Syntheses, Structures, and Bonding Analyses of Carbene-stabilized Stibinidenes

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Dedicated to Prof. E. Niecke on the occasion of his 80th birthday

Abstract: Reactions of two equivalents of LGa (L = HC[C(Me)NAr]₂; Ar = 2,6-*i*-Pr₂C₆H₃) with SbX₃ (X = Cl, Br) yield double-inserted products (LGaX)₂SbX (X = Cl **1**, Br **2**), which were isolated at –40 °C. Warming solutions of **1** and **2** to ambient temperature results in intramolecular elimination of LGaX₂ and formation of Ga-substituted stibinidenes L(X)GaSb as reaction intermediates, which were stabilized by coordination of strong σ -donating carbenes. Four carbene-stabilized stibinidenes ^{Me}CAAC-SbGa(X)L (^{Me}CAAC = [H₂C(CMe₂)₂NAr]C, Ar = 2,6-*i*-Pr₂-C₆H₃, X = Cl **3**, Br **4**) and IDipp-SbGa(X)L (IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene, X = Cl **5**, Br **6**) were characterized by single crystal X-ray diffraction and the nature of the bonding in **3–6** was further investigated by quantum chemical methods. The studies reveal substantial Sb–C_{carbene} π -backbonding contributions in **3** and **4**, whereas the IDipp-stabilized derivatives **5** and **6** exhibit Sb–C_{carbene} single bonds. DFT computations with and without dispersion corrections reveal that dispersion interactions mainly from the bulky aryl groups decisively contribute to the stability of **3–6**.

Introduction

Low-valent main group metal complexes have significantly contributed to a better understanding of the nature of the chemical bond in heavy main group element compounds. For instance, multiple bonding in compounds containing group 13, 14, and 15 elements differs fundamentally from the classical double and triple bonds observed with the lighter congeners - boron, carbon and nitrogen - which essentially leads to different structures, i.e., *trans-bent* orientations of heavier ethylene and acetylene analogues. Moreover, the electronic situation of the heavier element compounds often deviates from their lighter homologues, i.e., the increasing tendency of forming singlet ground states vs. triplet ground states species with increasing atomic number.^[1]

Low-valent and low-coordinate group 15 chemistry has been intensely studied since the isolation of the first diphosphene by Yoshifuji in 1981^[2] and a large number of dipnictenes RE=ER,^[3] and heterocyclic species [RE]_x have been reported.^[4] In contrast, monomeric pnictinidenes RE, which show interesting electronic

properties due to the presence of two electron lone pairs and one empty orbital (singlet state), or due to their behavior as diradicaloid species (triplet state), remained unknown. Unlike nitrenes and phosphinidenes, the triplet species of heavier group 15 elements are highly unstable and have only been investigated in the gas phase and in low-temperature matrices. However, Bertrand et al. recently reported on a stable singlet (phosphino)phosphinidene,^[5] and the corresponding (phosphino)arsinidene was observed as a transient species in solution.^[6] In addition, these reactive species were electronically stabilized by coordination to Lewis acidic metal centers as well as base-coordination.^[7] The coordination of strong σ -donating carbenes has resulted in the last decade in the synthesis of unforeseen main group element compounds with low coordination numbers and low formal oxidation states.^[8,9] The high synthetic potential of carbenes originates from the precise modulation of the bond strength in terms of σ -donor and π -acceptor bonding capacity.^[10]

Intramolecularly base-stabilized pnictinidenes (type **D**),^[11] and intermolecularly stabilized species containing strong σ -donors such as N-heterocyclic carbenes (NHCs, type **A**), including IDipp-PH^[12] and three NHC-AsH derivatives (NHC = IDipp; IMes, IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene); IAr*, Ar* = 2,6-CHPh₂-4-Me-C₆H₂),^[13] and cyclic alkyl(amino)carbenes (CAACs, type **B**),^[14] have been structurally characterized. However, the first intramolecularly (type **D**)^[15] and intermolecularly (type **B**)^[16] and **C**)^[17] base-stabilized stibinidenes were reported only recently, whereas transition metal-coordinated stibinidenes are known for decades.^[18] Based on spectroscopic, crystallographic, and computational analyses, Hudnall et al. concluded that DAC-SbPh (DAC = Me₂C[C(O)NMe]₂ **C**) shows significant π -backbonding contribution from the Sb(I) center to the carbene ligand, leading to a short Sb-C bond that is comparable to those observed in stibaalkenes.^[19] The Wiberg bond index (WBI) value of 2.842 shows formation of two Sb-C σ bonds and one π bond. Despite the almost identical Sb-C bond length of **B** compared to **C**, and a WBI value of 1.282, which proves partial Sb=C double bond character, ^{Cy}CAAC-SbCl (^{Cy}CAAC = [CyCC(Me)₂CH₂NDipp]C **B**) was described as base-stabilized stibinidene.

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Scheme 1. Base-stabilized stibinidenes (Ar = Mes, Dipp; Dipp = 2,6-*i*-Pr₂-C₆H₃; Mes = 2,4,6-Me₃-C₆H₂; dmp = 2,6-Me₂-C₆H₃). Only one mesomeric form is shown (for other important ones see Scheme 5).

Our interest in reactions of gallanediyl LGa with heavy group 15 element compounds (As, Sb, Bi) resulted in the synthesis of compounds with unusual bonding properties,^[20] i.e. Ga-substituted dipnictenes $[L(X)Ga]_2E_2$ ($X = \text{halogen}, NR_2, OR$),^[21] the first Sb analogues of bicyclo[1.1.0]butane $[L(X)Ga]_2Sb_4$ ($X = \text{halogen}, NR_2$),^[22] gallastibenes $L(X)GaSbGaL$ ($X = \text{halogen}$)^[23] and -arsenes $LGaAsCp^*$ ($Cp^* = C_5Me_5$)^[24] with Ga-pnictogen double bonds as well as Sb- and Bi-centered radicals.^[25] These reactions were found to occur via (stepwise) insertion of LGa into the pnictogen-X bond and subsequent elimination of $LGaX_2$. We herein present a comprehensive mechanistic study of the reactions of SbX_3 ($X = Cl, Br$) with two equivalents of LGa. The reactions proceed via formation of Ga-substituted stibinidenes as reaction intermediate, which were stabilized by carbene-coordination. The structure and bonding situation of four carbene-stabilized stibinidenes was studied in detail.

