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Articles

Synthesis and Characterization of the Monomeric Digallylphosphane and Digallylarsane Derivatives MesP{Ga(Trip)$_2$}$_2$·Et$_2$O and PhAs{Ga(Trip)$_2$}$_2$

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The compounds MesP{Ga(Trip)$_2$}$_2$·Et$_2$O, **1**, and PhAs{Ga(Trip)$_2$}$_2$ (Trip = 2,4,6-*i*-Pr$_3$C$_6$H$_2$), **2**, were synthesized by the reaction of Li$_2$ER (E = P and As and R = Mes and Ph, respectively) with 2 equiv of Trip$_2$GaCl in tetrahydrofuran solution. They were characterized by X-ray crystallography and variable temperature (VT) ^{1}H NMR and ^{31}P NMR spectroscopy. The structure of **1** displays an almost eclipsed C$_2$Ga–P(C)–GaC$_2$ core array with trigonal planar coordination at phosphorus. In contrast, **2** has trigonal pyramidal coordination at arsenic and large angles between the planes at Ga(1) or Ga(2) and the central AsGa$_2$ plane. These represent the first structurally characterized examples of monomeric digallylphosphanes and -arsanes. The detection of a rotational barrier around the Ga–P bonds in **1** is attributed to weak delocalized Ga–P–Ga π-bonding in a manner analogous to that in the allyl cation. Crystal data with Mo Kα (λ = 0.710 69 Å) at 130 K: **1**, C$_{70}$H$_{103}$Ga$_2$P, a = 15.641(5) Å, b = 20.112(5) Å, c = 22.278(6) Å, β = 97.61(2)°, monoclinic, space group $P2_1/c$, Z = 4, R = 0.063; **2**, C$_{66}$H$_{90}$Ga$_2$As, a = 13.395(5) Å, b = 14.438(7) Å, c = 18.693(7) Å, α = 105.80(3)°, β = 92.47(3)°, γ = 116.57(7)°, triclinic, space group $P\bar{1}$, Z = 2, R = 0.054.

Introduction

There has been widespread interest in multiple bonding between the main group 3 and 5 elements for many years. Much of this work has been concerned with B–N compounds.[1,2] In contrast, the importance of π-bonding for the heavier main group 3–5 compounds has only been recently established in the case of B–P or B–As species.[3,4] In addition, evidence for π-bonding in compounds where both of the main group 3 and 5 atoms are heavier members of their respective groups is currently very sparse. It has been shown by dynamic ^{1}H NMR studies that in the molecular species *t*-Bu$_2$GaPMes*(SiPh$_3$) there is a barrier of 12.7 kcal mol^{-1} to rotation around the Ga–P bond which is thought to be due to weak Ga–P π overlap.[5] Also a recent publication describing the Zintl anions M$_2$E$_4^{6-}$ (M = Al, Ga; E = P, As) which were characterized structurally (X-ray), reported shortened Ga–P (2.247(5) Å) and Ga–As (2.343(2) Å) bonds that are suggestive of multiple bonding.[6] In addition to differences of size and electronegativity between the heavier main group 3 and 5 elements, the magnitude of the inversion barrier at the pnictide element is usually quite large (>30 kcal mol^{-1}) and may strongly determine the extent of multiple bonding in these compounds. It has been shown that, in certain boron–phosphorus and boron–arsenic species, large and electropositive substituents at the pnictide serve to lower the inversion barrier and induce stronger multiple bonding.[4,7] In this paper further results in the use of this approach to induce multiple bonding between two heavier main group 3 and 5 elements are reported through the synthesis, structural (X-ray) and spectroscopic (^{31}P and variable temperature ^{1}H NMR) characterization of MesP{Ga(Trip)$_2$}$_2$·Et$_2$O, **1** and PhAs{Ga(Trip)$_2$}$_2$, **2**.

