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A General Pathway for the Synthesis of Gallastibenes containing Ga=Sb Double Bonds.

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Dedicated to Prof. W. A. Herrmann on the occasion of his 70th birthday.

Abstract: Reactions of three equivalents of LGa {L = HC[C(Me)N(2,6-*i*-Pr₂C₆H₃)₂] with SbX₃ (X = F, Cl, Br, I) proceed with insertion into the Sb-X bond, elimination of LGaX₂ and formation of LGaSbGa(X)L (X = F **1**, Cl **2**, Br **3**, I **4**) containing a Ga=Sb double bond. In contrast, the 2:1 molar ratio reaction of LGa and SbCl₃ initially gives the twofold insertion product [L(Cl)Ga]₂SbCl **7**, which could not be isolated due to its strong tendency toward elimination of LGaCl₂ and formation of distibene [L(Cl)GaSb]₂ **5** at 25 °C or cyclotristibine [L(Cl)GaSb]₃ **6** at 8 °C. The formation of **1** – **6** can be rationalized by formation of the Ga-substituted stibinidene L(X)GaSb as reaction intermediate.

Monomeric group 13/15 compounds of the general type RM=ER' containing a double bond between the lightest congeners of group 13 and group 15 elements (B and N) are very well known. The π -bonding contribution in boron-pnictogen compounds is rather strong and therefore, planar monomeric amino- R₂BNR'₂ and phosphinoboranes R₂BPR'₂ exhibit partial double bond character, while linear iminoboranes RBNR tend to show triple bond character.^[1] Although a large number of monomeric iminoboranes of the type RBNR' containing strong π -bonds have been synthesized, monomeric compounds containing B=P and B=As double bonds are still rare.^[2,3] In addition, very few monomeric aluminum, gallium and indium imides RMNR' have been structurally characterized,^[4] and their bonding nature was closely studied by quantum chemical calculations.^[5] In contrast, monomeric compounds RMER' containing double bonds between heavier group 13 (M = Al, Ga, In, Tl) and group 15 elements (E = P, As, Sb, Bi) are almost unknown.^[6]

Monomeric compounds typically tend to dimerize/oligomerize to give heterocyclic [RMER]_x (x = 2, 3) or cage-type complexes [RMER]_x (x > 4). Oligomerization can be suppressed by using sterically demanding substituents (kinetic stabilization) or chelating organic substituents such as β -diketimines, which sterically protect the metal center and also increase its coordination number. Electronic stabilization by coordination of the electron lone pair of the group 15 element to an electron acceptor (Lewis acid)^[7] or by intermolecular or intramolecular coordination of a Lewis base to the Lewis acidic group 13 metal center have been both successfully applied.^[4] To the best of our knowledge, [(Li(thf)₃)₂Ga₂(As(Si-*i*-Pr₃))₄] **A**,^[8] LGaAsCp* {L = HC[C(Me)N(2,6-*i*-Pr₂C₆H₃)₂] **B**,^[9] resulting from the reaction of Cp*AsCl₂ with two equivalents of LGa, and

LGa=SbGa(Cl)L **C**,^[10] which was formed by single electron reduction of the stibinyl radical L(Cl)Ga₂Sb· with KC₈ (Scheme 1), represent the only structurally characterized compounds containing Ga=E (E = As, Sb) double bonds, to date.

Scheme 1. Structurally characterized compounds of heavier group 13 (M = Al, Ga, In, Tl) and group 15 elements (P, As, Sb, Bi) containing π -bonding contribution; R = *i*-Pr₃Si, Ar = 2,6-*i*-Pr₂C₆H₃.

The synthesis of LGaSbGa(Cl)L **C** focused our interest on insertion reactions of LGa^[11] with group 15 metal halides. Insertion of LGa was observed with Bi(OR)₃, E(NR₂)₃ (E = As, Sb, Bi) and ECl₃ (E = As, Sb), yielding Ga-substituted dipnictogenenes [LGa(OR)Bi]₂ (R = C₆F₅, SO₂CF₃), [L(R₂N)GaE]₂ (E = As, Sb, Bi, NR₂ = NMe₂, NMeEt) and [L(Cl)GaE]₂ (E = As, Sb), all of which contain E=E double bonds.^[12] In addition, insertion of LGa into Bi-C and E-E bonds was observed in reactions using Et₃Bi and Et₄E₂ (E = Sb, Bi).^[13] This highlights the promising potential of LGa to serve as a selective reducing agent for the synthesis of intermetallic compounds. However, it remains unclear whether the reaction mechanism proceeds by a simple insertion reaction or by a complex reduction sequence.

To gain a deeper mechanistic understanding, we systematically investigated reactions of LGa with SbX₃ (X = F, Cl, Br, I) in different molar ratios and different reaction conditions. Reactions of three equivalents of LGa with SbX₃ at ambient temperature yielded LGaSbGa(X)L (X = F **1**, Cl **2** (= **C**^[10]), Br **3**, I **4**), which contain Ga=Sb double bonds (Scheme 2).

Scheme 2. Synthesis of **1** – **4**.