Results and Discussion

Synthesis and spectroscopic characterization. Insertion reactions of two equivalents of LGa with SbX_3 ($X = Cl, Br$) at low temperature proceed stepwise with initial formation of $L(X)GaSbX_2$, which could not be isolated, followed by the formation of the double-inserted products $[L(X)Ga]_2SbX$ ($X = Cl$ **1**, **Br 2**). Compounds **1** and **2**, which are stable in solution below $-40^\circ C$ as proven by VT NMR spectroscopy (**1**, Fig. S1, S2; **2**, Fig. S4, S5), were isolated as crystalline solids in good yields (79% **1**, 62% **2**) upon storage of concentrated solutions in toluene at $-78^\circ C$ for two days. Isolated crystals of **1** and **2** can be stored under Ar atmosphere at $-30^\circ C$ for several days without decomposition.

Scheme 2. Synthesis of **1** and **2**.

The 1H NMR spectra of **1** and **2** in toluene- d_8 each show a singlet for the γ -CH (**1**: 4.77 ppm; **2**: 4.80 ppm) and two single resonances for the methyl groups of the β -diketiminato ligand (**1**: 1.44, 1.44 ppm; **2**: 1.40, 1.41 ppm), whereas the magnetically inequivalent *i*-Pr groups exhibit four septets (**1**: 3.19, 3.33, 3.47, 3.73 ppm; **2**: 3.20, 3.38, 3.48, 3.86 ppm) and eight doublets (**1**: 1.36 – 0.94 ppm; **2**: 1.54 – 0.92 ppm) as was reported for the phosphorous analogues $[L(X)Ga]_2PX$ ($X = Cl, Br$).^[21a] Isolated samples of **1** and **2** were dissolved in toluene at $-78^\circ C$ and warmed to $0^\circ C$, yielding cyclotristibines $[L(X)GaSb]_3$ ($X = Cl, Br$). In remarkable contrast, dissolving of **1** and **2** in toluene at $25^\circ C$ selectively yielded distibines $[L(X)GaSb]_2$ ($X = Cl, Br$) (Scheme 3). In addition, the reaction of isolated samples of **1** and **2** with one equivalent of LGa yielded previously reported gallastibenes $LGaSbGa(X)L$ ($X = Cl, Br$) (Fig. S9).^[23,25]

Scheme 3. Thermal treatment of isolated samples of **1** and reactions with one equivalent of LGa, yielding cyclotristibines, distibines, and gallastibenes.

Our studies prove that **1** and **2** are formed as reaction intermediates in reactions of SbX_3 with two and three equivalents of LGa. The formation of cyclotristibines, distibines, and gallastibenes as well as $LGaX_2$ as side-product furthermore points to the presence of Ga-substituted stibinidenes $L(X)GaSb$ as a common reaction intermediate generated via intramolecular elimination of $LGaX_2$. Unfortunately, all attempts to isolate these reactive species failed. In contrast, coordination of strong σ -donating N-heterocyclic (IDipp) and cyclic alkylamino carbenes (MeCAAC) yielded four carbene-stabilized stibinidenes (Scheme 4), which were isolated as crystalline solids.

Scheme 4. Synthesis of MeCAAC - (**3**, **4**) and IDipp-stabilized stibinidenes (**5**, **6**).

Compounds **3** - **6** formed in good yields ($> 50\%$) according to *in situ* 1H NMR spectroscopic studies. Unfortunately, MeCAAC - $SbGa(X)L$ ($X = Cl$ **3**, **Br 4**) were only isolated in very low yields (**3** 7%, **4** $< 1\%$) due to their limited thermal stability in solution at ambient temperature as was shown by *in situ* 1H NMR spectroscopy (Fig. S13). Moreover, their solubility is comparable to that of the side product $LGaX_2$, thus causing problems in separating both compounds. In contrast, IDipp- $SbGa(X)L$ ($X = Cl$ **5**, **Br 6**) were isolated in 15% (**5**) and 29% (**6**) yields, respectively. To synthesize **5** and **6** in higher yields, we reacted the corresponding carbene adducts IDipp- SbX_3 ($X = Cl, Br$) (Fig. S20-23) with two equivalents of LGa under varying conditions (reaction time, temperature). Unfortunately, the reactions failed to produce **5** and **6** (Fig. S24, 25). Instead, $[L(X)GaSb]_2$ ($X = Cl, Br$) was formed in addition to $LGaX_2$ and IDipp, respectively. 1H NMR spectra of **3** - **6** show the expected resonances of the β -diketiminato ligand as well as of the MeCAAC (**3**, **4**) and IDipp (**5**, **6**) carbenes. The 1H NMR spectrum of **3** exhibits a single resonance for the γ -CH (5.00 ppm) and the methyl group (1.70 ppm) of the β -diketiminato, while the isopropyl groups show two septets (3.41, 4.03 ppm) and four doublets (1.07, 1.12, 1.27, 1.67 ppm), respectively. The methyl groups of the MeCAAC can

be assigned to the singlet at 0.82 and 1.24 ppm, whereas the methylene group shows a single resonance at 1.54 ppm. Furthermore, the isopropyl groups of the Dipp substituent of ^{Me}CAAC exhibit a septet at 2.69 ppm for the methine groups and a doublet at 1.44 ppm for the methyl groups. The ¹H NMR spectra of **5** and **6** also show two singlets for the γ-CH (**5**: 4.91 ppm, **6**: 4.97 ppm) and methyl groups (**5**: 1.55 ppm; **6**: 1.55 ppm) of the β-diketiminato ligand. The isopropyl groups of the β-diketiminato can be assigned to two septets (**5**: 3.03, 3.77 ppm; **6**: 3.06, 3.85 ppm) and five partially overlapping doublets (**5**: 0.98 – 1.37 ppm, **6**: 0.98 – 1.38 ppm), whereas the isopropyl groups of IDipp appear as one septet (**5**: 2.65 ppm; **6**: 2.66 ppm) and two doublets (**5**: 0.98, 1.20 ppm; **6**: 0.98, 1.21 ppm). In addition, singlet resonances at 6.26 (**5**) and 6.27 ppm (**6**) were observed for the olefinic methine groups of IDipp. As was reported for carbene-stabilized pnictogenes, the ¹³C NMR shifts of the carbene-carbon atoms in **3** – **6** are shifted to higher fields compared to the starting carbene.^{10b} The shifts observed for **3** – **6** are comparable to those reported by Bertrand et al. and Hudnall et al. for carbene-stabilized stibinidenes.^[16,17]

X-ray crystal structures. The structure of **2** was determined by single crystal X-ray diffraction (Figure 1). Compound **2** crystallizes in the monoclinic space group *P*2₁/*c* as observed for [LGa(Br)]₂PBr.^{21a}

