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ARTICLE

# Synthesis and X-ray Crystal Structures of Ga-substituted Distibenes $[L(X)GaSb]_2$

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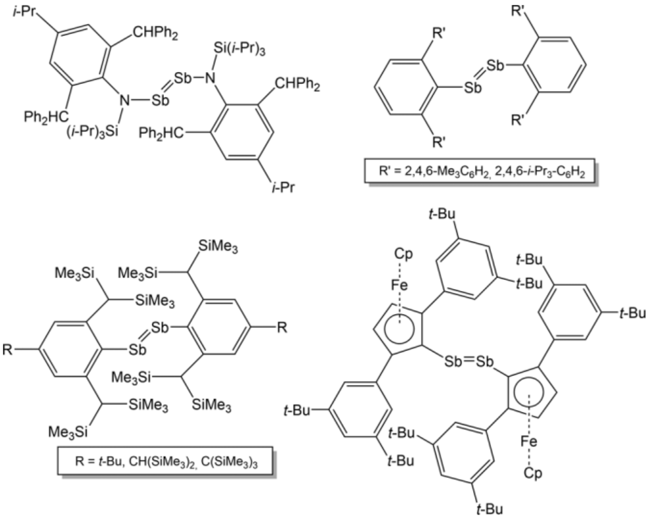
*Dedicated to Prof. A. Filippou on the Occasion of his 60th Birthday*

**Abstract**. The reactions of two equivalents of LGa {L = $HC[C(Me)N(2,6\text{-}i\text{Pr}_2C_6H_3)]_2$} with $SbX_3$ ($X$ = Br, I, OEt) proceed with elimination of $LGaX_2$ and formation of Ga-substituted distibenes $[L(X)GaSb]_2$ [$X$ = Br (**1**), I (**2**), OEt (**3**)]. Compounds **1** to **3** were characterized by heteronuclear NMR ($^1H$, $^{13}C$), IR and UV/Vis spectroscopy, elemental analysis, and single-crystal X-ray diffraction.

## Introduction

The interest in heavier main group element compounds containing an element–element double bond received a tremendous boost in the early 80ies of the last century, when *West* et al.[1] and *Joshifuji* et al.[2] reported on the first compounds containing Si=Si and P=P double bonds, respectively. Since then, numerous main group element compounds of group 13 to 16 elements containing homoleptic or heteroleptic double and triple bonds, which violate the so-called double bond rule,[3] according to which the formation of π bonds is restricted to elements of the second row of the periodic Table, have been reported,[4] their bonding situation analyzed by quantum chemical calculation,[5] and their interesting reactivity in particular in small molecule activation reactions studied.[6] In case of group 15 compounds, double-bonded species of the general type $RE{=}ER$ have been kinetically stabilized by use of sterically encumbered organic substituents (Scheme 1).[7] However, the low number of structurally characterized compounds of the type $R_2E_2$ (without transition metal complexes) containing As=As (11), Sb=Sb (7) and Bi=Bi (12) double bonds[8] compared to diphosphenes containing a P=P double bond (>75)[9]] indicate the lower bond strength of the $E{=}E$ double bond of heavier group 15 elements, resulting from the decreasing π-bond energy.[10] In addition, NHC-stabilized (NHC=N-heterocyclic carbene) diatomic molecules of the type $(NHC)_2E_2$ ($E$ = P, As, Sb), which formally contain the group 15 elements in the oxidation state 0, were prepared,[11] but these exhibit $E$–$E$ single bonds.



**Scheme 1.** Structurally characterized distibenes $R_2Sb_2$ containing a Sb=Sb double bond.

Distibenes have been kinetically-stabilized by use of sterically demanding substituents (Scheme 1).[12] Their electronic situation was investigated by quantum chemical calculation[13] and their chemical reactivity was studied in detail,[14] i.e. their coordination ability toward transition metals[15] and their reactivity in single electron reduction reactions, that yielded the corresponding radical anion,[16] respectively.

We recently observed that reactions of two equivalents of monovalent gallanediyl LGa {L = $HC[C(Me)N(2,6\text{-}i\text{Pr}_2C_6H_3)]_2$} with $EX_3$ ($E$ = As, Sb, Bi; $X$ = Cl, $NR_2$) yielded the corresponding Ga-substituted dipnictenes $[L(X)GaE]_2$ with a central $E{=}E$ double bond, under mild reaction conditions.[17] Upon heating, the distibenes $[L(X)GaSb]_2$, were converted into Sb analogues of bicyclo[1.1.0]butane $[L(X)Ga]_2(\mu,\eta^{1:1}\text{-}Sb_4)$ ($X$ = Cl, $NMe_2$, NMeEt).

