stacking interactions.[11] In fact, it is plausible that one or more of these factors may be active in achieving efficient and selective replication. Full details will be published elsewhere.

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$[\{Li(thf)_3\}_2Ga_2\{As(Si\mathit{i}Pr_3)\}_4]$—A Compound with Gallium–Arsenic Double Bonds**

Carsten von Hänisch* and Oliver Hampe

The synthesis of molecular compounds with multiple bonds between the heavier main-group elements is still a preparative challenge for the inorganic chemist. While various symmetric compounds with multiple bonds between two heavier atoms of Group 13 or 15 were synthesized in the last years,[1–3] most of the asymmetric compounds with multiple bonds between Group 13 and 15 elements contain one atom of the 2nd period of the periodic table.[3] Power and co-workers recently published compounds with aluminum– or gallium–nitrogen multiple bonds,[4] and compounds with boron–phosphorus and boron–arsenic double bonds $[Mes_2B{=}ER\{Li(thf)_3\}]$ (**1a**: E = P, R = $SiMe_3$; **1b**: E = As, R = Ph; Mes = mesityl) have also been described.[5] Partial multiple-bond character between the heavier elements of Group 13 and 15, however, can be observed in the ternary phases $Cs_6M_2E_4$ (M = Al, Ga; E = P, As) or in the molecular compounds $[\mathit{t}Bu_2GaPMes^*(SiPh_3)]$ and $[MesP\{Ga(Trip)_2\}_2]$ (Trip = 2,4,6-$\mathit{i}Pr_3C_6H_2$; Mes* = 2,4,6-$\mathit{t}Bu_3C_6H_2$).[6, 7] In contrast, multiple bonding between the heavier Group 13 and 15 elements can be excluded in the cyclic compounds $[RMER']_n$ (M = Al, Ga; E = P, As; R, R′ = alkyl, aryl; $n = 2$, 3), because of the ring folding and the pyramidal coordination of the phosphorus and arsenic atoms.[8] Molecular compounds with double bonds between gallium and arsenic are unknown to date.

We could synthesize the compound $[\{Li(thf)_3\}_2Ga_2\{As(Si\mathit{i}Pr_3)\}_4]$ (**2**) containing two As–Ga double bonds from the reaction of $GaCl_3$ with $Li_2AsSi\mathit{i}Pr_3$ [Eq. (1)].

$$2\,GaCl_3 + 4\,Li_2AsSi\mathit{i}Pr_3 \xrightarrow{\text{THF/heptane}} [\{Li(thf)_3\}_2Ga_2\{As(Si\mathit{i}Pr_3)\}_4]\ (\mathbf{2}) + 6\,LiCl \qquad (1)$$

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with two formula units per unit cell (Figure 1).[9] The central structural motive of **2** is a planar Ga_2As_2 four-membered ring with two further exocyclic As atoms bound to the Ga atoms. Each As atom is bonded to a tri(isopropyl)silyl group and each of the exocyclic As atoms is additionally bound to one $Li(thf)_3$ fragment.

The angular sum at the Ga atoms comes to 359.8(1)° thus, the coordination of these atoms is essentially trigonally planar. However, the As-Ga-As angles differ, the endocyclic As(1)-Ga-As(1′) angle is 98.36(3)°, and the As(1)-Ga-As(2) and As(1′)-Ga-As(2) angles are 121.51(4) and 139.90(4)°, respectively. The considerable difference between the exocyclic angles can be explained by the mutual repulsion of the neighboring $\mathit{i}Pr_3Si$ groups on As(1′) and As(2). The Li–As

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[*] Dr. C. von Hänisch, Dr. O. Hampe
Institut für Nanotechnologie
Forschungszentrum Karlsruhe
Postfach 3640, 76021 Karlsruhe (Germany)
Fax: (+49) 7247-82-6368
E-mail: carsten.vonhaenisch@int.fzk.de

