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ARTICLE

Synthesis and Structure of Gallaarsenes LGaAsGa(X)L featuring a Ga–As Double Bond

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Three equivalents of LGa {L = HC[C(Me)N(2,6-*i*-$Pr_2C_6H_3$)]$_2$} react with AsX_3 by insertion into two As–X bonds, elimination of $LGaX_2$, and formation of LGaAsGa(Cl)L (**1**) and LGaAsGa(Br)L (**2**). According to single crystal X-ray analysis, **1** and **2** each exhibit one Ga–As single bond and one Ga–As double bond. The π-bonding contribution (9.71 kcal/mol **1**; 9.71 kcal/mol **2**) was proven by temperature variable (VT) ^{1}H NMR spectroscopy, while the electronic structure of **1'** was studied by quantum chemical calculations.

Introduction

The number of p-block element compounds containing π-bonds typically decreases with increasing atomic number within each group. This observation was explained by the so-called "*double bond rule*",[1] which is often addressed to the weak π-bond interaction of heavier main group elements due to poor p-orbital overlap. Luckily, substantial progress has been made over the past years to develop fundamental concepts for the electronic and/or kinetic stabilization of heavy main group element compounds which feature multiple bonding or delocalized π-bonding contribution.[2]

A large number of stable homonuclear group 14 compounds with π-bonding interaction have been prepared since the initial report by West and co-workers on the synthesis of Mes_4Si_2 (Mes = 2,4,6-Me_3-C_6H_2), which represents the first organosilicon compound with a Si–Si double bond that was stable under ambient conditions[3]. Heteronuclear group 13/15 compounds with π-bonding contributions which are stable at ambient conditions were almost limited to monomeric amino- and phosphinoboranes $R_2EBR'_2$ (E = N, P),[4] as well as iminoboranes RNBR',[5] whereas π-bonded compounds of the even heavier elements remained almost unknown. The electronic structures of such compounds were investigated to some extent by quantum chemical calculations,[6] however structurally characterizable compounds were limited to (base-stabilized) boron-pnicogen compounds[7] and iminometallanes RMNR' (M = Al, Ga, In; type **A** and **B**) (Scheme 1).[8] Monomeric metallapnictenes of the general type RMER' (M = Al–Tl; E = N–Bi) tend to form head-to-tail adducts due to the presence of Lewis acidic and Lewis basic centres, hence they easily dimerize ([RMER']$_2$), trimerize ([RMER']$_3$) or oligomerize to form heterocyclic (x = 2, 3) or cage-type complexes [RMER']$_x$ (x > 4).[9] Sterically demanding substituents, which kinetically stabilize the monomeric unit (type **A**), as well as the addition of a Lewis base and/or Lewis acid, which coordinates with the existing Lewis acidic (M) and/or Lewis basic side (E), are both utilized to suppress oligomerization reactions.[10] Moreover, coordination of the group 13 metal by an N,N'-chelating β-diketiminate ligand, which results in an increase of the coordination number, was shown to effectively stabilize compounds with π-bonding contribution (type **B**).

Scheme 1. Structurally characterized group 13/15 compounds with π-bonding contributions.

Despite the progress that has been made within the last decades in the stabilization of π-bonded compounds of even heavier main group elements, the number of stable group 13/15 compounds containing a double bond is still low. To the best of our knowledge, LGaAsCp* **C**,[11] which was recently synthesized in our group by reacting Cp*$AsCl_2$ with two equivalents of LGa, as well as [{Li(thf)$_3$}$_2$Ga$_2${As(Si*i*Pr$_3$)}$_4$] **D**[12] represents the only structurally characterized gallaarsenes containing a Ga–As π-bond. In addition, we recently reported on the synthesis and solid state structures of a series of gallastibenes LGaSbGa(X)L of type **E** (X = F, Cl, Br, I),[13,14] as well as LGaSbTer **F** (Ter = 2,6-Mes_2-C_6H_3, Mes = 2,4,6-Me_3-C_6H_2),[15] which are the only structurally characterized compounds with Ga-Sb π-bonds. Gallastibenes of type **E** are generally accessible by reactions of SbX_3 with three equivalents of LGa,[14] and LGaSbGa(Cl)L was also formed by a single electron reduction reaction of the stibanyl radical L(Cl)Ga)$_2$Sb· with KC_8 (Scheme 1).[13] In contrast, reactions of LGa with EX_3 (X = halide, amide NR_2, alkoxide OR) in a 2:1 molar ratio yielded Ga-substituted dipnictenes of the general type [L(X)GaE]$_2$ containing As–As, Sb–Sb, and Bi–Bi double bonds,[16] respectively. These compounds

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are largely stabilized by dispersion interactions as shown by quantum chemical calculation.[17]

The synthesis of LGaSbGa(Cl)L **E** by reactions of three equivalents of LGa with SbX_3 prompted our interest to re-investigate reactions of LGa with AsX_3, hence we herein report on the synthesis of two gallaarsenes LGaAsGa(X)L **E** (X = Cl **1**, Br **2**). **1** and **2** were spectroscopically characterized in solution, while the solid-state structure of **1** was determined by single crystal X-ray analysis. In addition, the structure and electronic nature of the bonding interaction in **1'** was also investigated by quantum chemical calculations.