To further prove the influence of the $X$ substituent on the reactivity of the starting antimonides $SbX_3$, we systematically investigated reaction of two equivalents of LGa with two anti-

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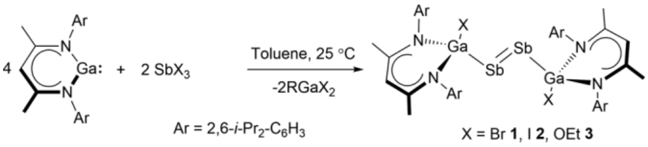
mony trihalides $SbX_3$ ($X$ = Br, I) and antimony triethoxide $Sb(OEt)_3$, respectively. The resulting Ga-substituted distibenes $[L(X)GaSb]_2$ [$X$ = Br (**1**), I (**2**), OEt (**3**)] (Scheme 2) were characterized by heteronuclear ($^1H$, $^{13}C$) NMR spectroscopy and single-crystal X-ray diffraction and the structural parameters within this class of compounds are compared. In addition, quantum chemical calculations were performed to investigate the electronic structure of **1**–**3**.



**Scheme 2.** Synthesis of **1** to **3**.

## Results and Discussion

Reactions of two equivalents of LGa with $SbX_3$ in toluene at ambient temperature proceeded with elimination of $LGaX_2$ ($X$ = Br, I, OEt), as was proven by in situ $^1H$ NMR spectroscopy, and formation of the Ga-substituted distibenes $[L(X)GaSb]_2$ [$X$ = Br (**1**), I (**2**), OEt (**3**)], which were isolated in high yields as green crystalline solids after recrystallization from solutions in toluene at ambient temperature.

**1**–**3** are soluble in benzene and toluene and can be stored in solution and as isolated crystals in an argon atmosphere at ambient temperature. The $^1H$ NMR spectra of **1**–**3** in [D$_6$]benzene show two septets and four doublets for the magnetically inequivalent *i*Pr groups of the β-diketiminate ligand and single resonances for the γ-CH and the methyl groups of the $C_3N_2M$ ring, whereas the $^{13}C$ NMR spectra of **1**–**3** each show 14 signals of the β-diketiminate groups (Table 1). Comparable findings were reported for dipnictenes of the general type $[L(Cl)GaE]_2$ ($E$ = As,[17c] Sb[17b]).

The UV/Vis spectra of solutions of **1**–**3** in toluene (Figure S12, Supporting Information) each show a maximum absorption at 354 nm, which agrees very well with the value reported by *Power* et al. for LGa (340 nm)[18] and thus can be assigned to the L($X$)Ga substituent, as well as a second absorption maximum at 437 (**1**) and 438 nm (**2**) due to the π–π* transitions. Comparable values were previously reported for other distibenes $R$Sb=Sb$R$.[7a] In contrast, no π–π* absorption was observed for **3**.

Single crystals of **1**–**3** were obtained upon storage of solutions in toluene at ambient temperature after 2 h (**1**), 3 h (**2**), and after 5 d at –30 °C (**3**). **1** and **2** crystallize in the triclinic space group $P\bar{1}$ with the molecule placed on center of inversion, whereas **3** crystallizes in the monoclinic space group $P2_1/c$, respectively (Figure 1, Figure 2, and Figure 3).[19]

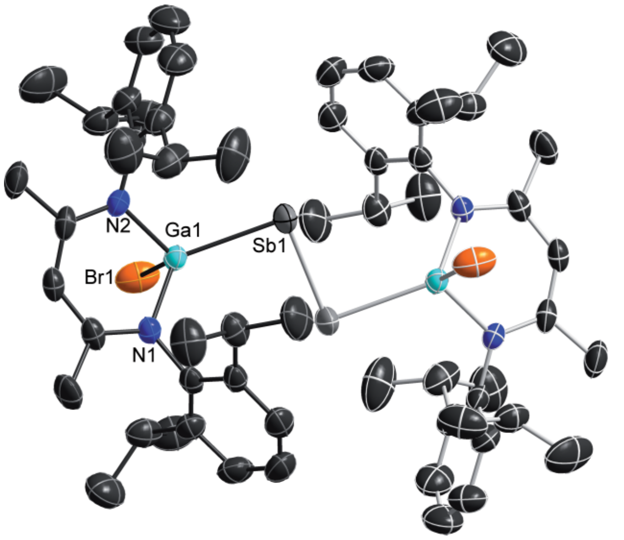


**Figure 1.** Solid state structure of **1**. Non-hydrogen atoms shown as thermal ellipsoids at 50 % probability levels; hydrogen atoms are omitted for clarity. Part depicted in pale colors is generated by symmetry.

