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# Neutral and Ionic Aluminum, Gallium, and Indium Compounds Carrying Two or Three Terminal Ethynyl Groups[†]

**Marcus Schiefer, N. Dastagiri Reddy, Hans-Jürgen Ahn, Andreas Stasch, Herbert W. Roesky,* A. Christine Schlicker, Hans-Georg Schmidt, Mathias Noltemeyer, and Denis Vidovic**

*Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4,*
*D-37077 Göttingen, Germany*

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The syntheses of the ionic compounds $[\mathrm{Li^+\cdot 2\ dioxane\ (2,6\text{-}\mathit{i}Pr_2C_6H_3N(SiMe_3)Al(C{\equiv}CSiMe_3)_3)^-}]\cdot 0.75$ dioxane (**1**), $[\mathrm{(Li^+)_2\cdot(dioxane)_7}]_{0.5}\ [\mathrm{2,6\text{-}\mathit{i}Pr_2C_6H_3N(SiMe_3)Ga(C{\equiv}CSiMe_3)_3{}^-}]\cdot 1.5$ dioxane (**2**), and $[\mathrm{(Li^+)_2\cdot(dioxane)_7}]_{0.5}\ [\mathrm{2,6\text{-}\mathit{i}Pr_2C_6H_3N(SiMe_3)In(C{\equiv}CSiMe_3)_3{}^-}]\cdot 1.5$ dioxane (**3**) by the reaction of the corresponding organo metal chloride with $\mathrm{LiC{\equiv}CSiMe_3}$ are reported. The neutral ethynyl compounds $\mathrm{Br{-}Al(C{\equiv}C\mathit{t}Bu)_2\cdot 2\ THF}$ (**4**), $\mathrm{Cl{-}Ga(C{\equiv}C\mathit{t}Bu)_2\cdot THF}$ (**5**), $\mathrm{Cl{-}In(C{\equiv}C\mathit{t}Bu)_2\cdot 2\ THF}$ (**6**), $\mathrm{Al(C{\equiv}C\mathit{t}Bu)_3\cdot C\{N(Me)CMe\}_2}$ (**7**), $\mathrm{Ga(C{\equiv}C\mathit{t}Bu)_3\cdot dioxane}$ (**8**), and $\mathrm{In(C{\equiv}C\mathit{t}Bu)_3\cdot NEt_3}$ (**9**) have been obtained in good yields from the reaction of $\mathrm{AlBr_3}$, $\mathrm{GaCl_3}$, and $\mathrm{InCl_3}$ with $\mathrm{LiC{\equiv}C\mathit{t}Bu}$ in the presence of a Lewis base. Compound **7** is the first heterocyclic carbene substituted ethynyl derivative. Aluminum and gallium compounds with three terminal ethynyl groups $\mathrm{Al(C{\equiv}CPh)_3\cdot NMe_3}$ (**10**) and $\mathrm{Ga(C{\equiv}CPh)_3\cdot NMe_3}$ (**11**) have been prepared by the reaction of $\mathrm{AlH_3\cdot NMe_3}$ or $\mathrm{GaH_3\cdot NMe_3}$ with three equivalents of phenylethyne. All the above-mentioned compounds have been structurally studied. In compound **1** the lithium ion is coordinated to the three terminal ethynyl groups, whereas in compounds **2** and **3** the lithium is coordinated to the solvent (dioxane). Compound **8** crystallizes as a coordination polymer with dioxane molecules bridging the individual gallium units.

## Introduction

Despite their synthetic use in organic chemistry[1a−c,2] only a few alkynyl derivatives of group 13 metals are known in the literature (Al,[1,3,4] Ga,[1e,5] In[2,5d,6]) and very few of them are structurally characterized (Al,[1c,d,3,4] Ga,[5] In[5d,6]). Recently we have reported the first ionic aluminum compounds carrying three terminal ethynyl groups and demonstrated that this type of compounds can show interesting structural properties.[4] This discovery has prompted us to explore the comparable compounds of Ga and In as well as their neutral analogues. Moreover, so far there is only one structural study on the analogous neutral trialkynyl derivatives of indium,[6b] and none have been reported for aluminum and gallium. In our continuing research on this class of compounds we have synthesized the first neutral halogeno compounds of Al, Ga, and In with two ethynyl moieties connected to the metal. Herein, we report the syntheses and structural analyses of $[\mathrm{Li^+\cdot 2\ dioxane\ (2,6\text{-}\mathit{i}Pr_2C_6H_3N(SiMe_3)Al(C{\equiv}CSiMe_3)_3)^-}]\cdot 0.75$ dioxane (**1**), $[\mathrm{(Li^+)_2\cdot(dioxane)_7}]_{0.5}\ [\mathrm{2,6\text{-}\mathit{i}Pr_2C_6H_3N(SiMe_3)Ga(C{\equiv}CSiMe_3)_3{}^-}]\cdot 1.5$ dioxane (**2**), $[\mathrm{(Li^+)_2\cdot(dioxane)_7}]_{0.5}$

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* Author to whom correspondence should be addressed. E-mail: hroesky@gwdg.de. Fax: (+49)551-393373.

[†] Dedicated to Professor T. Nakajima in recognition of his outstanding contribution to fluorine chemistry.

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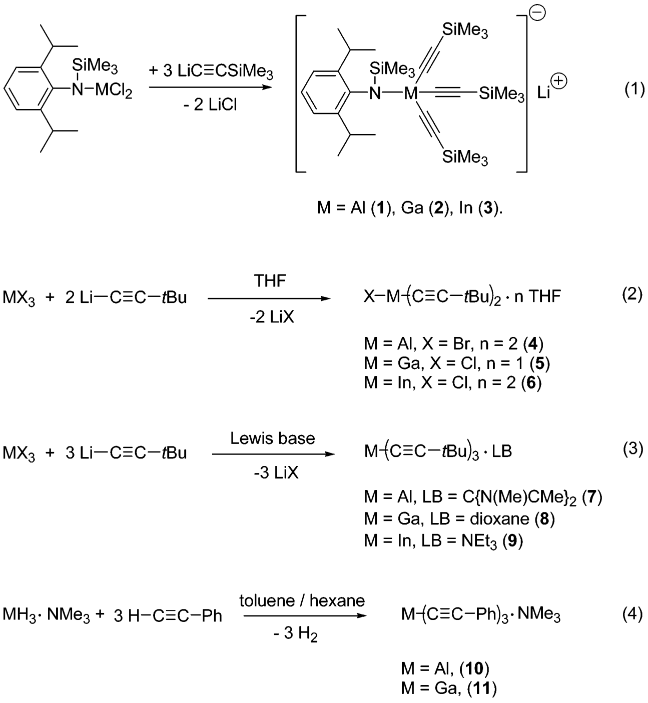
**Scheme 1**