Experimental Section

General Procedures. All experiments were performed either by using modified Schlenk techniques or a Vacuum Atmospheres HE 43-2 dry box under nitrogen. Solvents were freshly distilled from sodium-potassium alloy and degassed twice prior to use. ^{31}P and ^{1}H NMR spectra were recorded in C$_6$D$_6$ or C$_7$D$_8$ solutions by using a General Electric QE-300 spectrometer. Infrared spectra were recorded as a Nujol mull between CsI plates by using a Perkin-Elmer PE-1430 spectrometer. The reagents

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Table I. Selected Crystallographic Data and Structural Parameters for **1** and **2**

	1	**2**
formula	$C_{70}H_{103}PGa_2$	$C_{66}H_{90}AsGa_2$
fw	1114.9	1097.7
temp, K	130	130
cryst system	monoclinic	triclinic
a, Å	15.641(5)	13.395(5)
b, Å	20.112(5)	14.438(7)
c, Å	22.278(6)	18.693(7)
α, deg		105.80(3)
β, deg	97.61(2)	92.47(3)
γ, deg		116.57(3)
V, Å^3	6946(3)	3054(2)
space group	$P2_1/c$	$P\bar{1}$
Z	4	2
D_{calc}, g cm^{-3}	1.07	1.19
μ, cm^{-1}	0.83	1.46
2θ range, deg	0–54	1–50
no. of obsd reflcns	5913, $I > 3\sigma(I)$	7774, $I > 3\sigma(I)$
no. of variables	673	622
R, R_w	0.063, 0.067	0.054, 0.057

Table II. Selected Atom Coordinates (×10^4) for **1** and **2**

	x	y	z
	MesP{Ga(Trip)$_2$}$_2$·Et$_2$O, **1**		
P(1)	2861(2)	2678(1)	1847(1)
Ga(1)	1557(1)	2823(1)	2155(1)
Ga(2)	4101(1)	2155(1)	2206(1)
C(1)	2840(5)	2908(5)	1047(4)
C(10)	671(5)	3406(4)	1688(3)
C(25)	1152(5)	2393(4)	2860(3)
C(40)	4487(5)	1991(4)	3079(3)
C(55)	4936(6)	1909(4)	1653(4)
	PhAs{Ga(Trip)$_2$}$_2$, **2**		
As(1)	1143(1)	1181(1)	1735(1)
Ga(1)	1313(1)	881(1)	2935(1)
Ga(2)	2674(1)	2804(1)	1618(1)
C(1)	−217(4)	1339(4)	1593(3)
C(7)	420(4)	1157(5)	3715(3)
C(22)	2225(4)	115(4)	2926(3)
C(37)	4275(4)	3163(4)	1962(3)
C(52)	2371(4)	3670(4)	1055(3)

$MesPH_2$ and $Trip_2GaCl$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) were prepared by literature methods.[8,9] $PhAsH_2$ was obtained by reduction of $PhAsO(OH)_2$ (Aldrich) with zinc amalgam.[10] Compounds **1** and **2** gave satisfactory C, H analyses.

Synthesis. MesP{Ga(Trip)$_2$}$_2$·Et$_2$O (1). $MesPLi_2$ was synthesized by the slow addition of two equivalents of *n*-BuLi (1.6 M in hexanes) to $MesPH_2$ in Et_2O at 0 °C. After warming to room temperature and stirring for 1 h, a fine yellow precipitate of $MesPLi_2$ was isolated by filtration and dried under reduced pressure. A solution of $Trip_2GaCl$ (2.04 g, 4 mmol) in tetrahydrofuran (20 mL) was then added via cannula to a slurry of $MesPLi_2$ (0.33 g, 2 mmol) in tetrahydrofuran (30 mL). After stirring for 5 h, all volatile components were removed under reduced pressure and the residue was taken up in Et_2O (40 mL). Filtration through celite and reduction of the volume to 20 mL followed by cooling in a −20 °C freezer gave the product as moderately air sensitive pale yellow crystals. Yield: 1.21 g, 55%; mp 207–212 °C (dec. to yellow oil); ^1H NMR (C_6D_6): δ = 1.32 (d, p-CHMe_2), 1.40 (d, o-CHMe_2), 1.98 (s, p-Me), 2.90 (sept., p-CHMe$_2$), 3.05 (s, o-Me), 3.50 (sept., o-CHMe$_2$), 6.71 (s, m-H of Mes), 7.38 (s, m-H of Trip); ^{31}P NMR (C_6D_6): δ = −58.

