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Molecular Gallium Arsenide Phosphide Clusters Prepared from AsP_3, P_4, and $[\{GaC(SiMe_3)_3\}_4]$

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Abstract: Treatment of AsP_3 with 0.75 equivalents of $[\{GaC(SiMe_3)_3\}_4]$ resulted in selective insertion of three equivalents of $\{GaC(SiMe_3)_3\}$ into the three As–P bonds to give $[As\{GaC(SiMe_3)_3\}_3P_3]$ (**1**-As) with an intact *cyclo*-P_3 ring. This yellow compound has been characterized by NMR spectroscopy, combustion analysis, single-crystal X-ray diffraction, UV/Vis spectroscopy, Raman spectroscopy, and cyclic voltammetry (THF, 0.2 M [TBA] $[B(C_6F_5)_4]$; TBA = tetrabutyl ammonium). Computational models of **1**-As and the isomeric $[P\{GaC(SiMe_3)_3\}_3AsP_2]$ (**1**-P) have been investigated as well, revealing several interesting electronic features of these cage molecules. Following from the cyclic voltammetry studies of **1**-As that highlight an irreversible two-electron reduction at −2.2 V versus Fc/Fc^+, treatment with one equivalent of $[Mg(C_{14}H_{10})(thf)_3]$ resulted in two-electron reduction to provide $[As\{GaC(SiMe_3)_3\}_3P_3Mg(thf)_3]$ (**2**), in which the Mg^{2+} ion has inserted into one of the P–P bonds of the *cyclo*-P_3 ring. It was also found that treatment of AsP_3 or P_4 with one equivalent of $[\{GaC(SiMe_3)_3\}_4]$ resulted in formation of the quadruple insertion products $[As\{GaC(SiMe_3)_3\}_4P_3]$ (**3**) and $[P\{GaC(SiMe_3)_3\}_4P_3]$ (**4**), respectively.

Keywords: arsenic · gallium · phosphorus · single-source precursor

Introduction

Small inorganic cluster molecules are of considerable interest in terms of the development of theories of bonding and with respect to their physical properties as geared toward potential materials science applications.[1,2] A robust synthesis of the binary tetrahedral interpnictogen cluster AsP_3 has been developed recently.[3] While it is an endergonic compound, AsP_3 is kinetically stable over a wide temperature range and the compound can be isolated in pure form.[3,4] AsP_3 has been studied in detail with respect to its structural and electronic properties.[4,5] Early reactivity studies of AsP_3 demonstrated complexation of the intact tetrahedron to transition metal centers, single AsP_3 bond cleaveage reactions to generate arsatriphosphabicyclobutane structures, as well as reactions in which the AsP_3 tetrahedron is completely degraded to As and P units.[4] The single-bond cleavage reactions were particularly interesting as they were selective for cleavage of a single As–P bond over a P–P bond. It has been estimated that there is a 6 $kcal\,mol^{-1}$ difference between the As–P bond energy and the P–P bond energy in AsP_3.[4] With this piece of information in hand, we became interested in the possibility of discovering a reaction in which all three of the As–P bonds in AsP_3 might be selectively cleaved under certain conditions leaving an intact *cyclo*-P_3 ring, in line with our laboratory's interest in the chemistry of P_3-containing molecules.[3,4,6,7]

Uhl and co-workers have reported the synthesis of a novel tetragallane compound $[\{GaC(SiMe_3)_3\}_4]$, which exists as a tetramer in the solid state, but dissociates into monomeric $\{GaC(SiMe_3)_3\}$ fragments in dilute solutions and at elevated temperatures.[8] $[\{GaC(SiMe_3)_3\}_4]$ is synthetically available in good yield by the reduction of the corresponding alkyltrichlorogallate with Rieke magnesium,[9] and shows remarkable chemical reactivity similar to the more intensively investigated indium analogue $[\{InC(SiMe_3)_3\}_4]$.[10] Uhl and co-workers found that $[\{GaC(SiMe_3)_3\}_4]$ and P_4 undergo a slow reaction in boiling *n*-hexane to give yellow crystals of the novel trigallium tetraphosphorus compound $[P\{GaC(SiMe_3)_3\}_3P_3]$ in moderate (52 %) yield.[11] The structure of $[P\{GaC(SiMe_3)_3\}_3P_3]$ shows the insertion of three monomeric $GaC(SiMe_3)_3$ fragments into three of the six P–P bonds of the P_4 tetrahedron with a *cyclo*-P_3 ring intact and a lone gal-

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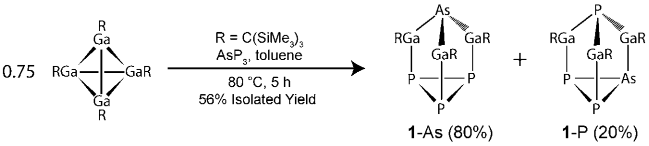
lium-bound P atom at the molecule's apex. This generates a molecular gallium phosphide core with a near C_{3v}-symmetric cage structure reminiscent of P_4S_3.[12] This reaction is a rare example of P_4 activation in which three P−P bonds are cleaved, while all four P atoms are incorporated into a single product molecule. This reaction type seemed ideally suited for an investigation involving AsP_3, in which case cleavage of all three As−P bonds would be expected on thermodynamic grounds.