$[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{In}(\text{C}{\equiv}\text{CSiMe}_3)_3{}^-]\cdot1.5$ dioxane (**3**), $\text{Br}-\text{Al}(\text{C}{\equiv}\text{C}t\text{Bu})_2\cdot2$ THF (**4**), $\text{Cl}-\text{Ga}(\text{C}{\equiv}\text{C}t\text{Bu})_2\cdot$THF (**5**), $\text{Cl}-\text{In}(\text{C}{\equiv}\text{C}t\text{Bu})_2\cdot2$ THF (**6**), $\text{Al}(\text{C}{\equiv}\text{C}t\text{Bu})_3\cdot\text{C}\{\text{N}(\text{Me})\text{CMe}\}_2$ (**7**), $\text{Ga}(\text{C}{\equiv}\text{C}t\text{Bu})_3\cdot$dioxane (**8**), $\text{In}(\text{C}{\equiv}\text{C}t\text{Bu})_3\cdot\text{NEt}_3$ (**9**), $\text{Al}(\text{C}{\equiv}\text{CPh})_3\cdot\text{NMe}_3$ (**10**), and $\text{Ga}(\text{C}{\equiv}\text{CPh})_3\cdot\text{NMe}_3$ (**11**).

## Results and Discussion

**Synthesis.** Compound **1** was obtained in good yield by treating six equiv of $\text{LiC}{\equiv}\text{CSiMe}_3$ with $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{AlCl}_2]_2$ in THF at 55 °C. Compound **1** is an air- and moisture-sensitive crystalline solid that decomposes above 300 °C without melting. Consequently we changed the central metal atom in **1** to gallium and indium which leads to the first examples of ionic compounds carrying three terminal ethynyl groups (**2** and **3**). The reaction between $[\text{Li}^+\cdot\text{Et}_2\text{O}\ (2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{GaCl}_3)^-]$ (**12**), which was prepared from the reaction of $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Li}$ and $\text{GaCl}_3$ in $\text{Et}_2\text{O}$, and three equiv of $\text{LiC}{\equiv}\text{CSiMe}_3$ in THF leads to the formation of **2**, whereas **3** was synthesized by using $[\text{Li}^+\cdot3\ \text{THF}\ (2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{InCl}_3)^-]$ and $\text{LiC}{\equiv}\text{CSiMe}_3$ (Scheme 1, eq 1).

Compounds **4**, **5**, and **6**, which each contain a halogen atom and two $t\text{BuC}{\equiv}\text{C}-$ moieties bonded to the metal were prepared by the reaction of the corresponding metal trihalide ($\text{AlBr}_3$, $\text{GaCl}_3$, $\text{InCl}_3$) and two equivalents of $\text{LiC}{\equiv}\text{C}t\text{Bu}$ (Scheme 1, eq 2). In our unsuccessful attempts using $\text{LiC}{\equiv}\text{CPh}$ instead of $\text{LiC}{\equiv}\text{C}t\text{Bu}$ formation of the expected products was not observed. Owing to the reactivity of M−X bonds (M = Al, Ga, In and X = Cl, Br) **4**, **5**, and **6** can be derivatized easily using monoanionic ligands.

In a facile reaction between $\text{MX}_3$ (M = Al, Ga or In, X = Br or Cl) and three equivalents of $\text{LiC}{\equiv}\text{C}t\text{Bu}$ in the presence of a Lewis base, **7**, **8**, and **9** were formed (Scheme 1, eq 3). However, a different approach was followed to synthesize compounds **10** and **11**. $\text{MH}_3\cdot\text{NMe}_3$ (M = Al or Ga) gave **10** and **11** in good yield when it was treated with an excess of phenylethyne in refluxing hexane and toluene, respectively, at 55 °C. Increasing the reaction temperature above 60 °C in toluene resulted in polymeric products, whereas decreasing the temperature resulted in either low yields or no reaction (Scheme 1, eq 4). For example, no reaction took place when a mixture of $\text{AlH}_3\cdot\text{NMe}_3$ and $\text{HC}{\equiv}\text{CPh}$ in toluene was stirred overnight at room temperature, but a significant amount of polymeric material was observed when the mixture was refluxed in toluene even for 1 h.

Compounds **1**−**11** were characterized by IR, NMR, and elemental analysis, and the data were found to be in good agreement with their solid-state X-ray structures. Suitable mass spectra containing the molecular ions were not obtained for most of the compounds (**1**−**11**) because of their low vapor pressure[5b] and low decomposition temperature. In the IR spectra of all compounds a sharp absorption band was observed around 2100 $\text{cm}^{-1}$ which can be attributed to the $\nu(\text{C}{\equiv}\text{C})$ stretching frequency.

**Structural Studies.** Crystallographic data for the structural analyses of compounds **1**−**11** are given in Table 1 and their molecular structures are shown in Figures 1−6. Tables 2 and 3 list important bond lengths and angles. Single-crystal X-ray analysis of **1** reveals that the lithium is coordinated to two ethynyl groups and two dioxane molecules. The three trimethylsilylethynyl groups and the $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)$ ligand form a slightly distorted tetrahedron around the Al. The Al−C bond distances in **1** (1.947(4)−1.979(4) Å) are comparable to those found in the previously reported structure of $[\text{Li}^+\cdot\text{dioxane}\ (2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Al}(\text{C}{\equiv}\text{CPh})_3)^-]_2\cdot2$ dioxane (1.943(3)−1.998(3) Å). However, while the average $\text{Li}-\text{C}_\alpha$ bond lengths (2.338 Å) of the two compounds are comparable (2.318 Å), the average $\text{Li}-\text{C}_\beta$ bond distance (2.751 Å) of **1** is longer than that of the latter compound (2.529 Å). This result can be attributed to the steric hindrance caused by the bulkier $\text{SiMe}_3$ group compared to the phenyl group.

The single-crystal X-ray analyses of **2** and **3** show that in contrast to **1** the lithium ion does not interact with the ethynyl groups. In **2** and **3** two lithium ions are bridged by a dioxane molecule and additionally each lithium ion is exclusively coordinated by three dioxane molecules. The different coordination behaviors of **1**, **2**, and **3** might be due to stronger polarized Al−C bond that initiates a stronger polar C≡C bond compared to those of the heavier congeners (Ga, In). The average Ga−C and In−C bond lengths are in the range of previously reported values.[5,6] The Ga−C≡C bond angles range from 169.9(6)° to 173.7(6)° and the In−C≡C-bond angles range from 168.1(2)° to 170.9(2)°. A closer look at the M−C≡C bond angle in **1**, **2**, and **3** discloses that the deviation of the bond angle from the ideal angle of 180° follows the order Al < Ga < In.

