Synthesis of heterobimetallic group 13 compounds via oxidative addition reaction of gallanediyl LGa and InEt₃

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Supporting Information Placeholder

ABSTRACT: Equimolar amounts of LGa (L = [(2,6-*i*-Pr₂-C₆H₃)NC(Me)]₂CH) and InEt₃ were found to react with insertion into the In-carbon bond and formation of LGa(Et)InEt₂ **1**, while in the presence of the N-heterocyclic carbene *It*Bu [C(N*t*-Bu₂CH)₂], the base-stabilized compound LGa(Et)Et₂In←*It*Bu **2** was formed which shows an abnormal binding mode of the NHC group. In addition, the reaction of InEt₃ with two equivalents of LGa occurred with double insertion and formation of [LGa(Et)]₂InEt **3**. **1** - **3** were characterized by heteronuclear NMR (¹H, ¹³C) and IR spectroscopy, their solid state structures were determined by single crystal X-ray analyses and their thermal stability was investigated by *in situ* NMR spectroscopy.

INTRODUCTION

Mono-valent group 13 diyls of the type RM [M = Al, Ga, In; R = Cp*, diketiminates, ...] have emerged from laboratory curiosities to versatile compounds in inorganic and organic syntheses¹ since the discovery of the first compound of this type, [Cp*Al]₄, more than 20 years ago.² Among many compounds, which have been synthesized and structurally characterized since then, the gallanediyl LGa (L = [(2,6-*i*-Pr₂-C₆H₃)NC(Me)]₂CH) containing the sterically crowded β-diketimate ligand, has been intensely studied in chemical reactions. LGa is monomeric in the solid state and in solution and the gallium valence shell contains two bond electron pairs, one electron lone pair and an empty p-orbital.³ As a consequence of this specific electronic situation, LGa can react both as electrophilic and nucleophilic reagent. LGa is a good σ-donor but a poor π-acceptor according to computational calculations as a result from the high s-character of the HOMO and the large energy difference (95.3-110 kcal/mol) between the donor orbital (HOMO) and the diffuse acceptor 4p-orbital (LUMO+1).⁴ The σ-donor capacity of LGa was shown with the synthesis of the Lewis acid-base adduct LGa→B(C₆F₅)₃⁵ and other p- or d-block metal complexes as well as with the synthesis of a large variety of late transition metal complexes,⁶ which are promising candidates for small molecules activation and cluster formation reactions.⁷ In addition to their general reactivity to act as σ-donor reagents, β-diketimate gallynes LGa also show powerful reducing activity as was demonstrated in reduction reactions of main group metal compounds such as SnCl₂. These reactions proceeded with oxidation of LGa and subsequent metal-metal bond formation, resulting in the formation of unprecedented gallyl-supported tin clusters [Sn₇{Ga(Cl)(L)}₂] and [Sn₁₇{Ga(Cl)(L)}₄].⁸ In addition, the galla-dibismuthenes [LGa(OR)Bi]₂ (R = C₆F₅, SO₂CF₃) containing Bi=Bi double bonds were obtained from reactions of

LGa with Bi(OR)₃,⁹ whereas reactions of LGa with GaX₃ (X = Me, Cl) occurred with insertion into the Ga-X bond and subsequent formation of the digallane LGa(X)GaX₂ and trigallane [LGa(X)]₂GaX, respectively.¹⁰ Analogous insertion reactions were reported for reactions with Me₂SnCl₂, SiCl₄ as well as *t*-BuCl.¹⁰