According to *in situ* ¹H NMR spectroscopic studies, **1** – **4** are almost quantitatively formed, however their isolation from the by-

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product LGaX_2 by fractional crystallization was rather difficult and required several (4-5) attempts. As a result, the isolated yields of **1** - **4** obtained in the form of air- and moisture-sensitive, crystalline red solids after workup, were relatively low (14-26%). **1** - **4** are soluble in *n*-hexane, benzene, and toluene and can be stored under argon atmosphere for 3-4 days without any sign of decomposition. ^1H and ^{13}C NMR spectra of **1** - **4** show the expected resonances of the β -diketiminate substituents. The strength of the Ga=Sb double bond in **1** and **3** was determined by variable-temperature (VT) ^1H NMR spectroscopy. As observed in compound **2**,^[10] the γ -CH signal of **3** splits into two peaks at -80°C (Fig. S12) with a maximum peak separation of 46.5 Hz, giving $\Delta G^\ddagger = 9.35 \text{ kcal mol}^{-1}$ for the rotation about the Ga=Sb bond.^[14] The resonance peaks corresponding to the *i*-Pr groups are split into three signals with a relative intensity of 1:1:2. These values agree well with those reported for **2** ($9.56 \text{ kcal mol}^{-1}$) and $\text{PhP}(\text{GaTrip}_2)_2$ (Trip = 2,4,6-*i*-Pr₃C₆H₂, $10.2 \text{ kcal mol}^{-1}$).^[15] In contrast, line broadening but no splitting occurred for the γ -CH and *i*-Pr resonance peaks of **1** even at -80°C (Fig. S11).

Dark red crystals of **1**, **3**, and **4** were obtained from solutions in *n*-hexane after storing for 2 days at 8°C . These compounds crystallize with one molecule in the asymmetric unit in the monoclinic space group $P2_1/n$ (**1**, **4**) and $P2_1/c$ (**3**).^[16] The crystal structure of **2**^[10] was previously reported.

Figure 1. Molecular structure of LGaSbGa(F)L 1 . H-atoms and second orientation of the disordered part have been omitted for clarity; displacement ellipsoids are drawn at the 50% probability level.

Compounds **1** (Fig. 1), **3** (Fig. S19) and **4** (Fig. S20) show angulated Ga_2Sb units as central structural motifs with comparable Ga1-Sb1-Ga2 bond angles except for **1** ($107.37(1)^\circ$), which has a smaller Ga1-Sb1-Ga2 bond angle compared to **2** - **4** ($113.18(1)^\circ$ **2**; $111.22(2)^\circ$ **3**; $111.78(2)^\circ$ **4**). Ga2 in **1** - **4** is threefold-coordinated and shows a planar coordination sphere, whereas Ga1 atoms adopt tetrahedral coordination spheres. Both Ga atoms in the $\text{C}_3\text{N}_2\text{Ga}$ rings of **1** - **4** are slightly out of plane.

Ga2-Sb1 bond distances (Table 1) in **1** ($2.4601(3) \text{ \AA}$), **3** ($2.4502(3) \text{ \AA}$) and **4** ($2.4496(8) \text{ \AA}$) are comparable to that observed in **2** (Ga2-Sb1 $2.4629(2) \text{ \AA}$).^[10] Due to the π -bonding contribution, Ga2-Sb1 bonds are substantially shorter than the Ga1-Sb1 bonds of the tetrahedrally-coordinated Ga atom ($2.5596(3) \text{ \AA}$ **1**; $2.5528(2) \text{ \AA}$ **2**; $2.5662(3) \text{ \AA}$ **3**; $2.5478(6) \text{ \AA}$ **4**). The calculated values for Ga-Sb bonds are $2.64 \text{ \AA}$ (single bond), $2.50 \text{ \AA}$ (double bond) and $2.48 \text{ \AA}$ (triple bond).^[17-19] As of now, **1** - **4** report the shortest Ga-Sb double bonds for compounds containing threefold-coordinated Sb atoms. For instance, the Ga2-Sb1 bonds are significantly shorter than the Ga-Sb σ -bonds found in Lewis acid base adducts,^[20] $[\text{R}_2\text{GaSbR'}_2]_3$ heterocycles ($2.663(2) - 2.722(3) \text{ \AA}$)^[21] and monomeric $[(\text{dmap})\text{Et}_2\text{GaSb}(\text{SiMe}_3)_2]$ ($2.648(1) \text{ \AA}$; dmap = 4-dimethylaminopyridine) with threefold-coordinated Sb atom.^[22] They are also shorter in comparison to Ga-Sb bonds observed in $(\text{LGa})_2\text{Sb}_4$ ($2.6637(11) - 2.6779(11) \text{ \AA}$),^[23] $[\text{L}(\text{X})\text{GaSb}]_2$ (X = NMe₂ $2.6200(4) \text{ \AA}$; NMeEt $2.6169(5) \text{ \AA}$; Cl $2.58178(19) \text{ \AA}$),^[12c,24] $[\{\text{L}(\text{X})\text{Ga}\}_2(\mu, \eta^{1:1}\text{-Sb}_4)]$ (X = NMe₂ $2.5975(5) \text{ \AA}$; Cl $2.6008(13) \text{ \AA}$),^[12c,24] and base-stabilized $[\text{Cl}(n\text{-Pr}_2\text{PhP})\text{GaSbSi-}i\text{-Pr}_3]_2$ ($2.635(1) - 2.655(1) \text{ \AA}$).^[25] On the other hand, the Ga-X bonds steadily increase in length ($1.7923(9) \text{ \AA}$ **1**; $2.2409(5) \text{ \AA}$ **2**; $2.3917(3) \text{ \AA}$ **3**; $2.6093(7) \text{ \AA}$ **4**) due to the increasing atomic radii, as expected. The Ga2-N bonds in **1** - **4** ($1.9281(12)$, $1.9582(12) \text{ \AA}$ **1**; $1.9244(14)$, $1.9595(14) \text{ \AA}$ **2**; $1.9531(16)$, $1.9207(16) \text{ \AA}$ **3**; $1.905(3)$, $1.958(2) \text{ \AA}$ **4**) are slightly shorter compared to those of the tetrahedrally-coordinated Ga1 atoms ($1.9761(11)$, $1.9855(12) \text{ \AA}$ **1**; $1.9806(15)$, $1.9880(14) \text{ \AA}$ **2**; $1.9766(16)$, $2.0033(16) \text{ \AA}$ **3**; $1.971(3)$, $2.006(2) \text{ \AA}$ **4**), yet they are significantly shorter than those observed in LGa ($2.0528(14) \text{ \AA}$, $2.0560(13) \text{ \AA}$).^[11] Shortening of the Ga-N bond typically occurs upon oxidative addition of LGa to organic and inorganic substrates.^[26]

Table 1. Selected bond lengths and angles in $\text{\AA}$ and $^\circ$ of **1** - **4**.