The solid-state molecular structures of **4** and **6**, which were determined by single-crystal X-ray analyses, reveal that they possess a trigonal bipyramidal structure with the aluminum in the center. The two $-\text{C}{\equiv}\text{C}t\text{Bu}$ groups and the halogen atom form the horizontal plane while the two THF molecules

**Table 1.** Crystallographic Data for the Structural Analyses of Compounds **1**−**11**

| | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| formula | $C_{41}H_{75}AlLiNO_{5.5}Si_4$ | $C_{50}H_{93}GaLiNO_{10}Si_4$ | $C_{50}H_{93}InLiNO_{10}Si_4$ | $C_{20}H_{34}AlBrO_2$ | $C_{16}H_{26}ClGaO$ | $C_{20}H_{34}ClInO_2$ |
| fw | 816.30 | 1057.27 | 1102.37 | 413.36 | 339.54 | 456.74 |
| $T$, K | 200(2) | 200(2) | 133(2) | 203(2) | 133(2) K | 293(2) |
| cryst syst | triclinic | triclinic | triclinic | monoclinic | monoclinic | monoclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 12.024(4) | 13.284(17) | 13.441(3) | 10.278(2) | 15.162(3) | 10.281(2) |
| $b$, Å | 19.507(8) | 15.030(14) | 15.106(3) | 12.082(2) | 11.267(2) | 12.472(3) |
| $c$, Å | 23.550(15) | 17.574(17) | 17.374(4) | 17.997(4) | 11.592(2) | 17.881(4) |
| $\alpha$, deg | 96.41(6) | 65.19(8) | 65.49(3) | 90 | 90 | 90 |
| $\beta$, deg | 94.38(3) | 84.09(7) | 83.97(3) | 91.59(3) | 111.02(3) | 90.66(3) |
| $\gamma$, deg | 107.574(17) | 79.29(7) | 78.81(3) | 90 | 90 | 90 |
| $V$, Å$^3$ | 5200.0(1) | 3130.0(1) | 3147.6(11) | 2233.8(8) | 1848.5(6) | 2292.5(8) |
| $D$ (calcd), g cm$^{-3}$ | 1.043 | 1.122 | 1.163 | 1.229 | 1.220 | 1.323 |
| $Z$ | 4 | 2 | 2 | 4 | 4 | 4 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 0.168 | 0.564 | 0.499 | 1.888 | 1.625 | 1.156 |
| no. of reflns collected | 14045 | 5964 | 58440 | 2920 | 3029 | 20942 |
| no. of indep reflns/$R$(int) | 13532/0.1123 | 5774/0.1077 | 10639/0.0752 | 2902/0.1261 | 3029 | 3883/0.1133 |
| data/restraints /params | 13532/1397/1013 | 5774/830/614 | 10639/0/604 | 2902/329/223 | 3029/190/224 | 3883/9/238 |
| $S$ | 1.022 | 1.032 | 1.001 | 1.040 | 1.009 | 1.056 |
| $R1$, $R2$ ($I > 2\sigma(I)$)[a] | 0.0695, 0.1795 | 0.0740, 0.1897 | 0.0256, 0.0654 | 0.0809, 0.2058 | 0.0368, 0.0919 | 0.0392, 0.0953 |
| $R1$, $R2$ (all data)[a] | 0.0924, 0.2013 | 0.0977, 0.2130 | 0.0296, 0.0664 | 0.0998, 0.2277 | 0.0401, 0.0936 | 0.0466, 0.0977 |
| $\Delta\rho$(min), $\Delta\rho$(max), e Å$^{-3}$ | 0.837, −0.676 | 0.858, −1.053 | 0.674, −0.718 | 1.689, −1.773[a] | 0.602, −0.796 | 1.582, −1.309 |

| | **7**·0.5 toluene | **8** | **9**·0.5 hexane | **10** | **11** |
|---|---|---|---|---|---|
| formula | $C_{28.5}H_{43}AlN_2$ | $C_{22}H_{35}GaO_2$ | $C_{27}H_{49}InN$ | $C_{27}H_{24}AlN$ | C27 H24 Ga N |
| fw | 440.63 | 401.22 | 502.49 | 389.45 | 432.19 |
| $T$, K | 200(2) | 133(2) | 133(2) | 150(2) | 203(2) |
| cryst syst | monoclinic | orthorhombic | trigonal | monoclinic | monoclinic |
| space group | $C2/c$ | $Pnma$ | $P\bar{3}c1$ | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 23.65(3) | 18.910(4) | 15.659(2) | 13.905(4) | 13.919(2) |
| $b$, Å | 12.913(4) | 17.713(4) | 15.659(2) | 11.914(3) | 11.9212(15) |
| $c$, Å | 18.980(5) | 6.8213(14) | 14.032(3) | 13.999(5) | 14.019(4) |
| $\alpha$, deg | 90 | 90 | 90° | 90 | 90 |
| $\beta$, deg | 93.64(8) | 90 | 90° | 94.16(4) | 94.363(16) |
| $\gamma$, deg | 90 | 90 | 120° | 90 | 90 |
| $V$, Å$^3$ | 5790(1) | 2284.8(8) | 2979.7(8) | 2313.1(12) | 2319.5(8) |
| $D$ (calcd), g cm$^{-3}$ | 1.012 | 1.166 | 1.120 | 1.118 | 1.238 |
| $Z$ | 8 | 4 | 4 | 4 | 4 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 0.086 | 1.215 | 0.804 | 0.099 | 1.198 |
| no. of reflns collected | 6032 | 10285 | 16974 | 2181 | 3241 |
| no. of indep. eflns/$R$(int) | 3790/0.0737 | 2012/0.0729] | 1712/0.0583] | 1751/0.0430 | 3022/0.1175 |
| data/restraints /params | 3790/42/315 | 2012/0/159 | 1712/239/153 | 1751/0/265 | 3022/0/265 |
| $S$ | 1.029 | 1.052 | 0.965 | 1.112 | 1.184 |
| $R1$, $R2$ ($I > 2\sigma(I)$)[a] | 0.0962, 0.2510 | 0.0233, 0.0687 | 0.0263, 0.0687 | 0.0890, 0.2373 | 0.0435, 0.1212 |
| $R1$, $R2$ (all data)[a] | 0.1339, 0.2958 | 0.0261, 0.0699 | 0.0416,0.0735 | 0.1198, 0.2802 | 0.0455, 0.1231 |
| $\Delta\rho$(min), $\Delta\rho$(max), e Å$^{-3}$ | 0.695, −0.459 | 0.369, −0.464 | 0.486, −0.287 | 0.351, −0.379 | 0.827, −0.706 |

[a] The largest difference peaks for compound **4** are near bromine and may be due to absorption effects.

