Phenylarsonates of Aluminum and Gallium: Synthesis and Structural Characterization of [^{t}BuAl(μ_3-O_3AsPh)]$_4$ and [^{t}Bu$_2$Ga(μ_2-O_2AsPh)]$_2$O

Mark R. Mason,* R. Mark Matthews,
Mark S. Mashuta, and John F. Richardson

Department of Chemistry and Center for Chemical Catalysis,
University of Louisville, Louisville, Kentucky 40292

Ashwani Vij

Department of Chemistry, University of Idaho,
Moscow, Idaho 83844

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Introduction

Microporous aluminophosphates[1] and gallophosphates[2] have been intensely studied as catalysts, catalyst supports, and sorbents since the initial discovery of aluminophosphates in 1982. The corresponding arsenate materials have not, however, been as extensively investigated. Xu and co-workers have synthesized a family of aluminoarsenates designated $AlAsO_4$-*n*[3] and a family of galloarsenates designated $GaAsO_4$-*n*.[4] Synthesis of these materials under hydrothermal conditions in the presence of a template results in the occlusion of organic amines or ammonium ions. Unlike the case for $AlPO_4$ and $GaPO_4$ materials, calcination of the arsenate materials does not result in retention of the microporous inorganic framework upon removal of the occluded organic material. Instead, arsenic sublimation and collapse of the porous inorganic structures occur above approximately 400 °C. The low thermal stability of known aluminoarsenates and galloarsenates, as well as the known toxicity of arsenic, limits industrial utility and most likely accounts for the relatively few reports on these materials.

Our interest in these materials is focused on the synthesis of new arsenate phases with improved thermal stability via a molecular precursor approach. This approach complements our previous research on cyclic and cubic phosphonate and phosphate derivatives of aluminum and gallium, which are molecular models of important secondary building units in, and potential molecular precursors to, $AlPO_4$ and $GaPO_4$ materials.[5−9] A desirable molecular precursor to thermally stable arsenate materials would be an organic-soluble double-four-ring (D4R) derivative with a cubic $M_4As_4O_{12}$ core capable of fluoride encapsulation. Encapsulation of fluoride in the D4R secondary building units of the gallophosphate cloverite has been suggested to account for the thermal stability of that material.[10] Here we report the synthesis and structural characterization of the first aluminoarsenate D4R derivative [^{t}BuAl(μ_3-O_3AsPh)]$_4$ (**1**) and the bicyclic galloarsonate [^{t}Bu$_2$Ga(μ_2-O_2AsPh)]$_2$O (**2**).

Experimental Section

General Procedures. All reactions were performed under an atmosphere of purified nitrogen using standard inert-atmosphere techniques. Pentane and tetrahydrofuran were distilled from sodium benzophenone ketyl prior to use. $CDCl_3$ was dried by storage over activated molecular sieves. Gallium trichloride was purchased from Strem Chemicals and was used without further purification. Phenylarsonic acid and aluminum trichloride were purchased from Aldrich and used as received. $^{t}Bu_3Ga$[11] and $^{t}Bu_3Al$[12] were prepared as previously described. Solution NMR spectra were recorded on a Bruker AMX-500 spectrometer using $CDCl_3$ as the internal lock. Chemical shifts are reported relative to TMS. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 5000 spectrometer for samples prepared as KBr pellets. High-resolution mass spectrometric analyses were provided by the Nebraska Center for Mass Spectrometry. Low-resolution mass spectral *m/z* values are reported for the predominant peak in the isotope pattern. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of [^{t}BuAl(μ_3-O_3AsPh)]$_4$ (1). A solution of $^{t}Bu_3Al$ (2.50 g, 12.6 mmol) in 15 mL of THF was added dropwise to a suspension of phenylarsonic acid (2.55 g, 12.6 mmol) in 15 mL of THF, and the resulting solution was stirred at room temperature for 15 h. The reaction solution was concentrated *in vacuo*, and the concentrate was cooled (−20 °C) overnight to yield **1** as a crystalline white solid. Yield: 2.01 g, 1.77 mmol, 56%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86 (d, 8H, Ph-ortho), 7.64 (t, 4H, Ph-para), 7.56 (t, 8H, Ph-meta), 0.86 (s, 36H, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.5 MHz): δ 133.3 (s, Ph-ortho), 130.4 (s, Ph-ipso), 130.2 (s, Ph-para), 129.4 (s, Ph-meta), 29.73 (s, $C(CH_3)_3$), 25.61 (br s, $C(CH_3)_3$). IR (KBr, cm^{-1}): 2940 (vs), 2837 (vs), 2699 (m), 1465 (s), 1445 (s), 1385 (m), 1336 (m), 981 (vs), 818 (s), 742 (s), 689 (s), 596 (s), 516 (vs), 470 (s). MS (EI) *m/z* (assignment, relative intensity): 1079 ($M^+ - {}^{t}Bu$, 100), 965 ($M^+ - 3{}^{t}Bu$, 6), 889 ($M^+ - 2{}^{t}Bu - C_4H_8 - Ph$, 3), 831 ($M^+ - 4{}^{t}Bu - Ph$, 20), 677 ($M^+ - 4{}^{t}Bu - 3Ph$, 12). HRMS (EI) *m/z* for $C_{36}H_{47}O_{12}Al_4As_4$ ($M^+ - {}^{t}Bu$): calcd, 1078.9193; found, 1078.9245. Anal. Calcd for $C_{40}H_{56}O_{12}Al_4As_4$: C, 42.27; H, 4.97; Al, 9.50; As, 26.37. Found: C, 42.82; H, 5.16; Al, 9.31; As, 26.71.