	1	2 ^[10]	3	4
Ga1-Sb1	2.5596(3)	2.5528(2)	2.5662(3)	2.5478(6)
Ga2-Sb1	2.4601(3)	2.4629(2)	2.4502(3)	2.4496(8)
Ga1-X1	1.7923(9)	2.2409(5)	2.3917(3)	2.6093(7)
Ga1-N1/2	1.9762(11), 1.9855(12)	1.9806(15), 1.9880(14)	1.9766(16), 2.0033(16)	1.971(3), 2.006(2)
Ga2-N3/4	1.9281(12), 1.9582(12)	1.9244(14), 1.9595(14)	1.9531(16), 1.9207(16)	1.905(3), 1.958(2)
Ga1-Sb1-Ga2	107.37(1)	113.18(1)	111.22(2)	111.78(2)
Sb1-Ga1-X1	123.97(3)	128.815(4)	124.147(11)	124.71(2)
N1-Ga1-N2	92.30(5)	93.16(6)	93.81(7)	94.20(10)
N3-Ga2-N4	95.24(3)	95.18(6)	95.69(7)	94.51(10)

Quantum chemical calculations were performed to understand the electronic structure of **1'** - **4'** in more detail. The *i*-

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Pr groups were replaced by Me groups in **1'** - **4'**. The calculated values (Table S3) for the Ga-Sb single (2.561 - 2.564 Å) and double bonds (2.444 - 2.447 Å) of **1'** - **4'** are not affected by the halide substituent and agree perfectly with those observed in the crystal structures (Table 1). In contrast, the Ga-Sb-Ga bond angles (93.47° **1'**, 101.37° **2'**, 102.97° **3'**, 104.03° **4'**) and X-Ga-Sb bond angles (114.98° **1'**, 123.94° **2'**, 124.67° **3'**, 124.91° **4'**) deviate from the experimental values, most likely due to the replacement of the *i*-Pr groups of the aryl substituent by sterically less demanding Me groups. In particular, the Ga-Sb-Ga bond angle of **1'** is significantly smaller than those of **2'** - **4'**; this is also observed with the corresponding bond angle of **1** in comparison to its derivative compounds (**2** - **4**). Based on NPA (Table S2), the σ -bond orbital is slightly polarized towards the Sb atom (54%), which shows a high p-character (11% s, 88% p), whereas a higher s-character is observed on the Ga atom (56% s, 44% p). In contrast, the π -bond orbital shows exclusive p-character on both atoms, and as previously reported, it is strongly polarized towards the Sb atom (82%).^[5c] The Mayer bond order is 1.52(1) in all the observed cases. The HOMO (Fig. 2) of **1'** - **4'** corresponds to the Ga-Sb π bond, and consists of a centered Sb lobe connecting both atoms above the Ga-Sb-Ga plane, including a second lobe in the opposite phase. The LUMO is exclusively located on the ligand and represents its delocalized electronic system.

Figure 2. Ground-state geometry optimized structure and calculated HOMO and LUMO of **1'**.

The natural charge on the double-bonded Ga2 atom in **1'** - **4'** is constant at 1.1 e, whereas the electric values for the Ga1 atom are significantly different (1.45 e **1'**; 1.18 e **2'**; 1.12 e **3'**; 1.02 e **4'**). As for the Sb atom, the natural charge value is slightly influenced (-0.75 e **1'**; -0.70 e **2'**; -0.68 e **3'**; -0.67 e **4'**) by the nature of the halide substituent. In this case, the charge increases with increasing electronegativity of the halide; this trend clearly reflects the increasing bond polarity within the Ga-X bond and consequently, the Ga1-Sb bond.

Our interest in the reaction mechanism for compounds containing Sb=Sb^[12] and Ga=Sb double bonds^[10] prompted us to re-investigated the reaction of SbCl₃ with two equivalents of LGa at different reaction temperatures. At ambient temperature, this reaction almost entirely yields the known Ga-substituted distibene [L(Cl)GaSb]₂ **5**,^[12c] whereas the cyclotristibine [L(Cl)GaSb]₃ **6** is formed in moderate yield at 8 °C (Scheme 3). **5** and **6** can be distinguished by NMR spectroscopy since the ¹H and ¹³C NMR spectra of **5**^[12c] clearly differ from those of **6**. Compound **6** shows the expected resonances of the three L(Cl)Ga substituents. The presence of two separate singlets in a 1:2 intensity ratio for the γ -CH protons (4.91, 4.95 ppm) indicate the occurrence of cis-trans isomerization in solution. Comparable findings were observed in

the ¹H NMR spectrum of cyclotristibine [(Me₃Si)₂CHSb]₃, showing two singlets for the methine protons in a relative intensity of 1:2.

Scheme 3. Synthesis of **5** and **6**.

Variable-temperature ¹H NMR studies of **6** show no dynamic behavior in solution, thus a reversible Sb-Sb bond breakage reaction of **6** into monomeric stibinidene L(Cl)GaSb, and its subsequent dimerization into the distibene [L(Cl)GaSb]₂ **5** can be excluded (Scheme 4 reaction (e)). However, **6** was found to slowly react at 78 °C in solution to a yet unknown compound with no sign of elemental antimony formation.