occupy the vertical axes. The M−C$_{alkynyl}$ bond lengths and M−C≡C bond angles of **4** and **6** are in good agreement with those of the previously reported structures.[1d,3,6] The C−M−C bond angle is found to be larger than 120° (**4**, 125.9(3)°; **6**, 130.6(2)°). Interestingly, in a similar compound, **5**, the gallium is coordinated by only one THF molecule and hence the geometry around the gallium is tetrahedral. As with the previously studied structures of tetra coordinated gallium compounds,[7] the L−Ga−LB (L = covalently bound ligand (alkynyl group or Cl in **5**), LB = coordinating Lewis base (THF in **5**)) bond angle is smaller than that of L−Ga−L. All the bond angles among the alkynyl groups and Cl around gallium (C(3)−Ga(1)−C(1), 124.6(1)°; (C(3)−Ga(1)−Cl(1), 113.1(7)°; C(1)−Ga(1)−Cl(1), 111.4(8)°) are larger than the tetrahedral angle (109°), while all the bond angles which arise from the THF oxygen (C(3)−Ga(1)−O(1), 100.5(3)°; C(1)−Ga(1)−O(1), 99.2(3)°; O(1)−Ga(1)−Cl(1), 103.8(3)°) are smaller. This can be attributed to the gallium atom approaching the ideal sp$^2$ hybridization with the THF oxygen atom presumably donating its electron pair to a gallium orbital of higher p character.[7] In other words, a strong covalent bond prefers utilizing a lower energy orbital with higher s character, whereas a weaker bond like a coordinative bond, involves an orbital of higher p character (Bent's rule).[7,8]

An important feature of **8** from a structural point of view is that it crystallizes as a coordination polymer, which was

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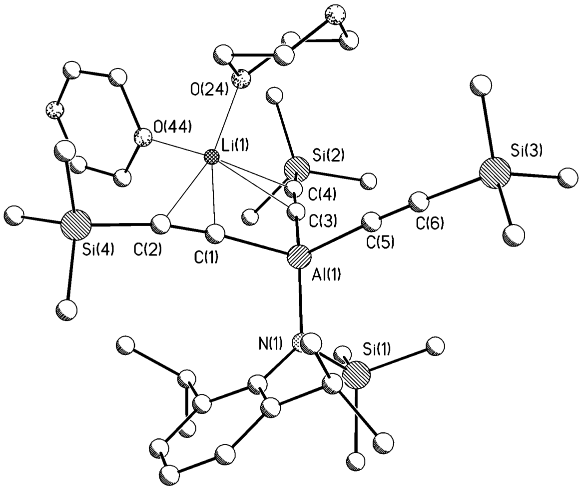

**Figure 1.** Stick and ball model of **1**. For clarity, the hydrogen atoms have been omitted.

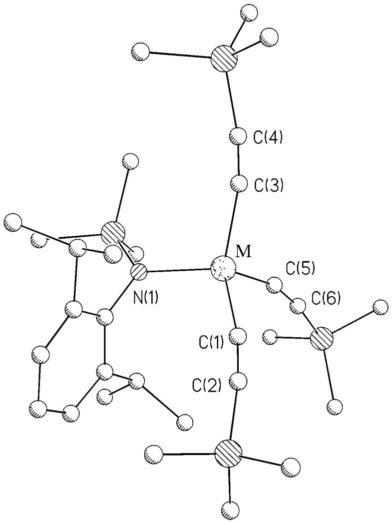

**Figure 2.** Stick and ball model of the anionic part of isomorphous compounds **2** (M = Ga) and **3** (M = In). All hydrogen atoms are omitted for clarity.

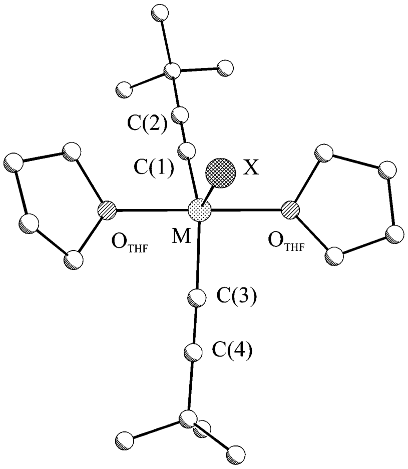

**Figure 3.** Stick and ball model of isomorphous compounds **4** (M = Al, X = Br) and **6** (M = In, X = Cl). All the hydrogen atoms are omitted for clarity.

determined by single-crystal X-ray studies. Each gallium unit, which represents a trigonal bipyramid, comprises three C≡C*t*Bu groups in the trigonal plane. Dioxane molecules link the gallium units while occupying the vertical axes of the trigonal bipyramid.

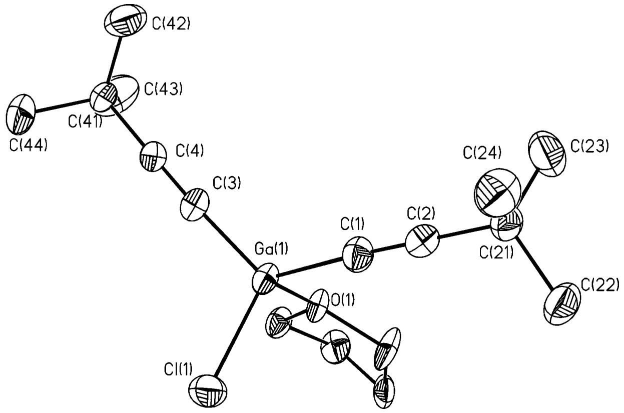

**Figure 4.** ORTEP plot of **5**. For clarity, the hydrogen atoms have been omitted. Nonhydrogen atoms are represented by thermal ellipsoids drawn at the 50% probability level.

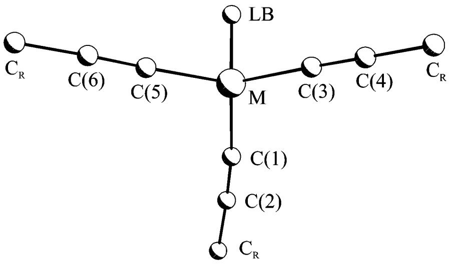

**Figure 5.** Stick and ball plot showing the basic structure of **7** (M = Al, $C_R$ = *t*Bu, LB = C{N(Me)CMe}$_2$), **9** (M = In, $C_R$ = *t*Bu, B = $NEt_3$), **10** (M = Al, $C_R$ = Ph, B = $NMe_3$), and **11** (M = Ga, $C_R$ = Ph, B = $NMe_3$).

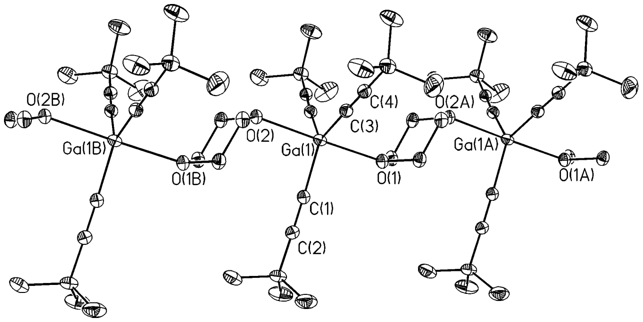

**Figure 6.** ORTEP plot showing the polymeric structure of **8**. All the hydrogen atoms are omitted for clarity. Nonhydrogen atoms are represented by thermal ellipsoids drawn at the 50% probability level.