Preparation of [^{t}Bu$_2$Ga(μ_2-O_2AsPh)]$_2$O (2). A solution of $^{t}Bu_3Ga$ (2.00 g, 8.30 mmol) in 15 mL of THF was added dropwise to a suspension of phenylarsonic acid (1.68 g, 8.30 mmol; Aldrich) in 15 mL of THF, and the resulting clear solution was refluxed for 2 h. Volatiles were removed *in vacuo* to yield a white solid, which was subsequently recrystallized from hot acetonitrile to afford clear colorless crystals. Yield of **2**: 1.65 g, 2.19 mmol, 53%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94 (d, 4H, Ph-ortho), 7.69 (t, 2H, Ph-para), 7.59 (t, 4H, Ph-meta), 1.17 (s, 18H, ^{t}Bu), 1.08 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.5 MHz): δ 134.4 (s, Ph-ortho), 131.0 (s, Ph-para), 130.3 (s, Ph-ipso), 129.8 (s, Ph-meta), 30.33 (s, $C(CH_3)_3$), 30.30 (s, $C(CH_3)_3$), 25.02 (s, $C(CH_3)_3$), 25.00 (s, $C(CH_3)_3$). IR (KBr, cm^{-1}): 3066 (w), 2927 (vs), 2836 (vs), 2699 (w), 1464 (s), 1445 (s), 1360 (m), 1089 (s), 896 (vs), 813 (s), 743 (s), 723 (s), 592 (m), 469 (m). MS (EI) *m/z* (assignment, relative intensity): 753 (MH^+, 0.2), 695 ($M^+ - {}^{t}Bu$, 100), 639 ($M^+ - {}^{t}Bu - C_4H_8$, 5), 581 ($M^+ - 3{}^{t}Bu$, 27), 525 ($M^+ - 3{}^{t}Bu - C_4H_8$, 22). HRMS (EI) *m/z* for $C_{24}H_{37}O_5{}^{69}Ga{}^{71}GaAs_2$ ($M^+ - {}^{t}Bu$): calcd, 694.9576; found 694.9570. Anal. Calcd for $C_{28}H_{46}O_5Ga_2As_2$: C, 44.72; H, 6.17; Ga, 18.54. Found: C, 44.67; H, 6.31; Ga, 19.56.