Figure 1. Solid state structure of [LGa(Br)]₂SbBr (**2**). Hydrogen atoms, disordered atoms, and solvent molecules have been omitted for clarity and thermal ellipsoids are shown with 50% probability level. Selected bond lengths [Å] and angles [°]: Sb(1)–Ga(2) 2.5993(13), Sb(1)–Ga(1) 2.6735(12), Br(1)–Ga(1) 2.3460(12), Br(2)–Ga(2) 2.3526(13), Ga(1)–N(1) 1.965(6), Ga(1)–N(2) 1.987(7), Ga(2)–N(4) 1.960(6), Ga(2)–N(3) 1.964(7), Br(3)–Sb(1)–Ga(2) 130.18(12), Br(3)–Sb(1)–Ga(1) 120.89(11), Ga(2)–Sb(1)–Ga(1) 108.68(4), N(1)–Ga(1)–N(2) 95.7(3), N(1)–Ga(1)–Sb(1) 118.6(2), N(2)–Ga(1)–Sb(1) 113.42(19), N(4)–Ga(2)–N(3) 95.3(3), N(4)–Ga(2)–Sb(1) 105.2(2), N(3)–Ga(2)–Sb(1) 138.4(2).

The Ga–Sb bond lengths are within the typical Ga–Sb single bond range reported for [L(X)Ga]₂Sb₂, [L(X)Ga]₂Sb₄, and L(X)GaSbGaL (X = halogen).^[21–23,25] The largest difference in the conformations of **2** and [LGa(Br)]₂PBr is the Br–Ga⋯Ga–Br torsion angle. The smaller angle of the P compound (~35°) allows an intramolecular CH⋯π interaction, while the larger

angle observed for **2** (~70°) leads to an intramolecular Br⋯π interaction. A more detailed structural comparison is not meaningful due to the disorder of the central units in **2** and in [LGa(Br)]₂PBr as well as the rather low quality of the crystal of **2**. Very few carbene-stabilized pnictinidenes were structurally characterized. CAAC–PCI, which was formed in the reaction of CAAC with PCI₃, shows an equilibrium between the CAAC-coordinated phosphinidene and the phosphalkene.^[26] In contrast, reactions of PX₃ with IDipp occurred with P–P bond formation, yielding [P₂(IDipp)₂Br₃]⁺Br[–],^[27] while reactions of IDipp with EBr₃ (E = Sb, Bi) only gave IDipp–EBr₃ adducts.^[28] Very recently, Gilliard et al. reported on the structure of the first base-stabilized bismuthinidene ^{Et}CAAC–BiPh.^[14d]

Figure 2. Solid state structure of **3**. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown with 50% probability level. The molecule is disordered over the mirror plane (2nd orientation omitted).

Figure 3. Solid state structure of **4**. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown with 50% probability level. The molecule is disordered over the mirror plane (2nd orientation omitted).

3 (Fig. 2) and **4** (Fig. 3) are isomorphous and crystallize in the orthorhombic space group *Pnma* with the molecule on the special position 4c (mirror plane). The molecular symmetry is lower than the symmetry of this position, hence the molecules are disordered. Lowering the symmetry did not resolve the disorder, thus the centrosymmetric space group was chosen. **5** (Fig. 4) and **6** (Fig. 5) crystallize in the monoclinic space groups *P2₁/n* and *P2₁/c* with one and two molecules in the asymmetric unit, respectively.

Figure 4. Solid state structure of **5**. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown with 50% probability level. The molecule is disordered over the mirror plane (2nd orientation omitted).

Figure 5. Solid state structure of **6**. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown with 50% probability level.

The Ga–Sb bonds in **3** and **4** are slightly longer than in **5** and **6** (Table 1). The bromine substituent appears to have a shortening effect on the bond regardless of which carbene is used. The Sb–C bonds of **3** (2.083(4) Å) and **4** (2.089(10) Å) are shorter than those of **5** (2.1585(16) Å) and **6** (2.148(5) Å), but compare well with those of ^{cy}CAAC–SbCl (2.082(5) Å) and DAC–SbPh (2.068(7) Å).^[16,17] The influence of the halide substituents on other structural parameters is almost negligible. However, ^{Me}CAAC-stabilized stibinidenes **3** and **4** show slightly elongated Ga–X bonds compared to **5** and **6**.

Table 1. Experimental bond lengths [Å] and angles [°] of **3** – **6**.^[a]

	3	4	5	6
Ga–Sb	2.605(1)	2.599(2)	2.571(1)	2.562(1)
C–Sb	2.083(4)	2.089(1)	2.159(2)	2.148(5)
Ga–X	2.245(1)	2.404(2)	2.228(1)	2.378(1)
Ga–N	2.035(2), 1.928(3)	1.972(5), 1.972(5)	2.008(2), 1.984(2)	1.996(4), 1.996(4)
C–Sb–Ga	107.2(2)	107.2(3)	112.0(1)	114.3(2)
X–Ga–Sb	120.4(1)	120.5(1)	123.5(1)	128.4(1)
N–Ga1–N	94.9(2)	94.8(3)	93.4(1)	93.5(2)

[a] Bond lengths rounded to three and bond angles to one decimal digit.

Quantum chemical calculations. The electronic nature of carbene-stabilized pnictinidenes can generally be described as base-stabilized neutral or zwitterionic pnictinidenes or as pnictaalkenes with a pnictogen-carbon double bond. Scheme 5 shows the major mesomeric forms for IDipp- and ^{Me}CAAC-coordinated stibinidenes.

Scheme 5. Major resonance forms of carbene stabilized stibinidenes (Ar = Dipp): base-stabilized neutral (left) and zwitterionic stibinidene (middle) and stibaalkene (right).

The electronic structure of carbene-stabilized pnictinidenes is largely influenced by the π -backbonding capacity

(electrophilicity) of the carbene. We considered NHCs to be suitable reagents for the stabilization of the stibinidene form since they are strong nucleophiles (σ -donor). On the other hand, the stronger π -accepting CAACs were expected to favor electron backdonation and therefore stabilize the stibaalkene form. Computational calculations were therefore performed to evaluate the bonding nature of **3** – **6** in more detail.

The computed structures of **3** – **6** agree very good with the experimental bond parameters observed in the solid-state structures of **3** – **6**. The deviations from the X-ray structure data for the Sb–C (<1.2%) and Ga–Sb (<0.8%) bond lengths and the C–Sb–Ga (<1.3%) bond angles are negligible (Table 2).

