted nature of the addition reaction. Rearrangement to the thermodynamically favoured *trans* isomer was shown to require the presence of a free coordination site on the metal atom to facilitate rearrangement *via* a bimolecular process.[17] The presence of four-coordinate metal centres in **3a** and **3b** was consequently found to stabilise the *cis*-hydrometallation products and increase the activation energy for the transformation to the *trans* products.



Scheme 3. ((i) to (v) refer to the discussion in the text)

The corresponding 1 : 2 addition products **4** (pyrrolidyl; (ii) in Scheme 3) and **5** (pyrrolyl; Scheme 4) were obtained accordingly in high yields (except **4b**) from the reaction of C_4H_8N-Si(C≡C-CMe_3)$_3$ and C_4H_4N-Si(C≡C-CMe_3)$_3$ (**2**), respectively, with two equivalents of H-M(CMe_3)$_2$. The comparatively low yield of compound **4b** is due to the formation of a mixture of **3b**, **4b** and **6** in a NMR spectroscopically determined ratio of 0.26, 0.52 and 0.22. After fractional recrystallisation of the mixture analytically pure **4b** was isolated in 40% yield. When the stoichiometric ratio of the starting materials was increased to a ratio of 1 : 3 (silane to hydride), the resonances of the monoaddition product **3b** disappeared and the NMR spectroscopically determined content of the condensation product **6** (elimination of $Ga(CMe_3)_3$, identified by NMR, *c.f.* ref. 18, 19) in the mixture increased to 44% (56% compound **4b**). Fractional crystallisation resulted in 28% yield of the pure product **6** ((iii) in Scheme 2). Surprisingly the product ratio (**4b** : **6**) did essentially not change when 3.2 or 4.5 equivalents of $H\text{-}Ga(CMe_3)_2$ were applied. Formally the formation of **6** may be rationalised by the addition of a sesquihydride of the type $[H\text{-}Ga(CMe_3)_2][H_2Ga\text{-}CMe_3]$ to the pyrrolidylsilane $C_4H_8N\text{-}Si(C{\equiv}C\text{-}CMe_3)_3$. A dimer of this unusual sesquihydride was recently synthesised in our group on a facile route by the treatment of $Ga(CMe_3)_3$ with the gallane-amine adduct $H_3Ga{\leftarrow}NMe_2Et$.[20] Its reaction with the alkynylsilane afforded selectively compound **6** which was isolated after recrystallisation from pentafluorobenzene in 62% yield. Compounds **4b** and **6** were both found to be thermally unstable in solution and reacted on heating by elimination of $H\text{-}Ga(CMe_3)_2$ or formally the unknown dihydride $H_2Ga\text{-}CMe_3$, respectively, to the 1 : 1 addition product **3b** ((iv and v in Scheme 2) and minor quantities of unidentified decomposition products.



5a, M = Al (*cis/cis*)
5b, M = Ga (*cis/cis*)

Scheme 4.

The particularly interesting structural motif of the monohydrometallation products **3a** and **3b** is the relatively strong intramolecular interaction between the pyrrolidine nitrogen atoms attached to silicon and the coordinatively unsaturated Al or Ga atoms which results in essentially planar four-membered Si-C-M-N heterocycles (puckering angles and other relevant parameters are summarised in Table 1 and Fig. 2). Ring closure leads to four-coordinate metal atoms, and the coordinative saturation of the metal atoms helps to stabilise the *cis* configuration in the olefin substituents. The endocyclic angles in the heterocycle are around 95º for C and Si, close to 90º for N and close to 81º for the metal atoms. In particular the acute angle at the sp^2-hybridised C atoms indicates a considerable ring strain in the molecules which is important for the future application of these compounds in secondary reactions. Ring opening may result in a situation similar to those of FLPs[1-4] which have a unique capability for the dipolar activation of small molecules. Only recently we have applied masked FLPs based on strained heterocycles with relatively weak Al-N interactions for the efficient activation of terminal alkynes, heterocumulenes or cyanamides.[21] The M-N bond lengths of **3a** and **3b** (208.5(1) and 222.3(2) pm) are at the long side of values typically observed for M-N-M[21,22] or Si-N→M[23] bridges. In few cases these Si-N→M interactions resulted in the formation of four-membered heterocycles similar to **3a** and **3b**.[23] Because of the lower electronegativity of Al, the more pronounced charge separation in Al-X bonds and the higher Lewis acidity of Al compared to Ga the M-N distances are shorter in the Al compound **3a**. The coordination of the N atom to the metal atom results in a considerable lengthening of the corresponding Si-N bond by more than 12 pm compared to that of the starting trialkynylsilane $C_4H_8N\text{-}Si(C{\equiv}C\text{-}CMe_3)_3$ (169.6(2) *vs.* 183.7(1) and 181.5(2) pm). Only recently we have shown for related germanium compounds[14] that this elongation corresponds to an activation of the E-N bonds and increases their reactivity considerably (*c.f.* introduction). A further weakening of the Si-N bond may result in the formation of silyl cations[15] or may at least facilitate insertion reactions into the Si-N bonds. The metal atoms in **3a** and **3b** deviate from the plane of the three adjacent C atoms by 46.4 (Al) and 41.0 pm (Ga).

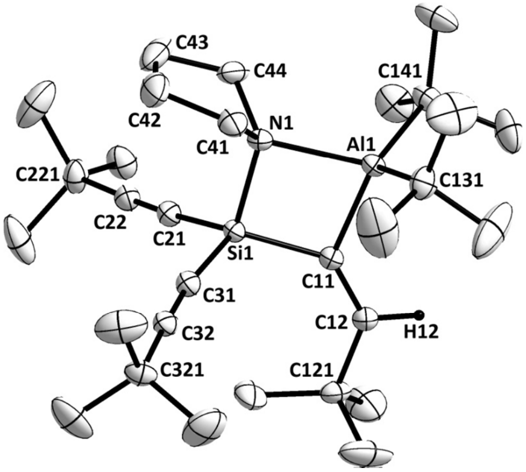


Figure 2. Molecular structure and atomic numbering Scheme of compound **3a**; a similar structure was observed for **3b**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms (except H(12), arbitrary radius) are omitted for clarity. Selected bond lengths (pm) and angles (º) of **3a** (M = Al) [**3b** (M = Ga)]: Si(1)–N(1) 183.7(1) [181.5(2)], C(21)–C(22) 119.8(2) [119.7(3)], C(31)–C(32) 120.2(2) [120.0(3)], M(1)–C(11) 200.0(1) [201.6(2)], M(1)–C(CMe_3) av. 201.8 [202.2], M(1)–N(1) 208.5(1) [222.3(2)], C(11)–Si(1)–N(1) 94.05(5) [96.35(7)], Si(1)–N(1)–M(1) 90.37(5) [88.81(6)], N(1)–M(1)–C(11) 81.96(5) [79.44(6)], M(1)–C(11)–Si(1) 93.43(6) [95.21(8)].

In the molecular structure of the 1 : 2 hydroalumination product **4a** (M = Al; Fig. 3) the Si atom is bonded to two alkenyl groups, an intact alkynyl substituent and the pyrrolidyl group. The crystals of the Ga analogue **4b** were of poor quality. The structure could not be refined to acceptable *R* values, but the preliminary results confirmed unambiguously the overall geometry of the molecule as shown in Scheme 3 and deduced from NMR spectra. A Si-C-M-N heterocycle similar to **3a** and **3b** is formed by an interaction of the N with the unsaturated Al atom (Al-N: 210.2(2) pm; Si-N 186.2(2) pm; Al 49.7 pm above the C_3 plane; see Table 1 and Fig. 3). The alkenyl group involved in this heterocycle has a *cis*-configuration. Interestingly, the second olefin unit of **4a** adopts the thermodynamically favoured *trans*-configuration. It is bonded to a terminal, nearly planar Al(CMe$_3$)$_2$ group that surprisingly does not interact with the C_α atom of the remaining alkynyl substituent as was observed in **5** and several related compounds[6,7,10] which typically showed Al···C_α contacts between 245 – 265 pm and a pronounced pyramidalisation of the metal atoms in the direction of the C_α atoms of the alkyne (Al 20 – 30 pm above the C_3 planes). Instead of these interactions we find two short Al(1)···H contacts (233 and 246 pm) to a methyl group of the vinylic *tert*-butyl substituent at C(121) and an concomitant pyramidalisation in that direction (*d* = 12 pm) as opposed to the direction of C_α. Interactions of this type between Main-Group metal atoms and C-H bonds (*pseudo*-agostic, anagostic) are well-known in the literature.[24]