X-ray Crystallography for 1. A crystal of **1** with dimensions 0.20 × 0.15 × 0.10 mm was obtained by crystallization from chlorobenzene. X-ray diffraction data were collected on a Siemens three-circle platform diffractometer equipped with a CCD detector maintained near −54 °C, and the *X*-axis fixed at 54.74°. The frame data were acquired with the SMART software using Mo Kα radiation (λ = 0.710 73 Å) from a

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Table 1. Crystallographic Data for $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3AsPh})]_4$ (**1**) and $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2AsPh})]_2\mathrm{O}$ (**2**)

	1	**2**
formula	$C_{40}H_{56}Al_4As_4O_{12}$	$C_{28}H_{96}As_2Ga_2O_5$
fw	1136.45	751.96
crystal system	rhombohedral	orthorhombic
space group	$R\bar{3}$	*Pbcn*
a, Å	15.8223(6)	18.819(4)
b, Å	15.8223(6)	8.959(2)
c, Å	36.439(2)	19.739(4)
V, Å^3	7900.2(6)	3328(2)
Z	6	4
D_{calcd}, g cm^{-3}	1.433	1.50
T, K	293(2)	296(3)
R (wR_2 or R_w)	0.0567 (0.1447)[a]	0.036 (0.041)[b]

[a] $R = \sum||F_\mathrm{o}| - |F_\mathrm{c}||/\sum|F_\mathrm{o}|$; $\mathrm{w}R_2 = [\sum[w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2]/\sum[w(F_\mathrm{o}^2)^2]]^{1/2}$. [b] $R = \sum||F_\mathrm{o}| - |F_\mathrm{c}||/\sum|F_\mathrm{o}|$; $R_\mathrm{w} = [\sum w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2]/\sum w(F_\mathrm{o}^2)]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3AsPh})]_4$ (**1**)

	Distances		
As(1)−O(1)	1.653(6)	Al(1)−O(2)	1.749(6)
As(1)−O(2)	1.636(6)	Al(1)−O(3)	1.765(6)
As(1)−O(4)	1.657(6)	Al(1)−O(4A)[a]	1.747(6)
As(2)−O(3)	1.634(6)	Al(2)−O(1)	1.750(6)
	Angles		
O(2)−As(1)−O(1)	110.4(3)	O(2)−As(1)−C(5)	109.1(3)
O(1)−As(1)−O(4)	110.8(3)	O(4)−As(1)−C(5)	107.8(3)
O(2)−As(1)−O(4)	110.4(3)	O(3)−As(2)−O(3A)[a]	111.0(2)
O(1)−As(1)−C(5)	108.4(3)	O(3)−As(2)−C(13)	107.9(2)
O(4A)−Al(1)−O(2)[a]	105.7(3)	O(4A)−Al(1)−C(1)[a]	112.3(4)
O(2)−Al(1)−O(3)	108.2(3)	O(3)−Al(1)−C(1)	112.3(3)
O(4A)−Al(1)−O(3)[a]	107.3(3)	O(1)−Al(2)−O(1A)[a]	106.9(2)
O(2)−Al(1)−C(1)	110.6(4)	O(1)−Al(2)−C(11)	112.0(2)
As(1)−O(1)−Al(2)	148.5(4)	As(2)−O(3)−Al(1)	148.0(4)
As(1)−O(2)−Al(1)	157.1(4)	As(1)−O(4)−Al(1B)[a]	143.1(4)

[a] A and B indicate symmetry-related atoms.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2AsPh})]_2\mathrm{O}$ (**2**)[a]

	Distances		
As−O(1)	1.661(4)	Ga−O(1)*	1.987(4)
As−O(2)	1.764(3)	Ga−O(3)	1.937(3)
As−O(3)	1.662(4)	Ga−C(1)	1.982(6)
As−C(9)	1.888(5)	Ga−C(5)	2.001(5)
	Angles		
O(1)−As−O(2)	106.7(1)	O(1)*−Ga−C(5)	106.1(2)
O(1)−As−O(3)	115.2(2)	O(3)−Ga−C(1)	107.2(2)
O(1)−As−C(9)	111.9(2)	O(3)−Ga−C(5)	110.2(2)
O(2)−As−O(3)	105.8(1)	C(1)−Ga−C(5)	125.5(2)
O(2)−As−C(9)	106.8(2)	As−O(1)−Ga*	131.6(2)
O(3)−As−C(9)	110.0(2)	As−O(2)−As*	114.9(3)
O(1)*−Ga−O(3)	98.2(1)	As−O(3)−Ga	128.4(2)
O(1)*−Ga−C(1)	106.2(2)		

[a] The asterisks indicate symmetry-related atoms.

