AD-A168 020 SYNTHESIS AND CRYSTAL STRUCTURE OF TRIS(DIMESITYLARSINO)GALLANE A MONOMER (U) DUKE UNIV DURHAM NC DEPT OF CHEMISTRY C G PITT ET AL 21 MAY 86 1/1

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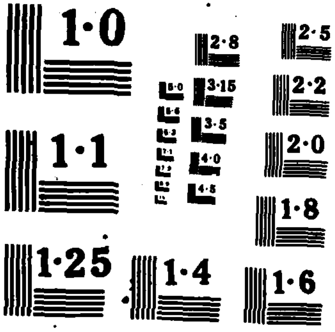

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Synthesis and Crystal Structure of Tris(dimesitylarsino)gallane, a Monomeric Tricoordinate Gallium-Arsenic Compound

by

C. G. Pitt, K. T. Higa, A. T. McPhail, and R. L. Wells

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Durham, NC 27706

May, 1986

Synthesis and Crystal Structure of Tris(dimesitylarsino)gallane, a Monomeric Tricoordinate Gallium-Arsenic Compound.

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The gallium-arsenic bond, in polymeric form, is expected to exhibit anisotropic conductivity by virtue of an extended p-π (Pi) system, isoelectronic with polyacetylene. Despite this potential and the current interest in gallium arsenide as a semiconductor,[1] knowledge of organogallium-arsenic synthetic chemistry was, until recently,[2] restricted to the work of Coates _et al_[3] in the 1960's. Coates used an alkane elimination reaction (Eq.1) to prepare monoarsinogallanes and showed that, in common

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$$R_2AsH + GaMe_3 \rightarrow 1/n\ (R_2AsGaMe_2)_n + CH_4 \qquad \begin{matrix} R = Me;\ n = 3 \\ R = Ph;\ n = 2 \end{matrix} \qquad (1)$$

with most Group 13(IIIA)-Group 15(VA) compounds, intermolecular As → Ga bonding to form four-coordinate gallium and arsenic dominates the structural properties of these compounds. In principle, intermolecular association can be suppressed by introduction of bulky substituents. However, in our hands, the yield of arsinogallanes prepared by the above alkane elimination (Eq.1) decreased to the point of impracticality as the steric bulk of the substituents was increased. Here we report the successful syntheses[4] of sterically hindered arsinogallanes using a lithium arsenide (Eq.2-5), and the crystal structure of tris(dimesitylarsino)gallane (**1**). The latter appears to be the first proven example of a monomeric tricoordinate 13-15 compound of the second and higher row elements.

$$R_2AsLi + GaCl_3 \rightarrow 1/n\ (R_2AsGaCl_2)_n + LiCl \qquad (2)$$

$$R_2AsLi + Me_2GaCl \rightarrow 1/n\ (R_2AsGaMe_2)_n + LiCl \qquad (3)$$

$$2R_2AsLi + GaCl_3 \rightarrow 1/n[(R_2As)_2GaCl]_n + 2LiCl \qquad (4)$$

$$3R_2AsLi + GaCl_3 \rightarrow (R_2As)_3Ga + 3LiCl \qquad (5)$$

R = mesityl

Heating dimesitylarsine with 1 equiv. of n-butyl lithium in ligroin at 40-50°C for 0.5 h afforded lithium dimesitylarsenide (**2**) as a yellow precipitate in 96% yield. Treatment of $GaCl_3$ with 1 equiv. of **2** in benzene (3 days, 25°C), filtration, then fractional crystallization, gave 90% of $(Mes_2AsGaCl_2)_n$ as a white crystalline solid, mp 145-146°C (dec.). Treatment of $GaCl_3$ with 2 equiv. of **2** in benzene (2 days, 25°C), filtration, and recrystallization, gave 67% of $[(Mes_2As)_2GaCl]_n$ as a yellow solid, mp 119-123°C (dec.). Reaction of $GaCl_3$ and 3 equiv. of **2** in benzene for 3 days at 25°C, filtration, then fractional crystallization, yielded 38% of **1** as an orange solid, mp 178°C (dec.). Treatment of Me_2GaCl with 1 equiv. of **2** in benzene (4 days, 25°C), filtration, and recrystallization, gave 68% of $(Mes_2AsGaMe_2)_n$ as a white solid, mp 200°C (dec.). Lack of suitable crystals and the limited solubility of the mono- and bisarsinogallanes (Eq. 2-4) prohibited determination of their degree of association.