PhAs{Ga(Trip)$_2$}$_2$ (2). The synthesis of **2** was analogous to that of **1**. Yield: 0.46 g, 21%, (air sensitive yellow crystals); mp >210 °C (dec. to red oil); ^1H NMR (C_6D_6): δ = 1.16–1.60 (mm, p-CHMe_2, o-CHMe_2), 2.78 (sept., p-CHMe$_2$), 3.10 (sept., o-CHMe$_2$), 6.65 (m, Ph), 7.10 (s, m-H of Trip), 7.32 (m, Ph).

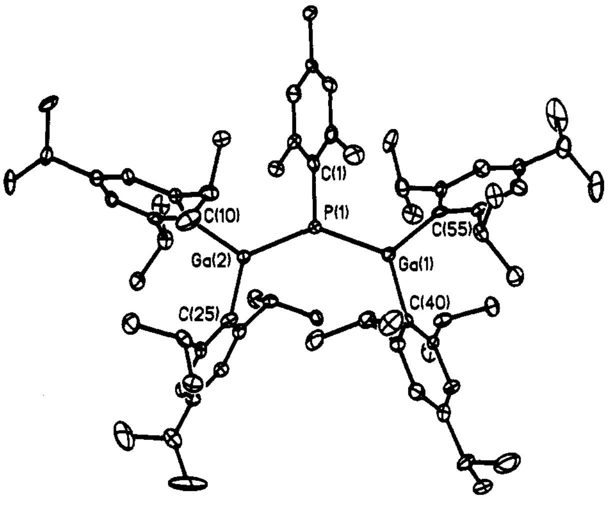

Figure 1. Computer-generated thermal ellipsoid (30%) plot of **1**. Hydrogen atoms and the disordered Et_2O molecule are omitted for clarity.

Table III. Important Bond Distances (Å) and Angles (deg) for **1** and **2**

	1		
P(1)–Ga(1)	2.256(3)	Ga(1)–C(25)	1.970(8)
P(1)–Ga(2)	2.258(3)	Ga(2)–C(40)	1.987(8)
P(1)–C(1)	1.837(9)	Ga(2)–C(55)	1.973(9)
Ga(1)–C(10)	1.998(8)		
Ga(1)–P(1)–Ga(2)	136.2(1)	P(1)–Ga(1)–C(25)	125.8(2)
Ga(1)–P(1)–C(1)	111.2(3)	C(40)–Ga(2)–C(55)	115.4(3)
Ga(2)–P(1)–C(1)	111.4(3)	P(1)–Ga(2)–C(40)	124.0(2)
C(10)–Ga(1)–C(25)	113.5(3)	P(1)–Ga(2)–C(55)	120.3(2)
P(1)–Ga(1)–C(10)	120.6(2)		
	2		
As(1)–G(1)	2.418(1)	Ga(1)–C(22)	1.978(7)
As(1)–Ga(2)	2.401(1)	Ga(2)–C(37)	1.998(6)
As(1)–C(1)	1.950(7)	Ga(2)–C(52)	1.991(7)
Ga(1)–C(7)	1.994(6)		
Ga(1)–As(1)–Ga(2)	115.9(1)	As(1)–Ga(1)–C(22)	109.9(2)
Ga(1)–As(1)–C(1)	108.3(2)	C(37)–Ga(2)–C(52)	119.6(2)
Ga(2)–As(1)–C(1)	105.6(2)	As(1)–Ga(2)–C(37)	119.1(2)
C(7)–Ga(1)–C(22)	127.0(3)	As(1)–Ga(2)–C(52)	120.7(1)
As(1)–Ga(1)–C(7)	122.4(2)		

X-ray Data Collection and the Solution and Refinement of the Structure. Crystals of **1** and **2** were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by silicon grease and immediately placed in the low temperature N_2 stream.[11] X-ray data were collected with a Siemens R3 m/V diffractometer equipped with a graphite monochromator and a locally modified Enraf-Nonius LT apparatus. Calculations were carried out on a Microvax 3200 computer using the SHELXTL PLUS program system. Neutral atom scattering factors and the correction for anomalous dispersion were from ref 12. The structures of **1** and **2** were solved from a Patterson map in the space groups $P2_1/c$ and $P\bar{1}$, respectively. A disordered Et_2O molecule cocrystallizes with **1**. Attempts to model this were unsuccessful. From the difference map it appears that this ether molecule is disordered over at least three different positions. Details of the data collection and refinement and important atom coordinates are provided in Tables I and II, respectively. Important bond distances and angles for the molecules of **1** and **2** are provided in Table III.