fine-focus tube. Cell constants were determined from sixty 30-s frames. A complete hemisphere of data was scanned on ω (0.3°) with a run time of 30 s/frame at the detector resolution of 512 × 512 pixels. Fifty frames were collected to determine crystal decay. The crystal showed no decomposition. An additional 1271 frames were collected for the data set. The frames were processed on an SGI-Indy/Indigo 2 workstation using the SAINT software to give the *hkl* file corrected for decay and for Lorentz and polarization effects. An absorption correction was performed using the SADABS program.[13] The structure was solved by direct methods using SHELXS-90[14] and refined by the least squares method on F^2, using SHELXL-93[15] incorporated in SHELXTL-PC V 5.03.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and refined as a riding model. The phenyl substituent on As(2) lies on the 3-fold axis, leading to a disordered phenyl substituent which was adequately modeled by restraining the C−C bond distances and angles to those in the ordered phenyl groups and making this ring and As(2) coplanar. A similar disorder was observed in the analogous aluminophosphonate $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3PPh})]_4$.[8] Of 15 871 data collected (maximum $2\theta = 56.7°$, Mo Kα, $\mu = 2.634$ mm^{-1}), 4251 were unique. The final residuals for 198 parameters refined against 1834 unique data with $I > 2\sigma(I)$ were $R_1 = 5.7\%$ and $\mathrm{w}R_2 = 14.5\%$. Selected crystallographic data for **1** are given in Tables 1 and 2.

X-ray Crystallography for 2. A colorless plate of **2** with dimensions of 0.46 × 0.33 × 0.20 mm was mounted on a glass fiber in a random orientation. Data were collected using Mo Kα radiation ($\lambda = 0.710\,73$ Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-crystal, incident-beam monochromator. Three representative check reflections showed a gradual loss of intensity which totaled 8.3% during the course of data collection. A linear decay correction was applied, as were Lorentz and polarization corrections. The structure was refined on a VAX computer using the MolEN[17] software package. The Patterson method revealed the positions of arsenic and gallium atoms; the remaining atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were located by difference maps and added to the structure factor calculations, but their positions were not refined. All non-hydrogen atoms were refined anisotropically. Thermal parameters for hydrogen atoms were set to $1.3B_{\mathrm{eq}}$ of the carbon atoms to which they were bound. Of 3341 data collected (maximum $2\theta = 49.9°$, Mo Kα, $\mu = 36.1$ cm^{-1}), 3333 were unique. The final residuals for 169 parameters refined against 2162 unique data with $I > 3\sigma(I)$ were $R = 3.6\%$ and $R_\mathrm{w} = 4.1\%$. Selected crystallographic data for **2** are given in Tables 1 and 3.

Results and Discussion

An equimolar reaction of phenylarsonic acid with $^t\mathrm{Bu_3Al}$ in THF yields $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3AsPh})]_4$ (**1**) in 56% yield. Compound **1** is highly symmetrical, as evidenced by a single *tert*-butyl resonance and a single set of phenyl resonances in the ^{1}H NMR spectrum. The 1:1 ratio of *tert*-butyl to phenyl substituents in the ^{1}H NMR spectrum, the lack of hydroxyl substituents on arsenic as evidenced by infrared spectroscopy, and the results of elemental analyses all confirm a formula $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3AsPh})]_n$. Successive loss of four *tert*-butyl and three phenyl substituents is evident in the electron impact mass spectrum, and exact mass measurement on the base peak at *m*/*z* 1078.9, assigned to the $\mathrm{M}^+ - {}^t\mathrm{Bu}$ fragment, confirms compound **1** to be a tetramer ($n = 4$) in the gas phase. Retention of the tetrameric structure in solution is consistent with NMR spectroscopic data, and a cubic tetrameric structure is confirmed for the solid state by X-ray crystallography.