The structure of **1**, determinined by single-crystal x-ray analysis[5], is illustrated in Figure 1, with selected bond lengths and bond angles listed in Table 1. The gallium atom is bonded to the three arsenic atoms in a trigonal planar configuration, and positioned 0.149 Å out of the plane formed by the three arsenic atoms. The Ga-As bond lengths at 2.498(1) 2.508(1) and 2.470(1) Å are all shorter than the mean Ga-As single bond length of 2.524 Å found in the 4-coordinate dimer, $(R_2AsGaPh_2)_2$, $R=CH_2SiMe_3$.[2c] The mean As-C bond length and C-As-C bond angle at 1.977 Å and 105.1°, respectively, are similar to the values of 1.976 Å and 108° observed in Mes_3As.[6] However, the geometry at the arsenic atoms is considerably distorted from tetrahedral with Ga-As-C angles ranging from 93.1(1)° to 112.1(1)°. The dimesitylarsino groups are oriented as staggered propeller blades when viewed down the Ga-As bonds. The dihedral angles between the normal to the plane through the arsenic atoms and those through the arsenic lone pair-As-Ga, which reflect the extent of As lone pair-Ga 4p orbital overlap, are 58°, 86°, and 52°, respectively, for As(1), As(2), and As(3).

The gallium and arsenic atoms are efficiently shielded from intermolecular associations by the bulky mesityl substituents. In addition to the outward extension of the mesityl groups from the Ga-As core, planes through C(17), C(27), C(39') and through C(19'), C(29'), C(37) lie approximately parallel to, but on opposite sides of, the As atom plane. The shortest Ga...H distances, at 2.58 Å and 2.47 Å, involve respectively C(17) and C(37) methyl group hydrogens and, accordingly, there is no evidence for any Ga-H bonding interaction.

The electronic spectrum of **1** exhibits bands at 224nm (ε 34,400) and 276 nm (ε 17,900). The long-wavelength band can be assigned to an As → π^* CT transition, based on studies of mesitylarsines and the same assignment to the 276 nm band of Mes_3As.[7] However, unlike the latter compound and 4-coordinate arsinogallanes, **1** is bright orange due to tailing of the 276 nm band into the visible region. This tailing is tentatively attributed to a partly obscured lower intensity As → Ga CT transition, although perturbation of the As → π^* transition resulting from reduction of the ionization potential of the As lone pair electrons by steric strain cannot be ruled out.

In summary, the coupling reaction of a lithium arsenide with gallium halides provides a useful method for the preparation of Ga-As compounds. Arsinogallanes containing large substituents, including bisarsino- and trisarsinogallanes, can be prepared. Permesitylation serves to suppress intermolecular As → Ga association, although the bond lengths and angles of **1** suggest steric effects minimize the ground state interaction of the As lone pair electrons and the vacant Ga 4p orbital.

Acknowledgement. The financial support of this work by the Office of Naval Research is gratefully acknowledged.

Supplementary Materials Available: Tables of positional and thermal parameters, bond lengths and angles, and displacements of atoms from least-squares planes for **1** (11 pages). Ordering information is given on any current mast head page. According to policy instituted January 1, 1986, the Tables of calculated and observed structure factors (47 pp.) are being retained in the editorial office for a period of one year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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4. Compounds were characterized by combustion analysis (C,H) and ^{1}H NMR spectroscopy or by comparison to an authentic sample.[2d] The ^{1}H NMR spectra were obtained in C_6D_6 at 25°C with benzene (7.150 ppm) as an internal standard using an IBM NR-80 spectrometer. $Mes_2AsGaCl_2$: 6.69s (4H), 2.45s (12H), 2.05s (6H). $(Mes_2As)_2GaCl$: 6.70s (8H), 2.34s (24H), 2.06s (12H). $(Mes_2As)_3Ga$: 6.63s (12H), 2.31s (36H), 2.05s (18H). $Mes_2AsGaMe_2$: 6.71 (4H), 2.43 (12H), 2.04 (6H), 0.209 (6H). Because of their extreme air sensitivity, all arsinogallanes were handled in a dry box under prepurified nitrogen.