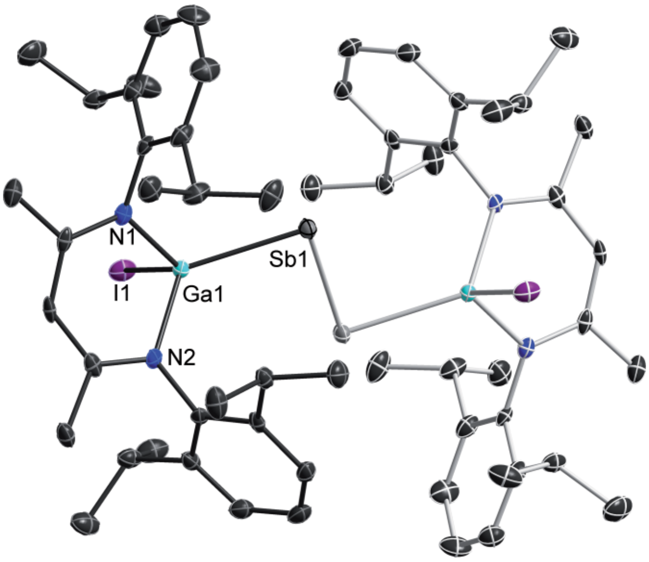


**Figure 2.** Solid state structure of **2**. Non-hydrogen atoms shown as thermal ellipsoids at 50 % probability levels; hydrogen atoms are omitted for clarity. Part depicted in pale colors is generated by symmetry.

**Table 1.** $^1H$ NMR chemical shifts of $[L(X)GaSb]_2$ $^{a)}$.

| $X$ = | γ-C*H* | C*H*Me$_2$ | CH*Me*$_2$ | CMe |
|---|---|---|---|---|
| Cl [17b] | 4.97 | 3.91, 3.05 | 1.30, 1.20, 1.11, 1.01 | 1.63 |
| Br (**1**) | 5.00 | 3.98, 3.05 | 1.40, 1.20, 1.12, 0.99 | 1.63 |
| I (**2**) | 5.06 | 4.04, 3.05 | 1.42, 1.21, 1.14, 0.97 | 1.62 |
| OEt (**3**) | 4.82 | 4.02, 2.99 | 1.51, 1.39, 1.29, 1.04 | 1.62 |
| NMe$_2$ [17a] | 4.75 | 3.62, 2.90 | 1.35, 1.29, 1.02, 1.00 | 1.61 |
| NMeEt [17b] | 4.78 | 3.95, 3.82, 2.90 | 1.32, 1.28, 1.03, 1.01 | 1.61 |

a) 300 MHz, 25 °C, [D$_6$]benzene.

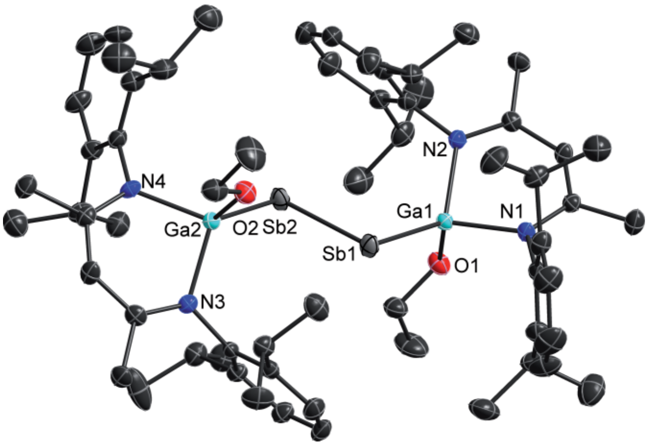


**Figure 3.** Solid state structure of **3**. Non-hydrogen atoms shown as thermal ellipsoids at 50 % probability levels; hydrogen atoms are omitted for clarity.

The centrosymmetric (**1**, **2**) $Sb_2$ units are coordinated by two LGa*X* groups [*X* = Br (**1**), I (**2**), OEt (**3**)] in a *trans*-bent orientation as is typically observed for distibenes. The Ga atoms are tetrahedrally coordinated and are slightly off the best plane of the ligand's backbone (**1**: 0.599(4) Å, **2**: 0.583(3) Å, **3**: 0.593(5) Å and 0.526(5) Å]. The Ga–*X* bond lengths [*X* = Cl 2.2319(4) Å,[17b] Br 2.4126(10) Å (**1**), I 2.6010(5) Å (**2**)] increase with increasing atomic number of the halogen atom (Table 2) and the Ga–N bond lengths [1.965(3), 1.959(3) Å (**1**), 1.940(2), 1.961(2) Å (**2**), 1.962(3), 1.969(3) Å (**3**)] are significantly shorter than those in gallanediyl LGa [2.0528(14) Å, 2.0560(13) Å][18] as is typically observed upon oxidation of the Ga atom in LGa.[20]

**Table 2.** Selected bond lengths /Å and angles /° of LGa*X* coordinated distibenes $[L(X)GaSb]_2$ [*X* = Br (**1**), I (**2**), OEt (**3**)].