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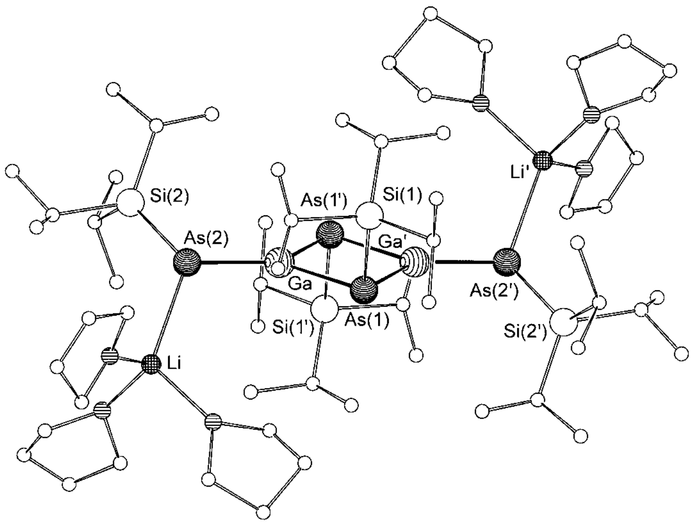

Figure 1. Molecular structure of **2**, selected bond lengths [pm] and bond angles [°]: Ga-As(1) 247.3(1), Ga-As(1′) 243.6(1), Ga-As(2): 231.8(1), As(1)-Si(1) 235.1(2), As(2)-Si(2) 231.3(2), As(2)-Li 260.6(2), Li-O 192.3(13)–200.6(15); As(1)-Ga-As(1′) 98.36(3), As(1)-Ga-As(2) 121.51(4), As(1′)-Ga-As(2) 139.90(4), Si(1)-As(1)-Ga 103.34(6), Si(1)-As(1)-Ga′ 110.45(6), Ga-As(1)-Ga′ 81.64(3), Si(2)-As(2)-Ga 107.99(6), Si(2)-As(2)-Li 121.4(3), Ga-As(2)-Li 113.8(3).

bond length (260.6(2) pm) which is slightly shorter than in **1b** (267.0(9) pm) and similar to the Li–As distance in [{(dme)-LiAs(SiMe$_3$)$_2$}$_2$] (259(2) pm; dme = 1,2-dimethoxyethane). In the latter compound the As atoms have a coordination number of four and the Li atoms are in bridging positions.[10]

Because of the electron deficiency at the Ga atoms and the lone pair at the arsenic centers the resonance structures **A** and **B** appear plausible for **2** (Figure 2). Whereas dative (p–p) π bonds in the Ga$_2$As$_2$ ring appear impossible because of the pyramidal coordination at As(1) and As(1′) (the angular sum at these atoms is 295.4(2)°). This situation is further reflected in the As(1)–Ga bond length of 245.5 pm (mean) which is at the lower end of the range for Ga–As single bonds (243–260 pm).[11] In contrast the As(2)–Ga bond is only 231.8 pm long. The angular sum at As(2) is with 343.2(1)° remarkably large and the As(1′)-Ga-As(2)-Si(2) torsion angle is only 14.6°. These values are in good agreement with the assumption of a dative (p–p) π overlap (resonance formula **B**). In **1a** the torsion angle for example is 23.15°, in **1b** the angular sum at the As atom is 341.4°.[5] The As–Li vector in **2** as well as in **1b** points out of the molecule plane; however, it has to be considered that the Li–As interaction is mainly of electrostatic nature. This ionic nature of the bond between the arsenic and the lithium atom is further confirmed by theoretical investigations of the similar boron–phosphors compound H$_2$B=PHLi.[12]

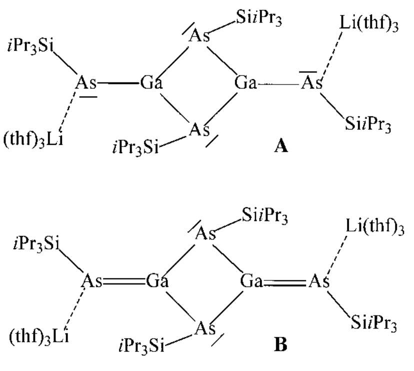

Figure 2. Resonance structures of **2**.

