Formation and Structural Characterization of the Mixed-Metal Pnicogen-Bridged Four-Membered Ring Compounds (Et$_2$O)$_2$Li[μ-E(SiMe$_3$)$_2$]$_2$GaH$_2$ (E = P, As)

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Two compounds with novel connectivities, (Et$_2$O)$_2$Li[μ-E(SiMe$_3$)$_2$]$_2$GaH$_2$ (E = P **(1)**, As **(2)**), formally lithium pnictidogallates, were synthesized in the reactions between LiGaH$_4$ and E(SiMe$_3$)$_3$ in diethyl ether *via* trimethylsilane elimination. No reaction took place for E = N under comparable conditions. Structural characterizations showed **1** and **2** to be isomorphous in the solid state and feature the planar four-membered rings of the {Li[μ-E]$_2$Ga} core.

Introduction

We have recently embarked on exploring a promising but rarely exploited[1] elimination−condensation pathway for making group 13(M)−15(E) element bonds, through trimethylsilane elimination or dehydrosilylation. In this regard, we rested our expectations on the results of our,[2] as well as those of others,[3] extensive studies on the related trimethylhalosilane elimination or dehalosilylation that has proven to be successful and led to a range of binary semiconducting materials such as nanocrystalline GaE (E = P,[2c,e,f,3d,e] As,[2b,e,3b,c,d] Sb[2g]) and InE′ (E′ = P,[2d,e,3a,e,f] As[2d,e]), as well as AlAs.[2a] We also expected the frailty of group 13 metal−hydrogen bonds[4] to be advantageous for designing the new trimethylsilane elimination−condensation precursor systems.

One of the outstanding synthetic challenges in the field of group 13−15 compounds is the preparation of single-source precursors to bulk ternary and quaternary materials. We already reported some model mixed-pnicogen compounds which supported the feasibility of such precursors and the resulting nanocrystalline ternaries GaAsP and InAsP.[2e,5] However, the preparation of group 13 mixed-metal precursors of this type has not been widely investigated.[2e,3e,5a] We report herein the synthesis and characterization, including X-ray single-crystal structure determinations, of two novel lithium derivatives of pnictidogallates, (Et$_2$O)$_2$Li[μ-E(SiMe$_3$)$_2$]$_2$-GaH$_2$ (E = P **(1)**, As **(2)**), that seem to be well suited for further conversion to the appropriate mixed-metal model compounds and precursors mentioned above. We note that the formation of **1** and **2** from the combination of LiGaH$_4$ and E(SiMe$_3$)$_3$ in diethyl ether is accompanied by facile trimethylsilane elimination chemistry. This is in marked contrast to what we could have expected on the basis of the reported reactions of LiGaH$_4$ with PR$_3$[6] and LiAlH$_4$ with NR$_3$.[7] In a few favorable cases, base displacement reactions took place, resulting in the formation of the relevant adducts, H$_3$Ga·PR$_3$ and

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$H_3Al\cdot NR_3$, and the precipitation of LiH and Li_3AlH_6, respectively.

Experimental Section

General Techniques. All experiments were carried out using standard vacuum/Schlenk techniques.[8] Solvents were dried and distilled from sodium benzophenone ketyl or Na/K alloy prior to use. $LiGaH_4$,[9] $P(SiMe_3)_3$,[10] and $As(SiMe_3)_3$[11] were prepared according to the literature methods. ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra were acquired on the Varian Unity 400 spectrometer at 25 °C from toluene-d_8 solutions and referenced by generally accepted methods. Mass spectra were collected on a JEOL JMS-SX 102A spectrometer operating in the EI mode at 20 eV. IR spectra were obtained from KBr pellets on a BOMEM Michelson MB-100 FT-IR spectrometer. Elemental analyses were provided by E+R Microanalytical Laboratory, Corona, NY. Melting behavior (uncorrected) was determined with a Thomas-Hoover Uni-melt apparatus for samples flame-sealed in glass capillaries. Single-crystal X-ray diffraction studies were performed at the University of Minnesota, X-ray Crystallographic Laboratory, Minneapolis, MN, on a Siemens SMART Platform CCD system using Mo Kα radiation (λ = 0.71073 Å) at 293 K for **1**[12] and 173 K for **2**.[13] All calculations were carried out using the SHELXTL V5.0 suite of programs;[14] the structures were solved by direct methods.