While the structure of **5**^[12c] was previously reported, single crystals of **6** were obtained at room temperature from saturated solutions of *n*-hexane after storing for 24 h. **6** crystallizes in the monoclinic space group *P*2₁/*n* with one molecule in the asymmetric unit. A highly disordered *n*-hexane molecule was also observed.^[16]

Figure 3. Molecular structure of [L(Cl)GaSb]₃ **6**. H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Sb1-Sb2 2.8205(3), Sb1-Sb3 2.8437(3), Sb2-Sb3 2.8241(3), Ga1-Sb1 2.6787(4), Ga2-Sb2 2.6235(4), Ga3-Sb3 2.6216(4), Ga1-Cl1 2.1754(8), Ga1-N1 2.011(2), Ga1-N2 1.954(3); Sb1-Sb2-Sb3 60.503(7), Sb1-Sb3-Sb2 59.687(7), Sb2-Sb1-Sb3 59.810(8), Ga1-Sb1-Sb2 112.728(11), Ga1-Sb1-Sb3 121.805(11), Ga2-Sb2-Sb1 97.379(11), Ga2-Sb2-Sb3 91.906(11), Ga3-Sb3-Sb1 113.165(11), Ga3-Sb3-Sb2 104.050(12), N1-Ga1-N2 95.62(10).

The Sb-Sb bonds (2.8205(3) - 2.8437(3) Å) in cyclotristibine **6** (Fig. 3) are significantly elongated compared to Sb=Sb double bonds reported for the Ga-coordinated distibenes [L(X)GaSb]₂ as

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mentioned before,^[12c,23,24] but agree very well with the Sb-Sb single bond values reported for distibines R_4Sb_2 , which were found to range from 2.797(3) to 3.030(3) Å,^[27] and cyclostibines $[RSb]_x$ ($x = 3 - 6$; 2.794(4) - 2.883(4) Å).^[28] In addition, the only structurally characterized cyclotristibine $[(Me_3Si)_2CHSb]_3$ showed almost identical Sb-Sb bond lengths (2.8188(6) - 2.8453(6) Å).^[29] As observed in $[(Me_3Si)_2CHSb]_3$, two of the $L(Cl)Ga$ substituents adopt cisoid positions relative to one another (Ga1, Ga3), while the Ga2 containing substituent adopts a *trans*-orientation. The Ga-Sb bond lengths range from 2.6216(4) to 2.6787(4) Å, which is typical for Ga-Sb single bonds.

The electronic properties of **6'** were studied by quantum chemical calculations. According to NBO analysis (Table S4), the single Sb-Sb bonds in **6'** (Mayer bond order = 0.94-0.98) are of predominantly p-character (92-95%). The Sb-Sb bonds are slightly polarized toward Sb(1) and Sb(3), resulting in a less negative Sb(2) atom (-0.11 e vs. -0.21 e (Sb1), -0.19 e (Sb3)). The Sb-Ga bonds are polarized toward the Sb atoms (62-64%) as found in **5'** (61-62%). The HOMO of **6'** is located on the Sb₃ center (Fig. 4) with expansion along the Sb-Ga bonds, including a small contribution from one ligand. The LUMO is located on one ligand, with smaller contributions from the Sb atoms. Although the *i*-Pr groups were changed to Me groups, the calculated structural parameters (Table S5) of the central Sb_3Ga_3 unit in **6'** are in good agreement with the parameters observed in the solid-state structure of **6**. The Sb-Sb (2.828 Å, 2.803 Å, 2.814 Å) and Ga-Sb bond lengths (2.598 Å, 2.646 Å, 2.607 Å) lie within 0.05 Å, while the Sb-Sb-Sb (60.5°, 59.6°, 60.0°) and Ga-Sb-Sb bond angles (117.1°, 112.9°, 96.7°, 94.0°, 85.1°, 105.9°) are within 5° of deviation, except for the Ga3-Sb3-Sb1 and Ga3-Sb3-Sb2 angles, which are respectively underestimated by 7.3° and 18.9°, due to the reduced steric demand of the Me-substituted ligand.

Figure 4. Calculated HOMO (left) and LUMO (right) of $[L'(Cl)GaSb]_3$ **6'**.

Since the temperature-dependent formation of **5** and **6** reveals an entropy-controlled reaction, we also investigated chemical energies of reactions (a) – (e) (Scheme 4). Quantum chemical calculations (Table 2) proved that the formation of cyclotristibines $[L'(Cl)GaE]_3$ (**c**) is energetically favored (ΔG : E = P -250, As -223, Sb -192 kJ/mol) compared to the formation of dipnictenes $[L'(Cl)GaE]_2$ (ΔG : E = P -223, As -196, Sb -165 kJ/mol), whereas the formation of the dipnictenes is entropically favored. This agrees very well with the experimental findings, since **6** is formed at low temperature (8 °C) and **5** at 25 °C.