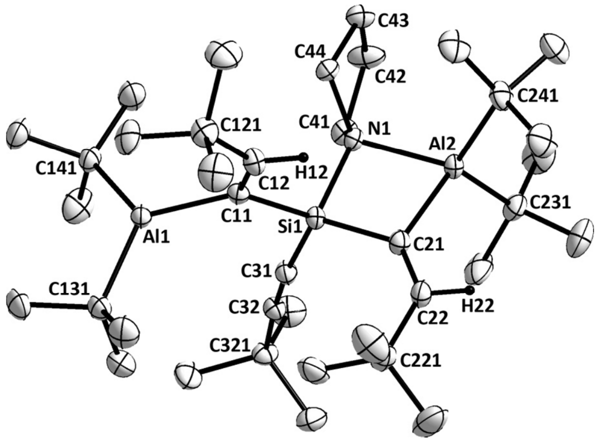


Figure 3. Molecular structure and atomic numbering Scheme of compound **4a**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms (except H(12) and H(22), arbitrary radii) and a molecule of cocrystallised pentafluorobenzene are omitted for clarity. Selected bond lengths (pm) and angles (°): Si(1)–N(1) 186.2(2), C(31)–C(32) 119.9(3), Al(1)–C(11) 197.3(2), Al(1)–C(*CMe*$_3$) av. 199.7, Al(2)–C(21) 199.5(2), Al(2)–C(*CMe*$_3$) av. 203.1, Al(1)–N(1) 210.2(2), C(21)–Si(1)–N(1) 93.19(9), Si(1)–N(1)–Al(2) 90.20(8), N(1)–Al(2)–C(21) 82.07(9), Al(2)–C(21)–Si(1) 94.2(1).

The molecular structures of the related pyrrolyl analogues **5** (Fig. 4) differ from those of **3** and **4** in so far as the Si-C-M-N heterocycles of the latter compounds are not formed which is essentially caused by the negligible basicity of the nitrogen atoms and the delocalisation of the lone pair of electrons into the aromatic system. Instead the atom Al(2) interacts with the atom C(41) of the pyrrolyl ring with a relatively short intramolecular Al(1)···C(41) distance of 239.4(2) pm (Al···H 216 pm). The corresponding Ga···C distance in **5b** (260.5(2) pm; Ga···H 240 pm) is expectedly much longer. The resulting structures may be described by a five-membered Al-C-Si-N-C heterocycle in an envelope conformation in which the atoms Si(1), C(21), M(2) and C(41) (M = Al, Ga) deviate only slightly from a coplanar arrangement [max. deviation from plane 5 pm for C(21) in **5a** and 4 pm for Ga(2) in **5b**]. The observed η^1-coordination (contact distances to other ring atoms are at least 50 (Al) or 40 (Ga) pm longer) of the pyrrole ring is very rare. Typical bonding modes between pyrrole substituents and metal atoms vary between η^2- and η^5-coordination.[25] As a consequence of this contact the Si(1)-N(1) distances are lengthened to 180.1(2) (**5a**) and 179.2(1) pm (**5b**) if compared to the free alkynylsilane **2**, and the metal atoms are 39.3 and 31.4 pm above the plane of the three adjacent C atoms. The second metal atom (Al(1), Ga(1)) has a relatively short contact to the C_{α} atom of the unreacted alkyne substituent (M(1)···C(31) 253 (**5a**) and 277 pm (**5b**)) which leads to an essentially planar four-membered M-C_{α}-Si-C heterocycle and a pyramidalisation of the metal atoms in the direction of C_{α} (Al 35.2, Ga 26.5 pm above the C_3 plane). In agreement with the above mentioned stabilising effect of four-coordinate Al or Ga atoms both olefinic substituents adopt a *cis* configuration. Overall geometry and bond lengths in these parts of the molecules compare well with those in related hydrometallated alkynylsilanes or –germanes.[6-14]

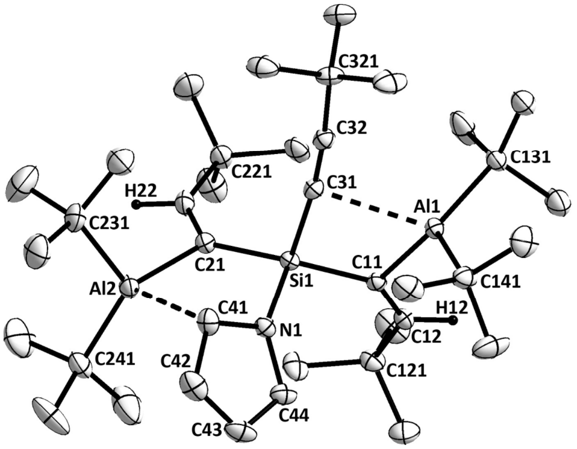


Figure 4. Molecular structure and atomic numbering Scheme of compound **5a**; a similar structure was observed for **5b**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms (except H(12) and H(22), arbitrary radii) are omitted for clarity. Selected bond lengths (pm) of compound **5a** (M = Al) [**5b** (M = Ga)]: Si(1)–N(1) 180.1(2) [179.2(1)], C(31)–C(32) 120.8(2) [120.1(2)], M(1)–C(11) 200.0(2) [201.0(2)], M(1)–C(*CMe*$_3$) av. 199.6 [av. 200.8], M(1)···C(31) 252.8 [277.0], M(2)–C(21) 200.5(2) [201.1(2)], Al(2)–C(*CMe*$_3$) av. 200.5 [av. 201.4], M(2)···C(41) 239.4(2) [260.5].

The unusual and unexpected molecular structure of compound **6** (Fig. 5) is complicated. It may be described as a bicyclic system with a six-membered N-Si-C-Ga-H-Ga heterocycle in a chair conformation which is bridged by the C_α atom of one of the alkenyl groups (C(11)) and has Si(1) and Ga(1) as the bridgehead atoms. Both Ga atoms are connected by a 3c-2e Ga-H-Ga bonding interaction. Ga(1) is additionally coordinated to a CMe_3 group, the atom N(1) and the alkenyl C atom C(11), Ga(2) to two CMe_3 groups and the C_α atom of the second alkenyl group C(21). A terminal alkynyl group (C≡C 120.4(2) pm) is bonded to Si(1) and deviates only slightly from linearity (Si-C≡C 177.1(1), C≡C-C 177.2(1)°). The typical (see above) Si-N-Ga-C heterocycle is formed by a Ga(1)-N(1) bonding interaction, but in contrast to the almost planar rings of the analogous structures discussed above it is folded across the C(11)···N(1) axis with a relatively large puckering angle of 34.9º. The bond lengths in the four-membered heterocycle are similar to those in the previously discussed compounds. But the Ga(1)-N(1) distance (210.31(9) pm) is the shortest one observed so far in this type of compounds and is in the range of Ga-N-Ga or Si-N→Ga bridges.[22,23] The Si(1)-N(1) bond is long (183.9(1) pm) compared to the pyrrolidyl starting material. The Ga-H distances are with 161(2) and 188(2) pm in the characteristic range of Ga-H-Ga bridges.[20,26-28] The shorter distance involves the sterically less shielded Ga-CMe_3 group in which the Ga atom (Ga(1)) is coordinated by the electronegative N atom. Both olefinic substituents adopt the *cis* configuration with Ga and H at the same side of the C=C bond.

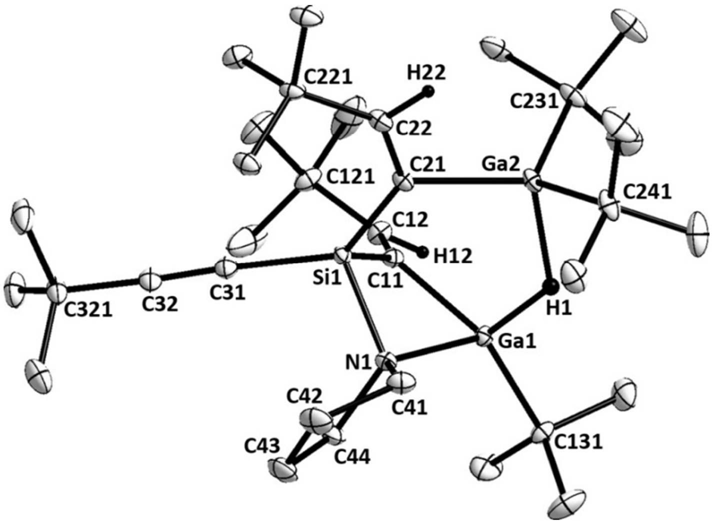


Figure 5. Molecular structure and atomic numbering Scheme of compound **6**. Displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms (except H(1), H(12) and H(22), arbitrary radii) are omitted for clarity. Selected bond lengths (pm) and angles (°) of **6**: Si(1) –N(1) 183.9(1), C(31)–C(32) 120.4(2), Ga(1)–C(CMe_3) 198.6(1), Ga(1)–N(1) 210.31(9), Ga(2)–C(21) 203.6(1), Ga(2)–C(CMe_3) av. 202.8, C(11)–Si(1)–N(1) 90.95(5), Si(1)–N(1)–Ga(1) 87.51(4), N(1)–Ga(1)–C(11) 79.94(4), Ga(1)–C(11)–Si(1) 90.53(5).

