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Communications

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

Sir:

The gallium-arsenic bond, in polymeric form, is expected to exhibit anisotropic conductivity by virtue of an extended pπ 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 1960s. Coates used an alkane elimination reaction (eq 1) to prepare monoarsinogallanes and showed that, in common with most group 13

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

(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

$$R_2AsLi + GaCl_3 \rightarrow (1/n)(R_2AsGaCl_2)_n + LiCl \tag{2}$$

$$R_2AsLi + Me_2GaCl \rightarrow (1/n)(R_2AsGaMe_2)_n + LiCl \tag{3}$$

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

$$3R_2AsLi + GaCl_3 \rightarrow (R_2As)_3Ga + 3LiCl \tag{5}$$

$$R = \text{mesityl}$$

the crystal structure of tris(dimesitylarsino)gallane (**1**). The latter appears to be the first proven example of a monomeric tricoordinate group 13-15 compound of the second and higher row elements.

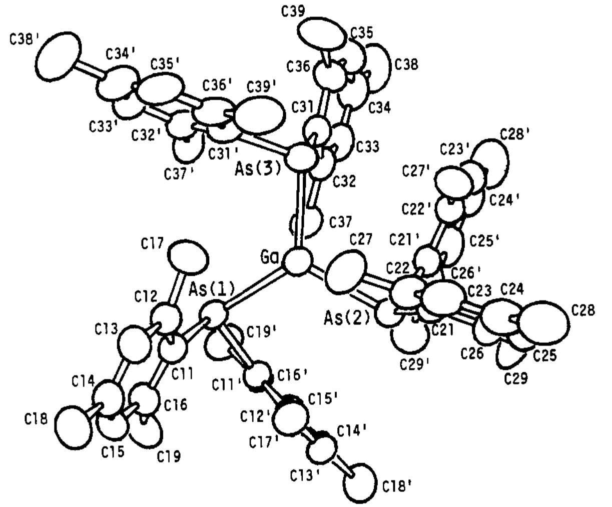

Figure 1. ORTEP drawing of tris(dimesitylarsino)gallane (hydrogen atoms omitted for clarity).

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

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

Heating dimesitylarsine with 1 equiv of *n*-butyllithium 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), followed by filtration and 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), followed by 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, followed by filtration and 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

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(2) (a) Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *Abstracts of Papers*, 189th National Meeting of the American Chemical Society, Miami Beach, FL; American Chemical Society: Washington, DC, 1985; INOR 26. (b) Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Chem. Soc., Chem. Commun.* **1986**, 487-488. (c) Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.*, in press. (d) Pitt, C. G.; Purdy, A. P.; Higa, K. T.; Wells, R. L. *Organometallics* **1986**, *5*, 1266-1268.

(3) (a) Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233-237. (b) Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241-3247.

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

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(4 days, 25 °C), followed by 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 bis(arsino)gallanes (eq 2–4) prohibited determination of their degree of association.

The structure of **1**, determinined by a single-crystal X-ray analysis,[5] is illustrated in Figure 1, with selected bond lengths and bond angles listed in Table I. The gallium atom is bonded to the three arsenic atoms in a trigonal-planar configuration and is 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 four-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 vector, 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), and C(39′) and through C(19′), C(29′), and C(37) lie approximately parallel to but on opposite sides of the As atom plane. The shortest Ga···H distances, at 2.58 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 224 nm (ϵ 34 400 M^{-1} cm^{-1}) and 276 nm (ϵ 17 900 M^{-1} cm^{-1}). The long-wavelength band can be assigned to an As → π^* CT transition, on the basis of studies of mesitylarsines and the same assignment to the 276-nm band of Mes_3As.[7] However, unlike the latter compound and four-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 bis(arsino)- and tris(arsino)gallanes, 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.

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

Registry No. **1**, 102651-38-7; **2**, 101860-09-7; $(Mes_2AsGaCl_2)_n$, 101836-85-5; $((Mes_2As)_2GaCl)_n$, 101836-87-7; $(Mes_2AsGaMe_2)_n$, 102634-11-7.

Supplementary Material Available: Tables of positional and thermal parameters, hydrogen atom coordinates, bond lengths and angles, and displacements of atoms from least-squares planes for **1** (11 pages). Ordering information is given on any current masthead page.