Table 2. Reaction energies (ΔH ; - ΔS in kJ/mol) calculated for the reactions (a) – (e) at 25 °C as shown in Scheme 4.

	a	b	c	d	e
P	-523; 127	200; -70	-300; 50	-256; 33	44; -17
As	-511; 134	185; -75	-272; 49	-228; 32	44; -17
Sb	-456; 128	163; -68	-241; 49	-197; 32	43; -16

The formation of **2**, **5** and **6** can be rationalized by the proposed reaction mechanism as depicted in Scheme 4. Comparable to the reaction of LGa with PX_3 ($X = Cl, Br$),^[12d] the twofold insertion reaction of LGa with $SbCl_3$ immediately yields $[L(Cl)Ga]_2SbCl$ **7**, which was proven by 1H NMR spectroscopy (Fig. S18). **7** shows the same resonance pattern of the two magnetically inequivalent $L(Cl)Ga$ substituents in the 1H NMR spectrum as was previously observed for $[L(Cl)Ga]_2PX$ ($X = Cl, Br$). **7** could not be isolated due to its strong tendency toward elimination of one equivalent of $LGaCl_2$. The as formed stibinidene $L(Cl)GaSb$ is proposed as reaction intermediate, but it could neither be isolated nor trapped, to date. Instead, the formation of **5** and **6**, which can be explained by dimerization or trimerization of the stibinidene, occurs. The formation of **2** can be rationalized by reaction of the proposed stibinidene $L(Cl)GaSb$ with another equivalent of LGa in a 1+1 addition. Alternatively, **2** can be formed by coordination of LGa to **7**, followed by elimination of $LGaCl_2$, or by insertion of LGa into the Sb-Cl bond of **7**, which yields the $Sb[Ga(Cl)L]_3$ intermediate, which then undergoes an intramolecular elimination of one equivalent of $LGaCl_2$ to give $LGa=SbGa(Cl)L$ **2**. However, a threefold insertion reaction of LGa was never detected, neither in the 3:1 molar reaction with $SbCl_3$ nor in any other reactions with group 15 compounds of the type ER_3 ($E = P - Bi, R = alkyl, NR_2$). In addition, the high steric demand of three LGa fragments attached to one central Sb atom seems to be far too large, hence the coordination mechanism should not be favored. Furthermore, *in situ* 1H NMR spectroscopic studies proved that **5** and **6** did not convert into **2** while reacting with additional equivalents of LGa (2 equiv. for **5**; 3 equiv. for **6**) at room temperature as well as upon heating to 80 °C for 2 h.

Scheme 4. Postulated reaction mechanism for the formation of **2**, **5** and **6** and calculated reactions (a) – (e).

The spectroscopic findings clearly prove that there is no (temperature-dependent) equilibrium between dimer **5** and trimer **6** in solution, and that the conversion of trimer **6** into monomeric stibinidene does not occur. Therefore, we propose that the stibinidene $L(Cl)GaSb$ is the key intermediate in these reactions; depending on the applied reaction conditions, compounds **2**, **5** or **6** is formed.

Reactions of LGa with SbX_3 can be compared to reactions of the cyclic alkyl(amino)carbene (cAAC) with PCl_3 ,^[30] which yield the cAAC-stabilized chlorophosphinidine. The former reaction proceeds with elimination of $[(cAAC)Cl]^+Cl^-$, and the final product exists in equilibrium between the cAAC-coordinated phosphinidine $cAAC \rightarrow PCl$ and the phosphalkene. In contrast, reactions of the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) with PX_3 yielded $[P_2(IPr)_2Br_3]Br$, which exhibits a P-P bond bridged by a bromine atom.^[31] On the other hand, reactions with EBr_3 (E = Sb, Bi) gave simple IPr- EBr_3 adducts, which do not undergo further Sb-Sb or Bi-Bi bond formation reactions.^[32] Finally, cAAC-stabilized stibinidene $cAAC-SbCl$ is obtained by reduction of $cAAC-SbCl_3$ with two equivalents of KC_8 ,^[33] while the NHC-stabilized phenylstibinidene is formed by reduction of $NHC \rightarrow SbCl_2Ph$ with magnesium.^[34]

To conclude, we report on a general synthetic pathway for compounds with Ga=Sb double bonds by reacting three equivalents of LGa with SbX_3 . The reactions proceed with a twofold insertion of LGa into two Sb-X bonds followed by an intramolecular elimination of $LGaX_2$ to ultimately form **1 - 4**. The reaction of $SbCl_3$ with two equivalents of LGa at 25 °C yields the distibene $[L(Cl)GaSb]_2$ **5**, whereas cyclotristibine $[L(Cl)GaSb]_3$ **6** is formed at 8 °C. The synthesis of **1 - 6** can be rationalized by the formation of the Ga-substituted stibinidene $L(X)Ga-Sb$ as a reactive intermediate, which either reacts with LGa in a 1+1 addition reaction to give **1 - 4**, or dimerizes/trimerizes into **5** and **6**, respectively. The proposed reaction mechanism for the general formation of group 13/15 compounds containing π -bonding contributions, as well as the chemical reactivity of **1 - 4** are currently under investigation. Moreover, trapping reactions of the proposed stibinidene are being performed.

Experimental Section

General Procedures. All manipulations were performed under argon atmosphere using standard Schlenk and glove-box techniques. Toluene and *n*-hexane were dried using a mBraun Solvent Purification System and degassed prior to use. The anhydrous nature of the solvents was verified by Karl Fischer titration. Deuterated solvents (benzene- d_6 , toluene- d_8) were dried over activated molecular sieves (4 Å). LGa was prepared according to literature method.^[11] SbX_3 (X = F, Cl, Br, I) were commercially available and purified prior to use. The identity of **2** was proven by comparing NMR spectra of a sample prepared as-described herein with known data of **2**.^[10]

Instrumentation. 1H (300 MHz) and $^{13}C\{^1H\}$ (75.5 MHz) NMR spectra (δ in ppm) were recorded using a Bruker Avance DPX-300 spectrometer and the spectra are referenced to internal C_6D_5H (1H : δ = 7.154; ^{13}C : δ = 128.39) and $C_6D_5CHD_2$ (1H : δ = 2.09; ^{13}C : δ = 20.40). IR spectra were measured with an ALPHA-T FT-IR spectrometer equipped with a single

reflection ATR sampling module. The spectrometer was placed in a glovebox to allow FT-IR measurements under inert gas atmosphere. Melting points were measured using a Thermo Scientific 9300 apparatus.