Compound **1** (Figure 1) crystallizes in the rhombohedral space group $R\bar{3}$ with one-third of the molecule in the asymmetric unit. Symmetry expansion around the 3-fold axis passing through As(2) and Al(2) yields the complete molecule with a cubic $\mathrm{Al_4As_4O_{12}}$ core analogous to the cubic $\mathrm{Al_4P_4O_{12}}$ cores in the crystallographically characterized aluminophosphates and aluminophosphonates $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3PPh})]_4$,[8] $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3P}^t\mathrm{Bu})]_4$,[8] $[\mathrm{MeAl}(\mu_3\text{-}\mathrm{O_3PMe})]_4$,[8] $[^i\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3P}^t\mathrm{Bu})]_4$,[18] and $[\mathrm{Al(PO_4)(HCl)(EtOH)_4}]_4$.[19] The $\mathrm{Al_4As_4O_{12}}$ core is best described as a cube with alternating aluminum and arsenic atoms at the

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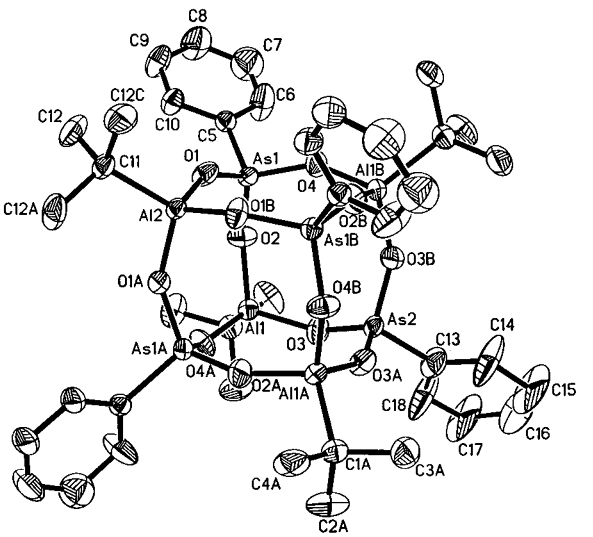

Figure 1. ORTEP drawing of $[^t\mathrm{BuAl}(\mu_3\text{-}\mathrm{O_3AsPh})]_4$ (**1**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

vertices, and a μ_2-oxo bridge along each edge. Aluminum and arsenic atoms are in distorted tetrahedral environments with O−Al−O and O−As−O angles ranging from 105.7(3) to 108.2(3)° and from 110.4(3) to 111.0(2)°, respectively. Aluminum−oxygen distances in **1** range from 1.747(6) to 1.765(6) Å, and As−O distances range from 1.634(6) to 1.657(6) Å. These distances are comparable to those previously reported for tetrahedral aluminum and arsenic atoms in the aluminoarsenates α-$\mathrm{AlAsO_4}$ (Al−O 1.741(2) Å, 1.743(2) Å; As−O 1.665(2) Å, 1.666(2) Å)[20] and $\mathrm{AlAsO_4}$-1 (Al-O 1.718−1.751 Å; As−O 1.649−1.698 Å).[3a] Intracage Al−As diagonal distances average 5.66 Å, suitable for encapsulation of fluoride.

By analogy to our previous results concerning the formation of $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2P(OH)Ph})]_2$ from reaction of phenylphosphonic acid with $^t\mathrm{Bu_3Ga}$,[5] we anticipated that reaction of phenylarsonic acid with $^t\mathrm{Bu_3Ga}$ would yield $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2As(OH)Ph})]_2$, potentially capable of subsequent thermolysis to form the gallium analog of **1**, $[^t\mathrm{BuGa}(\mu_3\text{-}\mathrm{O_3AsPh})]_4$. Instead, reaction of phenylarsonic acid with $^t\mathrm{Bu_3Ga}$ yields $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2AsPh})]_2\mathrm{O}$ (**2**) as a white crystalline solid in 53% yield after recrystallization from hot acetonitrile. Infrared spectroscopy clearly shows the absence of hydroxyl substituents on arsenic. A 2:1 ratio of *tert*-butyl to phenyl substituents in the ^{1}H NMR spectrum of **2** proves that the absence of hydroxyl substituents is not the result of $[^t\mathrm{BuGa}(\mu_3\text{-}\mathrm{O_3AsPh})]_n$ formation. The mass spectrum of **2** exhibits a weak molecular ion peak (*m/z* 753) and a base peak (*m/z* 695) assignable to the $\mathrm{M}^+ - {}^t\mathrm{Bu}$ fragment, each 18 units lower than would be expected for $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2As(OH)Ph})]_2$. This result suggests that the absence of hydroxyl substituents is due to dehydration during the formation of **2**. The lack of hydroxyl substituents on arsenic, the observation of two equally intense *tert*-butyl resonances in the ^{1}H NMR spectrum, the mass spectrometric data, and analytical results are all in agreement with the formulation of **2** as $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2AsPh})]_2\mathrm{O}$ containing an As−O−As linkage.