Synthesis of $(Et_2O)_2Li[\mu\text{-}P(SiMe_3)_2]_2GaH_2$ (1). A 0.24 g (3.0 mmol) sample of freshly prepared $LiGaH_4$ was dissolved in 10 mL of Et_2O, resulting in a slightly turbid solution. To this was added 1.50 g (6.0 mmol) of $P(SiMe_3)_3$ in 20 mL of Et_2O at room temperature. The mixture was stirred for 24 h, and a small amount of a gray solid was filtered out, affording a colorless solution. The volatiles were pumped out to about 5-10 mL, and the concentrated batch was stored in the freezer. After several hours at -30 °C, abundant colorless

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(12) Crystallographic data for **1** (293 K): $C_{20}H_{58}GaLiO_2P_2Si_4$, MW = 581.62, monoclinic, space group *C2/c*, *a* = 9.8572(6) Å, *b* = 18.7154-(11) Å, *c* = 20.7034(11) Å, β = 93.762(1)°, *V* = 3811.2(4) Å³, *F*(000) = 1256, *Z* = 4, D_c = 1.014 Mg/m³, μ = 9.44 cm⁻¹, specimen size (mm) 0.38 × 0.25 × 0.20, 9022 reflections collected, 3271 independent reflections (R_{int} = 0.0316); θ range for data collection, 1.97–24.96°. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C hydrogen atoms were placed in ideal positions and refined isotropically using a standard riding model; the Ga hydrogens were located on the difference map and refined isotropically. The diethyl ether ligand exhibited significant thermal motion, a probable consequence of the room temperature data collection. The final residuals were, for $I > 2\sigma(I) = 2117$, $R_1 = 0.0613$, $wR_2 = 0.1160$, and for all data $R_1 = 0.1057$, $wR_2 = 0.1317$. Some equations of interest: $R_{int} = \sum |F_o^2 - \langle F_o^2\rangle|/\sum |F_o^2|$; $R_1 = \sum ||F_o| - |F_c||/\sum ||F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$. A thermal ellipsoid diagram of **1** is available in the Supporting Information.
(13) Crystallographic data for **2** (173 K): $C_{20}H_{58}As_2GaLiO_2Si_4$, MW = 669.52, monoclinic, space group *C2/c*, *a* = 9.8900(2) Å, *b* = 18.2158-(4) Å, *c* = 20.4558(4) Å, β = 95.282(1)°, *V* = 3669.55(13) Å³, *F*(000) = 1400, *Z* = 4, D_c = 1.212 Mg/m³, μ = 26.83 cm⁻¹, specimen size (mm) 0.32 × 0.16 × 0.14, 9366 reflections collected, 3225 independent reflections (R_{int} = 0.0277); θ range for data collection, 2.00–24.99°. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C hydrogen atoms were placed in ideal positions and refined isotropically using a standard riding model; the Ga hydrogens were located on the difference map and refined isotropically. One ethyl group of the diethyl ether molecule was disordered over two sites in a 0.73:0.27 ratio; only one of these is shown in the final ellipsoid diagram. Sixteen restraints in positional and anisotropic displacement parameters were applied to better model the disorder. The molecule sits on a crystallographic two fold axis, so one-half is in the asymmetric unit. The final residuals were for $I > 2\sigma(I) = 2741$, $R_1 = 0.0346$, $wR_2 = 0.0829$, and for all data $R_1 = 0.0434$, $wR_2 = 0.0866$. For some equations of interest, see footnote 12. A thermal ellipsoid diagram of **2** is shown in Figure 1.
(14) SHELXTL-plus V5.0, Siemens Industrial Automation, Inc., Madison, WI.