The spectroscopic characterisation of compounds **2** to **6** supported the information from crystal structure determinations and demonstrated that the molecular structures of these compounds are largely retained in solution. The $\nu_{C\equiv C}$ stretching vibrations in the IR spectra were recently[9,27] shown to allow a differentiation between terminal and bridging alkynyl groups in aluminium or gallium functionalised mixed alkenyl-alkynylsilanes or -germanes. The absorptions of bridging alkynes are characteristically shifted by approximately 30 – 50 cm^{-1} to lower wavenumbers as compared to terminal groups. Pertinent data is summarised in Table 1 from which is evident that the values for terminal alkynyl substituents in compounds **3a**, **3b**, **4a** and **6** are very similar to those in the trialkynyl starting materials, while the alkynyl substituents that show an interaction between Al or Ga and C_α atoms in their crystal structures have significantly lower values (**5a**, **5b**). Interestingly the stretching vibrations observed for the gallium compound **4b** indicate an alkynyl-Ga interaction although it was clearly excluded by the crystal data for the Al analogue **4a**. The latter showed instead an interaction of the Al atom to a methyl group of the vinylic *tert*-butyl substituent. The results of the IR spectrum of **4b** may indicate that the weaker Lewis-acid Ga prefers the close contact to the ethynyl group over a Ga···H interaction. Regrettably the crystal structure determination of **4b** was of insufficient quality, and the preliminary data must therefore be handled with care. But it seems that indeed the Ga atom approaches the ethynyl group, which is a remarkable proof for the importance and relevance of these IR parameters.

Another important spectroscopic parameter for the assignment of the molecular structures is the value of the $^3J_{SiH}$ coupling constants between silicon and the vinylic H atom which allows the convenient differentiation between *cis*- ($^3J_{SiH} > 20$ Hz; Si and H in *trans*-position) and *trans*-hydrometallation products ($^3J_{SiH} < 20$ Hz; Si and H in *cis*-position) in solution.[6-10,17] Based on this indicator (Table 1) and in agreement with the solid state structures all compounds with the exception of **4a** adopted in solution a *cis* configuration for their olefinic substituents. Only compound **4a** featured a *cis*- ($^3J_{SiH} =$ 29.8 Hz) and a *trans*-substituent ($^3J_{SiH} = 15.8$ Hz), while its gallium analogue **4b** has two *cis*-configurated ethenyl groups.

The coordination of N to the Al or Ga atoms resulted for compounds **3a** and **3b**, as discussed above, in the formation of Si-C-M-N heterocycles. In solution the ring plane becomes a virtual mirror plane that is approximately perpendicular to the pyrrolidine ring. As a consequence only a single resonance was observed in the NMR spectra for both *tert*-butyl substituents of the $M(CMe_3)_2$ and $Si(C{\equiv}C\text{-}CMe_3)_2$ groups. In case of the gallium compound **3b** only two further sets of signals were observed for the pyrrolidine substituent (NCH_2 and CH_2) at room temperature while in **3a** four magnetically inequivalent protons were visible representing the different environments for protons in the vicinity of Al or Si. In the case of the gallium derivative **3b** the Ga-N bond is longer than the Al-N bond of **3a** and the protons equilibrate by a fast inversion of the pyrollidyl ring and a possible rotation about the Si-N bond after cleavage of the weak Ga-N bonding interaction. When **3b** was slowly cooled to 200 K both ^1H NMR signals began to broaden. The resonance of the NCH_2 protons split into two signals with chemical shifts (δ = 3.94 and 2.66) similar to those of the Al compound at room temperature. The resonance for the CH_2 protons disappeared in the baseline but did not resolve into two signals at 200 K. This observation is consistent with a deceleration of the structural change in the pyrrolidine heterocycle. Based on a coalescence temperature of T_C = 210 K the free activation energy $\Delta G^{\#}$ for this process was estimated to be 40 kJ/mol.[29]

The molecular structures of compounds **4a** and **4b** contain a chiral Si atom which should result in complicated NMR spectra with resonances for six or seven different *tert*-butyl groups. The real figure depends on the strength of the secondary metal-carbon or metal-hydrogen interactions (see discussion of the molecular structures) and the barrier of rotation about the M-C bonds between the three-coordinate Al or Ga atom (schematic drawings in Scheme 3) and the vinylic C atom. In accordance with this expectation seven *tert*-butyl resonances were detected for the Al compound **4a**. The hydrogen atoms of the C=C*H* and NC*H*₂ groups were also found to be magnetically inequivalent. In the ^1H NMR spectrum we observed a significant shift of the resonance of the vinylic *tert*-butyl group to a higher field compared to **3** or **5** (Table 1). The unusual chemical shift may be caused by the interaction of the CMe_3 group with Al(1) as found in the solid state and was similarly reported for agostic interactions in transition metal compounds.[24] Six resonances with a singlet for two equivalent *tert*-butyl groups resulted for **4b**, but only upon cooling of a sample in toluene to about 0 °C. At room temperature broad resonances occurred and four sharp singlets with an integration ratio of 2 : 2 : 2 : 1 were observed above 50 °C. The latter resonance belongs to the alkynyl *tert*-butyl group. Obviously the alkenyl groups became equivalent at elevated temperature which may be explained by a fast exchange of the N atom between both Ga atoms. This exchange process made both $Ga(CMe_3)_2$ groups equivalent, but due to a hindered rotation about the Ga-C(vinyl) bond the *tert*-butyl groups of a single GaR_2 group were inequivalent. The activation energy for this process was calculated from the NMR data to 59 kJ/mol.[29]

At room temperature, the ^1H NMR spectra of the pyrrolyl derivatives **5a** and **5b** showed one signal for the NC*H* and C*H* protons of the pyrrolyl group, respectively, and two equivalent vinyl substituents, but two signals for the magnetically inequivalent CMe_3 groups at the metal atoms. This is consistent with a dynamic behaviour similar to that of **4b** with the α-C atom and the pyrrolyl ring alternatively coordinated to both Ga atoms. When compound **5a** was cooled to 200 K this process became slow on the NMR timescale (*c.f.* Fig. 3) and as a consequence all four H atoms on the pyrrolyl substituent and all seven CMe_3 groups became inequivalent. The chemical shifts of the four pyrrolyl H atoms cover a broad range between $\delta = 6.16$ and 7.50. Based on averaged data of all involved H atoms $\Delta G^{\#}$ was estimated to 50 kJ/mol.[29]

The hydride adduct **6** showed a characteristic broad resonance for the bridging hydride at $\delta = 3.76$ in the ^1H NMR spectrum. The molecular backbone with a rigid bicycle (Fig. 5) resulted in all CMe_3 groups, the vinylic hydrogen atoms and all eight protons of the pyrrolidine heterocycle being magnetically inequivalent. Broad absorptions in the IR spectra at 1886 and 1614 cm^{-1} were in the characteristic range of Ga-H stretching vibrations and may verify the asymmetric Ga-H-Ga bridge.[27,28,30]

Conclusion

Hydrometallation of amino-tri(*tert*-butylethynyl)silanes with one or two equivalents of H-E$(CMe_3)_2$ (M = Al, Ga) afforded mixed alkenyl-dialkynyl- and dialkenyl-alkynylsilanes by the reduction of up to two of their C≡C triple bonds. The highly functionalised products have Lewis-acidic Al and Ga atoms in a geminal arrangement to the central four-coordinate Si atoms. The polarising capability of the coordinatively unsaturated Al and Ga atoms resulted in a fascinating variety of different intramolecular interactions. Depending on the molecular structures, the substitution pattern and the metal atoms close contacts have been observed to the N atom of the pyrrolidyl rings, the α-carbon atoms of the ethynyl groups which carry a relatively high partial negative charge, C-H bonds of a vinylic *tert*-butyl group or a C-H bond of the aromatic pyrrolyl ring. Particularly interesting are naturally those contacts which result in a potential activation by weakening and lengthening of specific bonds. Relatively strong interactions were observed to ethynyl C and amine N atoms which may facilitate (i) ring closure by 1,1-carbometallation or (ii) coordination and insertion of dipolar substrates. With their unique properties these compounds do not only possess fascinating molecular structures, but are also highly promising starting materials for interesting secondary reactions.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane with $LiAlH_4$; Et_2O and toluene with Na/benzophenone; 1,2-difluorobenzene and pentafluorobenzene with molecular sieves). *n*-BuLi and $H\text{-}C{\equiv}C\text{-}CMe_3$ were used as purchased. Pyrrole was distilled at atmospheric pressure. $SiCl_4$ was distilled and stored over Mg metal. $H_8C_4N\text{-}Si(C{\equiv}C\text{-}CMe_3)_3$,[9] $H\text{-}Al(CMe_3)_2$,[20,31] $H\text{-}Ga(CMe_3)_2$[20] and the sesquihydride $[H\text{-}Ga(CMe_3)_2]_2[H_2Ga\text{-}CMe_3]_2$[20] were obtained according to literature procedures. Microanalyses were carried out by the microanalytical laboratory of the Westfälische Wilhelms-Universität Münster. NMR spectra were recorded in C_6D_6 or C_7D_8 using the following Bruker instruments: Avance I (^1H, 400.13; ^{13}C, 100.62 MHz, ^{29}Si, 79.49 MHz, ^{15}N, 40.54 MHz) or Avance III (^1H, 400.03; ^{13}C, 100.59 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C NMR spectra were all proton decoupled. The assignment of NMR spectra is based on HSQC, HMBC, DEPT135, $^1H/^{29}Si$ HMBC, $^{29}Si\{^1H\}$ DEPT and H,H ROESY data. IR spectra were recorded as paraffin mulls between CsI plates on a Shimadzu Prestige 21 spectrometer, electron impact mass spectra with a Finnigan MAT 95 mass spectrometer.