| | 1 | 2 | 3 |
|---|---|---|---|
| Sb1–Ga1 | 2.6129(11) | 2.5919(5) | 2.6012(5) |
| Sb2–Ga2 | – | – | 2.5987(5) |
| Sb1–Sb1a/2 | 2.6442(11) | 2.6310(5) | 2.6495(4) |
| Ga1–*X*1 | 2.4126(10) | 2.6010(5) | 1.830(3) |
| Ga2–*X*2 | – | – | 1.824(3) |
| Ga1–N1 | 1.965(3) | 1.940(2) | 1.962(3) |
| Ga1–N2 | 1.959(3) | 1.961(2) | 1.969(3) |
| N1–C1 | 1.334(5) | 1.335(3) | 1.334(5) |
| N2–C3 | 1.335(5) | 1.325(3) | 1.332(5) |
| C1–C2 | 1.412(6) | 1.386(4) | 1.402(5) |
| C2–C3 | 1.396(6) | 1.402(4) | 1.397(5) |
| Ga1–Sb1–Sb1a | 90.92(3) | 89.69() | 92.24(2) |
| Ga2–Sb2–Sb1 | – | – | 88.31(2) |
| Sb1–Ga1–*X*1 | 116.79(3) | 116.21() | 117.87(9) |
| Sb2–Ga2–*X*2 | – | – | 110.26(10) |
| N1–Ga1–Sb1 | 121.14(8) | 111.88(7) | 110.61(9) |
| N2–Ga1–Sb1 | 111.57(9) | 121.14(6) | 121.30(9) |
| N1–Ga1–N2 | 96.55(13) | 96.64(9) | 94.47(13) |
| N1–C1–C2 | 123.5(4) | 123.0(2) | 122.8(3) |
| N2–C3–C2 | 122.5(3) | 124.2(3) | 124.7(4) |
| C1–C2–C3 | 129.7(3) | 128.9(3) | 127.7(4) |

The central Sb–Sb bond lengths [**1**: 2.6442(11) Å, **2**: 2.6310(5) Å, **3**: 2.6495(4) Å] are almost identical and agree very well with those of previously reported Ga-substituted distibenes $[L(X)GaSb]_2$ [*X* = Cl 2.6461(2) Å, NMeEt 2.6433(6) Å,[17b] $NMe_2$ 2.6477(3) Å[17a]] and distibenes *R*Sb=Sb*R* containing sterically demanding organic substituents, for which values from 2.64 to 2.70 Å were reported.[21] The Sb=Sb double bonds are shorter than Sb–Sb single bonds typically observed in distibines $R_4Sb_2$.[22] The Sb–Sb bond length in the parent system, HSb=SbH, was calculated by different groups, yielding values between 2.608 Å and 2.682 Å,[23] respectively. The Ga–Sb bond lengths [**1**: 2.6129(11) Å, **2**: 2.5919(5) Å, **3**: 2.6012(5), 2.5987(5) Å] are slightly shorter than the sum of the calculated single bond covalent radii for Ga (1.24 Å) and Sb (1.40 Å) atoms,[24] but comparable to Ga–Sb single bonds observed in other Ga-substituted distibenes $[L(X)GaSb]_2$ [*X* = Cl 2.58178(19) Å, NMeEt 2.6169(5) Å,[17b] $NMe_2$ 2.6200(4) Å[17a]], tetrastibines $[(LGaX)_2(\mu,\eta^{1:1}\text{-}Sb_4]$ [*X* = Cl 2.6008(13) Å,[17b] $NMe_2$ 2.5975(5) Å[17a]] as well as the stibanyl radical $[L(Cl)Ga]_2Sb^{\cdot}$ [2.5899(4), 2.5909(3) Å].[25]

In contrast, Ga–Sb single bonds in $[(LGa)_2(\mu,\eta^{2:2}\text{-}Sb_4)]$ [2.6637(11) Å],[26] dmap-$Ga(Et)_2Sb(SiMe_3)_2$ [dmap = 4-$Me_2NC_5H_4N$, 4-dimethylaminopyridine; 2.648(1) Å][27] as well as in four- and six-membered heterocycles $[R_2GaSbR'_2]_{x(x\,=\,2,\,3)}$, which were found to range from 2.666 Å to 2.772 Å,[28] are slightly elongated. Gallastibenes of the general type LGaSbGa(*X*)L, which contain a Ga=Sb double bond, showed significantly shorter Ga–Sb single bonds [F: 2.5596(3) Å, Cl: 2.5528(2) Å, Br: 2.5662(3) Å, I: 2.5478(6) Å] and Ga–Sb double bonds [F: 2.4601(3) Å, Cl: 2.4629(2) Å, Br: 2.4502(3) Å, I: 2.4496(8) Å], respectively.[25,29]

The Ga–Sb–Sb bond angles in **1** [90.92(3)°], **2** [89.685(15)°] and **3** [88.313(14)°, 92.238(15)°] agree almost perfectly with those in $[L(Cl)GaSb]_2$ [89.476(6)°],[17b] whereas those of the amido-substituted derivatives $[L(X)GaSb]_2$ [*X* = NMeEt 95.839(16)°,[17b] $NMe_2$ 94.710(8)°[17a]] are slightly enlarged, most likely resulting from the higher steric demand of the amido substituents. In addition, the calculated H–Sb–Sb bond angle of HSb=SbH (93.0°)[23] falls in between these values. The Ga–Sb–Sb bond angles in **1** to **3**, which are very close to 90°, indicate a high p orbital character within the bonding electron pairs and, as a consequence, high s character of the electron lone pair of the Sb atoms. Distibenes ArSb=SbAr containing sterically encumbered organic substituents (terphenyl ligands) show significantly larger C–Sb–Sb bond angles between 94.1° and 105.4° (7 hits in the CCDC database),[12] resulting from repulsive interactions between the bulky aryl ligands.