platelets of **1** were observed. The mother liquor was cold-decanted, and the crystals were allowed to dry shortly in the argon atmosphere at ambient temperature. Yield: 1.24 g or 71% based on idealized eq 1 (vide infra). The reactions were also carried out for the $LiGaH_4$ to $P(SiMe_3)_3$ ratios of 1:1 and 2:1. The colorless crystals isolated upon cooling the mixtures were shown by NMR and single-crystal X-ray diffraction studies to be **1** in both cases. For X-ray quality crystals, a few droplets of toluene were added to a concentrated ethereal solution of **1** before cooling it in the freezer to prevent a rapid desolvation of the crystals during capillary mounting in the drybox. The mounted crystals appeared opaque due to an unavoidable surface desolvation but in bulk were suitable for X-ray structure determination. Compound **1**, if evacuated for several minutes at room temperature, gradually lost the coordinated Et_2O molecules and was converted to an insoluble, polymeric white solid. The following characterization data were obtained for the freshly isolated and briefly dried **1** (argon atmosphere, 1-2 min), unless noted otherwise. Melting behavior: 94-97 °C dec; for sample evacuated for 30 min, 182-184 °C dec. Anal. Found (calcd for **1** with two coordinated Et_2O, i.e., $C_{20}H_{58}GaLiO_2P_2Si_4$, or with $^1/_2$ coordinated Et_2O, i.e., **1** - $^3/_2$ Et_2O): C, 35.85 (41.30 or 35.74); H, 9.29 (10.65 or 9.21); Ga, 15.09 (11.99 or 14.82); Li, 1.40 (1.19 or 1.48); P, 13.11 (10.65 or 13.17); P/Ga = 2.0/1.0; Ga/Li = 1.1/1.0. ^1H NMR:[15] δ 0.45 (t, $^3J_{P-H}$ = 2.4 Hz; $SiMe_3$), 1.05 (t, $^3J_{H-H}$ = 7.1 Hz; CH_3 in Et_2O), 3.29 (q, $^3J_{H-H}$ = 7.1 Hz; CH_2 in Et_2O), 4.7 (broad; Ga-H). $^{13}C\{^1H\}$ NMR: δ 4.3 (t, $^2J_{P-C}$ = 5.0 Hz; $SiMe_3$), 15.0 (s; CH_3 in Et_2O), 65.9 (s; CH_2 in Et_2O). $^{31}P\{^1H\}$ NMR: δ -277.7. MS [*m/e* (intensity) (ion)]: peak clusters around 568 (8) (trimer $[H_2GaP(SiMe_3)_2]_3 - 2SiMe_3 - 2Me - 2H$, M* $- 2SiMe_3 - 2Me - 2H$), 496 (65) (M* $- 3SiMe_3 - 2Me - H$ or dimer $[H_2GaP(SiMe_3)_2]_3 - 2H$ or M** $- 2H$), 424 (37) (M** $- SiMe_3 - H$), 409 (9) (M** $- SiMe_3 - Me - H$), 320 (23) (M** $- 2SiMe_3 - 2Me - 2H$), and 247 (100) (monomer $[H_2GaP(SiMe_3)_3] - 2H$; also contribution from $P(SiMe_3)_3$) at 250, 178 (33) ($P(SiMe_3)_2 + H$), 163 (17) ($P(SiMe_3)_2 - Me + H$), 147 (14) ($P(SiMe_3)_2 - 2Me$), and 73 (46) ($SiMe_3$). IR: ν(Ga-H) 1838 cm⁻¹.