Pyrrolyl-trichlorsilane (1). A solution of *n*-BuLi (50.3 mL, 100.6 mmol, 2 M in hexane) was added dropwise under strict exclusion of light to a solution of pyrrole (6.74 g, 7 mL, 100.6 mmol) in Et_2O (75 mL) at -78 ºC over a period of 1 h. The mixture was stirred for 1 h, the cooling bath was removed and the mixture was allowed to warm to room temperature overnight. The resulting suspension was cooled to -78 ºC and added to a cooled solution (-78 ºC) of excess $SiCl_4$ (25.64 g, 17.3 ml, 150.9 mmol) in Et_2O (100 mL) over a period of 2.5 h. Slow addition was achieved by means of a PTFE transfer cannula (30 cm, inner diameter 0.1 cm) and by careful adjustment of argon-pressure in regular intervals. The reaction mixture was stirred for another hour and then allowed to slowly warm to room temperature overnight. Volatiles were removed *in vacuo* und the obtained residue was distilled at 110 ºC / 3.5 x 10^{-1} mbar to give compound **1** as a colourless, hygroscopic and no longer light sensitive liquid (d = 1.36 g/mL). Yield: 12.53 g (62%). Microanalysis: not possible; compound is extremely hygroscopic, corrosive and damages CHN analysator. ^{1}H NMR (C_6D_6, 400.03 MHz, 300 K): δ = 6.78 (2 H, *pseudo*-t, outer line spacing 3 Hz, NC*H*), 6.25 (2 H, *pseudo*-t, outer line spacing 3 Hz, NCC*H*). ^{13}C NMR (C_6D_6, 100.61 MHz, 300 K): δ = 123.3 (N*C*H), 114.6 (NC*C*H). ^{29}Si NMR (C_6D_6, 79.47 MHz, 300 K): δ = -24.6. ^{15}N NMR (C_6D_6, 40.54 MHz, 300 K): δ = 158. IR (cm^{-1}; paraffin; CsI plates): 1763 m, 1719 w, 1576 s, 1570 s, 1560 s *v*(CN), *v*(CC) (pyrrole); 1464 vs, 1404 w, 1375 m (paraffin); 1287 vw, 1209 vs, 1198 vs, 1082 vs, 1043 s, 953 vw, 932 w, 870 vw, 814 w, 785 w; 733 vs (paraffin); 617 vs, 594 s, 575 vs, 511 vw, 474 w *v*(SiN), *v*(SiCl). Mass spectrum (EI+; 30 eV; 298 K): *m/z* (%) = 198 (1.0), 200 (0.8) [M^+ – H], 163 (1.3), 165 (0.6) [M^+ – H – Cl], 129 (1.6), 131 (0.4) [M^+ – 2Cl], 67 (100) [$C_4H_4NH^+$].

Pyrrolyl-tri(*tert*-butylethinyl)silane (2). A solution of *n*-BuLi (37.1 mL, 59.3 mmol, 1.6 M in hexane) was added to a solution of H-C≡C-CMe_3 (4.86 g, 7.25 mL, 59.3 mmol) in Et_2O (100 mL) at -78 ºC over a period of 1 h. The mixture was allowed to warm to room temperature overnight yielding a yellow solution, which was added to a solution of **1** (3.96 g, 19.8 mmol) in Et_2O (75 mL) at -110 ºC over a period of 3 h. The mixture was stirred for 3 h at the same temperature and allowed to slowly warm to room temperature overnight. The volatiles were removed *in vacuo*, the residue was treated with *n*-hexane (75 mL) and filtered. The filter cake was washed with *n*-hexane (25 mL) and the combined pale yellow filtrate was concentrated to give compound **2** as a colourless solid after recrystallisation from *n*-hexane at -30 ºC. Yield: 5.45 g (82%). M.P.: 138 °C. Microanalysis: found C 78.3, H 9.2, N 4.1; $C_{22}H_{31}NSi$ (337.57) requires C 78.3, H 9.3, N 4.2. ^1H NMR (C_6D_6, 400.13 MHz, 300 K): δ = 7.50 (2 H, *pseudo*-t, outer line spacing 3 Hz, NC*H*), 6.56 (2 H, *pseudo*-t, outer line spacing 3 Hz, NCC*H*), 0.99 (27 H, s, CMe_3). ^{13}C NMR (C_6D_6, 100.61 MHz, 300 K): δ = 124.2 (N*C*H), 118.5 (NC*C*H), 112.6 (Si-C≡*C*), 76.8 (Si-*C*≡C), 30.1 (C*Me₃*), 28.4 (*C*Me₃). ^{15}N NMR (C_6D_6, 40.53 MHz, 300 K): δ = 158. IR (cm^{-1}; paraffin, CsI plates): 2207 s, 2160 s ν(C≡C); 1736 w, 1701 m, 1578 s, 1570 s, 1560 m, 1545 m, 1541 m, 1522 vw, 1518 vw ν(CN), ν(CC) (pyrrole); 1458 vs, 1375 vs, 1364 s (paraffin); 1294 m, 1252 m $\delta(CH_3)$; 1198 s, 1113 w, 1082 s, 1069 s, 1045 s, 1030 m sh, 951 s, 930 s, 889 vw, 874 w, 835 m, 781 vs, 762 vs δ(CH), ν(CC); 729 vs (paraffin); 625 s, 592 s, 563 vs, 511 m, 467 s, 419 w ν(SiN), ν(SiC), δ(CC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 337 (100) [M^+], 322 (11) [$M^+ - CH_3$], 280 (7) [$M^+ - CMe_3$], 271 (6) [$M^+ - C_4H_4N$].

Compound 3a. A solution of C_4H_8N-Si(C≡C-CMe_3)$_3$ (0.349 g, 1.02 mmol) in toluene (10 mL) was treated at room temperature with a solution of H-Al(CMe_3)$_2$ (0.145 g, 1.02

mmol) in toluene (25 mL). The mixture was stirred for 30 min. The volatiles were removed *in vacuo* to give an amorphous solid which was recrystallised from a small quantity of 1,2-difluorobenzene at -15 ºC. Compound **3a** was obtained as a colourless solid which slowly decomposed *in vacuo*. Yield: 0.436 g (88%). M.p.: 127 °C. Microanalysis: found C 73.8, H 11.3, N 2.8; [$C_{30}H_{54}AlNSi$ (483.81)] requires C 74.5, H 11.2, N 2.9. ^{1}H NMR (C_6D_6, 400.03 MHz, 300 K): δ = 7.29 (1 H, s, $^3J_{HSi}$ = 31.5 Hz, C=C*H*), 3.90 and 2.83 (4 H, m br, NCH_2), 1.78 and 1.51 (4 H, m br, NCCH_2), 1.38 (18 H, s, Al(CMe_3)$_2$), 1.32 (9 H, s, C=CCMe$_3$), 1.04 (18 H, s, C≡CCMe$_3$). ^{13}C NMR (C_6D_6, 100.59 MHz, 300 K): δ = 171.2 (C=*C*-H), 143.6 (br, *C*=C-H), 120.3 (C≡C-CMe$_3$), 77.9 (*C*≡C-CMe$_3$), 52.9 (N*C*H$_2$), 40.1 (C=C*C*Me$_3$), 32.3 (Al(CMe$_3$)$_2$), 30.2 (C≡C-C*Me*$_3$), 29.9 (C=C-C*Me*$_3$), 28.5 (C≡C*C*Me$_3$), 24.2 (NC*C*H$_2$), 17.7 (br, Al*C*Me$_3$). ^{29}Si NMR (C_6D_6, 79.47 MHz, 300 K): δ = -39.5. IR (cm^{-1}; paraffin, CsI plates): 2199 s, 2154 vs *ν*(C≡C); 1605 vs, 1560 m *ν*(C=C); 1458 vs, 1379 vs (paraffin); 1304 w, 1294 w, 1254 s *δ*(CH_3); 1202 s, 1179 w, 1103 w, 1070 m, 1045 m, 1028 s, 1007 m, 962 m sh, 943 s, 916 s, 885 m, 847 vw, 808 s, 775 s *δ*(CH), *ν*(CC), *ν*(CN); 721 s (paraffin); 664 w, 592 s, 557 m, 473 m, 436 m, 420 m *ν*(SiC), *ν*(SiN), *ν*(AlN), *ν*(AlC), *δ*(CC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 426 (100) [M^+ – CMe$_3$], 356 (19) [M^+ – NC_4H_8 – CMe$_3$], 331 (9) [M^+ – NC_4H_8 – HC≡CCMe$_3$].