Table 2. Computed (PBE0-D3/def2-TZVP) bond lengths [Å] and angles [°] of LGa(X)Sb-MeCAAC (X = Cl **3***, Br **4***) and LGa(X)Sb-IDipp (X = Cl **5***, Br **6***)

	3 *	4 *	5 *	6 *
Ga–Sb	2.590	2.590	2.578	2.583
C–Sb	2.067	2.066	2.133	2.134
Ga–X	2.245	2.402	2.23	2.382
C–Sb–Ga	107.3	107.1	113.4	114.0
X–Ga–Sb	124.6	124.2	129.8	129.7

The π -backbonding contributions of the two carbenes were furthermore analyzed with natural bond orbital (NBO) analyses. Wiberg bond indices (WBI) clearly demonstrate that the Sb–C_{carbene} bonds in **3*** (1.19) and **4*** (1.18) show partial double bond character, whereas those in **5*** (0.97) and **6*** (0.96) should be rather described as true single bonds (Table 3).

Table 3. WBI, NPA atomic charges (q, e), and bond polarizations (P_{X,Y}) of **3*** – **6*** (PBE0-D3/def2-TZVP) and ^cCAAC–SbCl.

	WBI (Sb–C)	q (Sb, C _{carbene})	P _{Sb–C} (σ -bond) / %	P _{Sb–C} (π -bond) / %
3 *	1.19	0.02, 0.00	27 – 73	66 – 34
4 *	1.18	0.04, –0.01	26 – 74	67 – 33
5 *	0.97	–0.24, 0.15	24 – 76	-
6 *	0.96	–0.22, 0.15	24 – 76	-
^c CAAC–SbCl ^[16]	1.28	-	-	-

The Sb–C_{carbene} σ -bond in **3*** – **6*** results from the carbene lone-pair donating electron density into an Sb orbital with mainly p-character (86–90%) and is polarized towards the C_{carbene} center (73–76%). The partial π -backbonding as observed for **3*** and **4*** originates from one of the Sb lone-pair orbitals with exclusive p-character and is polarized towards the Sb center (66–67%). This Sb p-orbital was found to be the main contributor to the HOMO

of **3*** – **6*** (63% **3***/**4*** – 68% **5***/**6***) with minor contributions of the N p-orbitals and, in case of **5*** and **6***, the carbene backbone C–C π -bond (Fig. 6, Fig. 7).

Figure 6. HOMO of [LGa(Cl)Sb-MeCAAC] **3*** (A) and [LGa(Br)Sb-MeCAAC] **4*** (B) at the PBE0-D3/def2-TZVP level of theory. *i*-Pr groups are omitted for clarity.

Figure 7. HOMO of [LGa(Cl)Sb-IDipp] **5*** (A) and [LGa(Br)Sb-IDipp] **6*** (B) at the PBE0-D3/def2-TZVP level of theory. *i*-Pr groups are omitted for clarity.

The π -backbonding contribution of the Sb p-orbital to the C_{carbene} becomes visible in the extension of the HOMO over the Sb–C_{carbene} bond in **3*** and **4***, while this extension is missed in **5*** and **6***, and is furthermore reflected in the partial charges of Sb and C_{carbene}. In **5*** and **6***, the Sb atoms exhibit partial negative charges (–0.24/–0.22 e) and the C_{carbene} atoms partial positive charges (0.15 e), whereas in **3*** and **4***, the corresponding charges are distributed by π -backbonding, resulting in almost neutral atoms (Table 3). Comparable results were reported for NHC-stabilized arsinidenes NHC–AsH (NHC = IDipp, IMes, IAr*).^[13] The short As–C bonds point to substantial C=As double bond character as was proven by quantum chemical computations at the PBE1PBE/basis level of theory. Wiberg bond indices (1.26 – 1.27) compare well to values computed for **3*** and **4***. In contrast, germylidenylarsinidene LGeAs–C[N(*i*-Pr)C(Me)]₂ shows a significantly lower WBI of 0.99 (NHC), in accordance with an As–C single bond. This value agrees with those determined for **5*** and **6***. Replacing C[N(*i*-Pr)C(Me)]₂ by stronger electrophilic PPh₃ gave LGeAs–PPh₃, which shows a higher WBI of 1.12 due to larger π -backbonding contribution.^[29] EtCAAC–BiPh exhibits an even higher (about 42%) double bond character.^[14d] In addition, the Bi–C_{carbene} bond (2.199(2) Å) was shorter than the covalent bond Bi–C_{Ph} bond (2.278(2) Å), clearly indicating partial Bi–C_{carbene} double bond character.

London dispersion (LD) was proven to play a decisive role in the thermodynamic stability of main group compounds, in particular, for those coordinated by sterically bulky carbenes.^[30] In order to identify the effect of dispersion in carbene-stabilized stibinidenes, we computed the structures (Fig. S20) and reaction energies (ΔH^0 , Table 4) of **3'** – **6'** with and without LD corrections.

Table 4. Reaction energies in benzene solution (ΔH_0 : kcal mol⁻¹) with and without LD corrections (D3(BJ)) for the formation of **3'** – **6'** and distibenes [L(X)GaSb]₂ from stibinidenes L(X)GaSb (BP86/def2-SVP level of theory).

	ΔH_0 (D3(BJ))	ΔH_0	E_{disp}
3'	-67.4	-37.4	-30.1
4'	-67.7	-37.1	-30.6
5'	-52.5	-16.0	-36.6
6'	-53.0	-15.4	-37.5
[L(Cl)GaSb] ₂	-86.5	-54.0	-32.5
[L(Br)GaSb] ₂	-87.1	-53.5	-33.6

LD energies were estimated by the reaction energy differences, which is as large as 37.5 kcal mol⁻¹. IDipp-coordinated stibinidenes **5'** and **6'** show larger LD contributions than ^{Me}CAAC-stabilized species **3'** and **4'** due to their larger size, but shorter H...H contacts than in the corresponding distibene [L(Cl)Ga]₂Sb₂. This is supported by the non-covalent interaction (NCI) analysis (Fig. S21).^[31] Significant LD interactions involving the aryl groups and the Sb center contribute to the thermodynamic stabilities of **3'** – **6'**.

In addition, computation of the thermodynamics with dispersion correction of the reactions initiated from LGa and SbX₃ (Scheme 4) demonstrate, that stibinidenes L(X)GaSb are more reactive than double-insertion products [L(X)Ga]₂SbX **1** and **2**, while the highly exothermic product formation is the driving force for these reactions. LD was also found important in the formation of other products as compared to the uncorrected reaction energies (Scheme S1).