Results and Discussion

Treatment of one equivalent of AsP_3 with 0.75 equivalents of [{GaC(SiMe$_3$)$_3$}$_4$] in toluene at 80 °C over 5 h gave a reaction accompanied by a color change of the solution from red-orange to yellow and, upon cooling to 20 °C, precipitation of fibrous yellow needles. This yellow material was obtained in 56 % isolated yield and analysis clearly identified the product as the desired triple insertion product (Scheme 1). Although [As{GaC(SiMe$_3$)$_3$}$_3$P$_3$] (**1**-As) is the major species formed in the reaction, as determined by NMR interrogation of the crude reaction mixture, there is some formation of the isomeric triple insertion product [P{GaC(SiMe$_3$)$_3$}$_3$AsP$_2$] (**1**-P) as can clearly be seen by ^{31}P NMR spectroscopy, Figure 1. The ^{31}P NMR spectrum of **1**-As is simple, as expected, with only a singlet resonance at −192 ppm for the intact P_3 ring. The alternative structure **1**-P gives rise to a doublet at −174 ppm (2P) and an upfield triplet at −495 ppm (1P) with $^2J_{P\text{-}P}$ at 34 Hz, which is quite similar to the reported values of −202 (d, 3P) and −522 (q, 1P) with $^2J_{P\text{-}P}$ at 31 Hz for the all-phosphorus congener provided by Uhl and co-workers.[11] Perhaps the most exciting feature of this reaction of [{GaC(SiMe$_3$)$_3$}$_4$] with AsP_3 is that the insertion isomers are not formed in a statistical ratio and that there is a strong preference for selective cleavage of the As−P bonds over the P−P bonds.



Scheme 1. Preparation of [As{GaC(SiMe$_3$)$_3$}$_3$P$_3$] (**1**-As) and [P{GaC(SiMe$_3$)$_3$}$_3$AsP$_2$] (**1**-P).

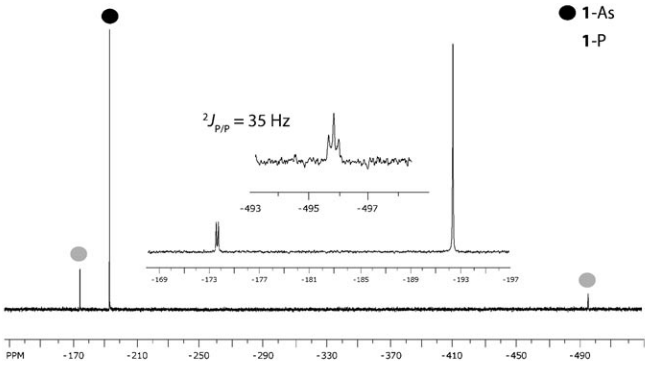


Figure 1. ^{31}P NMR spectrum of **1**-As and **1**-P prior to separation.

X-ray quality crystals of compound **1**-As were obtained as yellow needles from diffusion of pentane into a toluene solution at −35 °C and the thermal ellipsoid plot of the structure is shown in Figure 2.[13] Compound **1**-As crystallized in the hexagonal space group $P6_3$. The crystal structure of **1**-As confirms insertion of three {GaC(SiMe$_3$)$_3$} fragments into the As−P bonds of AsP_3 with an intact *cyclo*-P_3 ring and no compositional disorder of the arsenic and phosphorus positions, consistent with the NMR spectrum of the isolated powder, which indicates no contamination with **1**-P.[14] The Ga1−As1 interatomic distance is 2.426(1) Å and the Ga1−P1 interatomic distance is 2.397(2) Å; both values fall within expected ranges for the interatomic distances of crystallographically characterized compounds with Ga−As and Ga−P single bonds.[15] There are three equivalent P−P bonds in the molecule that have an interatomic distance of 2.213(3) Å. The Ga atoms are in an approximately trigonal planar coordination environment with a P1-Ga1-As1 angle of 115.08(5)°, a C1-Ga1-P1 angle of 120.08°, and a C1-Ga1-As1 angle of 124.6(2)°. The three Ga-As-Ga angles are equivalent and equal 83.86(4)°, distinctly acute for trisubstituted arsines.[16] This structure is not isostructural with the all-phosphorus analogue [P{GaC(SiMe$_3$)$_3$}$_3$P$_3$] prepared by Uhl and co-workers that crystallized in the orthorhombic