Despite these significant findings, there still remains interest in understanding the bonding situation in such intermetallic compounds and how the reactions occur in order to predict what kind of complexes are accessible. Due to our general interest in the synthesis, bonding situation and chemical reactivity of low-valent organometallics of group 12,¹¹ 13,¹² 14,¹³ and 15 elements,¹⁴ we became recently interested in insertion reactions of the gallanediyl LGa into metal-carbon as well as metal-metal bonds and reported on reactions with group 15 metalorganics such as Et₃Bi¹⁵ and Et₄E₂ (E = Sb, Bi),¹⁶ which proceeded with insertion into the Bi-C and E-E bond and subsequent formation of LM(Et)BiEt₂ and LM(EEt₂)₂, respectively. In addition, reactions of LGa with diisopropyltellane *i*-Pr₂Te and diphenylditellane Ph₂Te₂ were found to occur with insertion into the Te-Te and Te-C bond.¹⁷ We herein report on the reactions of LGa with InEt₃, yielding heterobimetallic group 13 element complexes containing direct In-Ga covalent bonds.

RESULTS AND DISCUSSION

The reaction of equimolar amounts of LGa and InEt₃ in toluene at 0 °C occurred with insertion of the gallane diyl into the In-C bond and formation of the heterobimetallic complex LGa(Et)InEt₂ **1** (Scheme 1). Solutions of **1** in benzene and toluene tend to decompose slowly at ambient temperature and the formation of LGaEt₂,¹⁵ InEt₃, which were clearly identified by their ¹H NMR spectra, and In metal has been observed within a day. The ¹H NMR spectrum of the reaction mixture

(Figure S15) shows the formation of LGaEt_2 and InEt_3 in 3:1 molar ratio, while the corresponding two equivalents of In metal was isolated in an independent large scale reaction and characterized by energy dispersive X-ray diffraction (EDX, Fig. S20). The observation of 3:1:2 stoichiometry of LGaEt_2 , InEt_3 and indium metal from **1** evidences the *in situ* formation of monovalent $[\text{InEt}]_x$, which further disproportionates into two equivalent indium metal and one equivalent InEt_3 as was observed. It should further be mentioned, that the formation of deeply colored solutions, which may indicate the presence of larger cluster-type complexes as was observed in reaction with SnCl_2 ,⁸ were not observed. In order to confirm the possible formation of In(I) in the reaction mixture, LGa was reacted with Cp^*InEt_2 . The reaction leads to the formation of LGaEt_2 and Cp^*In . However, we were able to isolate only 21% of the Cp^*In which might result from the simultaneous insertion of LGa into the In-C bond of both the In- Cp^* and In-Et moieties as well as due to a gradual decomposition of as-formed Cp^*In in solution.¹⁸

Compound **1** is quite stable below $-30\text{ }^\circ\text{C}$ both in its isolated pure form and in solution, while noticeable decomposition was observed at higher temperatures. Furthermore, **1** can be stabilized upon reaction with the strong σ -donor tBu [$\text{C}(\text{Nt-Bu}_2\text{CH})_2$], resulting in a quantitative formation of the respective NHC-stabilized compound $\text{LGa}(\text{Et})\text{Et}_2\text{In} \leftarrow \text{tBu}$ **2** (Scheme 1). It should be noted that the reaction of **1** with one additional equivalent of LGa , which can also serve as σ -donor, leads to twofold insertion and subsequent formation of $[\text{LGa}(\text{Et})]_2\text{InEt}$ **3** in good yield, while the reaction of **1** with two additional equivalents of LGa failed to give the threefold insertion product $[\text{LGa}(\text{Et})]_3\text{In}$. **2** and **3** are thermally more stable in solution than **1** and can be stored for several days at ambient temperature in solution and in its isolated form under argon atmosphere. **1** – **3** are moisture sensitive, yellow to orange crystalline solids but moderately stable toward air. They dissolve well in benzene, toluene and *n*-hexane.

Scheme 1. Synthesis and thermal stability of **1** – **3**.