Results

Structural Descriptions. MesP{Ga(Trip)$_2$}$_2$·Et$_2$O (1). The structure of **1** is illustrated in Figure 1. It consists of well separated molecules of MesP{Ga(Trip)$_2$}$_2$ which have no crystallographically

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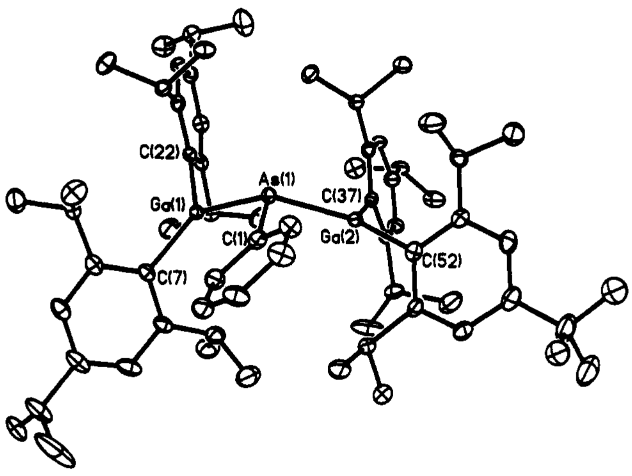

Figure 2. Computer-generated thermal ellipsoid (30%) plot of **2**. Hydrogen atoms are omitted for clarity.

imposed symmetry. The geometry at the phosphorus center is essentially planar. There is a wide Ga(1)–P(1)–Ga(2) angle of 136°, and narrower C–P–Ga angles of ca. 111°. The gallium centers have planar coordination with asymmetric P–Ga–C angles. Thus, the angles P(1)–Ga(1)–C(25) and P(1)–Ga(2)–C(40) are 125.8° and 124.0°, whereas the angles C(10)–Ga(1)–C(25) and C(40)–Ga(2)–C(55) are 113.5° and 115.4°, respectively. The P(1)–Ga(1) and P(1)–Ga(2) bond lengths are 2.256(3) Å and 2.258(3) Å. In addition, the angles between the perpendiculars to the planes at the gallium and phosphorus are 14.7° in the case of Ga(1) and 15.6°, for Ga(2). The angle between the plane of the mesityl ring and that at phosphorus is 62° and the corresponding values for the Trip rings range from 48.1° to 58°. The P(1)–C(1) bond length is 1.837(9) Å and the Ga–C bonds average ~1.98 Å in length.

PhAs{Ga(Trip)$_2$}$_2$ (2). Compound **2** crystallizes as discrete units of the title compound as shown in Figure 2. There is pyramidal geometry at arsenic (Σ°As = 330°) with the widest angle (116°) between the As–Ga bonds. In addition, there is a considerable difference in the angles between the planes at Ga(1) and Ga(2) and the AsGa$_2$ plane (81.3° and 41.7°). The bond lengths Ga(1)–As(1) and Ga(2)–As(1), 2.418(1) Å and 2.401(1) Å are also correspondingly different. The gallium centers have planar coordination with the angles around Ga(2) close to those expected for purely trigonal values. However, the angles at Ga(1) range from 109.9(2)° to 127.0(3)°. The angles between the Trip rings and the planes at Ga span the range 59° to 71° and the As–C and Ga–C bond lengths are 1.950(7) Å and 1.99 Å (av).

Variable Temperature ^{1}H NMR Studies. At T = 25 °C the ^{1}H NMR spectrum of **1** exhibits well defined doublets for the o-CH*Me*$_2$ and p-CH*Me*$_2$ groups. Increasing the temperature to T = 85 °C affords no change. Broadening of the o-CH*Me*$_2$ signal was observed below 10 °C and two broad peaks (1.52 and 0.70 ppm) appear on either side of the p-CH*Me*$_2$ signal at ~(–76 °C). However, in this case, overlap with the p-CH*Me*$_2$ signal prevents an accurate coalescence temperature assignment. The p-CH*Me*$_2$ signal was observed to split into two sets of peaks at ~(–62 °C) with a maximum peak separation of 20.4 Hz at (–84 °C). Insertion of these values into an approximate equation[13] gives $\Delta G^* = 10.6$ kcal mol^{-1} for the process. The o-*CH*Me$_2$ multiplet also splits into two sets of peaks at ~(–74 °C) which together with a peak separation of 45.6 Hz at –95 °C affords a barrier of 9.7 kcal mol^{-1}. In addition, the m-H (Trip) singlet splits into two singlets at ~(–58 °C) with a maximum peak separation of 79 Hz at –95 °C. This corresponds to a barrier of 10.2 kcal mol^{-1} for the dynamic process.