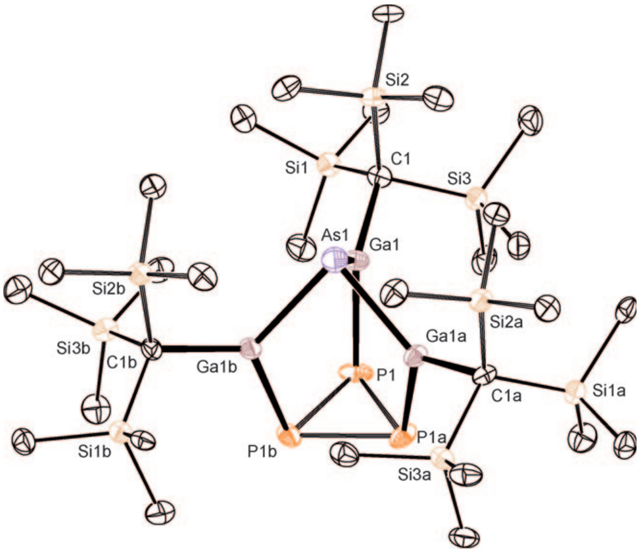


Figure 2. Thermal ellipsoid plot (50 % probability) of **1**-As with hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: Ga−C 2.005(6), Ga−P 2.3978(17), Ga−As 2.4260(10), Ga−Si 2.917(7), As−Ga 2.4260(10), P−P 2.213(3); C-Ga-P 120.08(17), C-Ga-As 124.67(17), P-Ga-As 115.08(5), C-Ga-Si 46.1(2), P-Ga-Si 97.04(18), As-Ga-Si 130.96(17), Ga-As-Ga 83.86(4).

space group *Pnma*.[11] Cluster compound **1**-As packs in a staircase pattern with the *cyclo*-P_3 ring of one molecule in line with the As atom of the next molecule, with one interstitial pentane molecule present per cluster, and with no close contacts between any of the molecules in the unit cell.

Molecular chemistry targeted at generating Ga–As bonds is of considerable interest due to the potential of such species to serve as single-source precursors to gallium arsenide solid-state materials.[1,2,17] Prior to 1986, there were no published examples of gallium arsenic compounds containing a single Ga_3As unit.[18] However, during that year Wells and co-workers reported the isolation and structural characterization of a compound with four-coordinate Ga and three-coordinate As in a 3:1 ratio with their synthesis of $[As\{GaBr_2(thf)\}_3]$.[18] In the concluding section of that report the authors state, “it should be noted that thus far we have been unsuccessful in our attempts to isolate a monomeric compound containing a Ga_3As unit having three coordinate Ga and As; however, it is expected that with the appropriate substituents on Ga this should be possible”.[18] This advance, the authors suggest, would be significant for the generation of single-source precursors for semiconductor synthesis. Since then, few reports of molecules containing three Ga–As bonds have been published,[19] and compound **1**-As represents the realization of Wells and co-workers goal of obtaining a Ga_3As unit with three coordinate Ga and As.

Charge analysis on a computational model of **1**-As, $[As(GaCH_3)_3P_3]$, reveals an intriguing feature of this cluster. Five different charge analyses are presented in Table 1; however, the discussion here will focus mainly on the Hirshfeld and Voronoi deformation density methods, as these have been shown to conform the best to chemical experience, and in this analysis, are mutually consistent.[20,21] The average charge on the three P atoms of the *cyclo*-P_3 ring is approximately −0.10, while the charge at the apical arsenic atom is −0.24 (Table 1).[14] This considerable negative charge at arsenic suggests that the arsenic atom in this structure could potentially have nucleophilic character. Mulliken, multipole-derived, and Bader charge analyses place the partial charge on the apical arsenic even more negative at −0.46, −0.58, and −0.70 respectively. Interestingly, Bader analysis suggests that in **1**-P, the apical P atom is even more negative with a charge of −0.81.

Table 1. Charge analysis for**1**-As and **1**-P model complexes computed in ADF.

Charge type	As		Ga		P[a]	
	1-As	**1**-P	**1**-As	**1**-P	**1**-As	**1**-P
Hirshfield	−0.20	−0.04	0.28	0.28	−0.09	−0.24/−0.10
Voronoi deformation density	−0.24	−0.05	0.22	0.22	−0.10	−0.29/−0.12
Mulliken	−0.45	−0.37	0.19	0.08	0.00	0.02/0.10
multipole-derived	−0.58	−0.66	0.26	0.19	−0.04	−0.14/0.15
Bader	−0.70	−0.16	0.90	0.92	−0.29	−0.81/−0.33

[a] For **1**-P apical/ring.