¹H and ¹³C NMR spectra of freshly prepared **1** show characteristic resonances of the organic substituents, i.e. the ¹H NMR

spectrum of **1** in C_6D_6 exhibits single resonances for the $\gamma\text{-CH}$ and two methyl groups of the $\text{C}_3\text{N}_2\text{Ga}$ ring at 4.83 and 1.48 ppm, while the magnetically inequivalent methyl and methine protons of the isopropyl substituents exhibit four doublets (1.39, 1.15, 1.12, 1.08 ppm) and two septets (3.56 and 3.01 ppm), respectively. Proton resonances of the Ga-Et group are shifted to higher field (0.85 and 0.37 ppm), whereas those of the InEt groups appear as a triplet and a multiplet at lower field (1.82 and 1.11 ppm). The ¹³C{¹H} NMR spectrum of **1** shows 18 signals including the characteristic resonances due to the $\gamma\text{-CH}$ (96.32 ppm), the remaining two $\text{C}_3\text{N}_2\text{Ga}$ ring carbons (167.98 ppm), the methine (29.23, 28.99 ppm) and the methyl carbon atoms of isopropyl groups (25.42, 25.07, 24.28, 23.36 ppm) as well as the methyl (13.52, 11.21 ppm) and methylene carbon atoms (7.23 ppm) of the ethyl groups.

The ¹H and ¹³C NMR spectra of **2** show additional resonances due to the carbene tBu . No significant chemical shifts were observed in the NMR spectra of **2** for the L and Et groups of **2** in comparison with **1**, which indicates that tBu binds only weakly in solution to the InEt_2 moiety. The ¹H NMR spectrum of **3** in toluene-*d*₈ exhibits very broad signals for the *i*-Pr groups of the β -diketiminate ligands [3.90–2.80 ppm, $-\text{CH}(\text{CH}_3)_2$; 1.33–1.07 ppm, $-\text{CH}(\text{CH}_3)_2$] and the GaEt groups (0.77 to -0.4 ppm). The $\gamma\text{-CH}$ and two methyl groups of the $\text{C}_3\text{N}_2\text{Ga}$ ring shows singlets at 4.70 and 1.47 ppm, respectively, while the InEt group appears as a triplet and a quartet at 1.97 and 1.00 ppm, respectively. At $-40\text{ }^\circ\text{C}$ (Figure S8), two separate singlets were observed for the $\gamma\text{-CH}$ (4.71, 4.65 ppm) and the ring NCCCH_3 (1.46, 1.45 ppm). Furthermore, the methine protons of the isopropyl substituents exhibit three multiplets (3.75, 3.48, 3.04 ppm) in 2:1:1 molar ratio. Due to the asymmetric nature of **3**, the region between 2.3 to -0.5 ppm shows several overlapping multiplets, which prohibits their assignment to appropriate groups. It should be noted that the signals do not correspond to those of a mixture of **1** and LGa at very low temperatures.

3 gradually decomposes at $80\text{ }^\circ\text{C}$ in C_6D_6 , yielding LGa and LGaEt_2 in 1:3 molar ratio after 24 h (Figure S16). The decomposition products confirm the activation of all In-Et groups. There are two possible pathways: (i) One of the $[\text{LGa}(\text{Et})]$ in **3** abstracts the remaining ethyl group from the indium center and leaves LGaEt_2 and an intermediate species $[\text{LGa}(\text{Et})\text{In}]$, which then disproportionate into indium metal, $\frac{1}{2}\text{LGaEt}_2$ and $\frac{1}{2}\text{LGa}$. (ii) Alternatively, **3** dissociates at high temperature into LGa and **1**, which then decomposes as observed previously with isolated **1**. In order to understand the reaction pathway, **3** was gradually heated in C_6D_6 and the reaction progress was monitored periodically by ¹H NMR spectroscopy. Compound **3** is thermally stable up to $50\text{ }^\circ\text{C}$ and starts to dissociate at $70\text{ }^\circ\text{C}$ with subsequent formation of LGa and **1** (Figure S17) as was observed for $[\text{LGa}(\text{Me})]_2\text{GaMe}$.¹⁰ Gradually formed (thermolabile) **1** decomposes under these conditions with formation of indium metal and LGaEt_2 . However, it should be noted that two new additional $\gamma\text{-CH}$ peaks (5.05, 4.80 ppm) appear at $80\text{ }^\circ\text{C}$ after 3 h, which couldn't be addressed to any known species yet (Figure S18). However, prolonged heating of **3** only afforded LGa and LGaEt_2 and In metal. Again, the formation of deeply colored solutions was not observed.