Results and discussion

Synthesis and characterization of 1 and 2 in solution.

Reactions of three equivalents of LGa[18] with AsX_3 at ambient temperature yielded LGaAsGa(X)L (X = Cl **1**, Br **2**). ^1H NMR spectroscopy studies proved that the reactions occur with double insertion of LGa into two As-X bonds, followed by elimination of $LGaX_2$ and formation of **1** and **2**, which were isolated as dark red, crystalline solids (Scheme 2). The insertion of LGa into the As-X bond can be described as an oxidative addition of AsX_3 to a monovalent gallanediyl LGa, similar to what has been observed by Braunschweig and co-workers in reactions of $AsCl_3$ with Pt(0) complexes PtL_2, yielding trans-$[PtCl(AsCl_2)L_2]$ complexes.[19] Oxidative addition reactions of E-Cl bonds of the heavier homologues (E = Sb, Bi) to Pt(0) centers were also reported.[20]

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

1 and **2** are air- and moisture-sensitive compounds. While **2** is reasonably soluble in both coordinating (THF, Et_2O) and non-coordinating solvents (*n*-hexane, benzene, toluene), the solubility of **1** in these solvents is rather limited. Both compounds can be stored as isolated crystalline solids as well as in solution in benzene under argon atmosphere for weeks without any sign of decomposition. The ^1H NMR spectra of **1** and **2** at ambient temperature each show only one set of resonances for both β-diketiminate substituents: singlet resonances for the γ-CH proton (4.84 ppm (**1**); 4.90 ppm (**2**)) and both Me groups (4.18 ppm (**1**); 1.50 ppm (**2**)), as well as one septet for the methine protons (3.16 ppm (**1**); 3.21 ppm (**2**)) and two doublets (1.18, 1.10 ppm (**1**); 1.26, 1.11 ppm (**2**)) for the methyl protons of the *i*-Pr groups, respectively. The ^{13}C spectra are in accordance with ^1H spectra and also show only one set of resonances for both β-diketiminate substituents. Comparable findings were previously reported for the Sb analogues LGaSbGa(X)L.[13,14] Since the two β-diketiminate ligands in both **1** and **2** are in principle magnetically inequivalent, these findings point to dynamic processes in solution. Cooling solutions of **1** and **2** in toluene-d_8 to –80 °C forms two well-separated γ-CH resonances for the two β-diketiminate ligands (Figs. S4, S8) with a maximum peak separation of 18 Hz (**1**) and 36 Hz (**2**), respectively. Two different processes are likely: halide anion exchange reaction between the Ga atoms or the rotation around the Ga–As double bond. Experimentally we can't distinguish between both processes. However, since any attempt to generate the corresponding cation $[LGaEGaL]^+$ (E = As, Sb) by halide abstraction reaction only proceeded with complete decomposition of the compounds, we believe that the rotation around the Ga–As double bond is more likely. The rotation energy ($\Delta G^{\neq}$ was calculated to 9.71 kcal mol^{-1} (**1**) and 9.44 kcal mol^{-1} (**2**),[21] which agree very well with the π-bonding contribution reported for LGaAsCp* (9.65 kcal mol^{-1})[11] and LGaSbGa(X)L **E** ($\Delta G^{\neq}$ = 9.56 kcal mol^{-1} (x = Cl); 9.35 (x = Br)),[13,14] whereas a slightly stronger π-bond was reported for $PhP(GaTrip_2)_2$ ($\Delta G^{\neq}$ = 10.2 kcal mol^{-1}, Trip = 2,4,6-*i*-$Pr_3C_6H_2$).[22] As observed for gallastibenes of type **E**, the *i*-Pr groups in **1** and **2** also split into three signals with a relative intensity of 1:1:2.

Solid state structure of 1.