Synthesis of $(Et_2O)_2Li[\mu\text{-}As(SiMe_3)_2]_2GaH_2$ (2). The preparation of **2** was carried out similarly, and on the same scale (0.24 g or 3.0 mmol of $LiGaH_4$ and 1.77 g or 6.0 mmol of $As(SiMe_3)_3$), as for **1**. Yield: 1.51 g or 75% based on eq 1 (vide infra). X-ray quality crystals of **2** were obtained at -30 °C from both the 1:1 and 1:2 ratio reactions in Et_2O. Melting behavior: beginning of melting at 60-70 °C (gas evolution); completion of melting at 90-95 °C (color change to yellow). Anal. Found (calcd for **2** with two coordinated Et_2O, i.e., $C_{20}H_{58}As_2GaLiO_2Si_4$, or with no coordinated Et_2O, i.e., **2** - 2 Et_2O): C, 27.80 (35.88 or 27.65); H, 7.33 (8.73 or 7.35); Ga, 13.25 (10.41 or 13.37); Li, 1.11 (1.04 or 1.33); As, 28.72 (22.38 or 28.75); As/Ga = 2.0/1.0; Ga/Li = 1.2/1.0. Freshly isolated **2**, as opposed to **1**, appeared not to lose its coordinated Et_2O molecules easily on evacuation. For example, ^1H NMR of a sample evacuated for 20 min at room temperature and run immediately showed the coordinated ether resonances that integrated with both the Ga-H and $SiMe_3$ proton resonances as expected (see Results and Discussion). ^1H NMR: δ 0.58 (intensity 50), 0.50 (intensity 100), 0.29 (intensity 25-50) (s; $SiMe_3$), 1.07 (t, $^3J_{H-H}$ = 7.0 Hz; CH_3 in Et_2O), 3.25 (q, $^3J_{H-H}$ = 7.0 Hz; CH_2 in Et_2O), 4.4 (broad; Ga-H). $^{13}C\{^1H\}$ NMR: δ 4.4 (intensity 100), 3.7 (intensity 25), 2.9 (intensity 50) (s; $SiMe_3$), 15.1 (s; CH_3 in Et_2O), 66.0 (s; CH_2 in Et_2O). MS [*m/e* (intensity) (ion)]: peak clusters around 294 (100) ($As(SiMe_3)_3$, M*), 279 (15) (M* $-$ Me), 221 (2) (M* $- SiMe_3$), 206 (52) (M* $-$

(15) Two small-intensity doublic resonances were also observed in the ^1H NMR spectrum of the raw decanted crystals of **1** (less than 10-15% of the main triplet): δ 0.42 (d, $^3J_{P-H}$ = 4.3 Hz), 0.54 (d, $^3J_{P-H}$ = 5.0 Hz). These were accompanied by the multiplet resonances in the $^{31}P\{^1H\}$ NMR spectrum: δ -247.1 (t, *J* = 61 Hz), δ -280.6 (second-order sextet).

SiMe$_3$ − Me), 191 (13) (M* − SiMe$_3$ − 2Me), 74 (5) (Et$_2$O or SiMe$_3$ + H), 73 (61) (SiMe$_3$), and 59 (9) (SiMe$_2$). IR: ν(Ga−H) 1834 cm^{-1}.

Results and Discussion

The high-yield syntheses of (Et$_2$O)$_2$Li[μ-E(SiMe$_3$)$_2$]$_2$-GaH$_2$ (E = P (**1**), As (**2**)), were accomplished by combination of LiGaH$_4$ and E(SiMe$_3$)$_3$ in diethyl ether at ambient temperatures according to the following idealized equation:

$$\text{LiGaH}_4 + 2\text{E(SiMe}_3)_3 \xrightarrow{\text{Et}_2\text{O}}$$

$$\text{(Et}_2\text{O)}_2\text{Li}[\mu\text{-E(SiMe}_3)_2]_2\text{GaH}_2 + 2\text{HSiMe}_3 \quad (1)$$
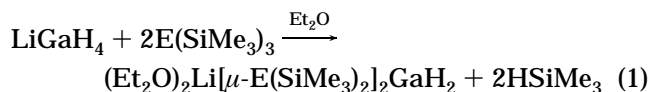
No reaction of any type occurred between LiGaH$_4$ and N(SiMe$_3$)$_3$ under comparable conditions. In the case of E = P, As, there appeared to be a large driving force toward the formation of such products with the Ga to E ratio of 1:2, irrespective of utilized ratios of the reagents. For example, **1** was isolated as the sole crystalline product from the reactions between LiGaH$_4$ and P(SiMe$_3$)$_3$ with ratios 2:1, 1:1, and 1:2; in all three cases, its identity was confirmed by NMR and X-ray single-crystal structural studies. Similarly, **2** was solely isolated in high yields for the LiGaH$_4$ to As(SiMe$_3$)$_3$ ratios of 1:1 and 1:2. No significant reactions took place between LiGaH$_4$ and P(SiMe$_3$)$_3$ in toluene, and most of the unreacted phosphine could be recovered.[16] Both **1** and **2** were stable for weeks and days, respectively, when stored as ethereal or toluene solutions/slurries at −30 °C. However, the room temperature stored toluene-d_8 solutions of both compounds showed signs of decomposition, as evidenced by NMR spectroscopy. Under these conditions, **1** slowly decomposed over the course of weeks with the formation of considerable amounts of P(SiMe$_3$)$_3$, some HSiMe$_3$, and H$_2$, while **2** was mostly decomposed after 1 day, yielding As(SiMe$_3$)$_3$, HSiMe$_3$, and H$_2$.

The most striking feature of **1** is its propensity to lose easily the coordinated ether molecules. Merely exposing it to an inert gas atmosphere made the colorless crystals look opaque, and their evacuation for several minutes turned them to a white powder. The evacuated, likely polymeric powdery product was practically insoluble in toluene,[16] slightly soluble in Et$_2$O, but well soluble in THF. This labile property of **1** made its characterization a rather difficult and ambiguous task. For example, the elemental analysis obtained for a sample that was dried for 2 min by exposure in the drybox atmosphere showed the correct Ga:P:Li ratio of approximately 1:2:1; however, the C and H contents were far off their theoretical values. On the other hand, a good match for all the analyzed elements could be obtained assuming only half a Et$_2$O molecule per core molecule (see Experimental Section). Apparently, mere handling of the sample during its preparation and analysis caused the release of most of the ether. Similarly, the melting point of **1** depended greatly on whether the sample was or was not evacuated. Significant variations in ether content

were further confirmed by ^{1}H NMR spectroscopy. For all investigated solutions, the integrated signals due to the ether molecules relative to the SiMe$_3$ protons varied from sample to sample and fell short of the theoretical values. However, the NMR studies gave several important clues as to the nature of the compound. First, both the SiMe$_3$ protons and carbons showed as triplets in the respective ^{1}H and ^{13}C{^{1}H} NMR spectra. This implied a symmetrical and planar four-membered ring containing two virtually coupled phosphorus atoms. A single resonance in the ^{31}P{^{1}H} NMR spectrum at −277.7 ppm complied well with such a notion. Second, the broad proton resonance at 4.7 ppm suggested the presence of terminal GaH$_2$ moieties in the structure.[17] The latter was also supported by IR spectrometry. The Ga−H stretching band for **1** was found at 1838 cm^{-1} in the range from 1800 to 2000 cm^{-1} typical for the {Ga− terminal H$_2$} symmetrical and antisymmetrical stretches.[17,18] Last, there was the mass spectrum of **1**, which was of little use in structural elucidation. It mainly showed ion fragments that could be assigned to free P(SiMe$_3$)$_3$ and the trimeric, dimeric, and monomeric units of [H$_2$GaP(SiMe$_3$)$_2$], as well as their fragmentation ions, and they all could be the possible decomposition byproducts of **1** under heat and electron impact conditions of the MS probe.