Single crystals of **1** – **3** suitable for X-ray diffraction analysis were grown from saturated *n*-hexane (**1**, **3**) and toluene (**2**)

solutions at -30 °C. **1** and **3** crystallize in the monoclinic space groups $C2/c$ (**1**) and $P2_1/c$ (**3**), whereas **2** crystallizes in triclinic space group $P-1$, respectively. Figures 1 – 3 show the solid state structures of **1** – **3**. Selected bond lengths and bond angles are given at the footnote of the figures and crystallographic details are summarized in table S1.

((Insert Table 1 here))

Figure 1. Molecular structure of LGa(Et)InEt_2 **1**. H-atoms, disordered Et group have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths and angles in Å and °: Ga(1)-N(1) 2.0022(18), Ga(1)-N(2) 1.9953(17), In(1)-Ga(1) 2.6268(3), Ga(1)-C(30) 1.987(2), In(1)-C(32) 2.187(3), In(1)-C(34) 2.189(11), N(1)-C(1) 1.317(3), N(2)-C(3) 1.328(3), C(1)-C(2) 1.408(3), C(2)-C(3) 1.397(3); N(2)-Ga(1)-N(1) 92.50(7), C(30)-Ga(1)-In(1) 118.45(7), C(34)-In(1)-Ga(1) 126.7(3), C(32)-In(1)-Ga(1) 124.44(7), C(32)-In(1)-C(34) 108.8(3), C(30)-Ga(1)-N(1) 111.98(8), C(30)-Ga(1)-N(2) 110.04(9), N(1)-Ga(1)-In(1) 111.24(5), N(2)-Ga(1)-In(1) 109.56(5).

Figure 2. Molecular structure of $\text{LGa(Et)Et}_2\text{In}<\text{IrBu}$ **2**. H-atoms, lattice solvent have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level. Ga(1)-N(1) 2.0278(12), Ga(1)-N(2) 2.0350(12), In(1)-Ga(1) 2.62080(19), Ga(1)-C(41) 2.0235(14), In(1)-C(43) 2.2209(15), In(1)-C(45) 2.2247(15), In(1)-C(30) 2.3148(15), N(1)-C(1) 1.3289(18), N(2)-C(3) 1.3263(18), C(1)-C(2) 1.402(2), C(2)-C(3) 1.401(2); N(2)-Ga(1)-N(1) 91.63(5), C(41)-Ga(1)-In(1) 115.85(4), C(43)-In(1)-Ga(1) 128.93(4), C(45)-In(1)-Ga(1) 113.87(4), C(30)-In(1)-Ga(1) 104.16(4), C(43)-In(1)-C(45) 103.51(6), C(43)-In(1)-C(30) 93.90(6), C(45)-In(1)-C(30) 109.81(5), C(41)-Ga(1)-N(1) 104.12(5), C(41)-Ga(1)-N(2) 103.24(5), N(1)-Ga(1)-In(1) 120.24(3), N(2)-Ga(1)-In(1) 117.99(3).