Dark red crystals of **1** and **2** were obtained from solutions of **1** and **2** in *n*-hexane after storing for two days at ambient temperature. Compound **1** crystallizes in the triclinic space group *P*-1 while **2** in the monoclinic space group $P2_1/n$, each with one molecule in the asymmetric unit. The Ga(1)–As(1) and Ga(2)–As(1) bond lengths in **1** and **2** each differ by almost 9 pm (**1**: Ga(2)–As(1) 2.2628(5) Å; Ga(1)–As(1) 2.35033(4) Å; **2** Ga(2)–As(1) 2.2591(11) Å; Ga(1)–As(1) 2.3580(11) Å), clearly proving the presence of a Ga–As single bond and a Ga–As double bond. The Ga(1)–As(1) double bonds in **1** and **2**, which represent the shortest Ga–As bond ever reported, are almost identical to the Ga–As double bond lengths recently reported for two independent molecules observed in the crystal of LGaAsCp* (2.2671(2), 2.2702(2) Å).[11] These values are well below the sum of the calculated covalent double-bond radii (Ga 2.17 Å, As 1.14 Å),[23] clearly proving the π-bonding contribution in **1** and **2**, but compare very well to calculated Ga–As bond lengths in HGaAsR (R = H, 2.245 Å, 2.272 Å; Me, 2.251 Å) and XGaAsH (X = F, 2.283 Å; Cl, 2.282 Å; Br, 2.284 Å; I, 2.285 Å), respectively.[24] In contrast, the Ga–As bond in the dianion $[Ga_2\{As(Si\textit{i}Pr_3)\}_4]^{2-}$ **D** (2.318(1) Å)[12] is 6 pm longer, and the intramolecularly base-stabilized diarsadigalletane $[t\text{-}BuGaAsC_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]_2$, which forms a four-membered ring without any (p-p)π bonding contribution, shows significantly longer Ga–As bonds of 2.457(3) Å.[25] This bond is even longer than the Ga(1)–As(1) single bond in **1** (2.3503(4) Å) and **2** (2.3580(11) Å).

Figure 1. Solid state structure of **1** including selected bond lengths (Å) and angles (°). Displacement ellipsoids are displayed at 50% probability levels. Second orientation of the disorder and hydrogen atoms omitted for clarity; As(1)–Ga(2) 2.2628(5), As(1)–Ga(1) 2.3503(4), Cl(1)–Ga(1) 2.2783(9), Ga(1)–N(2) 1.977(2), Ga(1)–N(1) 1.983(2), Ga(2)–N(3) 1.922(3), Ga(2)–N(4) 1.957(2), Ga(2)–As(1)–Ga(1) 111.419(19), N(2)–Ga(1)–N(1) 94.04(10), N(2)–Ga(1)–As(1) 107.88(7), N(1)–Ga(1)–As(1) 117.33(7), N(3)–Ga(2)–N(4) 95.54(11), N(3)–Ga(2)–As(1) 150.79(8), N(4)–Ga(2)–As(1) 110.96(7).

Figure 2. Solid state structure of **2** including selected bond lengths (Å) and angles (°). Displacement ellipsoids are displayed at 50% probability levels. Hydrogen atoms omitted for clarity; The model contains unresolvable twinning problems thus quantitative results may be unreliable. As(1)–Ga(2) 2.2591(11), As(1)–Ga(1) 2.3580(11), Br(3)–Ga(1) 2.3986(11), Ga(1)–N(2) 1.994(6), Ga(1)–N(1) 2.020(6), Ga(2)–N(3) 1.910(6), Ga(2)–N(4)

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1.957(6), Ga(2)–As(1)–Ga(1) 113.37(4), N(2)–Ga(1)–N(1) 94.4(2), N(2)–Ga(1)–As(1) 105.31(18), N(1)–Ga(1)–As(1) 120.12(17), N(2)–Ga(1)–Br(3) 103.96(18), N(1)–Ga(1)–Br(3) 101.29(17), As(1)–Ga(1)–Br(3) 126.18(4), N(3)–Ga(2)–N(4) 95.4(2), N(3)–Ga(2)–As(1) 153.88(17), N(4)–Ga(2)–As(1) 110.32(19).

The Ga(1)–As(1) single bonds in **1** and **2** are also substantially shorter compared to those found in four-membered heterocycles of the type $[R_2GaAsR'_2]_x$ (av. 2.541(15) Å)[26] and the six-membered heterocycles $[Me_2GaAs(i\text{-}Pr)_2]_3$ [2.498(2)-2.531(2) Å],[27] $[H_2GaAs(SiMe_3)_2]_3$ [2.4695(8)-2.4831(8) Å],[28] $[Br_2GaAs(CH_2SiMe_3)_2]_3$ [2.432(2)-2.464(1) Å].[29] $t\text{-}Bu_2GaAs(t\text{-}Bu)_2$, which is the only structurally characterized monomeric gallaarsane, also exhibits a roughly 10 pm longer Ga–As single bond (2.466(3) Å).[30] These structural findings most likely originate from the lower coordination number (2) of the As atom in **1** and **2** compared to those in the monomeric (3) and heterocyclic (4) compounds. The Ga(1)–As(1)–Ga(2) bond angles (111.42(2)° **1**, 113.37(4) **2**) are comparable to the Ga–As–C bond angles observed for **C** (110.92(5)°, 111.00(4)°) as well as the Ga–Sb–Ga bond angles in compounds of type **E**, which range from 107.37(1)° to 113.18(1)°,[13,14] whereas the Si(1)–As(1)–Ga bond angle (103.34(6)°) observed in **D** was slightly smaller.[11] The $Ga(2)N_2C_3$ metallacycles in **1** and **2** are almost planar (rms deviation from best plane 0.067 Å (**1**) and 0.054 (**2**)), whereas the $Ga(1)N_2C_3$ metallacycles significantly deviate from planarity (rms deviation from best plane 0.158 Å (**1**) and 0.155 Å (**2**)) due to the increased coordination number of the Ga atoms (4 vs. 3). The N(1)–Ga(1)–N(2) angles of 94.03(2)° (**1**) and 94.4(2)° (**2**) are slightly smaller than the N(3)–Ga(2)–N(4) angles of 95.55(2)° (**1**) and 95.4(2)° (**2**). The Ga(2) atoms adopt almost perfect trigonal-planar coordination spheres with the sums of bond angles $\Sigma\varphi(Ga)$ being 357.3° (**1**) and 359.6° (**2**); these values further indicate significant Ga-As π-bonding contribution.