Conclusions

In summary, detailed mechanistic studies on the reaction of two equivalents of LGa with SbX₃ suggest a stepwise reaction with formation of the double insertion products **1** and **2**. Isolated samples of **1** and **2** react at different temperatures to distibenes [L(X)GaSb]₂ and cyclotristibines [L(X)GaSb]₃, which do not undergo thermally induced interconversion reactions. Therefore, the reactions most likely proceed through formation of Ga-substituted stibinidenes L(X)GaSb as reaction intermediates, which were stabilized by carbene-coordination. ^{Me}CAAC-stabilized stibinidenes **3** and **4** exhibit substantial π -backbonding character, whereas IDipp-stabilized stibinidenes **5** and **6** show Sb-C_{IDipp} single bonds, therefore representing true carbene-stabilized stibinidenes. These findings are in agreement with the known electronic differences of ^{Me}CAAC and IDipp. Compared to IDipp, ^{Me}CAAC is a stronger σ -donor but also much stronger π -acceptor. DFT computations confirmed the expected partial π -backbonding character in **3'** and **4'** based on a higher WBI, an expansion of the HOMO along the Sb-C_{carbene} bond, and balanced partial charges. Dispersion interactions were found to substantially stabilize **3'** – **6'**.

Experimental Section

General Procedures. The reactions were performed under purified argon atmosphere using standard Schlenk and glove-box techniques. Solvents were dried using a MBraun Solvent Purification System and were carefully degassed. Karl Fischer titration of the dry solvents show water levels less than 2 ppm. Deuterated NMR solvents were stored over activated molecular sieves (4 Å) and degassed prior to use. LGa,^[32] ^{Me}CAAC,^[33] and IDipp^[34] were prepared according to literature methods. SbCl₃ and SbBr₃ were obtained from commercial sources and purified prior to use by distillation or sublimation.

Instrumentation. ¹H (300, 500, 600 MHz) and ¹³C{¹H} (75.5, 125, 150 MHz) NMR spectra (δ in ppm) were recorded using a Bruker Avance DPX-300 or Bruker Avance III HD spectrometer. Spectra are referenced to internal benzene-d₆ (¹H: δ = 7.154; ¹³C: δ = 128.39), toluene-d₈ (¹H: δ = 2.09; ¹³C: δ = 20.40) and thf-d₈ (¹H: δ = 3.58 ppm; ¹³C: δ = 67.21 ppm). 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. Melting points were measured using a Thermo Scientific 9300 apparatus.

Synthesis of [L(X)Ga]₂SbX (X = Cl **1, Br **2**).** LGa (200 mg, 0.41 mmol) and 0.205 mmol SbX₃ (X = Cl 47 mg, Br 74 mg) were filled in a Schlenk tube and cooled to -78 °C. 1.8 mL of toluene was added, and the suspension was stirred for 10 minutes at -78 °C. The reaction mixture

Scheme 6. Summary of the reaction products of two equivalents of LGa with SbX₃. Reaction energies with dispersion correction (ΔH_0 : kcal mol⁻¹, BP86-D3(BJ)/def2-SVP) are given for each step in benzene solution (Ar = 2,6-*i*-Pr₂-C₆H₃).

was slowly warmed to $-40\text{ }^{\circ}\text{C}$, upon which an orange precipitate formed. The solid was separated from the mother liquor by filtration at $-40\text{ }^{\circ}\text{C}$ and the volatiles were removed in vacuum. For purification, the raw product was washed three times at $-50\text{ }^{\circ}\text{C}$ with 1 mL of *n*-hexane.

1: Yield 192 mg (79%); m.p. $99\text{ }^{\circ}\text{C}$ (dec.); elemental analysis calcd (%) for $\text{C}_{58}\text{H}_{82}\text{N}_4\text{Cl}_3\text{Ga}_2\text{Sb}$: C 60.91, H 6.94, N 4.66; found: C 61.3, H 7.07, N 4.41. **$^1\text{H-NMR}$ (Tol- d_6 , 300 MHz, $-50\text{ }^{\circ}\text{C}$).** δ 7.07–7.15 (m, 6 H, C_6H_3), 4.77 (s, 1 H, $\gamma\text{-CH}$), 3.73 (sept, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 3.47 (sept, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 3.33 (sept, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 3.19 (sept, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 1.44 (s, 6 H, CCH_3), 1.36 (d, 6 H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.29 (d, 3 H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, 3 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.09 (d, 3 H, $^3J_{\text{HH}} = 6.4\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.97 (d, 3 H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.94 (d, 3 H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (THF- d_8 , 75 MHz, $-50\text{ }^{\circ}\text{C}$).** δ 170.5 (CCH_3), 170.4 (CCH_3), 146.4 (C_6H_3), 145.7 (C_6H_3), 143.4 (C_6H_3), 142.6 (C_6H_3), 142.6 (C_6H_3), 141.3 (C_6H_3), 138.6 (C_6H_3), 129.9 (C_6H_3), 129.2 (C_6H_3), 128.5 (C_6H_3), 127.9 (C_6H_3), 126.3 (C_6H_3), 125.9 (C_6H_3), 125.3 (C_6H_3), 124.5 (C_6H_3), 124.4 (C_6H_3), 99.0 ($\gamma\text{-CH}$), 30.9 ($\text{CH}(\text{CH}_3)_2$), 30.3 ($\text{CH}(\text{CH}_3)_2$), 29.0 ($\text{CH}(\text{CH}_3)_2$), 28.6 ($\text{CH}(\text{CH}_3)_2$), 28.4 ($\text{CH}(\text{CH}_3)_2$), 28.2 ($\text{CH}(\text{CH}_3)_2$), 25.4 ($\text{CH}(\text{CH}_3)_2$), 25.3 ($\text{CH}(\text{CH}_3)_2$), 24.8 ($\text{CH}(\text{CH}_3)_2$), 24.7 ($\text{CH}(\text{CH}_3)_2$), 24.5 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$), 23.6 (CCH_3), 21.8 (CCH_3). **IR.** ν 3062, 3024, 2961, 2923, 2867, 1520, 1461, 1433, 1382, 1359, 1316, 1260, 1177, 1099, 1020, 939, 863, 797, 762, 729, 694, 634, 528, 465, 442 cm^{-1} .