The synthesis of **1**–**3** demonstrates the high synthetic potential for bond activation reactions of gallanediyl LGa and for the stabilization of unusual bonding properties. It is noteworthy, that reactions of the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) with group 15 trihalides $EX_3$ (*E* = P, Sb, Bi; *X* = Cl, Br), which were recently reported by *Goichochea* et al.,[30,31] did not result in the formation of the corresponding dipnictenes. Instead, the reactions of IPr with $PX_3$ yielded $[P_2(IPr)_2Br_3]Br$, exhibiting a P–P single bond bridged by a bromine atom,[30] whereas the reactions with $EBr_3$ (*E* = Sb, Bi) only gave the simple adducts

IPr–$E$Br$_3$,[31] whereas Sb–Sb or Bi–Bi bond formation was not observed.

To investigate the bonding situation of **1** to **3** and the electronic nature within the Ga–Sb–Sb–Ga unit in more detail, the structures of $[\mathrm{L}(X)\mathrm{GaSb}]_2$ [$X$ = Br (**1**), I (**2**), OEt (**3**)] were investigated by quantum chemical calculations at the PBE0/def2-TZVP level of theory. The *i*Pr-groups were substituted by sterically less demanding Me groups.

The resulting structural parameters of the Ga–Sb–Sb–Ga unit coincide well with the experimentally values (Table 3). Sb–Sb bond lengths lay within 0.012 Å, Sb–Ga within 0.022 Å, Ga–$X$ within 0.025 Å and Ga–N within 0.032 Å deviation from the experimental values of **1** to **3**. The average deviation of the bond angles is greater for Sb–Ga–X (**1**: 3.69°, **2**: 4.52°, **3**: 3.39°) than for Ga–Sb–Sb (**1**: 1.72°, **2**: 0.08°, **3**: 1.68°), most likely resulting from the replacement of the *i*Pr groups by sterically less demanding Me groups.

**Table 3.** Selected experimental and calculated bond lengths /Å and angles /° of $[\mathrm{L}(X)\mathrm{GaSb}]_2$ [$X$ = Br (**1**), I (**2**), OEt (**3**)].

| | **1** | **2** | **3** |
|---|---|---|---|
| Sb–Ga$_{\mathrm{exp.}}$ | 2.6129(11) | 2.5919(5) | 2.6012(5), 2.5987(5) |
| Sb–Ga$_{\mathrm{calcd.}}$ | 2.621 | 2.613 | 2.653 |
| | 2.619 | 2.614 | 2.627 |
| Sb–Sb$_{\mathrm{exp.}}$ | 2.6442(11) | 2.6310(5) | 2.6495(4) |
| Sb–Sb$_{\mathrm{calcd.}}$ | 2.632 | 2.636 | 2.627 |
| Ga–$X_{\mathrm{exp.}}$ | 2.4126(10) | 2.6010(5) | 1.830(3), 1.824(3) |
| Ga–$X_{\mathrm{calcd.}}$ | 2.381 | 2.601 | 1.838 |
| | 2.394 | 2.601 | 1.833 |
| Ga–Sb–Sb$_{\mathrm{exp.}}$ | 90.92(3) | 89.69() | 92.24(2), 88.31(2) |
| Ga–Sb–Sb$_{\mathrm{calcd.}}$ | 87.0 | 89.7 | 89.3 |
| | 91.4 | 89.8 | 94.6 |
| Sb–Ga–$X_{\mathrm{exp.}}$ | 116.79(3) | 116.21() | 117.87(9), 110.26(10) |
| Sb–Ga–$X_{\mathrm{calcd.}}$ | 110.1 | 111.7 | 118.0 |
| | 116.1 | 111.7 | 116.9 |

The HOMO in the halide-substituted distibenes, which is located on the Ga–Sb–Sb–Ga motif, is dominated by contributions from the Sb=Sb double bond ($p_x$ and $p_y$ orbitals of the central Sb atoms). In addition, it shows a small contribution from the Ga–$X$ σ orbitals, as derived from Löwdin orbital populations. The LUMO is centered on both Sb atoms in all cases and is an almost exclusive representation of the Sb=Sb π* orbitals (Figure 4). The calculated HOMO-LUMO gap energies of **1** (274 kJ·mol$^{-1}$), **2** (281 kJ·mol$^{-1}$) and **3** (279 kJ·mol$^{-1}$) correspond to light absorption of 425–437 nm, which explains the observed yellow to green color of the compounds and which agree to the π–π* absorption bands observed for **1** and **2**.