Quantum chemical calculations.

To gain a deeper understanding in the electronic structure of the gallaarsenes, we computed the key geometries of **1'** utilizing density functional theory (DFT) approaches as implemented in the ORCA quantum chemistry package (version 4.0).[31] We first anchored our computational level with experiment by comparing the computed structures of **1** with that found by crystallography. DFT geometry optimized structures of **1′** (Cartesian coordinates summarized in Table S4) showed only very small differences in the central Ga(1)–As(1) (2.3503(4) Å **1**; 2.366 Å **1'**), Ga(2)–As(1) (2.2628(5) Å **1**; 2.259 Å **1'**), Ga(1)–Cl(1) (2.2783(9) Å **1**; 2.231 Å **1'**), Ga(1)–N(1/2) (1.983(2), 1.977(2) Å **1**; 2.004, 2.005 Å **1'**) and Ga(2)–N(3/4) bond lengths (1.922(3), 1.957(2)Å **1**; 1.962, 1.935 Å **1'**) as well as the Ga(1)–As(1)–Ga(2) bond angles (111.419(19)° **1**; 111.43° **1'**), respectively.

Natural bond orbital (NBO) analysis of **1'**, which was performed using the NBO 6.0 program,[32] reveals that the As(1)–Ga(2) σ-bonding orbital is composed of a nearly sp hybridized orbital at the Ga atom and a 85% p-character orbital at the As atom. An almost exclusive p-character (99%) of the π-bonding orbital at both elements and a Mayer bond order of 1.70 lead to the assumption of a covalent double bond. The σ-bond is slightly polarized towards the As atom (64%), while the π-bond is strongly (86%) polarized. Both orbitals are populated by 1.89 and 1.88 electrons, respectively. As expected, the As atom carries a more negative natural charge of −1.05 (vs. −0.70) in comparison to the Sb analogues[13,14] due to its enhanced electronegativity, which leads to an increased bond polarization towards As. The HOMO of **1** (Fig. 3) corresponds to the As(1)–Ga(2) π-bond, which is mainly localized along the bond axis with its core area on the As atom, and the two opposite lobes over and under the Ga–As–Ga plane.

Figure 3. HOMO and LUMO of **1'**.

Experimental

General procedures.

Argon gas was dried by passing the gas through pre-heated Cu_2O pellets and molecular sieves columns. The reactions were carried out using Schlenk and glove-box techniques. Toluene and *n*-hexane were passed through the columns of MBraun Solvent Purification System and collected in J-Young Schlenk flasks and stored under argon atmosphere. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. LGa (L = $HC[C(Me)N(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$)[18] was prepared according to literature methods, while $AsCl_3$ and $AsBr_3$ were commercially available and freshly distilled and degassed prior to use.

Materials and methods.

^1H (300 MHz; 600 MHz) and $^{13}C\{^1H\}$ (75.5 MHz; 150.9 MHz) NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer or a Bruker Avance III HD spectrometer and referenced to internal C_6D_5H (^1H: δ = 7.16; ^{13}C: δ = 128.06) or $C_6D_5CD_2H$ (^1H: δ = 2.08; ^{13}C: δ = 20.43).[33] IR spectra were recorded in a glovebox using an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Microanalyses were performed at the elemental analysis laboratory of University of Duisburg-Essen.

Crystallography.

The crystals of **1** and **2** were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (monochromatic $Mo_{K\alpha}$ radiation, λ = 0.71073 Å) at 100(2) K. The structures were solved by Direct Methods[34] and refined anisotropically by full-matrix least-squares on F^2.[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. As, Cl and a diisopropylphenyl (dipp) rest in **1** are disordered over two positions. The corresponding bond lengths of the two orientations of the dipp group were restrained to be equal (SADI). The residual density near a second dipp group suggests a disorder but refinement of the second orientation failed. The site occupations factor obtained in the attempts were < 10%.

The crystal of **2** was non-merohedrally twinned and an integration with two orientation matrices was attempted. The best results yielded a high percentage of unobserved reflections. The resulting model showed improved *R*-values

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($R1$=0.0688, $wR2$=0.1528), slightly lower residual electron density (still in unexpected places) and more reasonable weighting scheme. However, the resulting adp were unrealistic and in some cases anisotropic refinement was impossible even with standard ISOR restraints. Neither model will give reliable quantitative results and any conclusions beyond the connectivity should be carefully scrutinised.