The molecular structure of **1** is similar to those of recently reported group 13-bismuth compounds LM(Et)BiEt_2 , (M = Al, Ga, In),¹⁵ LGa(Me)GaMe_2 and **3** to $[\text{LGa(Me)}]_2\text{GaMe}$.¹⁰ Each Ga atom in **1** to **3** adopts a distorted tetrahedral geometry and the Ga atom is slightly out of the C_3N_2 plane (deviation from the best plane of the ligand backbone 0.616(3) Å **1**, 0.7040(17) Å **2**, 0.651(4) and 0.748(4) Å **3**). In **1** and **3**, the indium atoms adopt trigonal-planar coordination geometries and the sum of the bond angles is close to 360°. Bonding of IrBu to the InEt_2 moiety converts the planar geometry of indium (**1**) to a distorted tetrahedral geometry (**2**). The Ga-N distances in **1** – **3** are virtually the same [1.9953(17), 2.0022(18) Å (**1**); 2.0278 (12), 2.0350(12) Å (**2**); 2.020(3), 2.042(3), 2.016(3), 2.018(3) Å (**3**)] and the almost identical Ga-In bond distances of **1** and **2** [2.6268(3) Å (**1**), 2.62080(19) Å (**2**)] are slightly shorter than those found in **3** [2.6910(5), 2.6902(5) Å (**3**)]. In addition, they are comparable to the sum of covalent radii (Ga = 1.24 Å; In = 1.42 Å),¹⁹ indicating the formation of Ga-In σ -bonds.

Figure 3. Molecular structure of $[\text{LGa(Et)}]_2\text{InEt}$ **3**. H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level. Ga(1)-N(1) 2.020(3), Ga(1)-N(2) 2.042(3), Ga(2)-N(3) 2.018(3), Ga(2)-N(4) 2.016(3), Ga(1)-C(30) 2.014(3), Ga(2)-C(32) 1.986(4), Ga(1)-In(1) 2.6910(5), Ga(2)-In(1) 2.6902(5), In(1)-C(34) 2.223(4), N(1)-C(1) 1.333(5), N(2)-C(3) 1.323(4), N(3)-C(41) 1.322(5), N(4)-C(43) 1.330(5); N(1)-Ga(1)-N(2) 92.64(12), N(4)-Ga(2)-N(3) 90.97(13), Ga(2)-In(1)-Ga(1) 127.123(16), C(34)-In(1)-Ga(1) 122.02(11), C(34)-In(1)-Ga(2) 110.86(11), C(30)-Ga(1)-In(1) 113.84(11), C(32)-Ga(2)-In(1) 120.61(13), C(30)-Ga(1)-N(1) 106.86(13), C(30)-Ga(1)-

N(2) 102.33(14), C(32)-Ga(2)-N(3) 109.61(16), C(32)-Ga(2)-N(4) 109.40(16), N(1)-Ga(1)-In(1) 119.05(9), N(2)-Ga(1)-In(1) 119.08(8), N(3)-Ga(2)-In(1) 111.20(9), N(4)-Ga(2)-In(1) 111.07(9).

The molecular structure of **2** shows the presence of an abnormally-bonded NHC (a-NHCs), or so called mesionic carbene (MIC). A similar bonding mode was observed in the Lewis acid-base reaction of AlMe₃ with *l*Bu.²⁰ a-NHCs are typically less stable than the corresponding n-NHCs since the carbene-C atom is stabilized by only one N atom²¹ and the proton at C2 in imidazolium salts is much more acidic than the C4/5 proton, hence the conversion of an *a*-NHC into an *n*-NHC is thermodynamically favored.¹⁹ However, the formation of **2** most likely results from the high σ -donor capacity of a-NHCs, which is even substantially enhanced compared to classical imidazol-2-ylidenes (n-NHC), which are already considered as very strong σ -donor ligands.^{22a} Moreover, repulsive sterical interactions between the bulky *t*-Bu groups of the NHC base and the Et and L substituents bound to In and Ga further favor the formation of the a-NHC.²³

As expected, the Ga-C distances [1.987(2) Å (**1**); 2.0235(14) Å (**2**); 2.014(3), 1.986(4) Å (**3**)] are shorter than the In-C bonds [2.187(3), 2.189(11) Å (**1**); 2.2209(15), 2.2247(15) Å (**2**); 2.223(4) Å (**3**)], while the In-C distance to the coordinated a-NHC (2.3148 (15) Å) is even longer as was expected due to the dative bonding character. *l*Bu binds almost perpendicular to the Ga-In bond, showing a C30-In1-Ga1 bond angle of 104.16(4)°. The bite angle of the chelating ligand L 92.50(7)° (**1**), 91.63(5)° (**2**) and 92.64(12)° - 90.97(13)° (**3**) is comparable to those previously observed in these type of complexes. The Ga-In-Ga bond angle of **3** [127.123(16)°] is smaller than the same observed in [LGa(Me)]₂GaMe (138.37°).