In the case of **2**, at T = 25 °C, three doublets and two singlets are observed in the methyl region. There appears to be dynamic behavior in that the singlets collapse at about –30 °C and one of the doublets coalesces at –59 °C. However, modeling of this dynamic behavior is difficult owing to peak overlap.

Discussion

The synthesis of **1** and **2** arose from attempts to make gallylphosphide and -arsenide compounds analogous to the known borylphosphides[3,7] of formula R$_2$BPR′Li, by reaction of Trip$_2$GaCl with one equivalent of RELi$_2$ (E = P, As). These reactions yielded small amounts of **1** and **2** along with uncharacterizable oils. The synthesis of **1** and **2** in moderate yield was accomplished by isolation of the dilithium salts, RELi$_2$ (E = P, As) and subsequent treatment with two equivalents of Trip$_2$GaCl in tetrahydrofuran at room temperature. The use of main group 5 dilithium salts in the synthesis of low coordinate, heavier main group 3–5 compounds has been limited. This is due to an apparent preparative restriction to small substituents at phosphorus and arsenic. However, examples of their use have appeared in the synthesis of the main group 3–5 cluster [Ga$_4$(Trip)$_3${P(1-Ad)$_4$}P(H)(1-Ad)],[14] the cubane [*t*-BuGa(μ_3-PSiPh$_3$)]$_4$,[15] and the cyclic species [{2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$}GaPSiPh$_3$]$_2$[16] and [(2,4,6-Ph$_3$C$_6$H$_2$)GaP(*cyclo*-C$_6$H$_{11}$)]$_3$.[17] Although low coordinate Ga/E (E = P, As) compounds have been prepared with 1:1–3 stoichiometry,[18] **1** and **2** are the first examples of structurally characterized monomeric 2:1 compounds.

The structure of **1** possesses several features of interest. First, the digallylphosphane contains a planar three-coordinate phosphorus center. This is in contrast to related cyclic species [(2,4,6-Ph$_3$C$_6$H$_2$)GaP(*cyclo*-C$_6$H$_{11}$)]$_3$ (Σ°P = 315.7° to 331.1°)[17] and [*t*-BuGaPMes*]$_2$ (Mes* = 2,4,6-t-Bu$_3$C$_6$H$_2$, Σ°P = 314.7°)[19] which, for the most part, have strongly pyramidal coordination at the P atoms. The planarity of the core array in **1** almost extends to the GaC$_2$ planes at Ga(1) and Ga(2) which subtend relatively small interplanar angles of 14.7° and 15.6° with respect to the plane at phosphorus. Interestingly, this occurs despite the large size of the –GaTrip$_2$ groups which would be better accommodated sterically by larger interplanar angles. The wide angle, Ga(1)–P(1)–Ga(2), the asymmetric P–Ga–C and narrow C–Ga–C angles reflect the steric crowding in **1**. Similar structural characteristics were observed for the closely related diborylphosphane, (PhP(BMes$_2$)$_2$) allyl cation analogue in which a completely planar C$_2$B–P(C)–BC$_2$ array was observed.[20] This structural feature was attributed to B–P–B π-bonding which is maximized by having all three p-orbitals aligned parallel to each other even at the expense of greater steric congestion. The structural resemblance of PhP(BMes$_2$)$_2$ and the allyl cation to **1** suggest the possibility of a similar bonding scheme for the Ga–P–Ga p orbitals in **1**, as illustrated in Figure 3. This type of π-bonding in **1** is made possible by the reduction of the phosphorus inversion barrier through the bulky and electropositive nature of the two –GaTrip$_2$ groups. Further support for this interpretation are the Ga–P bond lengths (2.257 Å) which are the shortest observed to date for molecular Ga–P compounds.[6,18,19] The Ga–P distance may be compared with that observed for t-BuGa(P(H)Mes*)$_2$ (av

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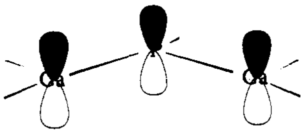

Figure 3. Schematic illustration of p-orbitals in **1** involved in delocalized π-bonding analogous to the allylic cation.