Quantum chemical calculations.

All quantum chemical calculations were employed with the ORCA quantum chemistry package (version 4.0).[31] Ground-state geometry optimizations were calculated with the PBE0 functional[36], the def2-SVP basis set on all C and H atoms and the def2-TZVP basis set on As, Ga, Cl and N.[37] The atom-pairwise dispersion correction with Becke-Johnson damping scheme (D3BJ)[38] was used to account for dispersion interactions. The RIJCOSX approximation was utilized to accelerate the calculations in conjunction with the appropriate auxiliary basis sets (def2/J).[39] Natural bond orbital analysis was performed using the NBO 6.0 program.[32] Vibrational frequency calculations were conducted to determine whether the optimized geometries are local minima on the potential energy surface.

Synthesis of LGaAsGa(Cl)L (1).

A solution of LGa (200 mg, 0.411 mmol) and $AsCl_3$ (24.8 mg, 0.137 mmol) in toluene (2.5 mL) was stirred for 2 days to yield a dark red solution and a bright green solid $(LGa(Cl)As)_2$. $(LGa(Cl)As)_2$ was filtered and all volatiles were removed *in vacuo*. The resulting residue was dissolved in *n*-hexane (1.3 mL) and stored at ambient temperature for several hours, to crystallize $LGaCl_2$. After the filtration, the mother liquor was dissolved in *n*-hexane (0.3 mL) again to afford **1** as dark red crystals. Yield: 25 mg (0.023 mmol, 17 %). M.p. 242 °C. Anal. Calcd. for $C_{58}H_{82}AsClGa_2N_4$: C, 64.20; H, 7.62; N, 5.16. Found: C, 62.70; H, 7.67; N, 4.95 %. IR (neat): ν 3061, 2959, 2923, 2864, 1524, 1435, 1368, 1318, 1255, 1175, 1088, 1019,931 859, 791, 757, 703, 636, 527, 439 cm^{-1}. ^1H NMR (toluene-d_8, 25 °C, 300 MHz): δ 7.05 (m, 12 H, aromatic H of Dipp group), 4.84 (s, 2 H, γ-C*H*), 3.16 (sept, $^3J_{HH}$ = 6.83 Hz, 8 H, $CH(CH_3)_2$), 1.48 (s, 12 H, $NCCH_3$), 1.18 (d, $^3J_{HH}$ = 6.72 Hz, 24 H, $CH(CH_3)_2$), 1.10 (d, $^3J_{HH}$ = 6.78 Hz, 24 H, $CH(CH_3)_2$). ^{13}C NMR (toluene-d_8, 25 °C, 75.5 MHz): δ 168.7 ($NCCH_3$), 143.9, 142.1 (C_6H_3), 127.4, 124.5 (C_6H_3), 98.2 (γ-CH), 29.2 ($CH(CH_3)_2$), 26.3, 24.6 ($CH(CH_3)_2$), 24.5 ($NCCH_3$).

Synthesis of LGaAsGa(Br)L (2).

A solution of LGa (185 mg, 0.381 mmol) and $AsBr_3$ (40 mg, 0.127 mmol) in toluene (3.5 mL) was stirred for 10 days to yield a red solution and a bright green solid $(LGa(Br)As)_2$. $(LGa(Cl)As)_2$ was filtered and all volatiles were removed *in vacuo*. The resulting residue was dissolved in *n*-hexane (1.4 mL) and stored at ambient temperature for 2l hours, to crystallize $LGaBr_2$. After the filtration, the mother liquor was dissolved in n-hexane (0.3 mL) again to afford **2** as red crystals. Yield: 16 mg (0.013 mmol, 10 %). M.p. 229 °C. Anal. Calcd. for $C_{58}H_{82}AsBrGa_2N_4$: C, 61.67; H, 7.32; N, 4.95. Found: C, 60.20; H, 7.32; N, 4.44 %. IR (neat): ν 3059, 2964, 2924, 2865, 1525, 1436, 1384, 1315, 1258, 1175, 1104, 1055, 1018, 936, 870, 795, 757, 637, 530, 441 cm^{-1}. ^1H NMR (benzene-d_6, 25 °C, 300 MHz): δ 7.13 (m, 12 H, aromatic H of Dipp group), 4.90 (s, 2 H, γ-C*H*), 3.21 (sept, $^3J_{HH}$ = 6.70 Hz, 8 H, $CH(CH_3)_2$), 1.50 (s, 12 H, $NCCH_3$), 1.26 (d, $^3J_{HH}$ = 6.70 Hz, 24 H, $CH(CH_3)_2$), 1.11 (d, $^3J_{HH}$ = 6.80 Hz, 24 H, $CH(CH_3)_2$). ^{13}C NMR (benzene-d_6, 25 °C, 75.5 MHz): δ 168.9 ($NCCH_3$), 144.0, 142.2 (C_6H_3), 127.5, 124.8 (C_6H_3), 98.4 (γ-CH), 29.3 ($CH(CH_3)_2$), 26.7, 24.8 ($CH(CH_3)_2$), 24.7 ($NCCH_3$). UV/Vis (toluene): $\lambda(\varepsilon)$ = 351 nm (16395 $M^{-1}\cdot cm^{-1}$).