A space-filling model of **1**-As shows that the apical arsenic atom, while recessed into the ligand pocket, is somewhat accessible (Figure 3). A side view of this model also reveals that the *cyclo*-P_3 ring is relatively exposed. These data beg the question as to what would be the preferred coordination mode if **1**-As were to serve as a bulky ligand.[16] An estimation of the cone angle for **1**-As using an Ni–As distance of 2.32 Å gives approximately 180°, with the Ni center well protected in the ligand pocket.[14]

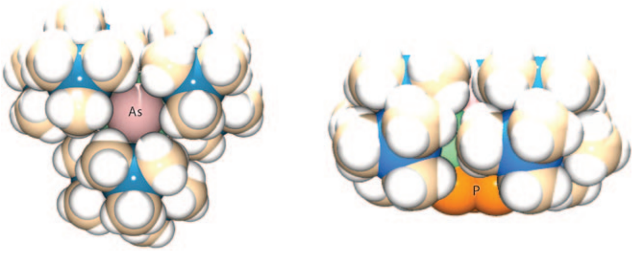


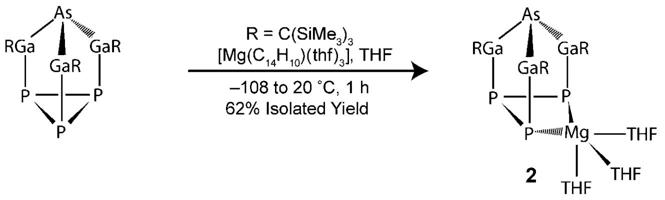
Figure 3. Space filling models of **1**-As; top view (left), side view (right).

A view of the computed HOMO of a computational model for **1**-As shows that it is largely phosphorus p orbital in character. The LUMO is characterized by the presence of low-lying empty Ga p orbitals, suggesing redox activity for **1**-As.[14] Comparing the charge distribution of **1**-As to that of **1**-P reveals in all analyses, quite different molecular polarities, (Table 1). This provides a rationale for the facile separation of **1**-As and **1**-P on crystallization; despite the structural similarity of the two isomers, this disparity likely inhibits co-crystallization.

The optical properties of **1**-As have been studied by UV/Vis absorption spectroscopy; this yellow compound displays two weak bands trailing into the visible region.[14] Compound **1**-As, however, does not display any fluorescence behavior when excited at 250, 300, or 340 nm. Raman spectroscopy with excitation at 785 nm gives a spectrum containing many strong bands in the 200 to 3000 cm^{-1} region.[14] Comparison of this Raman spectrum with that of the starting $[\{GaC(SiMe_3)_3\}_4]$ molecule allows us to partially deconvolute the contributions from the $C(SiMe_3)_3$ substituents. There is a strong resonance at 322 cm^{-1} that is suggestive of a P–P stretching mode of the *cyclo*-P_3 ring, especially given its similarity to the analagous mode in AsP_3.[3,14]

Cyclic voltammetry studies were also carried out to probe the electronic properties of this unusual cluster. Scanning cathodically in a solution of **1**-As in THF with 0.2 M [TBA] $[B(C_6F_5)_4]$ (TBA = tetrabutyl ammonium) as the supporting electrolyte, one sees a single irreversible two-electron reduction process centered at −2.2 V vs Fc/Fc^+; a cascade of irreversible one-electron oxidation processes are observed on the return wave following this reduction event.[14] Noting the propensity of **1**-As to undergo electrochemical two-electron reduction, next we turned to an examination of the chemical two-electron reduction of the compound.

Treatment of **1**-As with one equivalent of $[Mg(C_{14}H_{10})(thf)_3]$[22] in thawing THF results in a color progression from yellow, through green, and finally to a homogeneous red-orange (Scheme 2). This two-electron-reduced product is easily isolated by removal of THF from the crude reaction mixture and thoroughly washing the crude solids with benezene. Filtration effects the removal of anthracene, leaving a spectroscopically pure pink-orange powder. As isolated, $[As\{GaC(SiMe_3)_3\}_3P_3Mg(thf)_3]$ (**2**) is insoluble in hexane and pentane and is sparingly soluble in benzene and toluene, but it dissolves readily in THF or pyridine. Cooling an orange solution of the isolated powder in THF to −35 °C results in a reversible color change to green, indicative of thermochromic behavior.[23–25] The NMR spectral features of **2** are consistent with a structure in which a single P–P bond has been cleaved (Figure 4) with a doublet at −45.8 ppm (2P) and a triplet at −243.5 ppm (1P) with a $^1J_{P-P}$ of 49 Hz; these data compare favorably to those reported for structurally related cyclic tetraphosphines.[26–29] While DFT calculations show the LUMO of **1**-As to be mostly Ga p orbital in character, there is also a P–P antibonding contribution.[14] These calculations, along with the ^{31}P NMR data, suggest that the structure of compound **2** is one in which a single P–P bond of the *cyclo*-P_3 ring opens to incorporate the Mg^{2+} ion into a four-membered ring. Variable-temperature NMR experiments are consistent with a structural distortion on cooling below −20 °C with the ^{31}P NMR resonances broadening and shifting; at −65 °C the former doublet appears as a broad resonance at −21 ppm and the former triplet shifts to −207 ppm with the $^1J_{P-P}$ increasing to 121 Hz.[14] Compound **2** decomposes completely at 20 °C in THF over the course of four days into two, as yet unidentified, products.[14]