2: Yield 168 mg (62%); m.p. $92\text{ }^{\circ}\text{C}$ (dec.); elemental analysis calcd (%) for $\text{C}_{58}\text{H}_{82}\text{N}_4\text{Br}_3\text{Ga}_2\text{Sb}$: C 55.13, H 6.19, N 4.01; found: C 56.6, H 6.22, N 3.76. **$^1\text{H-NMR}$ (Tol- d_6 , 300 MHz, $-50\text{ }^{\circ}\text{C}$).** δ 7.11–7.17 (m, 6 H, C_6H_3), 4.80 (s, 1 H, $\gamma\text{-CH}$), 3.86 (sept, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 3.48 (sept, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 3.38 (sept, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 3.20 (sept, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 1 H, $\text{CH}(\text{CH}_3)_2$), 1.54 (d, 3 H, $^3J_{\text{HH}} = 6.4\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.41 (s, 3 H, CCH_3), 1.40 (s, 3 H, CCH_3), 1.38 (d, 3 H, $^3J_{\text{HH}} = 6.9\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.32 (d, 3 H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.30 (d, 3 H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, 6 H, $^3J_{\text{HH}} = 6.5\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.96 (d, 3 H, $^3J_{\text{HH}} = 6.9\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.92 (d, 3 H, $^3J_{\text{HH}} = 6.9\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (Tol- d_6 , 75 MHz, $-50\text{ }^{\circ}\text{C}$).** δ 170.1 (CCH_3), 169.6 (CCH_3), 146.3 (C_6H_3), 145.7 (C_6H_3), 143.3 (C_6H_3), 142.8 (C_6H_3), 142.2 (C_6H_3), 141.1 (C_6H_3), 129.7 (C_6H_3), 129.6 (C_6H_3), 129.3 (C_6H_3), 128.9 (C_6H_3), 128.7 (C_6H_3), 128.2 (C_6H_3), 128.0 (C_6H_3), 126.1 (C_6H_3), 125.8 (C_6H_3), 125.5 (C_6H_3), 124.3 (C_6H_3), 124.1 (C_6H_3), 99.1 ($\gamma\text{-CH}$), 30.9 ($\text{CH}(\text{CH}_3)_2$), 30.0 ($\text{CH}(\text{CH}_3)_2$), 29.0 ($\text{CH}(\text{CH}_3)_2$), 28.9 ($\text{CH}(\text{CH}_3)_2$), 28.3 ($\text{CH}(\text{CH}_3)_2$), 25.6 ($\text{CH}(\text{CH}_3)_2$), 25.3 ($\text{CH}(\text{CH}_3)_2$), 25.0 ($\text{CH}(\text{CH}_3)_2$), 24.9 ($\text{CH}(\text{CH}_3)_2$), 24.8 ($\text{CH}(\text{CH}_3)_2$), 24.7 ($\text{CH}(\text{CH}_3)_2$), 24.0 ($\text{CH}(\text{CH}_3)_2$), 23.6 (CCH_3), 21.9 (CCH_3). **IR.** ν 3065, 3018, 2957, 2923, 2865, 1522, 1461, 1433, 1383, 1360, 1314, 1255, 1177, 1095, 1015, 938, 860, 797, 757, 730, 694, 636, 526, 461, 440 cm^{-1} .

Synthesis of $[\text{L}(\text{X})\text{GaSb-MeCAAC}]$ ($\text{X} = \text{Cl}$ 3, Br 4). 0.0247 mmol $[\text{LGaX}]_2\text{SbX}$ ($\text{X} = \text{Cl}$ 30 mg, Br 33 mg) and 18 mg $^{\text{Me}}\text{CAAC}$ (0.049 mmol) were dissolved in 0.5 mL of benzene and stirred for 24 h at ambient temperature. The solvent was removed under vacuum and 0.7 mL of *n*-hexane were added to the resulting residue. The solution was stored for 2 h at $0\text{ }^{\circ}\text{C}$, yielding orange crystals of **3** and **4**. The product was recrystallized from a solution in *n*-hexane at $0\text{ }^{\circ}\text{C}$.

3: Yield 3 mg (7%); m.p. $195\text{ }^{\circ}\text{C}$ (dec.); elemental analysis calcd (%) for $\text{C}_{49}\text{H}_{72}\text{ClGaNa}_3\text{Sb}$: C 63.28, H 7.80, N 4.52; found: C 62.86, H 7.61, N 4.46. **$^1\text{H-NMR}$ (C_6D_6 , 300 MHz, $25\text{ }^{\circ}\text{C}$).** δ 6.90–7.13 (m, 9 H, C_6H_3), 5.00 (s, 1 H, $\gamma\text{-CH}$), 4.03 (sept, $^3J_{\text{HH}} = 6.7\text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 3.41 (sept, $^3J_{\text{HH}} = 6.7\text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 2.69 (sept, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 2 H, $\text{CNCCCH}(\text{CH}_3)_2$), 1.70 (s, 6 H, CCH_3), 1.67 (d, 6 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.54 (s, 2 H, CH_2), 1.44 (d, 12 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CNCCCH}(\text{CH}_3)_2$), 1.27 (d, 6 H, $^3J_{\text{HH}} = 6.9\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.24 (s, 6 H, $\text{NC}(\text{CH}_3)_2$), 1.12 (d, 6 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, 6 H, $^3J_{\text{HH}} =$

6.8 Hz, $\text{CH}(\text{CH}_3)_2$), 0.82 (s, 6 H, $\text{CC}(\text{CH}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 75 MHz, $25\text{ }^{\circ}\text{C}$).** δ 243.9 ($\text{CC}(\text{CH}_3)_2$), 167.8 (NCCH_3), 147.3 (C_6H_3), 146.0 (C_6H_3), 143.3 (C_6H_3), 142.8 (C_6H_3), 129.4 (C_6H_3), 127.0 (C_6H_3), 125.7 (C_6H_3), 125.0 (C_6H_3), 123.9 (C_6H_3), 97.6 ($\gamma\text{-CH}$), 74.7 ($\text{CC}(\text{CH}_3)_2$), 55.3 (CH_2), 52.4 ($\text{NC}(\text{CH}_3)_2$), 34.0 ($\text{NC}(\text{CH}_3)_2$), 29.9 ($\text{CH}(\text{CH}_3)_2$), 29.3 ($\text{CNCCCH}(\text{CH}_3)_2$), 28.9 ($\text{CNCC}(\text{CH}_3)_2$), 28.9 ($\text{CC}(\text{CH}_3)_2$), 28.1 ($\text{CH}(\text{CH}_3)_2$), 27.1 ($\text{CH}(\text{CH}_3)_2$), 25.0 ($\text{CH}(\text{CH}_3)_2$), 24.9 ($\text{CH}(\text{CH}_3)_2$), 24.8 ($\text{CH}(\text{CH}_3)_2$), 24.7 ($\text{CNCCCH}(\text{CH}_3)_2$), 24.3 ($\text{CH}(\text{CH}_3)_2$). **IR.** ν 3065, 3014, 2960, 2923, 2866, 1521, 1461, 1435, 1381, 1357, 1318, 1256, 1178, 1097, 1019, 938, 863, 797, 759, 728, 695, 635, 528, 463, 441 cm^{-1} .

