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Synthesis of the first diarsadigalletane

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Abstract

The diarsadigalletane [^{t}BuGaAsC$_6$H$_3$(CH$_2$NMe$_2$)$_2$] (1) has been prepared by treatment of [^{t}BuGaCl$_2$]$_2$ with Li$_2$AsC$_6$H$_3$(CH$_2$NMe$_2$)$_2$ in Et$_2$O solution. One of the Me$_2$N groups of each (Me$_2$NCH$_2$)$_2$C$_6$H$_3$ ring is coordinated to each of the gallium atoms in the As$_2$Ga$_2$ ring. Compound **1** is air and moisture stable.

Currently, compound semiconductors such as gallium arsenide and indium phosphide are prepared by thermolysis of Group 13 trialkyl/Group 15 trihydride mixtures [1]. The heightened interest in alternative precursors to III–V (Group 13–15) compound semiconductors stems not only from the desire to employ less toxic compounds, but also to achieve lower deposition temperatures and more precise control of stoichiometry. In particular, there has been a drive toward "single-source precursors" that feature prevenient bonds between the Group 13 and 15 elements [2]. To date, emphasis has been placed on dimers and trimers of empirical composition $R_2GaAsR'_2$ which feature thermally labile substituents R and R′ [2,3]. We now describe the synthesis and characterization of the first (intramolecularly base-stabilized) diarsadigalletane, $(RGaAsR')_2$.

A suspension of Li$_2$As[(Me$_2$NCH$_2$)$_2$C$_6$H$_3$] was prepared by addition of 5.5 mL of ^{t}BuLi (1.7 *M* in hexane) to a cooled (−78°C) solution of [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$] AsH$_2$ [4] (1.25 g, 4.66 mmol) in 25 mL of Et$_2$O. After allowing the stirred yellow suspension to warm to room temperature, it was added dropwise to a cooled (−78°C) solution of [^{t}BuGaCl$_2$]$_2$ [5] (0.92 g, 4.66 mmol of monomer) in 30 mL of Et$_2$O. The reaction mixture was allowed to warm to 25°C and was stirred for an additional 5 h at this temperature. After removal of the solvent and volatiles under vacuum, the resulting light yellow residue was extracted with 40 mL of toluene. Filtration, concentration, and cooling (−20°C) of this solution afforded light yellow crystalline **1** (m.p. 247–249°C) in 55% yield.

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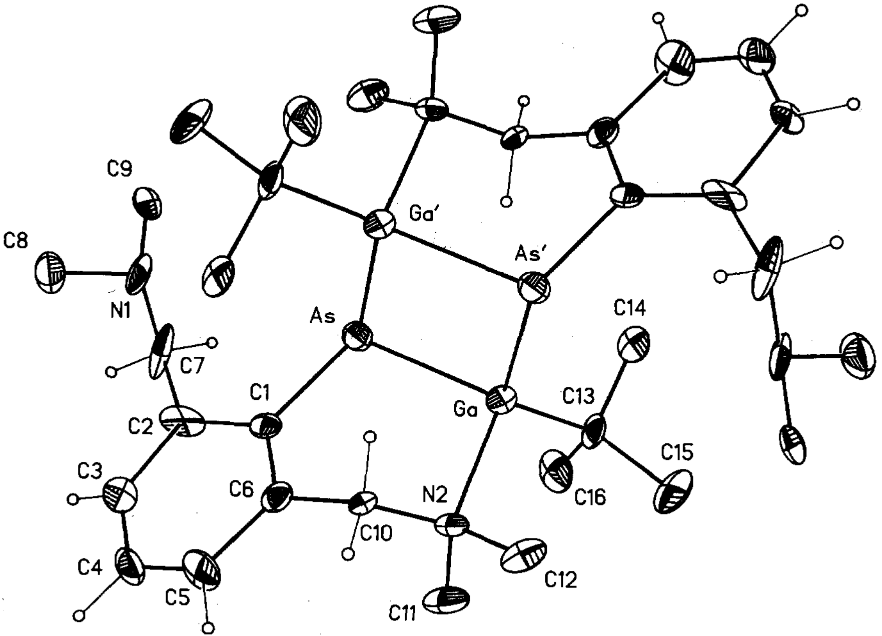

Fig. 1. ORTEP view of the structure of 1. Important bond distances (Å) and angles (deg): Ga–As, 2.457(3); Ga–N(2), 2.18(2); Ga–C(13), 2.00(2); As–C(1), 1.94(2); C(13)–Ga–As, 120.0(7); N(2)–Ga–As, 100.3(5); C(13)–Ga–N(2), 111.1(9); C(10)–N(2)–Ga, 108(1); As'–Ga–As 98.75(12); As'–Ga–C(13) 123.0(7); As'–Ga–N(2) 99.8(5); C(1)–As–Ga 104.2(6); Ga'–As–C(1) 108.7(6); Ga'–As–Ga 81.25(11).