Scheme 2. Preparation of $[As\{GaC(SiMe_3)_3\}_3P_3Mg(thf)_3]$ (**2**).

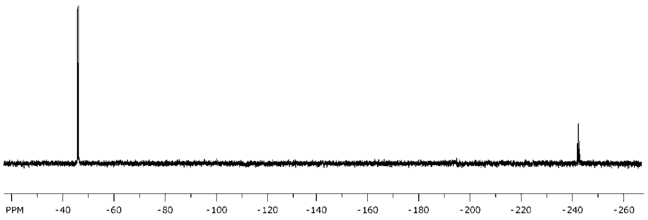


Figure 4. ^{31}P NMR spectrum of **2**.

Observation of an additional bond cleavage event in the reaction of **1**-As with $[Mg(C_{14}H_{10})(thf)_3]$ suggested that an additional equivalent of $\{GaC(SiMe_3)_3\}$ could potentially react with AsP_3 to give a quadruple insertion product in which one of the P–P bonds of the *cyclo*-P_3 ring is cleaved. Interestingly, treatment of AsP_3 with one equivalent of $[\{GaC(SiMe_3)_3\}_4]$ instead of 0.75 equivalents, indeed led to the formation of new reaction products. The ^{31}P NMR spectrum of this product mixture contains a triplet at −155 ppm and a doublet at 182 ppm in a 1:2 ratio for $[As\{GaC(SiMe_3)_3\}_4P_3]$ (**3**-As) and three doublets of doublets at 155, −163, and −257 ppm in a 1:1:1 ratio for $[P\{GaC(SiMe_3)_3\}_4AsP_2]$ (**3**-P; Figure 5 A). Once again a preference is observed in favor of apical As. These data suggest that the P_3 (AsP_2) ring has ruptured, giving the targeted quadruple insertion products shown in Scheme 3. For **3**-P, the fourth $\{GaC(SiMe_3)_3\}$ unit inserts into the As–P bond of the AsP_2 ring, exclusively. DFT calculations have confirmed that the observed ^{31}P chemical shifts are consistent with such a

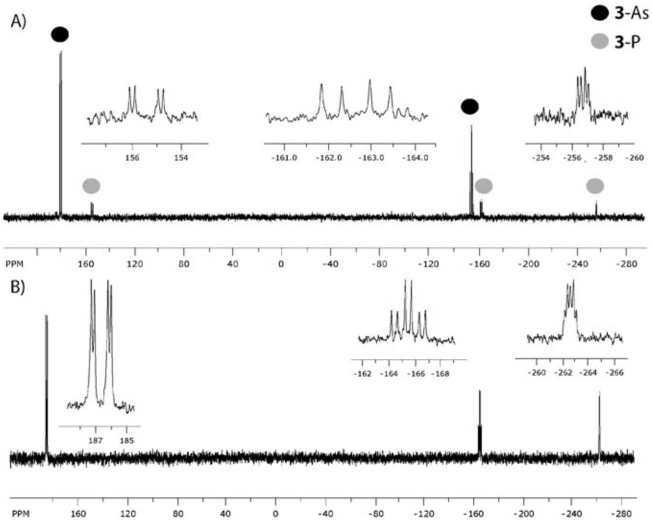
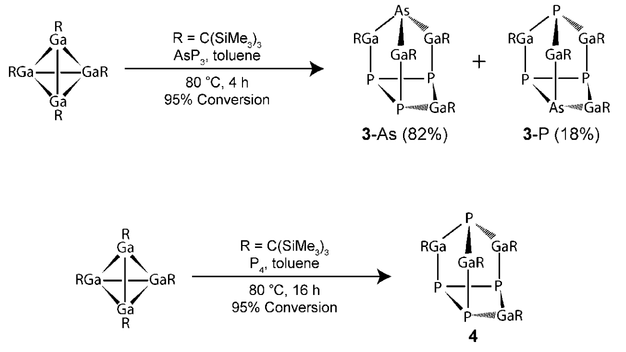


Figure 5. A) ^{31}P NMR spectrum of a mixture of **3**-As and **3**-P. B) ^{31}P NMR spectrum of **4**.