4: Yield <1%. Analytical data of isolated **4** could not be recorded due to very low yield. In one case we got a single crystal of **4**, that was used for structure determination. An *in situ* ^1H NMR spectrum of the reaction of $[\text{L}(\text{Cl})\text{Ga}]_2\text{SbCl}$ (**1**) with $^{\text{Me}}\text{CAAC}$ at the beginning and after 24 h in C_6D_6 is shown in Figure S13.

Synthesis of $[\text{L}(\text{X})\text{GaSb-NHC}]$ ($\text{X} = \text{Cl}$ 5, Br 6). 0.0125 mmol $[\text{LGaX}]_2\text{SbX}$ ($\text{X} = \text{Cl}$ 15 mg, Br 17 mg) and 5 mg IDipp (0.0125 mmol) were dissolved in 0.5 mL of benzene and stirred for 24 h at ambient temperature. The solvent was removed under vacuum and 0.7 mL of *n*-hexane were added to the resulting residue. The solution was stored for 6 d at $0\text{ }^{\circ}\text{C}$, yielding dark red crystals. The product was recrystallized from a solution in *n*-hexane at $0\text{ }^{\circ}\text{C}$.

5: Yield 2 mg (15%); m.p.: $102\text{ }^{\circ}\text{C}$. elemental analysis calcd (%) for $\text{C}_{56}\text{H}_{77}\text{ClGaNa}_4\text{Sb}$: C 65.10, H 7.51, N 5.42; found: C 64.79, H 7.32, N 5.26. **$^1\text{H-NMR}$ (C_6D_6 , 300 MHz, $25\text{ }^{\circ}\text{C}$).** δ [ppm]: 7.06–7.25 (m, 12 H, C_6H_3), 6.26 (s, 2 H, NCH), 4.91 (s, 1 H, $\gamma\text{-CH}$), 3.77 (sept, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 3.03 (sept, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 2.65 (sept, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 4 H, $\text{CH}(\text{CH}_3)_2$), 1.55 (s, 6 H, CCH_3), 1.37 (d, 6 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, 6 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.29 (d, 6 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, 12 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CNCCCH}(\text{CH}_3)_2$), 1.19 (d, 3 H, $^3J_{\text{HH}} = 6.9\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.99 (d, 3 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.98 (d, 12 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CNCCCH}(\text{CH}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 600 MHz, $25\text{ }^{\circ}\text{C}$).** δ [ppm]: 167.6 (CCH_3), 157.9 (C), 146.0 (C_6H_3), 143.9 (C_6H_3), 143.5 (C_6H_3), 136.3 (C_6H_3), 130.3 (NCH), 126.6 (C_6H_3), 124.8 (C_6H_3), 124.5 (C_6H_3), 124.4 (C_6H_3), 123.4 (C_6H_3), 98.0 ($\gamma\text{-CH}$), 29.9 ($\text{CH}(\text{CH}_3)_2$), 29.1 ($\text{CH}(\text{CH}_3)_2$), 28.9 ($\text{CH}(\text{CH}_3)_2$), 28.0 ($\text{CH}(\text{CH}_3)_2$), 25.1 ($\text{CH}(\text{CH}_3)_2$), 25.1 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$), 24.1 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{C}(\text{CH}_3)_2$). **IR ν [cm^{-1}]:** 3060, 2961, 2925, 2867, 1527, 1461, 1437, 1385, 1316, 1292, 1259, 1176, 1097, 1055, 1018, 936, 858, 796, 755, 737, 703, 637, 551, 528, 449, 396.

6: Yield 4 mg (29%); m.p.: $98\text{ }^{\circ}\text{C}$. elemental analysis calcd (%) for $\text{C}_{56}\text{H}_{77}\text{BrGaNa}_4\text{Sb}$: C 62.42, H 7.20, N 5.21; found: C 62.18, H 7.12, N 5.09. **$^1\text{H-NMR}$ (C_6D_6 , 300 MHz, $25\text{ }^{\circ}\text{C}$).** δ [ppm]: 7.06–7.25 (m, 12 H, C_6H_3), 6.27 (s, 2 H, NCH), 4.97 (s, 1 H, $\gamma\text{-CH}$), 3.85 (sept, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 3.06 (sept, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 2 H, $\text{CH}(\text{CH}_3)_2$), 2.66 (sept, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 4 H, $\text{CH}(\text{CH}_3)_2$), 1.55 (s, 6 H, CCH_3), 1.38 (d, 6 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, 6 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.29 (d, 3 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.27 (d, 6 H, $^3J_{\text{HH}} = 6.7\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, 12 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CNCCCH}(\text{CH}_3)_2$), 0.98 (d, 3 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CH}(\text{CH}_3)_2$), 0.98 (d, 12 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, $\text{CNCCCH}(\text{CH}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 600 MHz, $25\text{ }^{\circ}\text{C}$).** δ [ppm]: 167.7 (CCH_3), 158.2 (C), 146.0 (C_6H_3), 143.9 (C_6H_3), 143.6 (C_6H_3), 136.1 (C_6H_3), 130.3 (NCH), 126.7 (C_6H_3), 124.9 (C_6H_3), 124.7 (C_6H_3), 124.4 (C_6H_3), 123.4 (C_6H_3), 98.3 ($\gamma\text{-CH}$), 29.9 ($\text{CH}(\text{CH}_3)_2$), 29.6 ($\text{CH}(\text{CH}_3)_2$), 29.1 ($\text{CH}(\text{CH}_3)_2$), 28.1 ($\text{CH}(\text{CH}_3)_2$), 25.2 ($\text{CH}(\text{CH}_3)_2$), 25.1 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$), 24.1 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{C}(\text{CH}_3)_2$). **IR ν [cm^{-1}]:** 3062, 2060, 2927, 2866, 1526, 1462, 1434, 1385, 1315, 1293, 1259, 1174, 1097, 1016, 937, 854, 794, 754, 740, 703, 639, 548, 528, 455, 395.