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(5) Crystal data for tris(dimesitylarsino)gallane at 25 °C: $C_{54}H_{66}As_3Ga$, M_R 1009.61, triclinic, space group $P\bar{1}$ (from Laue symmetry and structure refinement), $a = 12.702$ (1) Å, $b = 17.500$ (2) Å, $c = 11.810$ (2) Å, $\alpha = 103.44$ (1)°, $\beta = 102.79$ (1)°, $\gamma = 77.79$ (1)°, $V_{obsd} = 2454.2$ Å^3, $Z = 2$, $D_{calcd} = 1.366$ g cm^{-3}, μ (Cu Kα radiation, $\lambda = 1.5418$ Å) = 32.6 cm^{-1}. Sample dimensions: 0.20 × 0.40 × 0.70 mm. Intensity data ($h,\pm k,\pm l$, $\theta_{max} = 67°$) for 8720 nonequivalent 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 and bond lengths and angles are included as supplementary material.

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A Cu–(μ-H) Bond Can Be Stronger Than an Intramolecular P→Cu Bond. Synthesis and Structure of $Cu_2(\mu\text{-}H)_2[\eta^2\text{-}CH_3C(CH_2PPh_2)_3]_2$[1a]

Sir:

We have reported earlier[1b] the dramatic influence of the identity of the phosphine on the aggregation and structure of phosphine adducts of CuH. We describe here the outcome of attempts to use a threefold symmetric tridentate phosphine in order to generate a four-coordinate complex containing a terminal hydride on Cu(I).

Hydrogenolysis (1 atm. 23 °C, 5 h) of the Cu–O bond of $(CuO\text{-}t\text{-}Bu)_4$ proceeds under mild conditions in THF in the presence of a stoichiometric amount (1 mol/mol of Cu) of $MeC(CH_2PPh_2)_3$ ("tripod") to produce *t*-BuOH and, as the only metal-containing product, a compound of empirical formula HCu(tripod) (isolated yield 75%). This compound is thermally unstable toward deposition of copper metal in toluene solution above 40 °C. The infrared spectrum of the compound shows an absorption assigned as ν(CuH) at 950 cm^{-1}, which shifts to 680 cm^{-1} when H_2 is replaced by D_2 in the synthesis ($\nu(H)/\nu(D)$ = 1.40). This frequency is too low to be the stretching mode of a terminal hydride.[2] Reinforcing this conclusion is the fact that the 220-MHz ^1H NMR spectrum shows an excessive number of aliphatic and of aromatic resonances for a threefold symmetric HCu(tripod) monomer.[3] The ^2H NMR of DCu(tripod) shows a broad yet unstructured resonance at a *positive* δ value (1.83 ppm), in the chemical shift region of the hydride ligands of $(HCuPPh_3)_6$ and $H_8Cu_8[Ph_2P(CH_2)_3PPh_2]_4$.[1b] The $^{31}P\{^1H\}$NMR spectrum at −40 °C provides further understanding of these data, exhibiting one broad (full width at half-height = 10 Hz) resonance at −21.0 ppm (intensity 2) and *two* sharp resonances (−28.9 and −29.7 ppm, total intensity 1). The latter values lie sufficiently close to the signal of free $CH_3C(CH_2PPh_2)_3$ in toluene at −40 °C (−27.3 ppm) to suggest a dangling (uncoordinated) phosphine arm. The two resonances of the dangling arms coalesce to a singlet at 20 °C, but these do not merge with the resonance of coordinated phosphine up to the sample decomposition temperature.

As anticipated by the spectroscopic data, an X-ray diffraction study shows the unit cell of HCu(tripod) to be composed of centrosymmetric dimers (Figure 1).[4] Two bridging hydrides link

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(1) (a) Taken from: Goeden, G. V. Ph.D. Thesis, Indiana University, 1982. (b) Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 7774.

(2) Muetterties, E. L. *Transition Metal Hydrides*; M. Dekker: New York, 1971.

(3) Chemical shifts in C_6D_6 at 19 °C: 0.91, 1.83, 2.20, 2.43, 2.66, 6.86, 7.02, 7.43, 8.02, 8.36 ppm. Free THF is also seen at 1.43 and 3.59 ppm. While the THF signals are sharp and well resolved, those of the tripod ligand are all broad.

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