Scheme 3. Preparation of $[As\{GaC(SiMe_3)_3\}_4P_3]$ (**3**-As), $[P\{GaC(SiMe_3)_3\}_4AsP_2]$ (**3**-P) and $[P\{GaC(SiMe_3)_3\}_4P_3]$ (**4**).

structure (Figure 6).[14] Compound **3**-As can also be cleanly generated by treatment of isolated **1**-As with 0.25 equivalents [{GaC(SiMe$_3$)$_3$}$_4$].

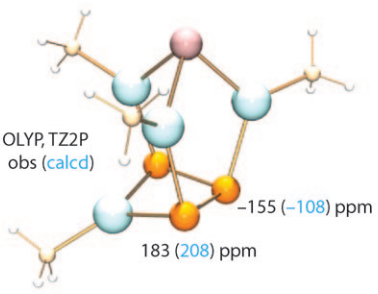


Figure 6. DFT geometry optimized computational model (As[GaCH$_3$]$_4$P$_3$) of the quadruple insertion product **3**-As.

This quadruple insertion reaction is not unique to AsP$_3$. When P$_4$ is treated with one equivalent of [{GaC(SiMe$_3$)$_3$}$_4$], [P{GaC(SiMe$_3$)$_3$}$_4$P$_3$] (**4**), the all-phosphorus analogue, is obtained cleanly from the reaction mixture (Figure 5B). The apical P atom in **4** resonates at −263 ppm in the ^{31}P NMR spectrum, suggestive of an opening of the Ga-P-Ga angles accompanying cleavage of the *cyclo*-P$_3$ ring. The basal P$_3$ unit has resonances at −167 and 187 ppm, similar to the analogous resonances in **3**. Both compounds **3** and **4** are unstable in solution towards reversion to [{GaC(SiMe$_3$)$_3$}$_4$] (this tetramer was readily idenitifed by ^{1}H NMR spectroscopy and single crystals were grown from the solution and identified by X-ray crystallography) and several unidentified products over time. At 10 °C, this decomposition process takes approximately two days to go to completion. Attempts to isolate crystals of **3** and **4** suitable for solid-state structural determination using X-ray diffraction methods were unsuccessful.

Conclusion

The reactivity of P$_4$ with monovalent Group III precursors has been of considerable interest for developing new models of bonding in cage molecules and clusters, as well as for investigating new starting materials for binary and ternary III/V semiconductor applications.[2,11,30,31] Indeed, several novel structure types have been identified over the past 20 years.[31] Herein, we have described the synthesis of new cage molecules with cores consisting of Ga, As, and P and stemming from insertion chemistry of the newly isolated AsP$_3$ molecule.[3–5] Both triple- and tetra-insertion products have been characterized. The redox chemistry of the triple insertion product was investigated and a two-electron reduced species bearing a Mg^{2+} counterion was isolated. Additionally, it was found that the quadruple insertion behavior of {GaC(SiMe$_3$)$_3$} was not unique to AsP$_3$ and an analogous product could be isolated and characterized in the case of P$_4$, as well in a reaction that can be described in terms of coalescing Ga$_4$ and P$_4$ tetrahedra. The new cage molecules reported herein resemble tiny semiconductor clusters and, as such, further exploration of **1**-As, and **3** as precursors to solid-state arsenide-phosphide materials will be of interest. In addition the reaction chemistry of **1**-As, in particular with respect to its application as a bulky arsine or *cyclo*-P$_3$ ligand, merits further exploration.