Ionic interactions between the negatively polarized As atom and the positively polarized gallium center have to be considered, too (resonance formula **A**). However, the observed drastic bond shortening can not be explained by these interactions alone. Overall the bonding description of **2** is closer to resonance form **B** than to form **A**. The sterically demanding and electropositive Si and Li substituents on As(2) facilitate this Ga–As π bonding by reducing the inversion barrier at the exocyclic As atoms.

Compound **2** can be formally separated into a [Ga$_2$(AsSi*i*Pr$_3$)$_4$]$^{2-}$ ion and two [Li(thf)$_3$]$^+$ ions. To support this ionic picture we performed electrospray mass spectrometry[13] and obtained the mass spectrum shown in Figure 3 upon adding a small amount of [12]crown-4 (probably acting as an Li$^+$-ion scavenger) to a THF solution of **2**. All the peaks observed in the mass spectrum were assigned as in Table 1. All the ion peaks are consistent with the picture that the ion [Ga$_2$(AsSi*i*Pr$_3$)$_4$]$^{2-}$ is unstable and undergoes rapid intermolecular reactions as well as partial hydrolysis with traces of water (possibly from the extremely hygroscopic crown ether). The most prominent ion peak corresponds to the singly charged [Ga$_2$(AsSi*i*Pr$_3$)$_5$H$_3$]$^-$ ion (peak II) around *m*/*z* 1303. Interestingly, the presence of peaks III and IIIa suggests the

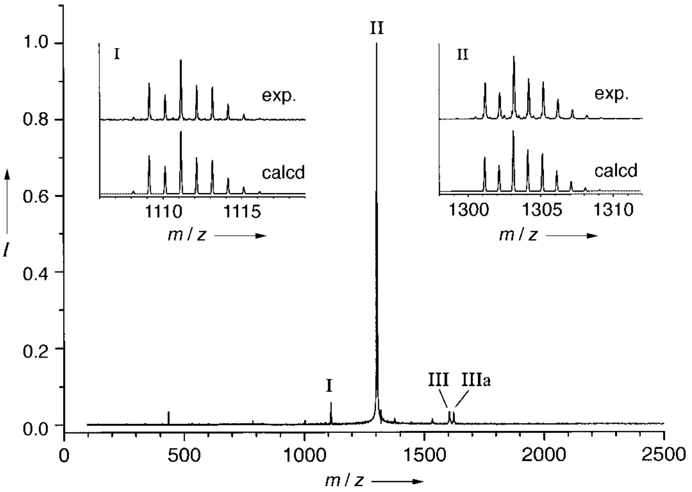

Figure 3. Negative-ion electrospray FT-mass spectrum of **2** (Insets: Comparison of experimentally observed and simulated isotope patterns).

Table 1. Assignment of negative ion mass peaks.

Peak	*m*/*z* found	*m*/*z* calcd	Ion
I	1111.14	1111.15	[Ga$_2$Li(AsSi*i*Pr$_3$)$_4$H$_4$O$_2$]$^-$
II	1303.18	1303.18	[Ga$_2$(AsSi*i*Pr$_3$)$_5$H$_3$]$^-$
III	1605.21	1605.16	[Ga$_3$(AsSi*i*Pr$_3$)$_6$H$_2$]$^-$
IIIa	1623.19	1623.17	[Ga$_3$(AsSi*i*Pr$_3$)$_6$H$_4$O)]$^-$

formation of a higher aggregate possibly with a spiro-like Ga_3As_6 unit with two four-membered rings connected by one central Ga atom.

The $[Ga_2(AsSi\mathit{i}Pr_3)_4]^{2-}$ ion shows a structural relationship with the Zintl ion $[Ga_2As_4]^{6-}$, which is contained in the ternary phase $Cs_6Ga_2As_4$.[6] This anion also has the shape of a Ga_2As_2 four-membered ring with two further exocyclic As atoms bonded to the Ga atoms. The exocyclic As–Ga bonds of the $[Ga_2As_4]^{6-}$ ions are 234.3 pm long, which is much shorter than usual for As–Ga single bonds, and suggests multiple-bond character. Because of the particular coordination numbers and conditions in this solid-state Zintl phase a comparison with the bonding situation in **2** is impossible. However, the $[Ga_2(AsSi\mathit{i}Pr_3)_4]^{2-}$ ion in **2** can be seen as a silyl derivative of the $[Ga_2As_4]^{6-}$ ion. Thus, **2** can be regarded as the first example of a silylated binary Zintl anion. So far only silylated Zintl anions of phosphorus and $[As_7(SiMe_3)_3]$ have been reported.[14]