General synthesis of $LGaSb=Ga(X)L$ (X = F **1, Cl **2**, Br **3**, I **4**).** A solution of SbX_3 (0.07 mmol) in 1 mL of toluene was added to a solution of LGa (100 mg, 0.21 mmol) in 2 mL of toluene and stirred for 24 h at ambient temperature. The solvent was removed in vacuum and 2 mL of *n*-hexane were added to the resulting residue, yielding a red solution and a colorless precipitate, which was isolated by filtration. The resulting red solution was concentrated to roughly 1 mL and stored at 8 °C for 48 h, yielding dark red crystals of **1 - 4** along with colorless crystals of $LGaX_2$. The red crystals were hand-picked under the microscope and fractionally crystallized 4-5 times in *n*-hexane to remove the residual $LGaX_2$. Yields are generally given for pure crystalline, isolated samples of **1 - 4**.

1: Yield 16 mg (0.014 mmol, 21 %). M.p. 215 °C. Anal. Calcd. for $C_{58}H_{82}N_4FGa_2Sb$: C, 62.45; H, 7.41; N, 5.02. Found: C, 62.51; H, 7.46; N, 4.97%. IR (neat): ν 3060, 2959, 2924, 2865, 1525, 1460, 1436, 1380, 1314, 1253, 1175, 1099, 1056, 1020, 940, 862, 794, 757, 705, 630, 529, 440 cm^{-1} . 1H NMR (C_6D_6 , 300 MHz, 25 °C): δ 7.22-7.10 (m, 6H, $C_6H_3(i-Pr)_2$), 4.84 (s, 1 H, $\gamma-CH$), 3.20 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.48 (s, 6 H, $ArNCCH_3$), 1.28 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.11 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6 , 600 MHz, 25 °C): δ 168.08 ($ArNCCH_3$), 143.87, 141.63, 127.37, 124.27 (C_6H_3), 97.91 ($\gamma-CH$), 28.85 ($CH(CH_3)_2$), 26.04 ($CH(CH_3)_2$), 24.48 ($CH(CH_3)_2$), 24.32 ($ArNCCH_3$). ^{19}F NMR (C_6D_6 , 282 MHz, 25 °C): δ -39.07 (s, GaF).

2: Yield 20 mg (0.018 mmol, 26 %). Anal. Calcd. for $C_{58}H_{82}N_4ClGa_2Sb$: C, 61.54; H, 7.30; N, 4.95. Found: C, 61.59; H, 7.26; N, 4.98%. 1H NMR (toluene- d_8 , 500 MHz): δ 7.16-7.06 (m, 6 H, $C_6H_3(i-Pr)_2$), 4.87 (s, 1 H, $\gamma-CH$), 3.15 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.51 (s, 6 H, $ArNCCH_3$), 1.24 (d, 12 H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 1.10 (d, 12 H, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$). ^{13}C NMR (toluene- d_8 , 150 MHz): δ 168.09 ($ArNCCH_3$), 143.71, 141.60, 127.27, 124.31 (C_6H_3), 98.28 ($\gamma-CH$), 29.01 ($CH(CH_3)_2$), 26.32 ($CH(CH_3)_2$), 24.40 ($CH(CH_3)_2$), 24.30 ($ArNCCH_3$).

3: Yield 11 mg (0.009 mmol, 14 %). M.p. 205 °C. Anal. Calcd. for $C_{58}H_{82}N_4BrGa_2Sb$: C, 59.22; H, 7.03; N, 4.76. Found: C, 59.29; H, 7.10; N, 4.78%. IR (neat): ν 3060, 2959, 2925, 2866, 1525, 1460, 1436, 1381, 1314, 1256, 1175, 1098, 1056, 1020, 939, 861, 794, 757, 705, 636, 615, 528, 440 cm^{-1} . 1H NMR (C_6D_6 , 300 MHz, 25 °C): δ 7.29-7.10 (m, 6H, $C_6H_3(i-Pr)_2$), 4.93 (s, 1 H, $\gamma-CH$), 3.23 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 1.53 (s, 6 H, $ArNCCH_3$), 1.33 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$), 1.11 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6 , 600 MHz, 25 °C): δ 168.25 ($ArNCCH_3$), 143.80, 141.64, 127.31, 124.49 (C_6H_3), 98.42 ($\gamma-CH$), 29.09 ($CH(CH_3)_2$), 26.57 ($CH(CH_3)_2$), 24.48 ($CH(CH_3)_2$), 24.38 ($ArNCCH_3$).

4: Yield 13 mg (0.011 mmol, 15 %). M.p. 203 °C. Anal. Calcd. for $C_{58}H_{82}N_4IGa_2Sb$: C, 56.94; H, 6.76; N, 4.58. Found: C, 57.01; H, 6.79; N, 4.62%. IR (neat): ν 3060, 2960, 2925, 2866, 1525, 1460, 1435, 1380, 1313, 1258, 1175, 1093, 1055, 1017, 939, 860, 793, 756, 704, 634, 616, 527, 438, 400, 382 cm^{-1} . 1H NMR (C_6D_6 , 300 MHz, 25 °C): δ 7.23-7.11 (m, 6 H, $C_6H_3(i-Pr)_2$), 4.93 (s, 1 H, $\gamma-CH$), 3.23 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.53 (s, 6 H, $ArNCCH_3$), 1.33 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$), 1.11 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6 , 600 MHz, 25 °C): δ 168.27 ($ArNCCH_3$), 143.78, 141.61, 127.31, 124.49 (C_6H_3), 98.42 ($\gamma-CH$), 29.09 ($CH(CH_3)_2$), 26.58 ($CH(CH_3)_2$), 24.48 ($CH(CH_3)_2$), 24.39 ($ArNCCH_3$).