Experimental Section

All manipulations were performed in a Vacuum Atmospheres model MO-40 M glove box under an atmosphere of purified dinitrogen. Solvents were obtained anhydrous and oxygen-free from a contour glass solvent purification system, or by analogous methods.[32] Celite 435 (EM Science), 4 Å molecular sieves (Aldrich), and alumina (EM Science) were dried by heating at 200 °C under dynamic vacuum for at least 24 h prior to use. All glassware was oven-dried at temperatures greater than 170 °C prior to use. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Labs. [D$_6$]Benzene and [D$_5$]pyridine were degassed and stored over molecular sieves for at least two days prior to use. The compounds AsP$_3$,[3,4] [{GaC(SiMe$_3$)$_3$}$_4$],[8,9,11] and [Mg(C$_{14}$H$_{10}$)(thf)$_3$][22] were synthesized according to reported methods. GaCl$_3$, anhydrous MgCl$_2$, MeLi (1.6 M solution), HC(SiMe$_3$)$_3$, and anthracene were purchased from Aldrich chemical company and used as received. NMR spectra were obtained on Varian Mercury 300 or Varian Inova 500 instruments equipped with Oxford Instruments superconducting magnets or on Bruker Avance 400 instruments equipped with Magnex Scientific superconducting magnets. ^{1}H NMR spectra were referenced to residual C$_6$D$_5$H (7.16 ppm) or C$_5$D$_4$N (8.74 ppm). ^{13}C NMR spectra were referenced to C$_6$D$_6$ (128.39 ppm) or C$_5$D$_5$N (150.35 ppm). ^{31}P NMR spectra were referenced externally to 85 % H$_3$PO$_4$ (0 ppm). Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, Indiana). For Raman studies, an Invictus solid-state laser at 785 nm, manufactured by Kaiser Optics, was routed through fiber-optic cables to a Hololab series 5000 Raman Microscope. The Raman scattering was observed through 180° reflectance through the objective of the Raman microscope. Each spectrum was corrected for dark current and cosmic ray interference using the Hololab software. UV/Vis spectra were obtained on a Cary 14 spectrophotometer, running the OLIS Globalworks software suite, in 1 cm quartz cells manufactured by Starna.

Preparation of [As{GaC(SiMe$_3$)$_3$}$_3$P$_3$] (1-As/P): AsP$_3$ (78 mg, 0.467 mmol) was dissolved in toluene (10 mL, freshly distilled from Na/benzophenone). [GaC(SiMe$_3$)$_3$]$_4$ (422 mg, 0.350 mmol) was also dissolved in toluene (10 mL). The two solutions were combined in a thick-walled glass reactor along with additional toluene (5 mL) to effect quantitative transfer of the reagents. The reaction mixture was heated with stirring for 5 h at 80 °C. During this time the solution lightened from red-orange to yellow-orange. On cooling, a copious amount of fibrous, yellow precipitate formed in the reaction flask. The solution was concentrated to 15 mL and cold pentane (5 mL) was added. The resulting yellow microcrystalline solids were collected by filtration and dried to constant mass giving 251 mg of cotton-like yellow solids. The filtrate was dried under reduced pressure and the residue was dissolved in toluene (5 mL) and placed in the freezer in order to obtain a second crop containing an additional 28 mg for a total of 279 mg (0.260 mmol, 56 % yield) of a 4:1 mixture of [As{GaC(SiMe$_3$)$_3$}$_3$P$_3$] (**1**-As) to [P{GaC(SiMe$_3$)$_3$}$_3$AsP$_2$] (**1**-P). ^{1}H NMR (20 °C, [D$_6$]benzene, 500 MHz): $\delta = 0.418$ (s, 27 H; **1**-As), 0.428 ppm (s, ≈7 H (20 % of total); **1**-P); ^{31}P{^{1}H} NMR (20 °C, [D$_6$]benzene, 202.5 MHz): $\delta = -192.39$ (s, 3 P; **1**-As), −173.61 (d, $^2J_{\text{P-P}} =$ 34 Hz, ≈0.75 P (20 % of total); **1**-P, ring P atoms), −495.84 ppm (t, $^2J_{\text{P-P}} =$ 34 Hz, ≈0.25 P (20 % of total); **1**-P, apical P atom); ^{13}C{^{1}H} NMR (20 °C, [D$_6$]benzene, 125.7 MHz): 6.6 (s, **1**-As, Me groups), 6.7 (s, **1**-P, Me groups), 27.6 (s, **1**-As, C bound to Ga), 27.8 ppm (s, , **1**-P, C bound to Ga); UV/Vis: λ (ε) = 294 (2866), 382 nm (1412 M^{-1} cm^{-1}); elemental analysis calcd (%) for $C_{30}H_{81}AsGa_3P_3Si_9$: C 33.62, H 7.62, P 8.67; found: C 33.53, H 7.24, P 9.07.