Single-crystal X-ray analyses of compounds **7**, **9**, **10**, and **11** show that all of them possess essentially the same distorted tetrahedral geometry around the metal atom. The phenomenon of deviation of bond angles from the ideal tetrahedral bond angle, which is observed in compound **5**, is also found in these structures. It is interesting to mention that compound **7** is the first aluminum alkynyl compound containing three terminal alkynyl groups and which is stabilized using a heterocyclic carbene. Obviously the carbene adduct is more stable than the corresponding $Me_3N$ derivative.

In summary we have shown that group 13 derivatives containing terminal alkynyl groups are easily prepared in the presence of a Lewis base. The coordination number of **4** is the preferred coordination pattern. However, the molecules

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**−**6**

| | **1**<br>M = Al, X = C(5) | **2**<br>M = Ga, X = C(5) | **3**<br>M = In, X = C(5) | **4**<br>M = Al, X = Br | **5**<br>M = Ga, X = Cl | **6**<br>M = In, X = Cl |
|---|---|---|---|---|---|---|
| M−C(1) | 1.972(5) | 1.966(8) | 2.148(2) | 1.937(7) | 1.911(2) | 2.104(4) |
| M−C(3) | 1.979(4) | 1.971(8) | 2.154(2) | 1.934(7) | 1.908(2) | 2.101(4) |
| M−C(5) | 1.947(4) | 1.970(8) | 2.169(2) | | | |
| M−C(1)−C(2) | 175.0(4) | 173.7(6) | 170.9(2) | 177.1(7) | 175.5(2) | 177.6(4) |
| M−C(3)−C(4) | 176.6(4) | 169.9(6) | 169.0(2) | 176.3(6) | 175.3(2) | 175.9(3) |
| M−C(5)−C(6) | 177.3(4) | 170.9(6) | 168.1(2) | | | |
| C(1)-M−C(3) | 103.0(2) | 111.8(3) | 112.5(7) | 125.9(3) | 124.6(1) | 130.6(2) |
| C(1)-M−X | 109.3(2) | 107.4(3) | 106.9(7) | 118.1(2) | 111.4(8) | 115.3(1) |
| C(3)-M−X | 108.9(2) | 111.8(3) | 112.5(7) | 115.9(2) | 113.1(7) | 114.0(1) |

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for Compounds **7**−**11**

| | **7**<br>M =Al | **8**<br>M = Ga | **9**<br>M = In | **10**<br>M = Al | **11**<br>M = Ga |
|---|---|---|---|---|---|
| M−C(1) | 1.940(2) | 1.933(2) | 2.116(3) | 1.913(1) | 1.940(4) |
| M−C(3) | 1.943(2) | 1.932(2) | [a] | 1.917(9) | 1.940(4) |
| M−C(5) | 1.939(3) | [a] | [a] | 1.930(1) | 1.929(4) |
| M−C(1)−C(2) | 171.7(2) | 178.5(2) | 172.3(3) | 174.1(8) | 172.0(4) |
| M−C(3)−C(4) | 176.0(2) | 178.0(1) | [a] | 179.3(8) | 173.8(3) |
| M−C(5)−C(6) | 171.3(2) | [a] | [a] | 174.6(7) | 178.6(4) |
| C(1)-M−C(3) | 109.7(1) | 120.6(4) | 116.4(5) | 116.0(4) | 113.2(2) |
| C(1)-M−C(5) | 115.9(1) | [a] | [a] | 112.2(4) | 116.3(2) |
| C(3)-M−C(5) | 112.8(9) | [a] | [a] | 114.8(4) | 115.8(2) |

[a] Symmetry transformations are used to generate equivalent atoms and hence these bond lengths and angles are same as the equivalent ones.

containing a metal−halogen bond (**4**, **5**, and **6**) utilize a trigonal bipyramidal surrounding. This geometry is also found in the coordination polymer of **8**.

Moreover, aluminum compounds containing terminal alkynyl groups are ideal precursors for the preparation of aluminum hydride clusters, which can be used for cluster surface chemistry.[9] Finally, the alkynyl compounds of group 13 are probably good precursors for the preparation of new materials. Research work in this direction is in progress.

## Experimental Section

All experiments were carried out using standard Schlenk techniques under a dry nitrogen atmosphere because of the sensitivity of the reactants and products toward air and moisture. A Braun MB 150-GI Box was used to store the compounds and to prepare the samples for spectroscopic characterization. All solvents were distilled from sodium/benzophenone and degassed prior to use. [Li$^+$·3THF (2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)InCl$_3$)$^-$],[10] C{N(Me)CMe}$_2$ (= 1,2,4,5-tetramethylimidazol-2-ylidene),[11] AlH$_3$·NMe$_3$,[12] GaH$_3$·NMe$_3$,[13] and [2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)AlCl$_2$]$_2$[4a] were prepared as described in the literature. NMR spectra were recorded on a Bruker Avance 200 or Bruker AC 250. $^1$H, $^{13}$C, and $^{29}$Si NMR data were referenced to trimethylsilane, whereas $^7$Li NMR data were referenced to LiCl. FT-IR spectra were measured on a Bio-Rad FTS-7 instrument as Nujol mulls in the range of 4000−400 cm$^{-1}$. Mass spectra were obtained on a Finnigan MAT 95. Melting points were measured in sealed glass tubes on a Büchi 540 instrument.