CONCLUSION

We showed that the redox transmetallation reaction of Et₃In to indium metal using the gallanediyl LGa initially starts with the insertion of one or two LGa moieties into one or two In-C bonds of InEt₃, resulting in the formation of the insertion complexes LGa(Et)InEt₂ **1** and [LGa(Et)]₂InEt **3**, respectively. **1** is thermolabile in solution, but can be stabilized by coordination of *l*Bu, yielding LGa(Et)Et₂In←*l*Bu **2** with an abnormal binding mode. A solution of **1** decomposes at ambient temperature in a controlled manner with quantitative formation of indium metal, LGaEt₂ and InEt₃, whereas thermal treatment of a solution of **3** at moderate temperatures (80 °C) yielded indium metal as well as LGa and LGaEt₂. The decomposition of **1** probably proceeds through formation of a monovalent In(I) species [EtIn]_x. This proposed reaction mechanism is supported by the analogous reaction of Cp*InEt₂, which proceeded with formation of Cp*In. The described reaction pathway therefore may offer a general synthetic pathway to (metalloid) low-valent main group element cluster compounds in the near future. It should be noted, that Aldridge et al. recently reported on the formation of the large metalloid In cluster In₁₉{B(NDippCH)₂}₆, which was obtained from the thermal decomposition of {(MeCCH₂)₂}[In{B(NDippCH)₂}]₂ in hexane at ambient temperature.²⁴

EXPERIMENTAL SECTION

General. All manipulations were performed in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Toluene and hexane were dried using a mBraun solvent purification system. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. The anhydrous nature of the solvents was verified by Karl Fischer titration. The ¹H (300 MHz) and ¹³C{¹H} NMR (75.5 MHz) spectra (δ in ppm) were recorded using a Bruker Avance DPX-300 spectrometer and were referenced to internal C₆D₅H (¹H: δ = 7.154; ¹³C: δ = 128.39) and C₆D₅CHD₂ (¹H: δ = 2.09; ¹³C: δ = 20.40). Microanalyses were performed at the elemental analysis laboratory of the University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. LGa,³ InEt₃,²⁴ and *l*Bu²⁵ were prepared according to literature methods. While purifying **1** and **2**, traces of grey precipitates was observed, which were filtered using a oven dried Teflon cannula (3.5 mm D) in which one end of the tip was wrapped with Whatman® glass microfiber filters (CAT No. 1823-025) using Teflon tape.