Conclusions

Two gallaarsenes LGaAsGa(X)L (X = Cl **1**, Br **2**) were synthesized by reactions of three equivalents of LGa with AsX_3. This reaction sequence has now established a general method for the synthesis of gallaarsenes and -stibenes of the desired type. **1** and **2** exhibit the shortest Ga–As bond lengths ever reported, which are roughly 5 pm shorter than the sum of the calculated covalent double-bond radii (2.31 Å). The π-bonding contributions of **1** and **2** were furthermore estimated by VT-NMR spectroscopy (9.71 kcal mol^{-1} **1**, 9.44 kcal mol^{-1} **2**). These findings undoubtedly prove the formation of Ga=As double bonds in **1** and **2**, which is also supported by results from quantum chemical calculations only to reveal substantial π-bonding contribution in **1'**.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ CCDC-1834971 (**1**) and CCDC-1958056 (**2**) contain the supplementary crystallographic data for this paper. These 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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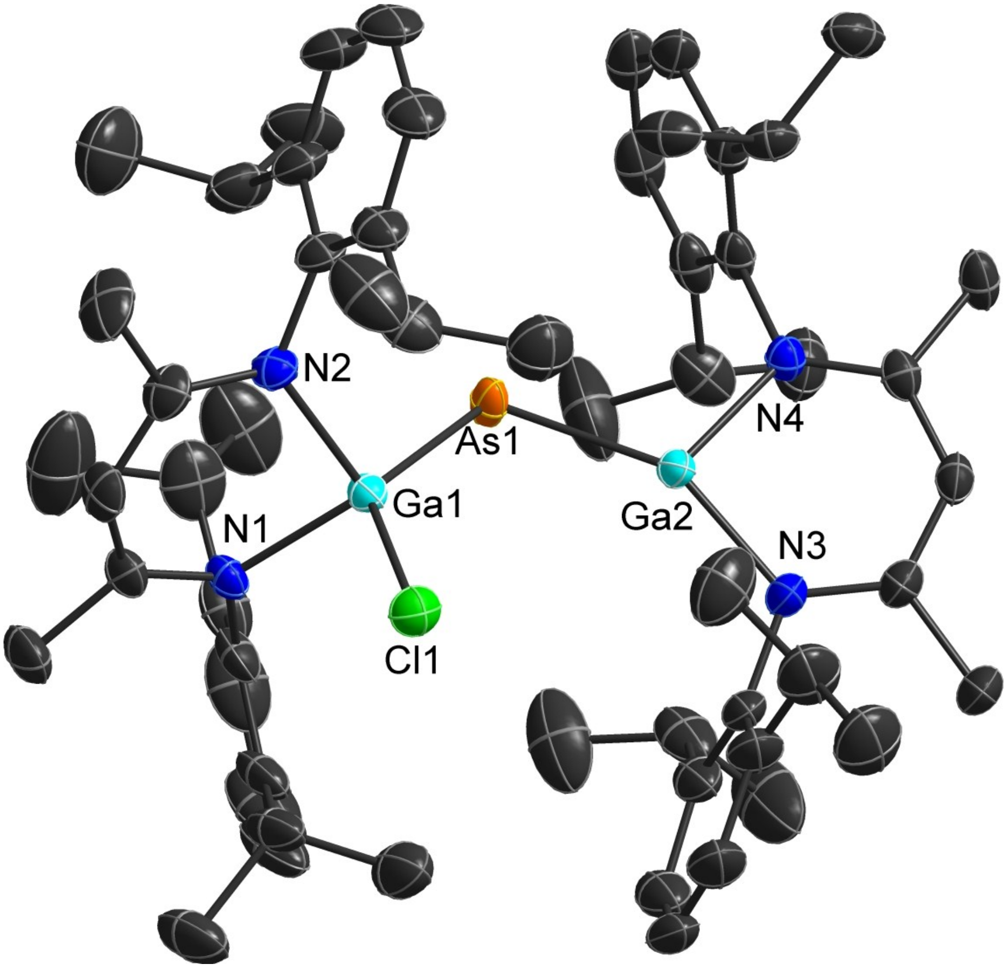

Figure 1. Solid state structure of 1 including selected bond lengths (Å) and angles (°). Displacement ellipsoids are displayed at 50% probability levels. Second orientation of the disorder and hydrogen atoms omitted for clarity; As(1)–Ga(2) 2.2628(5), As(1)–Ga(1) 2.3503(4), Cl(1)–Ga(1) 2.2783(9), Ga(1)–N(2) 1.977(2), Ga(1)–N(1) 1.983(2), Ga(2)–N(3) 1.922(3), Ga(2)–N(4) 1.957(2), Ga(2)–As(1)–Ga(1) 111.419(19), N(2)–Ga(1)–N(1) 94.04(10), N(2)–Ga(1)–As(1) 107.88(7), N(1)–Ga(1)–As(1) 117.33(7), N(3)–Ga(2)–N(4) 95.54(11), N(3)–Ga(2)–As(1) 150.79(8), N(4)–Ga(2)–As(1) 110.96(7).