**Synthesis of [Li$^+$·2 dioxane (2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)Al(C≡CSiMe$_3$)$_3$)$^-$]·0.75 dioxane (1).** A solution of HC≡CSiMe$_3$ (1.50 g, 15.3 mmol) in THF (75 mL) was treated at −78 °C with a solution of *n*-BuLi in hexane (2.5 M, 6.1 mL, 15.3 mmol). The mixture was stirred overnight at room temperature and [2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)AlCl$_2$]$_2$ (1.76 g, 2.55 mmol) was added at −78 °C. The resultant mixture was further stirred for 10 h at room temperature and 3 h at 55 °C. After the flask was cooled to room temperature, the volatiles were removed under vacuum and the residue was treated with hexane. The mixture was filtered, and the oily mass obtained after evaporating the hexane from the filtrate was dissolved in dioxane (15 mL). Storing the solution overnight at room temperature afforded colorless crystals of **1**. Yield: 2.83 g (74%). mp: > 300 °C. $^1$H NMR (200 MHz, THF-$d_8$): $\delta$ 6.90−6.60 (m, 3H, Ar*H*), 4.02 (m, $J$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 3.36 (s, 8H, dioxane), 1.24 (d, $J$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, $J$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.07 (s, 9H, Si(C*H*$_3$)$_3$), −0.04 (s, 27H, C≡CSi(CH$_3$)$_3$). $^7$Li NMR (97 MHz, THF-$d_8$): $\delta$ −0.3. $^{13}$C NMR (125 MHz, THF-$d_8$): $\delta$ 150.5, 147.6, 122.5, 120.9 (arom. *C*), 109.0 (br, Al−*C*), 95.3 (*C*−SiMe$_3$), 67.9 (dioxane), 27.7 (*C*H), 27.1 (*C*H$_3$), 3.4 (NSi(*C*H$_3$)$_3$), 1.0 (CSi(*C*H$_3$)$_3$). $^{27}$Al NMR (65 MHz, THF-$d_8$): $\delta$ 84.3. $^{29}$Si NMR (99 MHz, THF-$d_8$): $\delta$ −3.6, −25.3. IR (Nujol): $\tilde{\nu}$ = 2089, 2054, 1316, 1262, 1250, 1184, 1106, 1075, 931, 870, 853, 841, 795, 759, 733, 686, 451 cm$^{-1}$. MS (FAB): *m*/*z* (%) 566 ([M$^-$ − dioxane], 100). Anal. Calcd for C$_{38}$H$_{69}$AlLiNO$_4$Si$_4$ (with two dioxane molecules) (750.23): C, 60.84; H, 9.27; N 1.87. Found: C, 59.67; H, 9.11; N, 1.89.

**Synthesis of [(Li$^+$)$_2$·(dioxane)$_7$]$_{0.5}$ [2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)Ga(C≡CSiMe$_3$)$_3$$^-$]·1.5 dioxane (2).** To a solution of [Li$^+$·Et$_2$O (2,6-$^i$Pr$_2$C$_6$H$_3$N(SiMe$_3$)GaCl$_3$)$^-$] **12** (0.51 g, 1.0 mmol) in THF (75 mL) was added Me$_3$SiC≡CLi (0.31 g, 3.0 mmol). The resultant mixture was stirred for 24 h at room temperature and the solvent was removed under vacuum. Toluene (40 mL) was added to the residue, which was then filtered over Celite, and the filtrate was dried under vacuum. The residue from the filtrate was treated with dioxane (10 mL) at room temperature for 24 h and dried under vacuum. The crude product was recrystallized from toluene (30 mL) at −32 °C. Yield: 0.48 g (61%). mp: > 300 °C. $^1$H NMR (200 MHz, THF-$d_8$): $\delta$ 7.00−6.50 (m, 3H, Ar*H*), 4.05 (sept, $J$ = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 3.58 (s, 8H, dioxane), 1.21 (d, $J$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, $J$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.07 (s, 9H, Si(C*H*$_3$)$_3$), −0.03 (s, 27H, C≡CSi(C*H*$_3$)$_3$). $^7$Li NMR (97 MHz, THF-$d_8$): $\delta$ −0.5. $^{13}$C NMR (125 MHz, THF-$d_8$): $\delta$ 151.8, 148.1, 123.4, 120.6 (arom. *C*), 107.3 (br, Ga−*C*), 95.2 (*C*−SiMe$_3$), 27.6 (*C*H), 26.9 (*C*H$_3$), 3.6 (NSi(*C*H$_3$)$_3$), 1.0 (CSi(*C*H$_3$)$_3$). $^{29}$Si NMR (99 MHz, THF-$d_8$): $\delta$ −4.2, −25.2. IR (Nujol): $\tilde{\nu}$ = 2074, 2062, 1315, 1261, 1247, 1191, 1105, 1051, 1041, 936, 848, 759, 687 cm$^{-1}$. MS (EI): *m*/z (species, %) 616 ([M$^+$ − dioxane − H], 15), 511 ([M$^+$ − dioxane − Li − C≡CSiMe$_3$], 100). Anal. Calcd for C$_{38}$H$_{69}$GaLiNO$_4$Si$_4$ (792.98): C, 57.20; H, 8.80; N, 1.60. Found: C, 56.82; H, 8.39; N, 1.60.

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**Synthesis of $[(Li^+)_2\cdot(dioxane)_7]_{0.5}$ $[2,6\text{-}iPr_2C_6H_3N(SiMe_3)In(C\equiv CSiMe_3)_3^-]\cdot 1.5$ dioxane (3).** $Me_3SiC\equiv CLi$ (0.31 g, 3.0 mmol) was added to a solution of $[Li^+\cdot 3\ THF\ (2,6\text{-}iPr_2C_6H_3N(SiMe_3)InCl_3)^-]$ (0.69 g, 1.0 mmol) in toluene (60 mL) at −78 °C and the mixture was stirred for 3 d at room temperature before it was filtered over Celite. The volume of the filtrate was reduced to 10 mL and dioxane (5 mL) was added. Keeping the mixture at room temperature for 5 d yielded colorless crystals of compound **3**. The crystals were washed with pentane (3 mL) and dried under vacuum. Yield: 0.82 g (74%). mp: 160 °C. $^1$H NMR (200 MHz, THF-$d_8$): $\delta$ 7.00−6.50 (m, 3H, ArH), 4.02 (m, $J$ = 7.0 Hz, 2H, C$H$(CH$_3$)$_2$), 3.56 (s, 8H, dioxane), 1.18 (d, $J$ = 7.0 Hz, 6H, CH(C$H_3$)$_2$), 1.12 (d, $J$ = 7.0 Hz, 6H, CH(C$H_3$)$_2$), 0.06 (s, 9H, NSi(CH$_3$)$_3$), −0.02 (s, 27H, C≡CSi(CH$_3$)$_3$). $^7$Li NMR (97 MHz, THF-$d_8$): $\delta$ −0.2. $^{13}$C NMR (125 MHz, THF-$d_8$): $\delta$ 152.3, 147.3, 122.4, 120.1 (arom. $C$), 114.1 (br, In−$C$), 95.2 ($C$−SiMe$_3$), 27.5 ($C$H), 26.5 ($C$H$_3$), 3.6 (NSi($C$H$_3$)$_3$), 1.1 (CSi($C$H$_3$)$_3$). $^{29}$Si NMR (99 MHz, THF-$d_8$): $\delta$ −4.5, −25.2. IR (Nujol): $\tilde{\nu}$ = 2063, 2051, 1250, 1123, 1080, 1032, 941, 876, 845, 760, 722, 676, 606 cm$^{-1}$. Anal. Calcd for $C_{38}H_{69}InLiNO_4Si_4$ (792.98): C, 54.46; H, 8.30; N, 1.67. Found: C, 53.85; H, 7.71; N, 1.14.