Synthesis of $[L(Cl)GaSb]_3$ **6.** LGa (0.2 g, 0.410 mmol) was dissolved in 2 mL of benzene and $SbCl_3$ (0.047 g, 0.205 mmol) was added. The reaction mixture was quickly shaken, and the resulting solution was kept at 8 °C for 2 days, upon which the solution turned yellow-green. The solvent was removed in vacuo and the remaining residue dissolved in 1 mL of toluene. The solution was kept at 8 °C for 3 days to yield colorless crystals of

LGaCl₂, which were separated by filtration. The solution was concentrated to 0.6 mL and kept at 8 °C for another 2 days, resulting in the formation of yellow-orange crystals of **6**, which were separated from the solution, washed with 1 mL of *n*-hexane and dried under reduced pressure. The remaining solution was dried under reduced pressure, the residue was dissolved in 2 mL of *n*-hexane and kept at room temperature for 1 day to afford an additional amount of **6**. Yield: 0.057 g (0.029 mmol, 43%). M.p. 153 °C (dec.). Anal. Calcd. for C₈₇H₁₂₃N₆Cl₃Ga₃Sb₃: C, 54.04; H, 6.41; N, 4.35. Found: C, 54.11; H, 6.44; N, 4.38%. IR (neat): ν 2960, 2925, 2866, 1523, 1435, 1376, 1318, 1254, 1172, 1108, 1014, 938, 863, 798, 757, 635, 530, 436 cm⁻¹. ¹H NMR (C₆D₆, 300.1 MHz): δ 7.32–7.09 (m, 18 H, C₆H₃(*i*-Pr)₂), 4.95 (s, 2 H, γ -CH), 4.91 (s, 1 H, γ -CH), 3.73 (sept, 2 H, ³J_{HH} = 6.6 Hz, -CH(CH₃)₂), 3.53 (m, 6 H, -CH(CH₃)₂), 3.27 (sept, 2 H, ³J_{HH} = 6.9 Hz, -CH(CH₃)₂), 3.16 (sept, 2 H, ³J_{HH} = 6.6 Hz, -CH(CH₃)₂), 1.60 (s, 6 H, ArNCCH₃), 1.59 (s, 6 H, ArNCCH₃), 1.52 (s, 6 H, ArNCCH₃), 1.47 (m, 12 H, -CH(CH₃)₂), 1.39 (d, 6 H, ³J_{HH} = 6.9 Hz, -CH(CH₃)₂), 1.36 (d, 6 H, ³J_{HH} = 6.9 Hz, -CH(CH₃)₂), 1.25 (m, 18 H, -CH(CH₃)₂), 1.21 (d, 6 H, ³J_{HH} = 6.6 Hz, -CH(CH₃)₂), 1.12 (d, 6 H, ³J_{HH} = 6.9 Hz, -CH(CH₃)₂), 1.08 (d, 6 H, ³J_{HH} = 5.7 Hz, -CH(CH₃)₂), 1.06 (d, 6 H, ³J_{HH} = 6.3 Hz, -CH(CH₃)₂). ¹³C NMR (C₆D₆, 75.5 MHz): δ 169.30, 196.15, 168.74 (ArNCCH₃), 145.96, 145.80, 145.12, 144.60, 143.97, 142.58, 142.16, 141.71, 141.59, 127.45, 127.41, 125.50, 125.22, 124.64, 124.56, 124.37 (C₆H₃), 99.29, 98.38 (γ -CH), 29.82, 29.15, 28.66, 28.54, 28.46, 28.15 (-CH(CH₃)₂), 27.60, 27.14, 25.97, 25.60, 25.19, 25.14, 24.77, 24.68 (-CH(CH₃)₂), 24.53, 24.18, 24.12 (ArNCCH₃).

Synthesis of [L(Cl)Ga]₂SbCl **7.** LGa (0.2 g, 0.410 mmol) was dissolved in 2 mL of benzene, SbCl₃ (0.047 g, 0.205 mmol) was added and the mixture quickly shaken. The formation of **7** was proven by comparing the ¹H NMR spectrum of **7**, which was recorded immediately after the reagents were combined, with those of [L(Cl)Ga]₂PX (X = Cl, Br).^[12d] Unfortunately, any attempts to isolate a pure sample of **7** failed, to date, due to its strong tendency toward elimination of LGaCl₂, which can be also seen in the ¹H NMR spectrum of **7** (Fig. S18). Therefore, no further analytical data of **7** can be given. ¹H NMR (C₆D₆, 300.1 MHz): δ 7.17–6.99 (m, 6 H, C₆H₃(*i*-Pr)₂), 4.87 (s, 1 H, γ -CH), 3.77 (sept, 1 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 3.51 (sept, 1 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 3.34 (sept, 1 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 3.21 (sept, 1 H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 1.49 (s, 3 H, ArNCCH₃), 1.48 (s, 3 H, ArNCCH₃), 1.39 (d, 3 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.35 (d, 3 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.26 (d, 3 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.24 (d, 6 H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 1.12 (d, 3 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.11 (d, 3 H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 0.98 (d, 3 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 0.96 (d, 3 H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂).

Single-crystal X-ray diffraction: The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (monochromatic MoK α radiation, λ = 0.71073 Å) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97)^[35] and refined anisotropically by full-matrix least-squares on *F*² (SHELXL-2014).^[36] 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 central F-Ga-Sb-Ga moiety in **1** is disordered over two positions. The corresponding Sb/Ga bonds were restrained to be equal. **6** included a highly disordered *n*-hexane molecule that could not be modelled properly. The final refinement was done with a solvent free reflection data after PLATON/squeeze run.^[37] The solvent molecule was included in the sum formula.