Compound 3b. A solution of C_4H_8N-Si(C≡C-CMe$_3$)$_3$ (0.350 g, 1.04 mmol) in toluene (10 mL) was treated at room temperature with a solution of H-Ga(CMe$_3$)$_2$ (0.190 g, 1.02 mmol) in toluene (25 mL). The mixture was stirred for 30 min. Removal of all volatiles *in vacuo* yielded a colourless oil which was recrystallised from a small quantity of 1,2-difluorobenzene at -15 ºC to give compound **3b** as a colourless solid which slowly decomposed *in vacuo*. Yield: 0.412 g (76%). M.p.: 89 °C. Microanalysis: found C 68.3, H

10.3, N 2.7; [$C_{30}H_{54}GaNSi$ (526.55)] requires C 68.4, H 10.3, N 2.7. ^{1}H NMR (C_6D_6, 400.03 MHz, 300 K): δ = 6.99 (1 H, s, $^3J_{HSi}$ = 29.0 Hz, C=C*H*), 3.35 (4 H, m, NCH_2), 1.63 (4 H, m, NCCH_2), 1.43 (18 H, s, Ga$(CMe_3)_2$), 1.36 (9 H, s, C=CCMe_3), 1.07 (18 H, s, C≡CCMe_3). ^{1}H NMR (toluene-d_8, 400.13 MHz, 200 K): δ = 7.10 (1 H, s, $^3J_{HSi}$ = 29.2 Hz, C=C*H*), 3.94 and 2.66 (each 2 H, br, NCH_2), 1.65 (4 H, br, NCH_2CH_2), 1.55 (18 H, s, Ga$(CMe_3)_2$), 1.43 (9 H, s, C=CCMe_3), 1.03 (18 H, s, C≡CCMe_3). ^{13}C NMR (C_6D_6, 100.59 MHz, 300 K): δ = 167.3 (C=*C*CMe_3), 146.5 (*C*=CCMe_3), 119.7 (C≡*C*CMe_3), 78.7 (*C*≡CCMe_3), 52.7 (N*C*H_2), 39.8 (C=C*C*Me_3), 32.2 (Ga(C*Me*$_3$)$_2$), 30.3 (C≡CC*Me*$_3$), 30.1 (C=CC*Me*$_3$), 28.5 (C≡C*C*Me_3), 26.1 (br, Ga(*C*Me_3)$_2$), 24.7 (NC*C*H_2). ^{29}Si NMR (C_6D_6, 79.47 MHz, 300 K): δ = -42.2. IR (cm^{-1}; paraffin, CsI plates): 2201 s, 2154 vs *v*(C≡C), 1684 vw, 1607 vs, 1578 s, 1564 s *v*(C=C); 1458 vs, 1377 vs (paraffin); 1304 w, 1292 vw, 1254 vs $\delta(CH_3)$;1202 vs, 1167 w, 1103 m, 1042 vs, 1007 m, 964 s, 941 s, 926 s, 877 w, 851 vw, 810 s, 785 vs, 764 s δ(CH), *v*(CC), *v*(CN); 719 s (paraffin); 696 m, 681 m, 660 w, 590 vs, 557 w, 530 w, 490 vw, 459 s, 424 vs *v*(SiC), *v*(SiN), *v*(GaN), *v*(GaC), δ(CC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 468 (100) [$M^+ - CMe_3$], 399 (10) [$M^+ - NC_4H_8$ – butene].

Compound 4a. A solution of $C_4H_8N-Si(C≡C-CMe_3)_3$ (0.356 g, 1.04 mmol) in toluene (10 mL) was treated at room temperature with a solution of $H-Al(CMe_3)_2$ (0.304 g, 2.14 mmol) in toluene (25 mL). The mixture was stirred for 2 d. All volatiles were removed *in vacuo* and the residue was treated with a small quantity of pentafluorobenzene. Filtration to remove small quantities of solid material, concentration of the filtrate and storing the solution at -30 ºC yielded colourless crystals of compound **4a**. Yield: 0.531 g (81%). M.p.: 171 °C. Microanalysis: found C 72.2, H 11.7, N 2.2; [$C_{38}H_{73}Al_2NSi$ (626.09)] requires C 72.9, H 11.8, N 2.2. ^{1}H NMR (C_6D_6, 400.13 MHz, 300 K): δ = 7.41 (1 H, s,

$^{3}J_{\mathrm{HSi}}$ = 29.8 Hz, *cis*-C=C*H*), 7.21 (1 H, s, $^{3}J_{\mathrm{HSi}}$ = 15.8 Hz, *trans*-C=C*H*), 3.76 and 3.08 (each 1 H, m, NC(1)H_2), 3.43 and 2.78 (each 1 H, m, NC(4)H_2), 1.66 (2 H, m, NC(1)C(2)H_2), 1.58 (2 H, m, NC(4)C(3)H_2), 1.38 and 1.36 (each 9 H, s, *cis*-Al$(\mathrm{CMe_3})_2$), 1.26 and 1.20 (each 9 H, s, *trans*-Al$(\mathrm{CMe_3})_2$), 1.18 (9 H, s, *cis*-C=C$\mathrm{CMe_3}$), 1.14 (9 H, s, C≡C$\mathrm{CMe_3}$), 0.92 (9 H, s, *trans*-C=C$\mathrm{CMe_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$, 100.61 MHz, 300 K): δ = 175.7 (*trans*-C=*C*$\mathrm{CMe_3}$), 171.2 (*cis*-C=*C*$\mathrm{CMe_3}$), 145.4 (br, *cis*-*C*=C$\mathrm{CMe_3}$), 138.3 (br, *trans*-*C*=C$\mathrm{CMe_3}$), 122.0 (C≡*C*$\mathrm{CMe_3}$), 82.2 (*C*≡C$\mathrm{CMe_3}$), 53.3 (N*C(1)*$\mathrm{H_2}$), 51.7 (N*C(4)*$\mathrm{H_2}$), 39.2 (*cis*-C=C*C*$\mathrm{Me_3}$), 38.8 (*trans*-C=C*C*$\mathrm{Me_3}$), 32.9 and 31.9 (*cis*-Al$(\mathrm{CMe_3})_2$), 31.2 and 31.1 (*trans*-Al$(\mathrm{CMe_3})_2$), 30.3 (C≡CCMe_3), 30.2 (*cis*-C=CCMe_3), 28.7 (C≡C*C*$\mathrm{Me_3}$), 27.2 (*trans*-C=CCMe_3), 25.5 (NC(1)*C(2)*$\mathrm{H_2}$), 25.4 (NC(4)*C(3)*$\mathrm{H_2}$), 19.4 and 17,7 (br, *cis*-Al*C*$\mathrm{Me_3}$), 18.4 (*trans*-Al(*C*$\mathrm{Me_3})_2$). ^{29}Si NMR ($\mathrm{C_6D_6}$, 79.49 MHz, 300 K): δ = -24.0. IR ($\mathrm{cm^{-1}}$; paraffin, CsI plates): 2187 w, 2145 m ν(C≡C); 1699 w, 1599 vs, 1580 s, 1558 vs, 1549 vs ν(C=C); 1454 vs, 1373 vs (paraffin); 1294 w, 1250 s $\delta(\mathrm{CH_3})$; 1202 s, 1072 w, 1038 s, 1007 m, 1001 m, 932 m, 851 w, 810 m, 783 w, 766 m, 746 m δ(CH), ν(CC), ν(CN); 719 vs (paraffin); 667 m, 610 m, 590 m, 567 m, 501 sh, 486 s, 451 w, 436 w ν(SiC), ν(SiN), ν(AlN), ν(AlC), δ(CC). Mass spectrum (EI+; 20 eV; 353 K): *m/z* (%) = 568 (100) [$\mathrm{M^+ - CMe_3}$], 512 (14) [$\mathrm{M^+ - CMe_3}$ – butene], 426 (45) [$\mathrm{M^+ - Al(CMe_3)_2}$ – butane].