**Synthesis of Br−Al(C≡C*t*Bu)$_2$·2 THF (4).** To a solution of $AlBr_3$ (0.53 g, 2.0 mmol) in a mixture of hexane (2 mL) and THF (60 mL) was added LiC≡C*t*Bu (0.35 g, 4.0 mmol) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 2 d. The volatiles were removed under vacuum and the product was extracted with hexane (150 mL). Removal of hexane afforded a white solid, which was crystallized from hexane (10 mL). Yield: 0.55 g (67%). mp: 145 °C. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 3.78 (m, 8H, OC$H_2$−CH$_2$), 1.25 (m, 8H, OCH$_2$−C$H_2$), 1.22 (s, 18H, *t*Bu). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ 92.6 ($C$−*t*Bu), 67.9 (br, Al−$C$), 67.2 (THF), 30.9 (Me), 27.3 ($C$−Me$_3$), 25.8 (THF). IR (Nujol): ṽ = 2165, 2129, 1577, 1260, 1251, 1204, 1091, 1023, 923, 861, 803, 757, 632, 551, 484 cm$^{-1}$. Anal. Calcd for $C_{20}H_{34}AlBrO_2$ (413.37): C, 58.11; H, 8.29. Found: C, 57.30; H, 8.07.

**Synthesis of Cl−Ga(C≡C*t*Bu)$_2$·THF (5).** Compound **5** was prepared by using $GaCl_3$ (0.30 g, 1.70 mmol)) and LiC≡C*t*Bu (0.30 g, 3.41 mmol), and following the procedure mentioned for the preparation of **4**. Yield: 0.38 g (66%). mp: 110 °C. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 3.81 (m, 4H, OC$H_2$−CH$_2$), 1.17 (s, 18H, *t*Bu), 1.08 (m, 4H, OCH$_2$−C$H_2$). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ 116.4 ($C$−*t*Bu), 83.7 (br, Ga−$C$), 70.2 (THF), 31.2 (Me), 28.3 ($C$−Me$_3$)), 25.0 (THF). IR (Nujol): $\tilde{\nu}$ = 2177, 2144, 1378, 1366, 1260, 1253, 1204, 1096, 1017, 919, 861, 802, 749, 723, 630, 592, 488 cm$^{-1}$. Anal. Calcd for $C_{16}H_{26}ClGaO$ (339.56): C, 56.60; H, 7.72. Found: C, 56.29; H, 7.73.

**Synthesis of ClIn(C≡C*t*Bu)$_2$·2 THF (6).** Compound **6** was prepared by using $InCl_3$ (0.45 g, 2.0 mmol)) and LiC≡C*t*Bu (0.36 g, 4.0 mmol) and following the procedure given for **4**. Yield: 0.35 g (38%). mp: 112 °C. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 3.84 (m, 8H, OC$H_2$−CH$_2$), 1.30 (m, 8H, OCH$_2$−C$H_2$), 1.24 (s, 18H, *t*Bu). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ 118.2 ($C$−*t*Bu), 88.3 (br, In−$C$), 68.5 (THF), 31.6 (Me), 28.5 ($C$−Me$_3$), 25.3 (THF). IR (Nujol): $\tilde{\nu}$ = 2063, 2051, 1250, 1123, 1080, 1032, 941, 876, 845, 760, 722, 676, 606 cm$^{-1}$. Anal. Calcd for $C_{20}H_{34}ClInO_2$ (456.76): C, 52.59; H, 7.50. Found: C, 52.19; H, 7.64.

**Synthesis of Al(C≡C*t*Bu)$_3$·C{N(Me)CMe}$_2$ (7).** Toluene (25 mL) was added to a mixture of $AlCl_3$ (0.570 g, 4.27 mmol), C{N(Me)CMe}$_2$ (0.53 g, 4.27 mmol), and *t*BuC≡CLi (1.18 g, 13.5 mmol), and the resulting suspension was stirred for 6 h. The mixture was filtered and the solvent was removed in vacuo giving 1.54 g (3.90 mmol, 91%) (**7**) of a white solid. Crystals suitable for X-ray structural analysis of **7**·0.5 toluene were grown from a concentrated (ca. 0.5 g in 5 mL) solution in toluene at 4 °C. mp: 162 °C. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 3.59 (s br, 6 H, NC$H_3$), 1.24 (s, 27H, C(C$H_3$)$_3$), 1.19 (s br, 6H, C$H_3$−C−N). $^{13}$C NMR (126 MHz, $C_6D_6$): $\delta$ 165.3 (very br, N$C$Al), 124.9 (Me−$C$−N), 116.2 (br, $C$−*t*Bu), 93.8 (very br, Al−$C$), 34.1 (br, N$C$H$_3$), 31.8 (C($C$H$_3$)$_3$), 28.5 ($C$(CH$_3$)$_3$), 7.86 ($C$H$_3$−C−N). MS (EI): *m/z* (%) 394 (M$^+$, 8), 379 (M$^+$ − Me, 17), 337 (M$^+$ − *t*Bu, 100). IR (Nujol): $\tilde{\nu}$ = 2164, 2120, 1698, 1650, 1605, 1309, 1260, 1249, 1202, 1097, 1024, 917, 847, 746, 727, 697, 571, 532, 475, 402 cm$^{-1}$. Anal. Calcd for $C_{28.5}H_{43}AlN_2$ (incl. 0.5 toluene molecules) (440.63): C, 77.68; H, 9.84; N, 6.36. Found: C, 76.48; H, 9.65; N, 6.47.

**Synthesis of Ga(C≡C*t*Bu)$_3$·dioxane (8).** Compound **8** was prepared by using $GaCl_3$ (0.29 g, 1.64 mmol) and LiC≡C*t*Bu (0.44 g, 4.9 mmol) and following the procedure mentioned for **7**. Yield: 0.50 g (67%). mp: 330 °C. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 3.54 (s, 8H, dioxane), 1.15 (s, 27H, *t*Bu). $^{13}$C NMR (125 MHz, $C_6D_6$) $\delta$ 116.5 ($C$−*t*Bu), 86.3 (br, Ga−$C$), 67.3 (dioxane), 31.3 (Me), 28.3 ($C$−Me). IR (Nujol): $\tilde{\nu}$ = 2171, 2138, 1363, 1304, 1251, 1204, 1112, 1094, 1077, 1043, 1030, 889, 860, 803, 743, 609, 551, 478 cm$^{-1}$. MS (EI): *m/z* (%) 312 ([M$^+$ − dioxane], 10), 297 ([M$^+$ − dioxane − Me], 25), 231 ([M$^+$ − dioxane − C≡C*t*Bu], 100). Anal. Calcd for $C_{22}H_{35}GaO_2$ (401.24): C, 65.86; H, 8.79. Found: C, 65.46; H, 9.06.