Computational methods. All quantum chemical calculation were employed with the ORCA quantum chemistry package (version 4.0).^[38] Ground-state geometry optimizations of 1–6 were calculated with the composite approach PBEh-3c,^[39] utilizing the geometrical counterpoise correction (GCP)^[39b], the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ)^[39c]. The RIJK approximation was

employed to accelerate the calculations in conjunction with the appropriate auxiliary basis sets (def2-SV/J).^[40] Additionally, effective core potentials (ECP) were employed for the Sb and I atoms to accelerate geometry optimizations.^[41] Natural bond orbital analysis was performed using the NBO version 6.0.^[42] Frequency calculations at 298 K were conducted in order to gain the thermal components of the Gibbs free enthalpy and to characterize the optimized structures as minima on the potential energy surface. All isopropyl groups were changed to methyl groups in the QM calculations to accelerate convergence.

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- [16] **1**: [C₅₈H₈₂FGa₂N₄Sb], *M* = 1115.46, dark red crystal, (0.391 × 0.242 × 0.194 mm); monoclinic, space group *P*2₁/*n*; *a* = 12.8718(4) Å, *b* = 22.7600(8) Å, *c* = 19.8971(7) Å; α = 90°, β = 105.093(2)°, γ = 90°, *V* = 5628.0(3) Å³; *Z* = 4; μ = 1.469 mm⁻¹; ρ_{calc} = 1.316 g · cm⁻³; 220987 reflections (θ_{max} = 36.054°), 25625 unique (*R*_{int} = 0.0310); 652 parameters; largest max./min in the final difference Fourier synthesis 1.332 e · Å⁻³/ -0.567 e · Å⁻³; max./min. transmission 0.75/0.63; *R*₁ = 0.0319 (*I* > 2 σ (*I*)), *wR*₂ = 0.0809 (all data). **3**: [C₅₈H₈₂BrGa₂N₄Sb], *M* = 1176.37, dark red crystal, (0.173 × 0.156 × 0.050 mm); monoclinic, space group *P*2₁/*c*; *a* = 13.5074(11) Å, *b* = 17.0023(14) Å, *c* = 25.653(2) Å; α = 90°, β = 95.300(4)°, γ = 90°, *V* = 5866.3(8) Å³; *Z* = 4; μ = 2.088 mm⁻¹; ρ_{calc} = 1.332 g · cm⁻³; 148480 reflections (θ_{max} = 33.246°), 22429 unique (*R*_{int} = 0.0474); 615 parameters; largest max./min in the final difference Fourier synthesis 1.336 e · Å⁻³/ -0.864 e · Å⁻³; max./min. transmission 0.75/0.63; *R*₁ = 0.0374 (*I* > 2 σ (*I*)), *wR*₂ = 0.0884 (all data). **4**: [C₅₈H₈₂Ga₂IN₄Sb], *M* = 1223.36, dark red crystal, (0.174 × 0.099 × 0.078 mm); monoclinic, space group *P*2₁/*n*; *a* = 17.535(5) Å, *b* = 16.851(5) Å, *c* = 19.787(6) Å; α = 90°, β = 92.757(17)°, γ = 90°, *V* = 5840(3) Å³; *Z* = 4; μ = 1.942 mm⁻¹; ρ_{calc} = 1.391 g · cm⁻³; 70576 reflections (θ_{max} = 30.508°), 17797 unique (*R*_{int} = 0.0533); 615 parameters; largest max./min in the final difference Fourier synthesis 1.482 e · Å⁻³/ -1.580 e · Å⁻³; max./min. transmission 0.75/0.58; *R*₁ = 0.0374 (*I* > 2 σ (*I*)), *wR*₂ = 0.1026 (all data). **6**: [C₉₃H₁₃₇Cl₃Ga₃NeSb₃], *M* = 2019.84, pale brown crystal, (0.402 × 0.096 × 0.053 mm); monoclinic, space group *P*2₁/*n*; *a* = 13.5514(7) Å, *b* = 34.4970(18) Å, *c* = 20.9888(11) Å; α = 90°, β = 106.346(3)°, γ = 90°, *V* = 9415.3(9) Å³; *Z* = 4; μ = 1.825 mm⁻¹; ρ_{calc} = 1.425 g · cm⁻³; 259042 reflections (θ_{max} = 33.196°), 35417 unique (*R*_{int} = 0.0569); 950 parameters; largest max./min in the final difference Fourier synthesis 3.320 e · Å⁻³/ -1.315 e · Å⁻³; max./min. transmission 0.75/0.57; *R*₁ = 0.0453 (*I* > 2 σ (*I*)), *wR*₂ = 0.1230 (all data). The crystallographic data (without structure factors) were deposited as „supplementary publication no. CCDC-1829496 (1), CCDC-1829497 (3), CCDC-1829499 (4) and CCDC-1829498 (6)“ at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).
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COMMUNICATION

A general pathway for the synthesis of gallastibenes LGaSbGa(X)L ($\text{X} = \text{F}$ **1**, Cl **2**, Br **3**, I **4**) containing $\text{Ga}=\text{Sb}$ double bonds by reactions of three equivalents of LGa [$\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_2$] with SbX_3 is presented. In contrast, the reaction of two eq. of LGa with SbCl_3 at 25°C yields distibene [L(XGaSb)_2] **5**, while cyclotristibine [L(X)GaSb_3] **6** is formed at 8°C .

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A General Pathway for the Synthesis of Gallastibenes containing $\text{Ga}=\text{Sb}$ Double Bonds.

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