Compound 4b. A solution of $\mathrm{C_4H_8N\text{-}Si(C{\equiv}C\text{-}CMe_3)_3}$ (0.341 g, 1.00 mmol) in toluene (10 mL) was added at room temperature to a solution of H-Ga$(\mathrm{CMe_3})_2$ (0.368 g, 1.99 mmol) in toluene (25 mL). The mixture turned brown and was stirred for 3 d. All volatiles were removed *in vacuo* and the oily residue was recrystallised from pentafluorobenzene at -45 ºC to give a brownish solid which was found to be a mixture of **4b** (*ca.* 60 %), **3b** (*ca.* 10 %) and **6** (*ca.* 30 %). Repeated fractional crystallisation from pentafluorobenzene at -45 ºC yielded pure **4b** as colourless crystals. Yield: 0.283 g (40%). M.p.: 125 °C. Microanalysis: found C 64.2, H 9.8, N 2.0; [$C_{38}H_{73}Ga_2NSi$ (711.54)] requires C 64.1, H 10.3, N 2.0. ^{1}H NMR (C_6D_6, 400.13 MHz, 275 K): δ = 6.84 (1 H, s, $^{3}J_{\mathrm{HSi}}$ = 24.1 Hz, C=C*H*), 6.48 (1 H, s, $^{3}J_{\mathrm{HSi}}$ = 28.5 Hz, NGaC=C*H*), 3.38 and 3.32 (each 2 H, m, NC*H$_2$*), 1.64 and 1.63 (each 2 H, m, NCC*H$_2$*), 1.43 (18 H, s, Ga(CMe$_3$)$_2$), 1.41 and 1.31 (each 9 H, s, NGa(CMe$_3$)$_2$), 1.23 (9 H, s, NGaC=CCMe$_3$), 1.13 (9 H, s, C=CCMe$_3$), 1.12 (9 H, s, C≡CCMe$_3$). ^{1}H NMR (C_6D_6, 400.13 MHz, 300 K): δ = 6.82 (1 H, br, C=C(1)*H*), 6.48 (1 H, br, C=C(2)*H*), 3.36 (4 H, br, NC*H*), 1.66 (4 H, m, NCH$_2$C*H*), 1.40 (18 H, s, NGa(CMe$_3$)$_2$), 1.36 (18 H, br, Ga(CMe$_3$)$_2$), 1.17 (18 H, br, C=CCMe$_3$), 1.14 (9 H, s, C≡CCMe$_3$). ^{1}H NMR (C_6D_6, 400.13 MHz, 350 K): δ = 6.63 (2 H, br, C=C*H*), 3.37 (4 H, *pseudo*-t, outer line spacing: 11.2 Hz, NC*H*), 1.71 (4 H, m, NCH$_2$C*H*), 1.36 (18 H, s, NGa(CMe$_3$)$_2$), 1.32 (18 H, s, Ga(CMe$_3$)$_2$), 1.18 (18 H, s, C=CCMe$_3$), 1.17 (9 H, s, C≡CCMe$_3$). ^{13}C NMR (C_6D_6, 100.61 MHz, 275 K): δ = 164.8 (NGaC=*C*CMe$_3$), 164.1 (C=*C*CMe$_3$), 157.1 (*C*=CCMe$_3$), 142.5 (NGa*C*=CCMe$_3$), 122.7 (C≡*C*CMe$_3$), 84.1 (*C*≡CCMe$_3$), 52.0 (N*C*H$_2$), 39.1 (C=C*C*Me$_3$), 38.4 (NGaC=C*C*Me$_3$), 32.2 and 31.8 (NGaC*Me$_3$*), 31.0 (Ga(C*Me$_3$*)$_2$), 30.6 (C≡CC*Me$_3$*), 30.1 (NGaC=CC*Me$_3$*), 29.9 (C=CC*Me$_3$*), 29.7 (NGa*C*Me$_3$; second resonance of this group not observed), 29.2 (Ga(*C*Me$_3$)$_2$), 28.8 (C≡C*C*Me$_3$), 25.8 (NC*C*H$_2$). ^{29}Si NMR (C_6D_6, 79.49 MHz, 280 K): δ = -29.1. IR (cm^{-1}; paraffin, CsI plates): 2151 m, 2133 m *v*(C≡C); 1576 vs sh, 1558 vs *v*(C=C); 1458 vs, 1400 m, 1377 vs (paraffin); 1306 w, 1250 m δ(CH$_3$); 1202 m, 1169 w, 1111 vw, 1072 vw, 1049 w, 1030 vw, 1007 vw, 930 w, 880 vw, 851 vw, 812 m, 795 m, 762 w δ(CH), *v*(CC), *v*(CN); 719 s (paraffin); 706 m, 681 w, 650 vw, 623 vw, 592 vw, 559 m, 517 vw, 482 w, 467 m, 444 m *v*(SiC), *v*(SiN), *v*(GaN), *v*(GaC), δ(CC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 654 (12) [M^+ – CMe_3], 468 (100) [M^+ – $Ga(CMe_3)_2$ – butane].

Compound 5a. A solution of compound **2** (0.354 g, 1.05 mmol) in toluene (15 mL) was treated at room temperature with a solution of H-$Al(CMe_3)_2$ (0.306 g, 2.15 mmol) in toluene (25 mL). The mixture was stirred for 16 h. The solvent was removed *in vacuo* and the residue recrystallised from 1,2-difluorobenzene at -15 ºC to give a colourless solid. Yield: 0.53 g (81%). M.p.: 158 °C. Microanalysis: found C 73.2, H 11.0, N 2.3; $C_{38}H_{69}Al_2NSi$ (621.99) requires C 73.4, H 11.2, N 2.3. ^1H NMR (C_6D_6, 400.03 MHz, 300 K): δ = 7.26 (2 H, s br, NC*H*), 6.97 (2 H, s, $^3J_{HSi}$ = 30.8 Hz, C=C*H*), 6.75 (1 H, s br, NCHC*H*), 1.35 and 1.01 (each 18 H, s, $Al(CMe_3)_2$), 1.12 (18 H, s, C=$CCMe_3$), 1.11 (9 H, s, C≡$CCMe_3$). ^1H NMR (toluene-d_8, 400.13 MHz, 200 K): δ = 7.50 (1 H, br, NC*H*), 7.20 (1 H, s, $^3J_{HSi}$ = 31.2 Hz, C=C*H*), 7.11 (1 H, *pseudo*-t, outer line spacing: 3.0 Hz, NCHC*H*), 6.97 (1 H, br, NC*H*), 6.81 (1 H, s, $^3J_{HSi}$ = 31.4 Hz, C=C*H*), 6.16 (1 H, *pseudo*-tr, outer line spacing: 4.5 Hz, NCHC*H*), 1.44 and 1.43 (each 9 H, s, $Al(CMe_3)_2$), 1.17 and 1.14 (each 9 H, s, C=C-CMe_3), 1.04 and 1.03 (each 9 H, s, $Al(CMe_3)_2$), 1.04 (9 H, s, C≡$CCMe_3$). ^{13}C NMR (C_6D_6, 100.59 MHz, 300 K): δ = 169.1 (C=*C*CMe_3), 142.9 (br, *C*=$CCMe_3$), 130.3 (C≡*C*CMe_3), 83.1 (*C*≡$CCMe_3$), 39.4 (C=C*C*Me_3), 31.8 and 31.1 (Al(C*Me₃*)₂), 30.4 (C≡CC*Me₃*), 29.4 (C=CC*Me₃*), 29.3 (C≡C*C*Me_3), 19.4 and 19.2 (br, Al(*C*Me_3)₂), N*C*H, NCH*C*H not observed. ^{29}Si NMR (C_6D_6, 79.47 MHz, 300 K): δ = -39.0. IR (cm^{-1}; paraffin, CsI plates): 2156 m, 2114 s ν(C≡C); 1784 vw, 1599 vs, 1558 vs ν(C=C), pyrrole; 1458 vs, 1375 vs (paraffin); 1294 m, 1254 m, 1242 m δ(CH_3); 1233 m, 1200 m, 1167 s, 1078 m, 1070 w, 1051 vs, 1028 m, 999 m, 939 s, 905 m, 889 s, 851 w, 810 vs, 762 m, 752 m δ(CH), ν(CC); 721 vs (paraffin); 691 m, 640 m, 629 s, 606 m, 583 m, 556 s, 538 m, 519 m, 469 s, 426 m ν(SiC), ν(SiN), ν(AlN), ν(AlC), δ(CC). Mass spectrum (EI+; 20 eV; 373 K): *m/z* (%) = 564 (58) [M$^+$ – CMe$_3$], 422 (100) [M$^+$ – Al(CMe$_3$)$_2$ – butane].