Preparation of $[As\{GaC(SiMe_3)_3\}_3P_3Mg(thf)_3]$ (2): $[Mg(C_{14}H_{10})(thf)_3]$ (27 mg, 0.065 mmol) was dissolved in THF (7 mL) and was frozen in the cold well. Compound **1**-As (70 mg, 0.065 mmol) was likewise suspended in THF (8 mL) and was separately frozen. Upon thawing the solution of $[Mg(C_{14}H_{10})(thf)_3]$ was added to the solution of **1**-As and the reaction mixture was allowed to warm to room temperature and stir for 1 h. During this time the solution went from a yellow-orange suspension through a bright grass-green color then to a heterogeneous red-orange color. After 1 h of stirring the reaction mixture was taken to dryness under reduced pressure and the resulting red residue was stirred in hexane (10 mL) for 5 min and then taken to dryness again. The resulting residue was slurried in benzene (20 mL) for 20 min and was then filtered and the pink solids were isolated. These solids were recrystallized at −35 °C in a 1:1 mixture of THF and toluene, giving green microcrystals of **2** after 7 h. These solids were isolated and dried to an orange solid with a constant mass of 53 mg (0.04 mmol, 62 % yield). It is worth noting that the red-orange to green color change is fully reversible; room temperature solutions of **2** are red-orange and solutions below approximately −20 °C are green. ^1H NMR (20 °C, $[D_5]$pyridine, 400 MHz): $\delta = 0.55$ ppm (s, 81 H); $^{31}P\{^1H\}$ NMR (20 °C, $[D_8]$THF, 162 MHz): $\delta = -243.5$ (t, $^1J_{P\text{-}P} = 49$ Hz, 1 P), −45.8 ppm (d, $^1J_{P\text{-}P} = 49$ Hz, 2 P); $^{13}C\{^1H\}$ NMR (20 °C, $[D_5]$pyridine, 100.5 MHz): $\delta = 7.4$, 26.3 (THF), 27.2, 68.26 ppm (THF); elemental analysis calcd (%) for $C_{42}H_{105}AsGa_3MgO_3P_3Si_9$: C 38.44, H 8.06, P 7.08; found: C 38.02, H 7.95, P 6.98.

Preparation of $[As\{GaC(SiMe_3)_3\}_4P_3]$ (3-As/P): AsP_3 (65 mg, 0.387 mmol) was dissolved in toluene (10 mL, freshly distilled off of Na/benzophenone). $[\{GaC(SiMe_3)_3\}_4]$ (467 mg, 0.387 mmol) was also dissolved in toluene (10 mL). The two solutions were combined in a thick-walled glass reactor along with additional toluene (5 mL) to effect quantitative transfer of the reagents. The reaction mixture was heated with stirring for 4 h at 80 °C. During this time the solution remained red-orange during the course of the reaction. The final reaction mixture showed greater than 95 % conversion to a of a 4:1 mixture of $[As\{GaC(SiMe_3)_3\}_4P_3]$ (**3**-As) and $[P\{GaC(SiMe_3)_3\}_4AsP_2]$ (**3**-P). On sitting at room temperature or below, **3**-As/P readily reverts to $[\{GaC(SiMe_3)_3\}_4]$ and other unidentified products. $^{31}P\{^1H\}$ NMR (20 °C, $[D_6]$benzene, 202.5 MHz): $\delta = -256.7$ (dd, $^2J_{P\text{-}P} = 55$ Hz, $^2J_{P\text{-}P} = 27$ Hz, 0.3 P; **3**-P), −162.9 (dd, $^1J_{P\text{-}P} = 135$ Hz, $^2J_{P\text{-}P} = 56$ Hz, 0.3 P; **3**-P), −155.2 (d, $^1J_{P\text{-}P} = 138$ Hz, 2 P; **3**-As), 155.4 (dd, $^1J_{P\text{-}P} = 137$ Hz, $^2J_{P\text{-}P} = 27$ Hz, 0.3 P; **3**-P), 183.1 ppm (t, $^1J_{P\text{-}P} = 138$ Hz, 1 P; **3**-As).

Preparation of $[P\{GaC(SiMe_3)_3\}_4P_3]$ (4): P_4 (48 mg, 0.387 mmol) was dissolved in toluene (10 mL freshly distilled from Na/benzophenone). $[\{GaC(SiMe_3)_3\}_4]$ (467 mg, 0.387 mmol) was also dissolved in toluene (10 mL). The two solutions were combined in a thick-walled glass reactor along with additional toluene (5 mL) to effect quantitative transfer of the reagents. The reaction mixture was heated with stirring for 16 h at 80 °C. During this time the solution remained red-orange during the course of the reaction. The final reaction mixture showed greater than 95 % conversion to compound **4**. On sitting at room temperature or below, **4** readily reverts to $[\{GaC(SiMe_3)_3\}_4]$ (^1H NMR: $\delta = 0.51$ ppm; unit cell obtained on single crystals grown from a solution of **4** toluene at −35 °C) and other unidentified products. $^{31}P\{^1H\}$ NMR (20 °C, $[D_6]$benzene, 202.5 MHz): −263.0 (m, 1 P), −166.7 (td, $^1J_{P\text{-}P} = 132$ Hz, $^2J_{P\text{-}P} = 56$ Hz, 1 P), 186.6 ppm (dd, $^1J_{P\text{-}P} = 132$ Hz, $^2J_{P\text{-}P} = 56$ Hz, 2 P).

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[14] Please see the Supporting Information document for further details.
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