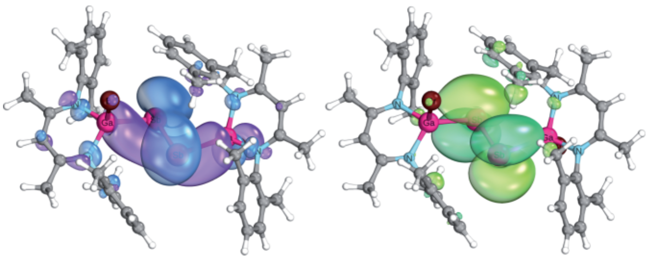


**Figure 4.** Exemplary HOMO (left) and LUMO (right) of **1**.

The charge distribution in the $[\mathrm{Ga}(X)\mathrm{Sb}]_2$ unit is mainly influenced by the halide substituent ($X$). As was expected, the natural charge of the halide atoms increases with their electronegativity values (F: –0.76 *e*, Cl: –0.52 *e*, Br: –0.50 *e*, I: –0.40 *e*), resulting in a higher positive charge at the central gallium atom (F: 1.48 *e*, Cl: 1.18 *e*, Br: 1.14 *e*, I: 1.03 *e*). As a result, the charge at the Sb atom becomes more negative (F: –0.15 *e*, Cl: –0.13 *e*, Br: –0.10 *e*, I: –0.10 *e*). This is also reflected in the polarization of the Sb–Ga bond. The polarization of the bond towards the central Sb atom increases in the order 59, 60, 62, and 63 % from I to F, in conjunction with the increasing electronegativity of the halide. On the other hand, the electronic character of the Sb–Sb and Sb–Ga bonding orbitals is not largely influenced by the halide substituent $X$. The Sb σ bonds have almost 90 % and the π bond 99 % p character in all cases. The Sb lone-pairs also have a constant 76–78 % s character.

The bond polarization of the Sb–O bond and the orbital characters in **3** fall between the values of the F and Cl substituted molecules, as was expected from the electronegativity and steric demand of the OEt substituent. Only the charge of the central oxygen atom is more negative (–0.96 *e*) than the corresponding F (–0.76 *e*), since it can withdraw electron density not only from the Ga but also from the adjacent C atom.

## Conclusions

Distibenes containing a Sb=Sb double bond can generally be synthesized by reaction of two equivalents of LGa with antimony trihalides Sb$X_3$ ($X$ = Br, I) and triethoxide $\mathrm{Sb(OEt)_3}$. The reactions proceed with insertion of two gallandiyls into two Sb–$X$ bonds, followed by elimination of LGa$X_2$ and $\mathrm{LGa(OEt)_2}$, respectively, and formation of $[\mathrm{L}(X)\mathrm{GaSb}]_2$ [$X$ = Br (**1**), I (**2**), OEt (**3**)]. Comparable reactions were previously observed between L$M$ ($M$ = Al, Ga) and $EX_3$ and $E(\mathrm{NR_2})_3$ ($E$ = As, Sb, Bi; $X$ = halide), hence this reaction pathway offers a general route to metal-substituted dipnictogenes of the general type $[\mathrm{L}(X)ME]_2$.[17] Quantum chemical calculations with these complexes are currently performed to prove if the L($X$)Ga substituents only serve as kinetically stabilizing (sterically demanding) ligand or if dispersion interactions between the ligands, as was recently reported for main group element compounds,[32] also lead to a stabilization of such molecules.

## Experimental Section

**General Procedures:** All manipulations were performed using Schlenk-line and glove-box techniques in a purified argon atmosphere. Toluene and hexane were obtained after passing these solvents through activated alumina columns with an MBraun Solvent Purification System. Deuterated NMR solvents were dried with potassium, purified by distillation, stored over activated molecular sieves (4 Å) and degassed prior to use. Karl Fischer titration of the dry solvents show values less than 3 ppm. LGa[18] was prepared according to literature methods, whereas $\mathrm{SbBr_3}$ and $\mathrm{SbI_3}$ were obtained from commercial sources. $\mathrm{Sb(OEt)_3}$ was prepared by literature method.[33] Table S1 (Supporting

Information) summarizes the $^1$H NMR values of the side-products LGa$X_2$ ($X$ = Cl, Br, I) in $C_6D_6$.

**Instrumentation:** $^1$H (300 and 500 MHz) and $^{13}$C{1H} (75.5 MHz) NMR spectra ($\delta$ in ppm) were recorded with a Bruker Avance DPX-300 spectrometer and the spectra were referenced to internal $C_6D_5H$ ($^1$H: $\delta$ = 7.154; $^{13}$C: $\delta$ = 128.39 ppm) and $C_6D_5CHD_2$ ($^1$H: $\delta$ = 2.09; $^{13}$C: $\delta$ = 20.40 ppm). Microanalyses were performed at the Elemental Analysis Laboratory of the University of Duisburg-Essen. IR spectra were measured with an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. UV/Vis spectra were recorded with a Varia Carry 300. The melting points were measured with a Thermo Scientific 9300 apparatus.