The characterization data for **2** paralleled in many cases those for **1**. The notable example was the unsatisfactory match between the calculated and determined element contents. However, an acceptable match was obtained assuming no ether molecules in the material (see Experimental Section), which could result from a relatively fast decomposition of **2** at ambient temperatures. In contrast with that, the integrated ^{1}H NMR signals for freshly made solutions indicated two Et$_2$O molecules per one GaH$_2$ moiety. In this regard, the symmetrical, broad proton resonance at 4.4 ppm was consistent with the presence of the terminal GaH$_2$ group in the molecule, as was the IR Ga−H stretching band at 1834 cm^{-1}.[17,18] But, surprisingly, both ^{1}H and ^{13}C-{^{1}H} NMR spectra obtained for the freshly prepared toluene-d_8 solutions of **2** consistently showed three major peaks in the SiMe$_3$ region. The proton resonances at δ 0.58, 0.50, and 0.29 integrated with an approximately 1:2:1 ratio, while the carbon resonances at δ 4.4, 3.7, and 2.9 had their relative intensities close to 100:25:50. The combined area of all three proton signals was approximately twice as large as the area due to the Et$_2$O resonances, and this implied two ether molecules per combined SiMe$_3$ protons (assuming two As(SiMe$_3$)$_2$ groups per one GaH$_2$ group). Since a similar ratio was obtained for the relative quantities of the Ga hydrides and Et$_2$O protons, we concluded that one GaH$_2$ group was correlated with all three SiMe$_3$ species. These results were quite different from the respective simple NMR data for **1**. Apparently, **2** either was losing its symmetry or formed a mixture of closely related, oligomeric species in the toluene solution. In this regard,

(16) A very small amount of a toluene-soluble byproduct was detected by NMR (^{31}P{^{1}H} NMR: δ −265.8); this new compound, [H$_2$GaP(SiMe$_3$)$_2$]$_3$, was also synthesized in our laboratory from an independent reaction between H$_3$Ga·NMe$_3$ and P(SiMe$_3$)$_3$. Similarly, [H$_2$GaAs(SiMe$_3$)$_2$]$_3$ was obtained from the combination of H$_3$Ga·NMe$_3$ and As(SiMe$_3$)$_3$. Research to be published.

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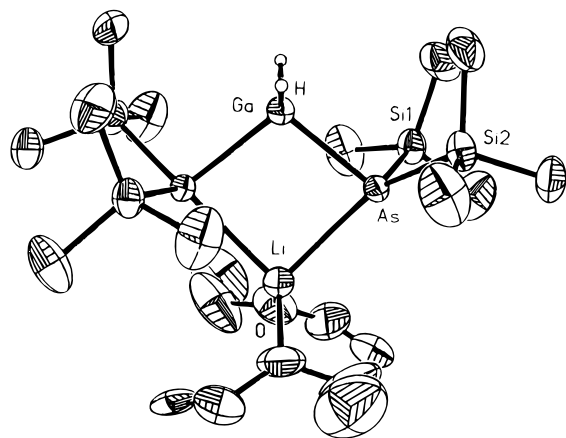
Figure 1. Thermal ellipsoid diagram (35% probability ellipsoids) showing the molecular structure of **2**. All C hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2, with Estimated Standard Deviations in Parentheses

	1 (E = P)	**2** (E = As)
Bond Lengths		
Ga−H	1.58(4)	1.51(5)
E−Ga	2.4122(12)	2.4941(5)
E−Li	2.716(8)	2.736(6)
E−Si(av)	2.236(2)	2.3360(11)
Li−O	1.967(8)	1.937(6)
Bond Angles		
H−Ga−E	109(2)	108(2)
E−Ga−E	101.62(6)	101.65(2)
E−Li−E	87.0(3)	89.9(2)
Ga−E−Li	85.7(2)	84.21(12)
O−Li−O	108.4(6)	113.9(5)
O−Li−E(av)	115.1(2)	112.69(13)
Si(1)−E−Si(2)	105.47(7)	103.56(4)
Si(1)−E−Li	113.80(7)	112.44(4)
Si(2)−E−Li	136.40(7)	141.89(4)
Si−E−Ga(av)	103.37(6)	101.46(3)

the species were observed by NMR to decrease in the same manner, preserving the original ratio, if the NMR sample was stored and decomposing at room temperature. In addition to these major resonances assigned to **2**, the NMR spectra, even for freshly made solutions, showed signals due to free As(SiMe₃)₃, which grew with time, and which were indicative of compound's thermal frailty. Consistent with the above was the MS spectrum for **2** that showed the prevalent As(SiMe₃)₃ ion and its logical fragmentation ions. It was apparent that, although isolated **1** was losing the ether much more easily than its isolated As analog **2**, it was decomposing in the solution much more slowly than **2**.