Synthesis of 1. A mixture of InEt₃ (0.0252 g, 20 μ L, 0.125 mmol) and LGa (0.0608 g, 0.125 mmol) in 2 mL of toluene was stirred at 0 °C for 30 min. The solvents were removed under reduced pressure and the residue was dissolved in 0.6 mL of *n*-hexane. Storage of the solution at -30 °C for 3 days afforded analytically pure form of **1** as yellow-orange crystals. Yield: 89% (0.077 g). Anal. Calcd for C₃₅H₅₆GaInN₂: C, 60.98; H, 8.19; N, 4.06. Found: C, 60.67; H, 8.07; N, 4.01%. ¹H NMR (C₆D₆, 300 MHz): δ 7.13-6.92 (m, 6H, C₆H₃(*i*-Pr)₂), 4.83 (s, 1H, γ -CH), 3.56 (sept, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂), 3.01 (sept, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂), 1.82 (t, ³J_{HH} = 7.0 Hz, 6H, InCH₂CH₃), 1.48 (s, 6H, ArNCCH₃), 1.39 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂), 1.16-1.06 (m, 22H, CH(CH₃)₂, InCH₂CH₃), 0.85 (t, ³J_{HH} = 7.0 Hz, 3H, GaCH₂CH₃), 0.37 (q, ³J_{HH} = 7.0 Hz, 2H, GaCH₂CH₃). ¹³C NMR (C₆D₆, 75.5 MHz): δ 168.0 (ArNCCH₃), 144.0 (C₆H₃), 143.9 (C₆H₃), 142.3 (C₆H₃), 127.0 (C₆H₃), 124.7 (C₆H₃), 124.6 (C₆H₃), 96.3 (γ -CH), 29.2 (CH(CH₃)₂), 29.0 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 20.5 (ArNCCH₃), 13.5 (InCH₂CH₃), 11.2 (GaCH₂CH₃), 7.2 (GaCH₂CH₃). IR (neat): ν 3063, 2959, 2923, 2856, 1562, 1519, 1440, 1385, 1312, 1263, 1178, 1106, 1020, 936, 856, 796, 759, 637, 522, 443 cm⁻¹.

Decomposition of 1: A solution of **1** (0.215 g, 0.312 mmol) in 3 mL of toluene was stirred at ambient temperature for 24 h. The reaction mixture was filtered and the grey precipitate was washed with 10 mL of *n*-hexane. The combined filtrates were concentrated under reduced pressure and stored at -30 °C. Colorless crystals of LGaEt₂, which was identified by NMR spectroscopy,¹⁵ were formed within 2 days. Yield: 94% (0.1603 g, LGaEt₂); 96% (0.0230 g, In metal).

Reaction of LGa with Cp*InEt₂: A solution of Cp*InEt₂ (0.1168 g, 0.379 mmol) in 3 mL of toluene was added to a solution of LGa (0.185 g, 0.379 mmol) in 5 mL of toluene at ambient temperature and the reaction mixture was stirred for 24 h. The solvents were removed under reduced pressure and the residue was sublimed at 55 °C (10⁻³ mbar). Yield of isolated Cp*In: 21 % (20 mg).

Synthesis of 2. A mixture of InEt₃ (0.0882 g, 70 μ L, 0.437 mmol) and *l*Bu (0.0787 g, 0.437 mmol) in 5 mL of toluene was stirred at ambient temperature for 1 h. LGa (0.213 g, 0.437 mmol) dissolved in 5 mL of toluene was added and the reaction mixture was stirred for additional 4 h. The golden yellow solution was concentrated to 5 mL and stored at -30 °C for 24 h to afford pure form of **2** as yellow crystals. Yield: 73% (0.277 g). Anal. Calcd for C₄₆H₇₆N₄GaIn: C, 63.53; H, 8.81; N, 6.44. Found: C, 63.19; H, 8.69; N, 6.31%. ¹H NMR (C₆D₆, 300 MHz): δ 7.11-6.92 (m, 6H, C₆H₃(*i*-Pr)₂), 6.79 (s, 2H, *NCH*), 4.83 (s, 1H, γ -CH), 3.55 (sept, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂), 3.01 (sept, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂), 1.82 (t, ³J_{HH} = 7.0 Hz, 6H, InCH₂CH₃), 1.52 (s, 18H, *l*Bu, C(CH₃)₃), 1.49 (s, 6H, ArNCCH₃), 1.39 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂), 1.16-1.07 (m, 22H, CH(CH₃)₂, InCH₂CH₃), 0.84 (t, ³J_{HH} = 7.0 Hz, 3H, GaCH₂CH₃), 0.37 (q, ³J_{HH} = 7.0 Hz, 2H, GaCH₂CH₃). ¹³C NMR (C₆D₆, 75.5 MHz): δ 213.3 (*l*Bu, NCN), 168.0 (ArNCCH₃), 144.0 (C₆H₃), 144.0 (C₆H₃), 142.3 (C₆H₃),