**Synthesis of In(C≡C*t*Bu)$_3$·NEt$_3$ (9).** Compound **9** was prepared by using $InCl_3$ (0.22 g, 1.0 mmol) and LiC≡C*t*Bu (0.26 g, 3.0 mmol) and following the procedure given for **4**. A mixture of triethylamine (25 mL) and THF (25 mL) was used instead of pure THF. Yield: 0.38 g (83%). mp: 220 °C. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 2.66 (m, $J$ = 7.2 Hz, 6 H, C$H_2$CH$_3$), 1.19 (s, 27H, *t*Bu), 1.08 (t, $J$ = 7.2 Hz, 9H, CH$_2$C$H_3$). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ 119.2 ($C$−*t*Bu), 90.3 (br, In−C), 48.2 (N−$C$H$_2$), 31.6 (Me), 28.5 ($C$−Me$_3$), 10.7 (CH$_2$−$C$H$_3$). IR (Nujol): $\tilde{\nu}$ = 2160, 2124, 1400, 1362, 1328, 1261, 1249, 1204, 1171, 1101, 1053, 1026, 908, 807, 748, 735, 547, 453 cm$^{-1}$. Anal. Calcd for $C_{24}H_{42}InN$ (459.42): C, 62.74; H, 9.22; N, 3.05. Found: C, 61.93; H, 8.75; N, 2.31.

**Synthesis of Al(C≡CPh)$_3$·NMe$_3$ (10).** To a suspension of $AlH_3\cdot NMe_3$ (1.00 g, 11.2 mmol) in hexane (50 mL) phenylethyne (5.00 g, 49.0 mmol) was added and stirred at room temperature for 1 h. The reaction mixture was refluxed for 1 h and filtered. All the solvent and the excess of phenylethyne were removed from the filtrate under vacuum, and the residue obtained was crystallized from toluene (10 mL) to obtain colorless crystals of **10**. Yield: 3.2 g, (73%). mp: 183 °C (decomp). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 7.47 (m$_c$, *m*-C$_6$H$_5$, 6H), 7.25 (m$_c$, *o*- and *p*-C$_6$H$_5$, 9H), 2.80 (s, CH$_3$, 9H). $^{13}$C NMR: $\delta$ 132.0, 128.0, 127.7, 124.6 (arom. $C$), 107.5 (C$_6$H$_5$−$C$), 101.2 (br, Al−$C$), 47.4 ($C$H$_3$). IR (Nujol): $\tilde{\nu}$ = 2125, 1594, 1570, 1378, 1212, 990, 816, 757, 693, 611 cm$^{-1}$. Anal. Calcd for $C_{27}H_{24}AlN$ (389.45): C, 83.27; H, 6.21; N, 3.60. Found: C, 84.01; H, 6.12; N, 3.29.

**Synthesis Ga(C≡CPh)$_3$·NMe$_3$ (11).** To a solution of $GaH_3\cdot NMe_3$ (3.00 g, 22.7 mmol) in toluene (150 mL) phenylethyne (23.1 g, 227 mmol) was added and the mixture was stirred overnight at 55 °C. After the mixture was cooled to room temperature the volatiles were evaporated under vacuum. The resulting residue was once again dissolved in toluene (50 mL) and filtered. The amount of filtrate was reduced to 7 mL and stored at 4 °C overnight to give **11** as colorless crystals. Yield: 6.96 g (16.1 mmol, 71%). mp: 151 °C. $^1$H NMR (500.13 MHz, $C_6D_6$): $\delta$ 7.51−7.49 (m, *o*-C$_6$H$_5$, 6H), 6.97−6.95 (m, *m*- and *p*-C$_6$H$_5$, 9H), 2.23 (s, CH$_3$, 9H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ 132.3, 128.4, 128.0, 125.1 (arom. $C$), 107.2 (C$_6$H$_5$−$C$), 99.2 (br, Ga−$C$), 47.3 ($C$H$_3$). IR (Nujol): $\tilde{\nu}$ = 3053, 2137, 1597, 1570, 1210, 996, 796, 764, 692, 568, 535, 384 cm$^{-1}$. MS (EI): *m/z* (%) 431 (M$^+$, 30), 372 ([M$^+$ −

$NMe_3$], 100). Anal. Calcd for $C_{27}H_{24}GaN$ (432.21): C, 75.03; H, 5.60; Ga, 16.13; N, 3.24. Found: C, 75.10; H, 5.60; Ga, 15.30; N, 3.33.

**Synthesis of [$Li^+ \cdot Et_2O$ (2,6-*i*$Pr_2C_6H_3N(SiMe_3)GaCl_3)^-$] (12).** A solution of 2,6-*i*$Pr_2C_6H_3N(SiMe_3)Li$ (12.77 g, 50.0 mmol) in diethyl ether (150 mL) was treated with a solution of $GaCl_3$ (8.80 g, 50.0 mmol) in diethyl ether (50 mL) at −78 °C while stirring. The mixture was slowly warmed to room temperature and stirred for 4 h. All the volatiles were removed under vacuum. The residue was washed with cold pentane (10 mL), and the product was extracted with $CHCl_3$ (100 mL) using a Soxhlet apparatus. Yield: 6.49 g (26%). mp: 98 °C. $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 7.20−6.70 (m, 3H, ArH), 3.87 (sept, 2H, $CH(CH_3)_2$), 3.38 (q, $J = 6.8$ Hz, 4H, $OCH_2$), 1.14 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 1.13 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 1.11 (t, $J = 6.8$ Hz, 6H, $OCH_2CH_3$), 0.07 (s, 9H, $Si(CH_3)_3$). $^{13}C$ NMR (125 MHz, THF-$d_8$): $\delta$ 148.3, 147.0, 124.2, 123.0 (arom. *C*), 66.3 ($OCH_2$), 27.8 (*C*H), 26.0 ($CH_3$), 15.7 ($CH_2CH_3$), 3.1 ($NSi(CH_3)_3$). $^7Li$ NMR (97 MHz, $C_6D_6$): $\delta$ −0.43. MS (EI): *m*/*z* (%) 389 ([$M^+ - LiCl - Et_2O$], 30), 354 ([$M^+ - Cl - LiCl - Et_2O$], 15), 248 ([$M^+ - GaCl_2 - LiCl - Et_2O$], 100). IR (Nujol): $\tilde{\nu} = 1433, 1336, 1317, 1249, 1186, 1105, 1041, 915, 886, 870, 834, 803, 751$ $cm^{-1}$. Anal. Calcd for $C_{19}H_{36}Cl_3GaLiNOSi$ (505.61): C, 45.14; H, 7.18; N, 2.77. Found: C, 45.48; H, 7.32; N, 2.70.

**X-ray Crystallography.** Data for all compounds were collected on a Stoe four-circle diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods and refined anisotropically with SHELXTL.[14]

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for the structures of **1**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.