5. Crystal data for tris(dimesitylarsino)gallane at 25°C: $C_{54}H_{66}As_3Ga$, mol wt 1009.61, triclinic, space group $\underline{P\bar{1}}$ (from Laue symmetry and structure refinement), $\underline{a}$ = 12.702(1) Å, $\underline{b}$ = 17.500(2) Å, $\underline{c}$ =

11.810(2) Å, α = 103.44(1)°, β = 102.79(1)°, γ = 77.79(1)°, V_o = 2454.2 $Å^3$, Z = 2, D_{calc} = 1.366 g cm^{-3}, μ(Cu-Kα radiation, λ = 1.5418 Å) = 32.6 cm^{-1}. Sample dimensions: 0.20 x 0.40 x 0.70 mm. Intensity data ($h \pm k \pm l$, θ_{max} = 67°) for 8720 non-equivalent forms were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-Kα radiation, incident-beam graphite monochromator; ω-2θ scans). Those 7083 reflections with $I > 3.0\sigma(I)$ were retained and corrected for Lorentz and polarization effects. An empirical absorption correction (relative range of transmission factors 0.63 - 1.0), based on a series of ϕ scans at χ ca. 90°, was also applied to these data. The structure was solved by direct methods (MULTAN11/82). All hydrogen atoms were located by difference Fourier synthesis. Full-matrix least-squares refinement of atomic parameters (anisotropic carbon, arsenic, and gallium; isotropic hydrogen) converged to R = 0.040 (R_w = 0.056). The function minimized in the least-squares calculations was $\sum w(\|F_o| - |F_c\|)^2$, where w = $1/\sigma^2(|F_o|)$. All calculations were performed on a PDP11/44 computer by use of the Enraf-Nonius SDP suite of programs. Tables of atomic parameters, bond lengths and angles are included as supplementary material.

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Figure 1. ORTEP Drawing of Tris(dimesitylarsino)gallane (hydrogen atoms have been omitted for clarity)