**General Procedure for the Synthesis of 1 and 2:** LGa (100 mg, 0.205 mmol) and Sb$X_3$ ($X$ = Br, 23.4 mg, 0.103 mmol; I 23.4 mg, 0.103 mmol) were dissolved in 2 mL of toluene in a Schlenk tube and stirred at room temperature for 2 d. The solution was concentrated in vacuo and 2 mL of hexane were added. Yellowish-green crystals of **1** and **2**, which were formed upon storage at ambient temperature, were isolated by filtration and recrystallized from toluene solution to afford pure form of **1** and **2**.

**[L(Br)GaSb]$_2$ (1):** Yield: 44 mg (65 %). Mp.: 239 °C (dec.). $C_{58}H_{82}N_4Br_2Ga_2Sb_2$ (M = 1378.15 g·mol$^{-1}$): calcd. C 50.55 H 6.00 N 4.07 %; found: C 49.95 H 6.07 N 4.24 %; found: C 49.5 H 6.22 N 3.16 %. **$^1$H NMR** ($C_6D_6$, 300 MHz, 25 °C): $\delta$ = 7.12–6.92 (m, 12 H, C$_6$*H*$_3$–2,6-*i*Pr$_2$), 5.00 (s, 2 H, $\gamma$-C*H*), 3.98 [sept, $^3J_{H,H}$ = 6.7 Hz, 4 H, C*H*(CH$_3$)$_2$], 3.05 [sept, $^3J_{H,H}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.63 (s, 12 H, ArNCC*H*$_3$), 1.40 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 1.20 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 1.12 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 0.99 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$]. **$^{13}$C NMR** ($C_6D_6$, 75 MHz, 25 °C): $\delta$ = 169.3 (ArNCCH$_3$), 146.3 (*C*$_6$H$_3$), 142.7 (*C*$_6$H$_3$), 141.2 (*C*$_6$H$_3$), 125.6 (*C*$_6$H$_3$), 124.2 (*C*$_6$H$_3$), 98.4 ($\gamma$-*C*H), 29.74 [*C*H(CH$_3$)$_2$], 28.2 [*C*H(CH$_3$)$_2$], 28.2 [CH(*C*H$_3$)$_2$], 25.9 [CH(*C*H$_3$)$_2$], 24.9 [CH(*C*H$_3$)$_2$], 24.5 [CH(*C*H$_3$)$_2$], 24.1 (ArNC*C*H$_3$). **IR**: $\tilde{\nu}$ = 3060, 3018, 2962, 2923, 2864, 1150, 1518, 1460, 1437, 1385, 1360, 1316, 1289, 1258, 1173, 1100, 1018, 935, 862, 794, 771, 756, 712, 635, 523, 441 cm$^{-1}$. **UV/Vis** (toluene): $\lambda$ ($\varepsilon$) = 355 (41280), 437 nm (5377 M$^{-1}$·cm$^{-1}$).

**[L(I)GaSb]$_2$ (2):** Yield: 49 mg (67 %). Mp.: 173 °C (dec.). $C_{58}H_{82}N_4I_2Ga_2Sb_2$ (M = 1472.12 g·mol$^{-1}$): calcd. C 47.13 H 6.00 N 3.79 %; found: C 47.02 H 5.87 N 3.59 %; found: C 48.0 H 5.92 N 3.59 %. **$^1$H NMR** ($C_6D_6$, 300 MHz, 25 °C): $\delta$ = 7.12–6.99 (m, 12 H, C$_6$*H*$_3$–2,6-*i*Pr$_2$), 5.06 (s, 2 H, $\gamma$-C*H*), 4.04 [sept, $^3J_{H,H}$ = 6.7 Hz, 4 H, C*H*(CH$_3$)$_2$], 3.05 [sept, $^3J_{H,H}$ = 6.7 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.62 (s, 12 H, ArNCC*H*$_3$), 1.42 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 1.21 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 1.14 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 0.97 [d, 12 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$]. **$^{13}$C NMR** ($C_6D_6$, 75 MHz, 25 °C): $\delta$ = 169.4 (ArNCCH$_3$), 146.4 (*C*$_6$H$_3$), 142.9 (*C*$_6$H$_3$), 141.2(*C*$_6$H$_3$), 125.8 (*C*$_6$H$_3$), 124.3 (*C*$_6$H$_3$), 98.8 ($\gamma$-*C*H), 29.7 [*C*H(CH$_3$)$_2$], 29.6 [*C*H(CH$_3$)$_2$], 28.4 [CH(*C*H$_3$)$_2$], 25.0 [CH(*C*H$_3$)$_2$], 24.6 [CH(*C*H$_3$)$_2$], 24.6 [CH(*C*H$_3$)$_2$], 24.2 (ArNC*C*H$_3$). **IR**: $\tilde{\nu}$ = 3060, 3018, 2962, 2922, 2864, 1551, 1519, 1460, 1437, 1385, 1360, 1312, 1286, 1234, 1174, 1098, 1057, 1018, 981, 936, 862, 794, 770, 756, 710, 635, 524, 500, 438 cm$^{-1}$. **UV/Vis** (toluene): $\lambda$ ($\varepsilon$) = 354 (31949), 436 nm (2656 M$^{-1}$·cm$^{-1}$).