The CI-mass spectrum of 1 * is consistent with a dimeric formulation, $[^tBuGaAs(\{Me_2NCH_2\}_2C_6H_3)]_2$. Moreover, the ^1H NMR spectrum * indicates the presence of equal abundances of ^tBu and $(Me_2NCH_2)_2C_6H_3$ substituents. However, note that although the ^tBuGa protons are equivalent, the Me_2N groups are non-equivalent and appear in relative abundances 1 : 1 : 2. A plausible structure for 1 therefore involves one coordinated and one free Me_2NCH_2 moiety for each aryl ring. Such a view is consistent both with the $^{13}C\{^1H\}$ spectral data * and with the observation that pairs of meta ring carbons and C–H protons are non-equivalent. Doubts remain, however, regarding connectivity since the coordinated Me_2N groups could be attached to either gallium or arsenic. An X-ray analysis was therefore undertaken. Unfortunately, crystals of 1 diffract X-rays very weakly. Nevertheless, after several attempts we were able to collect a set of diffraction data of mediocre quality.

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* MS (+CI, CH_4): 786 (M^+), 729 ($M^+ - {}^tBu$), 539 ($M^+ - {}^tBu - (Me_2NCH_2)_2C_6H_3$), 393 ($M^+/2$), 266 $[\{(Me_2NCH_2)_2C_6H_3\}As]$, 191 ($(Me_2NCH_2)_2C_6H_3$), 57 ($^tBu$). HRMS (+CI, CH_4): calcd: 784.14485, exp: 784.14450. ^1H NMR (300.15 MHz, 298 K, C_6D_6): $\delta = 1.03$ (s, 18H, $(CH_3)_3CGa$), 1.80 (s, 6H, $(CH_3)_2N$), 2.34 (s, 12H, $(CH_3)_2N$), 2.66 (s, 6H, $(CH_3)_2N$), 2.93 (d, 2H, CH_2N, $J = 12.6$ Hz), 3.84 (d, 2H, CH_2N, $J = 13.5$ Hz), 4.37 (d, 2H, CH_2N, $J = 13.5$ Hz), 4.56 (d, 2H, CH_2N, $J = 12.3$ Hz), 6.66 (d, 2H, *meta*-H, $J = 6.6$ Hz). 7.02 (t, 2H, *para*-H, $J = 7.5$ Hz), 7.64 (d, 2H, *meta*-H, $J = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, 298 K, C_6D_6): $\delta = 27.1$ (s, (CGa), 31.2 ($(CH_3)_3CGa$), 31.4 ($(CH_3)_2N$), 45.9 ($(CH_3)_3N$), 48.5 ($(CH_3)_2N$), 66.5 (CH_2N), 72.7 (CH_2N), 124.5 (*ipso*-C), 129.5 (*ortho*-C), 131.1 (*ortho*-C), 139.5 (*meta*-C), 145.4 (*meta*-C), 147.4 (*para*-C).

Crystal data: $C_{32}H_{56}N_4As_2Ga_2$, $M = 786.10$, monoclinic, space group $P2_1/n$, $a = 7.952(7)$, $b = 12.428(5)$, $c = 18.394(6)$ Å, $U = 1817(3)$ Å^3, $D_c = 1.44$ g cm^{-3}, $Z = 2$, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu(\text{Mo-}K_\alpha) = 33.14$ cm^{-1}. A total of 2902 reflections was collected on an Enraf Nonius CAD-4 diffractometer with 2θ between 2 and 50° using the $\theta/2\theta$ scan mode. The data were corrected for decay and Lorentz-polarization effects. The structure was solved by Patterson methods and refined (full-matrix least-squares) using 2040 reflections having $i > 6.0\sigma(I)$. The final R and R_w values were 12.24 and 14.10% respectively. The X-ray analysis indicates that individual molecules of **I** reside on a center of inversion (Fig. 1) and that there are no unduly short intermolecular contracts. As a consequence of the site symmetry the four-membered arsenic-gallium ring is planar. The intra-ring bond angles at As and Ga are 81.25(11) and 98.75(12)° respectively. One of the Me_2N groups of each $(Me_2NCH_2)_2C_6H_3$ ring is coordinated to each of the Ga atoms; the other is uncoordinated. Since each Ga is tetracoordinate, the geometry is approximately tetrahedral. Note, however, that there are considerable distortions from the ideal tetrahedral value, the angles ranging from 98.75(12) (As'–Ga–As) to 123.0(7) (As'–Ga–C(13)). The geometry at As is also tetrahedral thus indicating the sterochemical activity of the lone pair and implying little or no circumannular $p\pi$–$p\pi$ bonding in the As_2Ga_2 ring. This conclusion is borne out by the As–Ga bond distance (2.454(5) Å) which is close to the sum of single bond covalent radii for As and Ga (2.46 Å [6]). Evidently such π-type interactions are thwarted in **1** by the presence of strong intramolecular N → Ga dative bonds. This same feature is presumably responsible for the observation that the diarsadigalletane is stable to air and moisture. The Ga–N(2) bond distance in **1** (2.18(2) Å) is comparable to those in adducts such as $Me_3Ga \cdot NH_2(^tBu)$ (2.12(1) Å [7]) and $^tBu_3Ga \cdot NH_2Ph$ (2.246(9) Å [8]).

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