Compound 5b. A solution of C_4H_4N-Si(C≡CCMe$_3$)$_3$ **2** (0.268 g, 0.79 mmol) in toluene (15 mL) was treated at room temperature with a solution of H-Ga(CMe$_3$)$_2$ (0.301 g, 1.66 mmol) in toluene (25 mL). The mixture was stirred for 16 h resulting in a colour change from colourless to deep orange. All volatiles were removed *in vacuo* and the residue was recrystallised from 1,2-difluorobenzene at 2 ºC to give **4b** as a colourless solid. Yield: 0.445 g (80%). M.p.: 162 °C. Microanalysis: found C 64.3, H 9.8, N 1.9; [$C_{38}H_{69}Ga_2NSi$ (707.47)] requires C 64.5, H 9.8, N 2.0. ^{1}H NMR (C_6D_6, 400.13 MHz, 300 K): δ = 7.20 (2H, *pseudo*-t, outer line spacing 3 Hz, NC*H*), 6.62 (2 H, *pseudo*-t, outer line spacing 3 Hz, NCHC*H*), 6.51 (2 H, s, $^3J_{HSi}$ = 27.7 Hz, C=C*H*), 1.42 and 1.09 (each 18 H, s, Ga(CMe$_3$)$_2$), 1.19 (18 H, s, C=CCMe$_3$), 1.13 (9 H, s, C≡CCMe$_3$). ^{13}C NMR (C_6D_6, 100.61 MHz, 300 K): δ = 163.6 (C=*C*CMe$_3$), 146.3 (br, *C*=CCMe$_3$), 122.7 (C≡*C*CMe$_3$), 122.1 (br, N*C*H), 118.8 (NC*C*H), 83.1 (*C*≡CCMe$_3$), 39.1 (C=C*C*Me$_3$), 31.9 and 31.1 (Ga(C*Me$_3$*)$_2$), 30.7 (C≡CC*Me$_3$*), 29.9 and 29.3 (br, Ga(*C*Me$_3$)$_2$), 29.7 (C=CC*Me$_3$*), 28.8 (C≡C*C*Me$_3$). ^{29}Si NMR (C_6D_6, 79.49 MHz, 300 K): δ = -42.8. IR (cm^{-1}; paraffin, CsI plates): 2168 m, 2129 s *v*(C≡C); 1566 vs, 1497 m,sh *v*(C=C); 1447 vs, 1377 vs (paraffin); 1304 vw, 1292 w, 1254 m, 1246 m δ(CH$_3$); 1229 m, 1200 s, 1188 sh, 1179 vs, 1070 vs, 1049 vs, 1030 m, 1022 m, 1015 m, 1005 m, 939 m, 920 m, 907 m, 883 m, 856 vw, 841 w, 808 s sh, 800 s, 750 s δ(CH), *v*(CC); 719 vs (paraffin); 675 m, 640 w, 627 m, 610 w, 588 vw, 561 s, 521 w, 471 m, 455 w sh, 428 m *v*(SiC), *v*(SiN), *v*(GaN), *v*(GaC), δ(CC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 650 (42) [M$^+$ – CMe$_3$], 464 (100) [M$^+$ – Ga(CMe$_3$)$_2$ – butane].

Compound 6 (from [H-Ga(CMe$_3$)$_2$]$_2$[H$_2$Ga-CMe$_3$]$_2$). A solution of C$_4$H$_8$N-Si(C≡C(CMe$_3$)$_3$ (0.164 g, 0.48 mmol) in toluene (15 mL) was added at room temperature to a solution of [H-Ga(CMe$_3$)$_2$]$_2$[H$_2$Ga-CMe$_3$]$_2$ (0.200 g, 0.32 mmol; excess) in toluene (15 mL). The mixture was stirred for 3 d, the solvent was removed *in vacuo* and the residue recrystallised from pentafluorobenzene at -30 ºC to give colourless crystals of compound **6**. Yield: 0.196 g (62%).

Compound 6 (from H-Ga(CMe$_3$)$_2$). A solution of C$_4$H$_8$N-Si(C≡CCMe$_3$)$_3$ (0.364 g, 1.07 mmol) in toluene (20 mL) was treated at room temperature with a solution of H-Ga(CMe$_3$)$_2$ (0.591 g, 3.20 mmol) in toluene (25 mL). The mixture was stirred for 3 d. Removal of all volatiles *in vacuo* yielded a pale yellow solid which was dissolved in a small quantity of pentafluorobenzene. The solution was concentrated and stored at -45 ºC to give a colourless solid consisting of a mixture of **5b** (*ca.* 33 %) and **6**. Recrystallisation from pentafluorobenzene at -15 ºC yielded as a first fraction compound **5b** and from the mother liquor compound **6**. Yield: 0.195 g (28%). M.p.: 130 °C. Microanalysis: found C 62.8, H 10.1, N 2.3; [C$_{34}$H$_{65}$Ga$_2$NSi (655.40)] requires C 62.3, H 10.0, N 2.1. ^{1}H NMR (C$_6$D$_6$, 400.13 MHz, 300 K): δ = 7.19 (1 H, s, $^3J_{HSi}$ = 28.0 Hz, NGaC=C*H*), 6.97 (1 H, s, $^3J_{HSi}$ = 24.0 Hz, (Me$_3$C)$_2$GaC=C*H*), 3.76 (1 H, s, Ga*H*), 3.31 and 2.81 (each 1 H, m, NC(1)*H$_2$*), 3.21 and 2.93 (each 1 H, m, NC(4)*H$_2$*), 1.77 and 1.43 (each 1 H, m, NC(1)C(2)*H$_2$*), 1.58 and 1.44 (each 1 H, m, NC(4)C(3)*H$_2$*), 1.48 (9 H, s, NGa-CMe$_3$), 1.41 and 1.24 (each 9 H, s, Ga(CMe$_3$)$_2$), 1.41 (9 H, s, NGaC=CCMe$_3$), 1.27 (9 H, s, (Me$_3$C)$_2$GaC=CCMe$_3$), 1.12 (9 H, s, C≡CCMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100.61 MHz, 300 K): δ = 168.6 (NGaC=*C*) 165.6 ((Me$_3$C)$_2$GaC=*C*), 146.8 ((Me$_3$C)$_2$Ga*C*=C), 144.8 (NGa*C*=C), 120.7 (C≡*C*CMe$_3$), 82.6 (*C*≡CCMe$_3$), 52.0 (N*C(4)*H$_2$), 49.5 (N*C(1)*H$_2$), 38.3 ((Me$_3$C)$_2$GaC=C*C*Me$_3$), 37.3 (NGaC=C*C*Me$_3$), 33.8 (NGa-C*Me$_3$*), 33.7

and 30.5 (Ga(C*Me₃*)₂), 32.4 (NGaC=CC*Me₃*), 30.2 (C≡CC*Me₃*), 30.0 ((Me₃C)₂GaC=CC*Me₃*), 28.7 (C≡C*C*Me₃), 26.4 and 25.1 (Ga*C*Me₃), 26.2 (NC(4)*C(2)*H₂), 25.2 (NGa*C*Me₃), 24.8 (NC(1)*C(2)*H₂). ^{29}Si NMR (C_6D_6, 79.49 MHz, 300 K): δ = -27.0. IR (cm^{-1}; paraffin, CsI plates): 2193 w, 2149 s *ν*(C≡C); 1886 w br, 1614 w br *ν*(Ga-H); 1531 m, 1510 w *ν*(C=C); 1454 vs, 1377 vs (paraffin); 1304 vw, 1252 m δ(CH_3); 1202 m, 1179 m, 1136 vw, 1111 vw, 1070 s, 1053 m, 1007 m, 926 m, 833 w, 810 m, 793 m, 779 w, 764 w δ(CH), *ν*(CC), *ν*(CN); 718 m (paraffin); 681 w, 637 w, 525 m, 480 w, 463 m, 440 m *ν*(SiC), *ν*(SiN), *ν*(GaN), *ν*(GaC), δ(CC). Mass spectrum (EI+; 20 eV; 298 K): *m/z* (%) = 598 (66) [M^+ – CMe_3], 468 (8) [M^+ – $Ga(CMe_3)_2$ – 2H], 412 (100) [M^+ – $Ga(CMe_3)_2$ – butane].