Computational details. The geometries of all species under consideration were fully optimized in the gas phase at the PBE0-D3/def2-

TZVP level of theory as implemented in the ORCA 4.0 program^[35-38] with a corresponding small-core relativistic effective core potential for Sb employing ultrafine grid.^[39] The stationary points were characterized as minima on the potential energy surface by vibrational analysis (the number of imaginary frequencies (NImag) was equal to zero) and the structures obtained were used for the subsequent computations. NBO analyses^[40] were performed with the NBO 6.0 program.^[41] Geometries for reaction energies were optimized in gas phase at the BP86-D3(BJ)/def2-SVP level of theory with Gaussian09 Program.^[42-44] Geometry optimization was also carried out without the empirical dispersion correction (DFT-D3) as a reference to evaluate dispersion energy.^[36] Single-point energies in solvent (benzene) were calculated by SMD model with def2-TZVP basis set.^[45]

Single-crystal X-ray analyses. The crystals were mounted on nylon loops in inert oil. Data of 2 to 5 were collected on a Bruker AXS D8 Venture diffractometer with Photon II detector (mono-chromated CuK α radiation, λ = 1.54178 Å, micro-focus source) at 123(2), 120(2), 120(2) and 131(2) K, respectively. Data of 6 were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoK α radiation, λ = 0.71073 Å) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97)^[46] and refined anisotropically by full-matrix least-squares on F² (SHELXL-2017).^[47,48] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2/3). Hydrogen atoms were refined using a riding model or rigid methyl groups. In **2** the central Sb-Br unit is disordered over two positions. The ADP of the toluene molecule suggest disorder however it was not possible to separate different orientations. RIGU restraints were applied to the solvent's ADP. In **3** the molecule is disordered over a mirror plane. RIGU restraints were applied to all ADP. Lowering the symmetry did not resolve the disorder. The crystal of **4** was a non-merohedral twin and the model was refined against HKLF5 data. As vast parts of the molecule are disordered RIGU restraints were applied to all ADP. The aromatic C-C bond lengths were restrained to be equal (SADI). **5** contains a highly disordered benzene molecule, whose electron density was removed by a Platon/SQUEEZE run. It was included in the sum formula for completeness.^[49] In **6** a dipp group is disordered over two positions. RIGU and ISOR restraints were applied to the ADP of the corresponding atoms. The bond lengths within the phenyl ring were restrained to be equal (SADI). The structure contains two highly disordered n-hexane molecules that could not be modelled properly. The final refinement was done with a solvent free dataset from a SQUEEZE/Platon run. The solvent molecules were included in the sum formula for completeness. The unit cell parameters suggest pseudo-merohedral twinning however the obvious twin laws yielded a BASF of 0. Consequently, the high R_{int} is likely caused by the weak diffraction of the tiny crystal.

2: [C₆₅H₉₀Br₃Ga₂N₄Sb], *M* = 1428.32, colorless crystal, (0.122 × 0.062 × 0.027 mm); monoclinic, space group *P*2₁/c; *a* = 13.9460(5) Å, *b* = 24.3834(11) Å, *c* = 19.1527(8) Å; α = 90°, β = 91.365(2)°, γ = 90°, *V* = 6511.0(5) Å³; *Z* = 4; μ = 6.689 mm⁻¹; ρ_{calc} = 1.457 g·cm⁻³; 125208 reflections (θ_{max} = 80.404°), 14083 unique (*R*_{int} = 0.1740); 716 parameters; largest max./min in the final difference Fourier synthesis 2.217 e·Å⁻³/ -1.731 e·Å⁻³; max./min. transmission 0.75/0.53; *R*₁ = 0.0931 (*I* > 2 σ (*I*)), *wR*₂ = 0.2611 (all data). **3:** [C₄₉H₇₂ClGa₂N₃Sb], *M* = 930.01, yellow crystal, (0.151 × 0.108 × 0.076 mm); orthorhombic, space group *Pnma*; *a* = 10.0803(3) Å, *b* = 19.1276(7) Å, *c* = 24.5267(8) Å; α = 90°, β = 90°, γ = 90°, *V* = 4729.0(3) Å³; *Z* = 4; μ = 5.997 mm⁻¹; ρ_{calc} = 1.306 g·cm⁻³; 48321 reflections (θ_{max} = 79.045°), 5271 unique (*R*_{int} = 0.0430); 508 parameters; largest max./min in the final difference Fourier synthesis 1.257 e·Å⁻³/ -0.941 e·Å⁻³; max./min. transmission 0.75/0.66; *R*₁ = 0.0387 (*I* > 2 σ (*I*)), *wR*₂ = 0.0913 (all data). **4:** [C₄₉H₇₂BrGa₂N₃Sb], *M* = 974.47, pale yellow crystal, (0.122 × 0.047 × 0.041 mm); orthorhombic, space group *Pnma*; *a* = 10.1139(3) Å, *b* = 19.1231(6) Å, *c* = 24.5563(6) Å; α = 90°, β = 90°, γ = 90°, *V* = 4749.4(2) Å³; *Z* = 4; μ = 6.440 mm⁻¹; ρ_{calc} =

1.363 g·cm⁻³; 5782 reflections (θ_{max} = 79.414°), 5782 unique (*R*_{int} = 0.1010); 454 parameters; largest max./min in the final difference Fourier synthesis 1.594 e·Å⁻³/ -0.701 e·Å⁻³; max./min. transmission 0.75/0.48; *R*₁ = 0.0698 (*I* > 2 σ (*I*)), *wR*₂ = 0.1905 (all data). **5:** [C₆₂H₈₃ClGa₂N₄Sb], *M* = 1111.24, orange crystal, (0.332 × 0.231 × 0.211 mm); monoclinic, space group *P*2₁/n; *a* = 12.8959(5) Å, *b* = 15.5258(6) Å, *c* = 31.0579(12) Å; α = 90°, β = 98.7069(11)°, γ = 90°, *V* = 6146.7(4) Å³; *Z* = 4; μ = 4.702 mm⁻¹; ρ_{calc} = 1.201 g·cm⁻³; 146208 reflections (θ_{max} = 79.356°), 13276 unique (*R*_{int} = 0.0471); 587 parameters; largest max./min in the final difference Fourier synthesis 1.716 e·Å⁻³/ -0.518 e·Å⁻³; max./min. transmission 0.75/0.47; *R*₁ = 0.0317 (*I* > 2 σ (*I*)), *wR*₂ = 0.0889 (all data). **6:** [C₆₂H₉₁BrGa₂N₄Sb], *M* = 1163.76, orange crystal, (0.063 × 0.061 × 0.047 mm); monoclinic, space group *P*2₁/c; *a* = 17.7535(19) Å, *b* = 17.693(2) Å, *c* = 38.637(4) Å; α = 90°, β = 90.929(7)°, γ = 90°, *V* = 12134(2) Å³; *Z* = 8; μ = 1.587 mm⁻¹; ρ_{calc} = 1.274 g·cm⁻³; 241231 reflections (θ_{max} = 28.458°), 30382 unique (*R*_{int} = 0.1478); 1284 parameters; largest max./min in the final difference Fourier synthesis 2.402 e·Å⁻³/ -1.433 e·Å⁻³; max./min. transmission 0.75/0.63; *R*₁ = 0.0668 (*I* > 2 σ (*I*)), *wR*₂ = 0.1679 (all data).

The crystallographic data of **2** – **6** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1579373 (**2**), -1583617 (**3**), -1579371 (**4**), -1579372 (**5**) and -579351 (**6**). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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