Experimental Section

2: A butyllithium solution (1.6 M; 3.55 mL, 5.68 mmol) was added to a solution of $H_2AsSi\mathit{i}Pr_3$ (0.66 g, 2.84 mmol)[15] in THF (5 mL) of at 0 °C. After stirring for 1 h, this solution was added to a –50 °C solution of $GaCl_3$ (0.25 g, 1.42 mmol; 99.99 %) in heptane (20 mL). The reaction mixture was allowed to warm to room temperature and then stirred for additional 24 h. The resulting red solution was filtered to remove the precipitated LiCl. Subsequently this solution was reduced to about 10 mL in vacuo. After two days large orange crystals of **2** formed. Yield: 0.37 g (34 %); elemental analysis (%) calcd for $C_{60}H_{132}As_4Ga_2Li_2O_6Si_4$ (1515.0): C 47.57, H 8.78; found: C 45.77, H 8.24; ^{1}H NMR ([D$_6$]benzene): $\delta = 3.720$ (m, 12 H, $(CH_2C\mathit{H}_2)_2O$), 1.593 (m, 21 H, *i*Pr) 1.540 (m, 12 H, $(C\mathit{H}_2CH_2)_2O$), 1.449 pm (m, 21 H, *i*Pr); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): $\delta = 68.7$ (s, $(CH_2\mathit{C}H_2)_2O$), 25.7 (s, $(\mathit{C}H_2CH_2)_2O$), 21.3 (s, $\mathit{C}H_3$), 20.5 (s, $\mathit{C}H_3$), 16.5 (s, $\mathit{C}H$), 15.6 pm (s, $\mathit{C}H$); $^{29}Si\{^1H\}$ NMR ([D$_6$]benzene): $\delta = 26.7$ pm (br); UV/Vis (suspension in mineral oil): $\lambda_{max} = 410$ nm (sh), 270 nm.

ESI-FTMS: Mass spectra were taken in a Fourier-Transform Ion Cyclotron Resonance Mass Spectrometer (Bruker Daltonics, APEX II) equipped with an electrospray source (Analytica of Branford).

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[9] STOE-IPDS, Schneider-rotating anode, graphite monochromator, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; **2**: $a = 1124.8(2)$, $b = 2430.4(5)$, $c = 1487.1(3)$ pm, $\beta = 99.99(3)^\circ$, $V = 4003.8(14) \times 10^6$ pm^3; monoclinic, $P2_1/n$, $Z = 2$, $\rho_{calcd} = 1.146$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.408$ mm^{-1}, $T = 200$ K, $2\Theta_{max} = 46^\circ$; 19418 reflections measured, 5525 independenr reflections, ($R_{int} = 0.0414$), 4787 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2, 290 parameters (As, Ga, Si, O, Li atoms refined aniosotropically, C atoms refined isotropically with split positions, the positions of H atoms where not determind), $R1 = 0.0620$, $wR2 = 0.1942$ (all data), residual electron density: 0.575 e Å^{-3}. CCDC-174606 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Total Synthesis of Woodrosin I**

Alois Fürstner,* Fabien Jeanjean, and Patrick Razon

Plants belonging to the *Convovulacaeae* family are rich sources of alkaloids and resin glycosides. Although intriguingly complex in detail, the latter invariably contain (11*S*)-hydroxyhexadecanoic acid (jalapinolic acid) as a common aglycon, which is usually tied back to form a characteristic macrolide ring that spans two or more sugar units of their oligosaccharide backbones.[1] The biological functions and physiological properties of resin glycosides are far from fully understood; however, diverse and promising effects have been described for some of these compounds, for example,

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[*] Prof. A. Fürstner, Dr. F. Jeanjean, Dr. P. Razon
Max-Planck-Institut für Kohlenforschung
45470 Mülheim/Ruhr (Germany)
Fax: (+49) 208-306-2994
E-mail: fuerstner@mpi-muelheim.mpg.de

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