Unfortunately, all the data did not unambiguously provide the atomic connectivities for **1** and **2**, and, especially, the bonding mode of the lithium atom could not be unequivocally deduced. In this regard, the relevant compound obtained from the reaction between LiAlH₄ and 2 equiv of HN(SiMe₃)₂ via dihydrogen elimination, (Et₂O)₂Li[μ-H]₂Al[N(SiMe₃)₂]₂, consisted of the hydrogen-bridged four-membered {Li[μ-H]₂Al} core and two terminal N(SiMe₃)₂ groups.[19] This kind of atomic connectivities was, however, in contrast with the picture emerging from the characterization data for both compounds, as discussed above.

The X-ray single-crystal structure determinations confirmed that, in fact, **1** and **2** were isostructural in the solid state. As an example, Figure 1 shows a thermal ellipsoid diagram of **2** in which all C-hydrogens are omitted for clarity, but the Ga hydrides are retained. Table 1 contains the most important bond distances and angles for **1** and **2**. Both molecules feature a planar four-membered "kite-shaped" ring of the {Li[μ-E]₂Ga} core with two bridging pnicogen atoms, which can be contrasted with the hydrogen-bridged ring of {Li[μ-H]₂Al} in (Et₂O)₂Li[μ-H]₂Al[N(SiMe₃)₂]₂.[19] Each molecule possesses crystallographically imposed twofold rotational symmetry, the two-fold axis passing through Ga and Li in the ring. Significant ring strain in **1** and **2** is suggested by the acute Ga−E−Li angles of 85.7(2)° and 84.21(12)°, respectively. A slight shortening of otherwise typical Li−O distances[20] from 1.967(8) Å in **1** to 1.937(6) Å in **2**, accompanied by an opening of the O−Li−O bond angle from 108.4(6)° to 113.9(5)°, respec-

tively, supports more tightly bound Et₂O molecules in **2**. The Ga−H bond lengths in **1**, 1.58(4) Å, and in **2**, 1.51(5) Å, are in the typical range for terminal Ga−H distances (both in Lewis acid−base adducts of {GaH₃} and in derivatives containing the GaH₂ moiety), as exemplified by structural studies of the following compounds: Ga₂H₆ (gas phase),[18c] 1.519(35) Å for the terminal hydrogens (but 1.710(38) Å for the bridging hydrogens); [Me₂NGaH₂]₂ (gas phase),[18a] 1.487(36) Å; a solid product from the reaction between H₃Ga·NMe₃ and 1,4-di-*tert*-butyl-1,4-diazabutadiene[17b] containing a terminal GaH₂ group, 1.57(8) and 1.54(12) Å; and H₃Ga·P(C₆H₁₁)₃,[6a] 1.35, 1.55, and 1.54 Å (mean 1.48 Å).

There are no structurally characterized phosphidogallanes, and only a few gallane organophosphine adducts of the H₃Ga·PR₃ type have been structurally authenticated. For these and for some calculated cases, the following relevant Ga−P bond lengths have been derived: H₃Ga·P(C₆H₁₁)₃,[6a] 2.460(2) Å; (H₃Ga)₂·(PMe₂-CH₂)₂,[6a] 2.399(4) Å; H₃Ga·PH₃ (calculated),[6a] 2.576 and 2.731 Å; H₃Ga·P(*t*-Bu)₃,[6b] 2.444(6) Å; and H₃Ga·PMe₃ (calculated),[6b] 2.550 Å. The Ga−P bond length in **1**, 2.4122(12) Å, is rather short compared with those above. However, more appropriate is comparison with the Ga−P average distances in the four-membered ring compounds such as [Cl₂GaP(SiMe₃)₂]₂[21] (2.379(2) Å), [Br₂GaP(SiMe₃)₂]₂[2b] (2.386(2) Å), and [I₂GaP(SiMe₃)₂]₂[5d] (2.397(3) Å). The slightly longer Ga−P bond in **1** could reflect the competition between the Ga and Li centers in the mixed-metal ring of {Li[μ-P]₂Ga} for electron density from the bridging P centers. However, the Li−P distance in **1**, 2.716(8) Å, is one of the longest, if not the longest, for relevant lithium phosphide structures, still being in the range of the sum of the elements' atomic radii, 2.83 Å. For example, the following Li−P distances are found: [LiP(SiMe₃)₂]₆[22a] solvent-free ladder, 2.38(1)−2.63(1) Å; [Li(Et₂O)PPh₂]ₙ[20a] polymeric chain, 2.483(10)−2.496(10) Å; [Li(THF)₂P(SiMe₃)₂]₂[22b] planar dimer, 2.62(2) Å; [Li(DME)P(SiMe₃)₂]₂[22c] planar