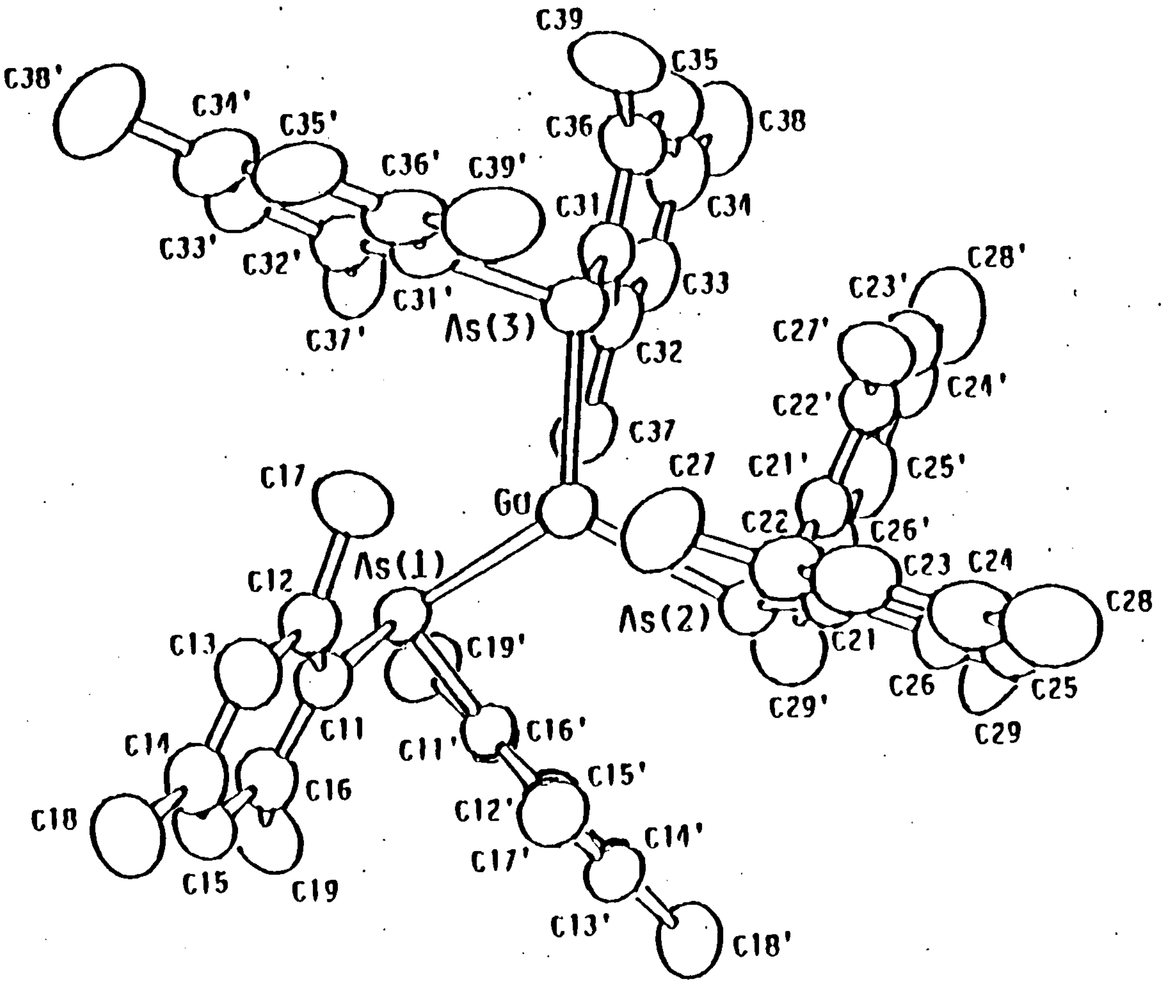
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Table 1. Selected Bond Lengths and Bond Angles of Tris(dimesitylarsino)gallane, with Estimated Standard Deviations in Parentheses.

Bond Lengths (Å)		Bond Angles (deg.)	
Ga-As(1)	2.498(1)	As(1)-Ga-As(2)	117.59(2)
Ga-As(2)	2.508(1)	As(1)-Ga-As(3)	124.37(2)
Ga-As(3)	2.470(1)	As(2)-Ga-As(3)	116.97(2)
As(1)-C(11)	1.978(3)	Ga-As(1)-C(11)	112.1(1)
As(1)-C(11')	1.976(3)	Ga-As(1)-C(11')	93.1(1)
As(2)-C(21)	1.983(3)	C(11)-As(1)-C(11')	105.3(1)
As(2)-C(21')	1.983(4)	Ga-As(2)-C(21)	110.8(1)
As(3)-C(31)	1.970(3)	Ga-As(2)-C(21')	98.3(1)
As(3)-C(31')	1.975(3)	C(21)-As(2)-C(21')	104.5(1)
		Ga-As(3)-C(31)	106.6(1)
		Ga-As(3)-C(31')	108.2(1)
		C(31)-As(3)-C(31')	105.4(1)

Abstract

Four mono-, bis-, and trisarsinogallanes were prepared from the reaction of lithium dimesitylarsenide with gallium chlorides. One of these, tris(dimesitylarsino)gallane, $(Mes_2As)_3Ga$ (1), was characterized by single crystal x-ray analysis and shown to be the first example of a monomeric tricoordinate gallium-arsenic compound. Orange crystals of 1 belong to the triclinic system space group $P\bar{1}$, with a = 12.702(1) Å, b = 17.500(2) Å, c = 11.810(2) Å, α = 103.44(1)°, β = 102.79(1)°, γ = 77.79(1)°, V=2454.2 Å^3, Z = 2. The gallium atom is bonded to the three arsenic atoms in a trigonal planar configuration, [Ga-As = 2.498(1), 2.508(1), and 2.470(1) Å; As-Ga-As = 117.59(2), 124.37(2), and 116.97(2)°], and lies 0.149 Å out of the plane through the As atoms. The color of 1 is the result of tailing of a 276 nm CT band into the visible.

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