X-Ray crystallography. Crystals suitable for X-ray crystallography were obtained by recrystallisation from *n*-hexane (**2**), 1,2-difluorobenzene (**3a**, **3b**, **4a**, **4b**) or pentafluorobenzene (**5a**, **6**). Intensity data was collected on Bruker APEX II, IPDS-II and D8-Venture diffractometers with monochromated MoK_α and CuK_α radiation (**2**, **4a**). The collection method involved ω scans. Data reduction was carried out using the program SAINT+.[32] The crystal structures were solved by Direct Methods using SHELXTL.[33,34] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL.[33,34] Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Compound **6** crystallizes with one molecule of pentafluorobenzene per formula unit, the solvent molecule is disordered statistically over all F/H-positions. Two CMe_3 groups of compound **2** and one of compounds **3a**, **3b**, **4a** and **4b** were disordered and refined in split positions (**2** 0.45 : 0.32 : 0.23, 0.45 : 0.35 : 0.20; **3a** 0.55 : 0.45; **3b** 0.54 : 0.46; **4a** 0.43 : 0.57; **4b** 0.56 : 0.44). The interaction of methyl hydrogen atoms with the aluminium atom Al(1) in compound **4a** was verified by an analysis of the difference Fourier map. The positions of residual electron density found for all three hydrogen atoms bonded to C(121) were almost identical to the calculated, ideal ones which were applied for the final refinement of the structure. Molecular structures were drawn with the DIAMOND program package.[35]

Crystal data for **2**: $C_{22}H_{31}NSi$, $M = 337.57$, orthorhombic, $a = 10.0207(2)$ Å, $b = 13.4721(2)$ Å. $c = 16.8224(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2271.02(7)$ Å^3, $T = 153(2)$ K, space group $P2_12_12_1$, $Z = 4$, $\mu(\mathrm{CuK}\alpha) = 0.906$ mm^{-1}, 16167 reflections measured, 4542 independent reflections ($R_{int} = 0.0322$). The final R values were $R_1 = 0.0390$ ($I > 2\sigma(I)$) and w$R(F^2) = 0.0944$ (all data). The goodness of fit on $F^2 = 1.059$.

Crystal data for **3a**: $C_{30}H_{54}AlNSi$, $M = 483.81$, monoclinic, $a = 28.593(1)$ Å, $b = 15.1324(6)$ Å. $c = 18.5944(8)$ Å, $\alpha = 90°$, $\beta = 124.746(1)$, $\gamma = 90°$, $V = 6610.9(5)$ Å^3, $T = 153(2)$ K, space group $C2/c$, $Z = 8$, $\mu(\mathrm{MoK}\alpha) = 0.113$ mm^{-1}, 43426 reflections measured, 9237 independent reflections ($R_{int} = 0.0249$). The final R values were $R_1 = 0.0487$ ($I > 2\sigma(I)$) and w$R(F^2) = 0.1428$ (all data). The goodness of fit on $F^2 = 1.034$.

Crystal data for **3b**: $C_{30}H_{54}GaNSi$, $M = 526.55$, monoclinic, $a = 28.468(1)$ Å, $b = 15.2259(7)$ Å. $c = 18.6308(8)$ Å, $\alpha = 90°$, $\beta = 124.829(1)°$, $\gamma = 90°$, $V = 6629.0(5)$ Å^3, $T = 153(2)$ K, space group $C2/c$, $Z = 8$, $\mu(\mathrm{MoK}\alpha) = 0.882$ mm^{-1}, 36363 reflections measured, 6366 independent reflections ($R_{int} = 0.0239$). The final R values were $R_1 = 0.0326$ ($I > 2\sigma(I)$) and w$R(F^2) = 0.0920$ (all data). The goodness of fit on $F^2 = 1.043$.

Crystal data for **4a**·C_6F_5H: $C_{44}H_{74}Al_2F_5NSi$, $M = 794.09$, orthorhombic, $a = 20.7949(4)$ Å, $b = 11.5692(2)$ Å. $c = 40.0587(9)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 9637.3(3)$ Å^3, $T = 153(2)$ K, space group $Pbca$, $Z = 8$, $\mu(\mathrm{CuK}\alpha) = 1.169$ mm^{-1}, 59102 reflections measured, 9671 independent reflections (R_{int} = 0.1396). The final R values were R_1 = 0.0647 ($I > 2\sigma(I)$) and w$R(F^2)$ = 0.1768 (all data). The goodness of fit on F^2 = 1.081.

Crystal data for **5a**: $C_{38}H_{69}Al_2NSi$, M = 621.99, monoclininc, a = 12.6637(6) Å, b = 16.9211(8) Å. c = 19.3879(8)(3) Å, α = 90°, β = 90.479(2)°, γ = 90°, V = 4154.4(3) Å^3, T = 153(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 0.122 mm^{-1}, 34357 reflections measured, 10348 independent reflections (R_{int} = 0.0721). The final R values were R_1 = 0.0504 ($I > 2\sigma(I)$) and w$R(F^2)$ = 0.1332 (all data). The goodness of fit on F^2 = 1.021.

Crystal data for **5b**: $C_{38}H_{69}Ga_2NSi$, M = 707.47, monoclinic, a = 12.6965(3) Å, b = 16.9151(4) Å. c = 19.3913(5) Å, α = 90°, β = 90.589(1), γ = 90°, V = 4164.3(2) Å^3, T = 153(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 1.346 mm^{-1}, 71404 reflections measured, 12161 independent reflections (R_{int} = 0.0500). The final R values were R_1 = 0.0325 ($I > 2\sigma(I)$) and w$R(F^2)$ = 0.0785 (all data). The goodness of fit on F^2 = 1.031.

Crystal data for **6**: $C_{34}H_{65}Ga_2NSi$, M = 655.40, orthorhombic, a = 11.5215(2) Å, b = 20.1495(4) Å. c = 32.8729(6) Å, α = β = γ = 90°, V = 7631.5(2) Å^3, T = 100(2) K, space group $Pbca$, Z = 8, μ(MoKα) = 1.464 mm^{-1}, 128527 reflections measured, 11143 independent reflections (R_{int} = 0.0383). The final R values were R_1 = 0.0236 ($I > 2\sigma(I)$) and w$R(F^2)$ = 0.0586 (all data). The goodness of fit on F^2 = 1.046.

Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC–992855 to –992861 (**2**, **3a**, **3b**, **4a**, **4b**, **5a**, **6**).

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Notes and references

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Table 1. Selected structure, NMR and IR parameters

Compound	M···N/C[a]	M···C_α≡C	Si-C-M-N puckering angle (°)[b]	C=C(H)^t*Bu* (^{1}H)	$^3J_{SiH}$	IR ν(C≡C)
C_4H_8N-Si(C≡C-$CMe_3)_3$	-	-	-	-	-	2199 / 2158
2	-	-	-	-	-	2207 / 2160
3a	208.5(1)	-	4.8	1.32	31.5	2199 / 2154
3b	222.3(2)	-	4.7	1.36	29.0	2201 / 2154
4a	210.2(2)	(353.7)	6.0	0.92 / 1.18	29.8 / 15.8	2187 / 2145
4b	-	-	-	1.13 / 1.23	28.5 / 24.1	2151 / 2133
5a	239.4(2)	252.8	-	1.12	30.8	2156 / 2114
5b	260.5	277.0	-	1.19	27.7	2168 / 2129
6	210.31(9)	-	34.9	1.27 / 1.41	28.0 / 24.0	2193 / 2149

[a]Pyrrolyl C atom; [b]across the C(11)···N(1) axes

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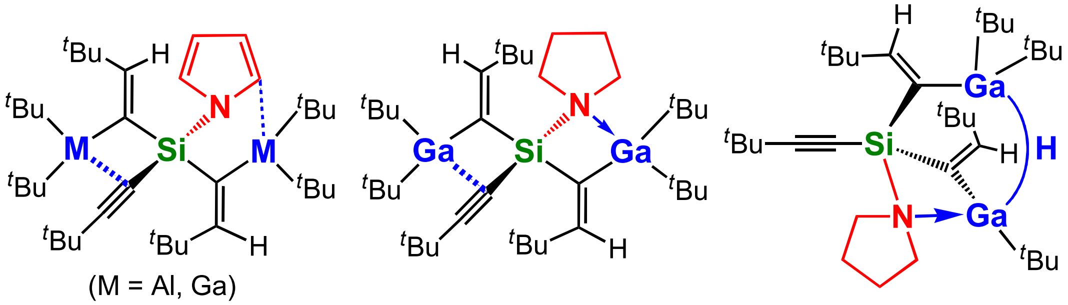

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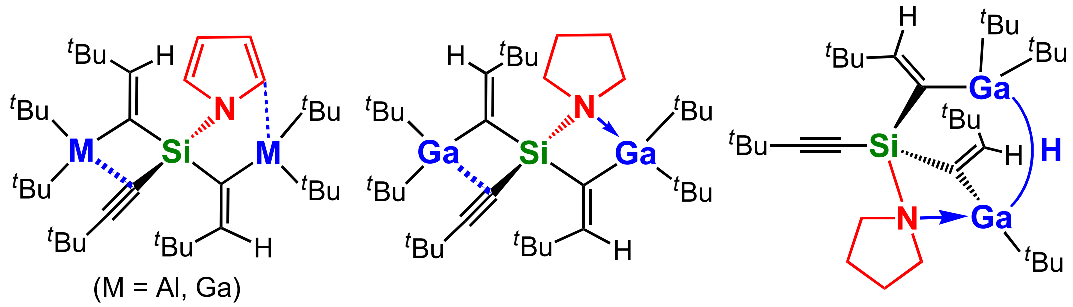

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[†] Electronic supplementary information (ESI) available. CCDC 992855 – 992861. For ESI and crystallographic data in CIF or other electronic format see DOI: …………