The molecular structure of **2** (Figure 2) is confirmed in the solid state by X-ray crystallography. The bicyclic $\mathrm{Ga_2As_2O_5}$ core is composed of two μ_2-$\mathrm{O_2AsPh}$ groups bridging two distorted tetrahedral gallium centers, forming a $\mathrm{Ga_2As_2O_4}$ heterocycle. The $\mathrm{Ga_2As_2O_5}$ core is completed by a μ_2-oxo bridge between the two arsenic centers. The two $^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2AsPh})$ monomer units are related by a crystallographically imposed 2-fold rotation axis passing through the oxo bridge, O(2), between arsenic centers. Arsenic−oxygen bond distances within the eight-membered heterocycle are comparable to those observed in $\mathrm{GaAsO_4}$-2 (1.652−1.696 Å)[4b] and in the aluminoarsenates noted above.[3] Distances for the As−O−As linkage are significantly longer (1.764(3) Å). Gallium−oxygen distances in **2** are within the range reported for the related heterocycles $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2P(OH)Ph})]_2$ (1.944(4) Å),[5] $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2PPh_2})]_2$ (1.950(8), 1.969(7) Å),[21] and $[\mathrm{Me_2Ga}(\mu_2\text{-}\mathrm{O_2PPh_2})]_2$ (1.9384(12), 1.9295(12) Å).[22]

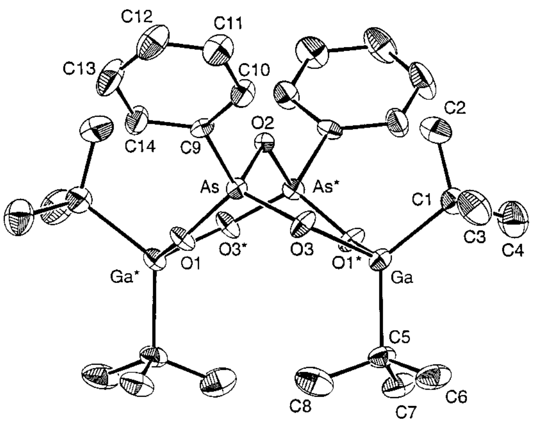

Figure 2. ORTEP drawing of $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2AsPh})]_2\mathrm{O}$ (**2**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Formation of **2** can be rationalized by elimination of water from $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2As(OH)Ph})]_2$ with the formation of two favorable six-membered rings. Phenylarsonic acid is known to eliminate water to form As−O−As linkages under mild heating.[23] A metal-mediated condensation of phenylarsonic acid has also been reported to occur during the solvothermal synthesis of $[(\mathrm{V_2O_3})(\mathrm{Ph_6As_6O_{14}})]$.[24] Reaction of phenylarsonic acid and $^t\mathrm{Bu_3Ga}$ at 0 °C followed by warming to room temperature also produced only **2**, ruling out dehydration during recrystallization from hot acetonitrile. Attempts to convert **2** to $[^t\mathrm{Bu_2Ga}(\mu_2\text{-}\mathrm{O_2As(OH)Ph})]_2$ by addition of water resulted in no reaction, as monitored by ^{1}H NMR spectroscopy.

Hydrolysis could potentially yield elimination of 2 equiv of isobutane with the formation of an oxo bridge between the gallium centers. We are pursuing synthetic routes to similar molecules with an adamantane-like $\mathrm{M_2P_2O_6}$ core (M = Al, Ga). Organic-soluble precursors with $\mathrm{M_2P_2O_6}$ adamantane cores may be unique precursors for the synthesis of new phosphate materials.

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Supporting Information Available: Tables of crystal data and refinement details, positional and thermal parameters, and complete bond distances and angles for **1** and **2** (12 pages). Ordering information is given on any current masthead page.

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