905x868mm (96 x 96 DPI)

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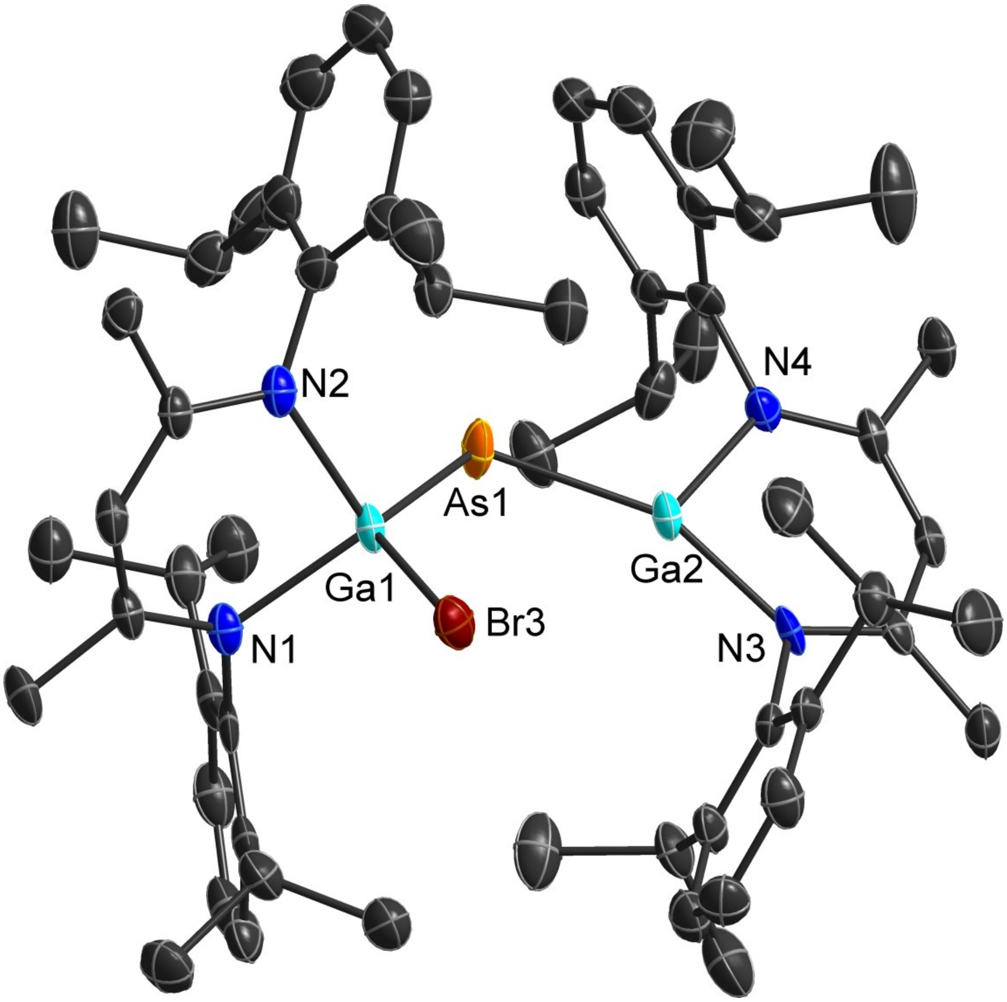

Figure 2. Solid state structure of 2 including selected bond lengths (Å) and angles (°). Displacement ellipsoids are displayed at 50% probability levels. Hydrogen atoms omitted for clarity; The model contains unresolvable twinning problems thus quantitative results may be unreliable. As(1)–Ga(2) 2.2591(11), As(1)–Ga(1) 2.3580(11), Br(3)–Ga(1) 2.3986(11), Ga(1)–N(2) 1.994(6), Ga(1)–N(1) 2.020(6), Ga(2)–N(3) 1.910(6), Ga(2)–N(4) 1.957(6), Ga(2)–As(1)–Ga(1) 113.37(4), N(2)–Ga(1)–N(1) 94.4(2), N(2)–Ga(1)–As(1) 105.31(18), N(1)–Ga(1)–As(1) 120.12(17), N(2)–Ga(1)–Br(3) 103.96(18), N(1)–Ga(1)–Br(3) 101.29(17), As(1)–Ga(1)–Br(3) 126.18(4), N(3)–Ga(2)–N(4) 95.4(2), N(3)–Ga(2)–As(1) 153.88(17), N(4)–Ga(2)–As(1) 110.32(19).

