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Preliminary Communication

Synthesis and structure of $[\overline{(\mathrm{CH_2})_4\mathrm{Ga}}\text{-}\mu\text{-}\mathrm{As^tBu_2}]_2$. The first example of a gallacyclopentane

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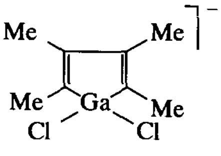
Abstract

The first gallacyclopentane, $[\overline{(\mathrm{CH_2})_4\mathrm{Ga}}\text{-}\mu\text{-}\mathrm{As^tBu_2}]_2$ (**4**) has been synthesized in 61% yield by treatment of $\mathrm{Li(CH_2)_4Li}$ with $\mathrm{Cl_2GaAs^tBu_2}$ in $\mathrm{Et_2O}$ solution. The structure of **4** has been established by X-ray crystallography: monoclinic, space group *I* 2/*m* (No. 12) with $a = 8.624(6)$, $b = 11.389(12)$, $c = 14.921(13)$ Å, $\beta = 95.330(10)°$, and $Z = 4$ (monomeric units).

Key words: Gallium; Arsenic; Cyclopentane; Crystal structure

Gallium-arsenic compounds of the type $[\mathrm{R_2GaAsR'_2}]_n$ (R = R′ = alkyl) have attracted attention as single-source precursors for chemical beam epitaxy of gallium arsenide films [1,2]. Vapor-phase pyrolysis studies [3] of $[\mathrm{Me_2Ga}\text{-}\mu\text{-}\mathrm{As^tBu_2}]_2$ (**1**) and $[\mathrm{Et_2Ga}\text{-}\mu\text{-}\mathrm{As^tBu_2}]_2$ (**2**) at 10^{-2} Torr revealed that Me and Et ligand loss occurred at 700 K and 600–625 K respectively. This ≈ 100 K difference in Ga–alkyl bond cleavage temperature could be ascribed to facile loss of $\mathrm{C_2H_4}$ via a β-hydride shift mechanism in the case of **2**. However, since the order of radical stability is ethyl > methyl, it is plausible that Ga–C bond homolysis could play an important or even dominant role in the thermolysis of **2**. Since the β-hydride shift process has been shown to be inhibited in tetramethylene metallacycles [4], it was relevant to attempt the preparation of a GaAs precursor featuring a $\overline{(\mathrm{CH_2})_4\mathrm{Ga}}$ moiety. A second reason for undertaking the present work concerns the paucity of information on gallacycles. In fact, the only previous gallacycle of which we are aware is the gallate **3** which has not been structurally characterized [5]. Herein we describe the synthesis and X-ray crystal structure determination of **4**, the first gallacyclopentane.



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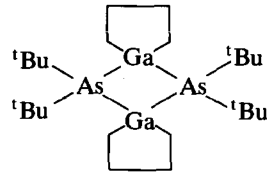

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An intermediate of empirical composition $[\mathrm{Cl_2GaAs^tBu_2}]_n$ was prepared *in situ* by the addition of 49 ml of a 0.10 M solution of $\mathrm{LiAs^tBu_2}$ (4.9 mmol) in $\mathrm{Et_2O}$ to a suspension of $\mathrm{GaCl_3}$ (0.87 g, 4.9 mmol) in $\mathrm{Et_2O}$ at −78°C. The stirred solution was allowed to warm slowly to 25°C, and after 2 h at this temperature it was re-cooled to −78°C and 19.6 ml of a 0.25 M (4.9 mmol) solution of $\mathrm{Li(CH_2)_4Li}$ in $\mathrm{Et_2O}$ [6] was added via syringe. The mixture was warmed slowly, then stirred at ambient temperature for several hours. The solution was then filtered, the solvent and volatiles were removed, and the residue was dissolved in toluene. Slow cooling of this solution to −25°C produced 0.94 g (3.0 mmol, 61% yield) of white crystals of **4** (m.p. 288–291°C).

The dimeric formulation $[\mathrm{(CH_2)_4GaAs^tBu_2}]_2$ is consistent with the CI mass spectrum which exhibits a parent peak at m/e 630. Moreover, the ^{1}H and ^{13}C{^{1}H} NMR spectra are also in accord with the above formulation. The presence of a $\overline{\mathrm{Ga(CH_2})_4}$ gallacycle was suggested by the presence of a AA′BB′ spin system in the ^{1}H spectrum. *

In order to provide more detailed structural information, an X-ray crystal structure determination of **4** was carried out. ** Like other dimers of the type $[\mathrm{R_2Ga}\text{-}\mu\text{-}\mathrm{AsR'_2}]$ [7], **4** features a rhombic $\mathrm{Ga_2As_2}$ core (Fig. 1) and there are no unduly short intermolecular contacts. It is of interest to compare the structure of **4** with those of the acyclic analogues, $[\mathrm{R_2Ga}\text{-}\mu\text{-}\mathrm{As^tBu_2}]_2$ (R = Me [8], Et [9], ^{n}Bu [8]). The incorporation of

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* ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz): δ 1.38 (s, 18H, $\mathrm{As^tBu_2}$), 1.96 (t, 4H, $\mathrm{C}H_2$–C–Ga), 1.00 (t, 4H, $\mathrm{C}H_2$–Ga). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 75.5 MHz): δ 39.75 (C–As), 32.79 ($\mathrm{CH_3}$), 30.28 (*C*–C–Ga), 15.07 (*C*–Ga). Mass spectrum (CI, $\mathrm{CH_4}$) *m*/*e* 630 ($\mathrm{M^+}$), 441 ($\mathrm{M^+ - As^tBu_2}$), 313 ($\mathrm{M^+/2}$). Analysis. Found: C, 45.63%; H, 8.29% Calcd: C, 45.76%; H, 8.32%.