127.0 (C_6H_3), 124.7 (C_6H_3), 124.6 (C_6H_3), 115.4 (IrBu, NCCN), 96.3 (γ -CH), 56.2 (IrBu, $C(CH_3)_3$), 31.8 (IrBu, $C(CH_3)_3$), 29.2 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$), 20.5 (ArNCCCH₃), 13.5 (InCH₂CH₃), 11.2 (GaCH₂CH₃), 7.3 (GaCH₂CH₃). IR (neat): ν 2920, 2843, 1556, 1531, 1403, 1312, 1239, 1185, 1118, 984, 936, 850, 795, 747, 649, 619, 546, 437 cm^{-1} .

Synthesis of 3. A solution of InEt₃ (0.0378 g, 30 μ L, 0.187 mmol) in 3 mL of toluene was added dropwise to a toluene solution (10 mL) of LGa (0.182 g, 0.374 mmol). After stirring for 24 h, the solution was concentrated to 2 mL and stored at 0 °C to give red crystals of **3**. Yield: 73% (0.160 g). Anal. Calcd for C₆₄H₉₇N₄Ga₂In: C, 65.32; H, 8.31; N, 4.76. Found: C, 65.03; H, 8.22; N, 4.57. ¹H NMR (300 MHz, toluene-*d*₈): δ 7.14–7.04 (m, 6H, $C_6H_3(i-Pr)_2$), 4.70 (s, 1H, γ -CH), 3.52 (br m, 4H, $CH(CH_3)_2$), 1.97 (t, ³J_{HH} = 7.0 Hz, 3H, InCH₂CH₃), 1.47 (s, 6H, ArNCCCH₃), 1.15 (br, 6H, GaCH₂CH₃), 1.13 (2 d, 24H, $CH(CH_3)_2$), 0.97 (q, ³J_{HH} = 7.0 Hz, 2H, InCH₂CH₃), 0.60 (br, 4H, GaCH₂CH₃). IR (neat): ν 3057, 2959, 2923, 2862, 1556, 1519, 1446, 1391, 1319, 1263, 1172, 1106, 1020, 936, 856, 796, 753, 643, 607, 522, 443 cm^{-1} .

Single crystal X-ray diffraction. Crystallographic data of **1**–**3**, which were collected on a Bruker D8 Kappa APEX2 diffractometer (MoK α radiation, λ = 0.71073 Å) at 100(1) K, are summarized in Table S1. The solid-state structures of **1**–**3** are shown in Figures 1–3. The structures were solved by Direct Methods (SHELXS-97)²⁶ and refined anisotropically by full-matrix least-squares on F² (SHELXL-2014)^{27,28}. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups.

The crystallographic data of **1** to **3** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1048240 (**1**), CCDC-1048239 (**2**) and CCDC-1048238 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

Electronic Supplementary Information (ESI) available: Cif files of **1**, **2** and **3**. In addition, NMR and IR spectra of **1**–**3**, Et₃In-IrBu, Et₃In, LGaEt₂, Cp*InEt₂ and ¹H NMR spectra of thermal treatment of **1** and **2** as well as crystallographic details are given in the SI. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

The authors declare no competing financial interest.

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Table of Contents (TOC) entry.

InEt₃ reacts with different amounts of gallanediyl LGa with insertion into the In-carbon bond and formation of LGa(Et)InEt₂ **1** and [LGa(Et)]₂InEt **3**. Thermolabile **1**, which decomposes in solution with subsequent formation of LGaEt₂, InEt₃ and elemental In, can be stabilized by reaction with the N-heterocyclic carbene ItBu [C(N*i*-Bu₂CH)₂], yielding the base-stabilized compound LGa(Et)Et₂In←ItBu **2** with an abnormal bonded NHC group.

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