877x872mm (96 x 96 DPI)

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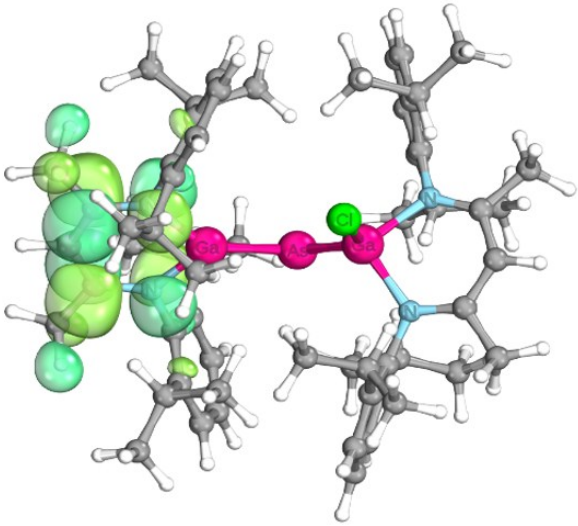
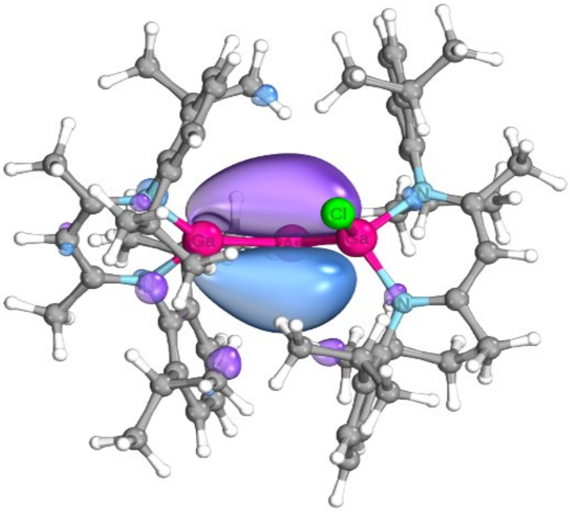


LUMO



HOMO

Figure 3. HOMO and LUMO of 1'.

97x185mm (150 x 150 DPI)

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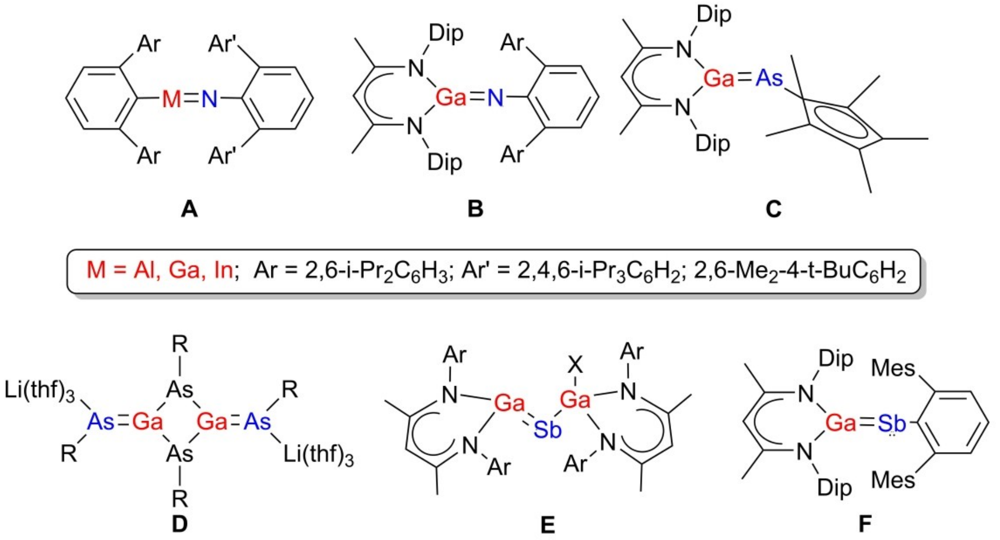

Scheme 1. Structurally characterized group 13/15 compounds with π-bonding contributions.

1289x706mm (96 x 96 DPI)

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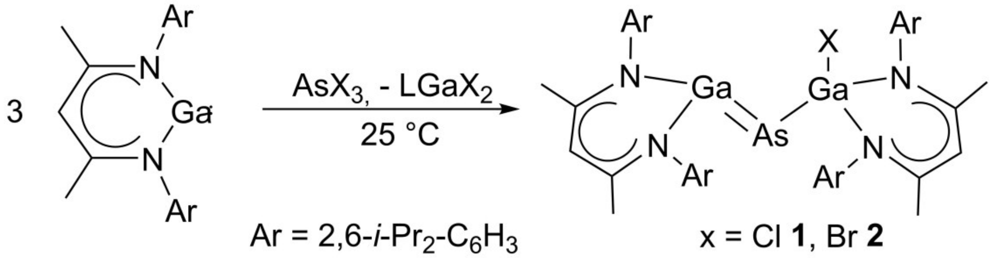

Scheme 2. Synthesis of 1 and 2

973x265mm (96 x 96 DPI)