**[L(EtO)GaSb]$_2$ (3):** RGa (0.116 g, 0.239 mmol) and Sb(OEt)$_3$ (0.031 g, 20 µL, 0.119 mmol) were dissolved in 0.5 mL of *n*-hexane and stirred at ambient temperature for 2 h to yield a yellow-brown solution, which was heated at 70 °C for 1 h to ensure the reaction completion. Cooling to ambient temperature and storage for 2 h yielded pale yellow crystals, which were isolated by filtration. Twofold recrystallization from solutions in *n*-hexane (0.5 mL) at room temperature finally yielded pure **3**. M. p. 216–217 °C. Yield 42 mg (0.032 mmol, 54 %). $C_{62}H_{92}N_4O_2Ga_2Sb_2$: calcd. C 56.92; H 7.09; N 4.28 %; found: C 56.97; H 7.03; N 4.31 %. **$^1$H NMR** ($C_6D_6$, 300 MHz, 25 °C): $\delta$ = 7.14–6.92 (m, 12 H, C$_6$*H*$_3$-2,6-*i*Pr$_2$), 4.83 (s, 2 H, $\gamma$-C*H*), 4.03 [sept, $^3J_{H,H}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$], 3.90 [quartet, $^3J_{H,H}$ = 6.9 Hz, 4 H, OC*H*$_2$CH$_3$], 3.01 [sept, $^3J_{H,H}$ = 6.6 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.63 (s, 12 H, ArNCC*H*$_3$), 1.40 [d, 12 H, $^3J_{H,H}$ = 6.6 Hz, CH(C*H*$_3$)$_2$], 1.38 (triplet, $^3J_{H,H}$ = 6.6 Hz, 6 H, OCH$_2$C*H*$_3$), 1.30 [d, 12 H, $^3J_{H,H}$ = 6.9 Hz, CH(C*H*$_3$)$_2$], 1.05 [d, 24 H, $^3J_{H,H}$ = 6.6 Hz, CH(C*H*$_3$)$_2$]. **$^{13}$C NMR** ($C_6D_6$, 75 MHz, 25 °C): $\delta$ = 168.71 (ArN*C*CH$_3$), 145.61, 142.88, 142.49, 127.10, 124.98, 124.23 (*C*$_6$H$_3$), 97.68 ($\gamma$-*C*H), 63.15 (O*C*H$_2$CH$_3$), 29.10 [*C*H(CH$_3$)$_2$], 27.76 [*C*H(CH$_3$)$_2$], 26.03 [CH(*C*H$_3$)$_2$], 25.20 [CH(*C*H$_3$)$_2$], 25.01 [CH(*C*H$_3$)$_2$], 24.70[CH(*C*H$_3$)$_2$], 24.30 (ArNC*C*H$_3$), 21.30 (OCH$_2$*C*H$_3$). **IR** (neat): $\tilde{\nu}$ = 2954, 2925, 2861, 2837, 1558, 1528, 1464, 1441, 1394, 1318, 1260, 1172, 1108, 1061, 1020, 938, 904, 857, 792, 757, 606, 530, 436 cm$^{-1}$. **UV/Vis** (toluene): $\lambda$ ($\varepsilon$) = 354 nm (16760 M$^{-1}$·cm$^{-1}$).

**Single Crystal X-ray Diffraction:** Crystallographic data of **1** to **3**, which were collected with a Bruker AXS D8 Kappa diffractometer with APEX2 detector (Mo-$K_\alpha$ radiation, $\lambda$ = 0.71073 Å) at 296(2) K (**1**) and 100(2) K (**2**, **3**), are summarized in Table S1 (Supporting Information). The solid-state structures of **1** to **3** are shown in Figure 1, Figure 2, and Figure 3, bond lengths and angles of **1** to **3** are summarized in Table 2. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on $F^2$ (SHELXL-2016).[34,35] 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 crystals of **1** cracked and lost crystallinity upon cooling. Consequently, the measurement was done at room temperature. Unfortunately, the grease used to mount the crystal was not viscous enough and the crystal slipped during the measurement. As a result, only part of the obtained frames could be successfully integrated, and the completeness of the data set is low.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1827131 (**1**), CCDC-1827132 (**2**), and CCDC-1837837 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**Supporting Information** (see footnote on the first page of this article): A CIF file giving X-ray crystallographic data of **1** and **2**, $^1$H NMR spectra of LGa$X_2$ ($X$ = Cl, Br, I) as well as spectroscopic details ($^1$H, $^{13}$C NMR. IR, UV/Vis) and crystallographic details of **1**–**3**.

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**Keywords:** Gallium; Antimony; Multiple bonds; X-ray diffraction

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*J. Krüger, J. Schoening, C. Ganesamoorthy, L. John, C. Wölper, S. Schulz** ........................................................ **1–8**

Synthesis and X-ray Crystal Structures of Ga-substituted Distibenes [L(*X*)GaSb]$_2$