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dimer, 2.559(4) Å; [Li(DME)PH$_2$]$_n$[22c] polymeric chain, 2.537(5)−2.596(5) Å; and [Li$_2$(μ_3-t-Bu$_2$-P)(μ_3-t-Bu$_2$-P)-(THF)]$_2$[22d] ladder, 2.498(9)−2.669(9) Å. Apparently, a bonding compromise between the angle strain in the kite-shaped ring, steric interactions between the ligands on the P and Li centers, and decreased effective acidity of the gallium center results in the slightly elongated Ga−P and Li−P bonds in **1**.

The referencing of structural data for **2** is even more handicapped due to an apparent lack of any structures for either arsenidogallanes or gallane arsine adducts. A few structurally characterized lithium arsenides provide the following Li−As distances: [Li(THF)$_2$As-(SiMe$_3$)$_2$]$_2$[23a] distorted planar dimer, 2.67(1)−2.70(1) Å; {Li[μ_2-As(SiMe$_3$)$_2$][μ_3-As(SiMe$_3$)$_2$](THF)}$_2$[23a] ladder, 2.53 (average for four-coordinate Li)−2.63 Å (average for five-coordinate Li); [Li(Et$_2$O)$_2$AsPh$_2$]$_2$[20b] planar dimer, 2.708(9) and 2.757(9) Å; Li(1,4-dioxane)$_3$AsPh$_2$[20b] monomer, 2.660-(10) Å; [Li(DME)As(SiMe$_3$)$_2$]$_2$[23b] planar dimer, 2.59(2) Å; and [Li(THF){As(t-Bu)As(t-Bu)$_2$}]$_2$[23c] planar dimer, 2.58(2) Å. The Li−As bond length in **2**, 2.736(6) Å, falls in the range of rather long distances of this type, similarly as does the Li−P bond length in **1**. However, the Li−As distance in **2** is only slightly longer than the Li−P distance in **1**, i.e. 2.736(6) vs 2.716(8) Å, and this

implies a relatively more favorable Li−As bonding interaction in the dimeric core of **2**. The Ga−As bond length in **2**, 2.4941(5) Å, seems to be typical for four-coordinate Ga and As centers such as those found, for example, in the relevant dimeric structures of [I$_2$GaAs-(SiMe$_3$)$_2$]$_2$[24a] (average 2.471(4) Å), {[(Me$_3$SiCH$_2$)$_2$-As]$_2$GaBr}$_2$[24b] (average Ga−As ring distance, 2.517(1) Å), and [(Me$_3$SiCH$_2$)$_2$GaAs(SiMe$_3$)$_2$]$_2$[24c] (average 2.567-(1) Å).

Currently, we are doing extensive work on the preparation of other lithium pnictido−group 13 element derivatives similar in type to **1** and **2**, and on exploring alternative dehydrosilylation systems for the formation of group 13−15 bonds. We are also studying a further conversion of **1** and **2** to appropriate mixed-metal compounds and precursors by reactions with R$_n$MX$_{3-n}$ (R = H, alkyl, aryl, SiMe$_3$; X = halogen; n = 0, 1, 2).

Supporting Information Available: Thermal ellipsoid diagram for **1** and tables of bond distances, bond and torsion angles, anisotropic temperature factor parameters, and atomic fractional coordinates for **1** and **2** (9 pages). Ordering information is given on any current masthead page.

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