Ga–P = 2.325(5) Å)[19] which is a putative Ga–P analogue of the allyl anion. The longer Ga–P distances in this species suggest that π-delocalization is not extensive. The Ga–P distances in **1** are also significantly shorter than the Ga–P bond length (2.295(3) Å) seen in t-Bu$_2$GaP(Mes*)SiPh$_3$.[5] This might be a result of greater steric crowding in t-Bu$_2$GaP(Mes*)SiPh$_3$ which inhibits a closer approach of the gallium and phosphorus atoms. A variable temperature ^{1}H-NMR study of **1** was thus undertaken to examine the strength of the Ga–P π bonding in **1**. For compound **1**, two dynamic processes may occur; aromatic ring flip or rotation about the Ga–P bond. The VT ^{1}H-NMR study of **1** yields three similar ΔG^* values averaging ~10.2 kcal mol^{-1} which suggest that a single dynamic process occurs. Certain features of the spectrum of compound **1** suggest that restricted rotation around the Ga–P is being observed. For example, the p-CHMe_2 resonances of **1** split into two signals, which is inconsistent with a ring flip process. Most probably the restricted rotation is due to an allylic type of Ga–P–Ga π bonding. It is notable that the observed strength (ca. 10.2 kcal mol^{-1}) of this π-bond is less than that observed for t-Bu$_2$GaP(Mes*)SiPh$_3$ in spite of shorter Ga–P distances in **1**. We attribute this apparent anomaly to the greater planarity at phosphorus in **1** which gives rise to a shorter Ga–P bond owing to a change in σ-orbital hybridization. Steric considerations may also play a role in differences in the π-bonding strengths between the two compounds.

The most important structural feature in PhAs{Ga(Trip)$_2$}$_2$, **2** is the pyramidal coordination at arsenic. This may either reflect the larger (up to 10 kcal mol^{-1}) inversion barrier at arsenic in comparison to phosphorus[21] or the lower congestion at arsenic owing to longer As–Ga bonds. It could also be argued that Ga–As p–p π-bonding is inherently weaker than that in the Ga–P bond which would make planarity at arsenic less likely. However, comparison of the strength of related B–P and B–As π-bonding shows that, for these pairs of atoms, there is only a small difference in their relative strength.[8] In any case, it is apparent that Ga–As π-bonding in unable to completely overcome the larger inversion barrier. Nonetheless, the arsenic center in **2** is less pyramidal (Σ°As = 330°) than in the related compounds, (t-Bu)$_2$GaAs(t-Bu)$_2$, (Ga–As = 2.466(3) Å, Σ°As = 317°),[22] (η^1-C$_5$Me$_5$)$_2$GaAs(SiMe$_3$)$_2$, (Ga–As = 2.433(4) Å, Σ°As = ~320°),[23] and Ga(AsMes$_2$)$_3$, (Ga–As = ~2.49 Å, Σ°As = 311–320°).[24] Presumably, the flattening at arsenic in **2** is due to the greater electropositive character of the ligand triads (CGa$_2$ vs GaC$_2$) surrounding arsenic and perhaps the bulk of the –GaTrip$_2$ groups. In addition, the Ga–As bond lengths (2.401(1) Å and 2.418(1) Å) are notably shorter than in the above compounds. However, the Ga–As distance (2.401(4) Å) in [(THF)Br$_2$Ga]$_3$As,[25] in which four coordination at the gallium centers prevents Ga–As π-bonding, is comparable. This observation along with the large angles between the arsenic lone pair and the empty gallium 4p orbitals in **2** suggests that multiple bond character similar to that proposed for **1** cannot be extensive.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Full tables listing data collection parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters and a figure showing variable temperature ^{1}H NMR spectra (23 pages). Ordering information is given on any current masthead page.

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