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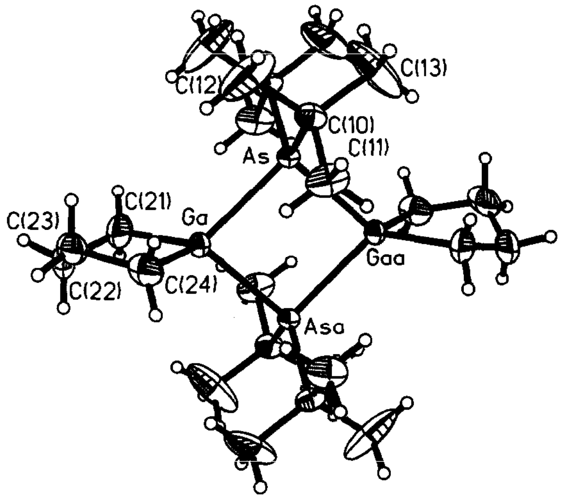

Fig. 1. Molecular structure of 4 (50% probability ellipsoids). For clarity only the asymmetric unit is numbered. Only one of the two butylene bridges in the disordered gallacycle is shown. Selected bond distances (Å) and angles (°): As–Ga 2.512(2), As–C(10) 2.014(3), Ga–C(21) 2.002(4), Ga–C(24) 1.992(4), Ga–As–GaA 94.03(7), C(10)–As–Ga 113.14(9), C(10)A–As–Ga 112.56(9), C(10)–As–C(10)A 110.6(2), As–Ga–AsA 85.97(7), C(21)–Ga–C(24) 93.6(2), C(24)–Ga–As 119.77(9), C(21)–Ga–As 120.31(9).

gallium into a carbocyclic ring has several structural consequences. As expected, the most dramatic change is closure of the C–Ga–C bond angle from an average of 110.9(7)° in the acyclic alkyl derivative to 93.6(2)° in 4. The effects on the Ga_2As_2 core are more subtle, namely a decrease in the Ga–As bond distance from an average of 2.548(6) Å in the acyclic alkyls to 2.512(2) Å in the gallacyclopentane. There is also a slight ($\approx 1°$) opening and closing of the As–Ga–As and Ga–As–Ga angles, respectively. The metric parameters for the As^tBu_2 moiety are unexceptional and do not need comment.

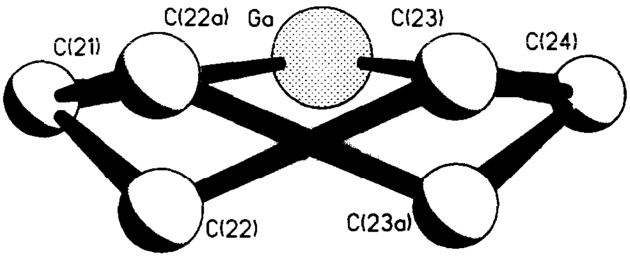

Fig. 2. Disorder model for the gallacycle of 4. The solid lines show the two conformations of the disordered butylene bridge with the carbon–carbon distances fixed at 1.541 Å. The dotted lines show fixed distances between the two disordered bridges. The parallel distances have been fixed to be of equal length.

Carbon atoms C(22) and C(23) of the gallacyclopentane ring were found to be disordered. The disorder was modeled satisfactorily with occupation factors of 50% for each carbon atom. As shown in Fig. 2, this disorder is due to the twisted conformation of the GaC_4 ring.

Preliminary studies indicate that 4 undergoes thermolysis at 50 K higher than does 2. However, vapor-phase pyrolysis and temperature-programmed desorption studies will be necessary to elucidate the gas-phase and surface-bound thermolysis mechanisms for 4. Such studies are in progress.

Acknowledgments

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[**] Crystal data: $C_{12}H_{26}AsGa$, colorless rods, 0.25 mm × 0.4 mm × 0.5 mm, monoclinic, $I\,2/m$ (No. 12); $a = 8.624(6)$, $b = 11.389(12)$, $c = 14.921(13)$ Å, $\beta = 95.330(10)°$, $Z = 4$; $V = 1459(2)$ Å^3, $T = 163$ K; F.W. = 314.97 g mol^{-1}; $D_c = 1.434$ Mg m^{-3}; Mo Kα radiation, $\mu = 4.105$ mm^{-1}, 3661 (1771 independent) data collected $3.0° \leq 2\theta \leq 55.0°$; 1522 observed reflections with $F_o > 4\sigma(F_o)$ semi-empirical absorption correction applied (SHELXA-90, Version 1.0 [10]), structure solved by direct methods (SHELXS-90, Beta-Test Version [11]) and refined by full matrix least squares (SHELXL-93, MsDos 32 bit Version [12]); all non-hydrogen atoms anisotropic, 152 parameters, data-to-parameter ration = 18.2:1 (all reflections) 15.5:1 (observed reflections), final $R_1 = 0.0346$, $wR_2 = 0.0938$, goodness of fit $S = 1.392$ (all 1771 reflections), $wR_2 = 0.0702$ (1770 reflections) $R_1 = 0.0274$, $S = 1.043$ (observed reflections).

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