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# Formation and Structural Characterization of the Mixed-Metal Pnicogen-Bridged Four-Membered Ring Compounds $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2GaH_2$, E = P, As

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**Summary:** Two compounds with novel connectivities, $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2GaH_2$, 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 compounds (**1**) and (**2**) to be isomorphous in the solid state and feature the planar four-member rings of the $\{Li[\mu\text{-}E]_2Ga\}$ core.

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## 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, namely, through trimethylsilane elimination or dehydrosilylation. In this regard, we rested our expectations on the results of our,[2] as well as 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, $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2GaH_2$, 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 based on 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, $H_3Ga\cdot PR_3$ and $H_3Al\cdot NR_3$, 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 Na benzophenone ketyl or Na/K alloy prior to use. $LiGaH_4$,[9] $P(SiMe_3)_3$,[10] $As(SiMe_3)_3$[11] were prepared by 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 $K_\alpha$ radiation ($\lambda = 0.71073$ 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, 1.50 g (6.0 mmol) of $P(SiMe_3)_3$ in 20 mL of $Et_2O$ was added 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 to 10 mL and the concentrated batch was stored in the freezer. After several hours at -30 °C, abundant colorless 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 equation 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 de-solvation of the crystals during capillary mounting in the dry-box. The mounted crystals appeared opaque due to an unavoidable surface de-solvation but in bulk were suitable for a X-ray structure determination. Compound **(1)**, if evacuated for several minutes at room temperature, was gradually losing 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 to 2 minutes), unless noted otherwise. Melting behavior: 94-97 $^oC$ (decomposition); for sample evacuated for 30 minutes, 182-184 $^oC$ (decomposition). 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] $\delta$ 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: $\delta$ 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: $\delta$ −277.7. MS: [m/e (intensity)(ion)]: peak clusters around: 568 (8)(trimer $[H_2GaP(SiMe_3)_3]_3$ - 2$SiMe_3$ - 2Me - 2H, $M^*$ - 2$SiMe_3$ - 2Me - 2H), 496 (65)($M^*$ - 3$SiMe_3$ - 2Me - H or dimer $[H_2GaP(SiMe_3)_3]_2$ - 2H or $M^{**}$ - 2H), 424 (37)($M^{**}$ - $SiMe_3$ - H), 409 (9)($M^{**}$ - $SiMe_3$ - Me - H), 320 (23)($M^{**}$ - 2$SiMe_3$ - 2Me - 2H), 247 (100)(monomer $[H_2GaP(SiMe_3)_3]$ - 2H; also, contribution from $P(SiMe_3)_3$) at m/e 250, 178 (33)($P(SiMe_3)_2$ + H), 163 (17)($P(SiMe_3)_2$ - Me + H), 147 (14)($P(SiMe_3)_2$ - 2Me), 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 equation 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 compound **(2)**, as opposed to compound **(1)**, appeared not to lose its coordinated $Et_2O$ molecules easily on evacuation. For example, $^1H$ NMR of a sample evacuated for 20 minutes 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: R&D section). $^1H$ NMR: $\delta$ 0.58 (intensity 50), 0.50 (intensity 100), 0.29 (intensity 25 to 50) (s, $SiMe_3$), 1.07 (t, $^3J_{H\text{-}H}$ = 7.0 Hz; $CH_3$ in $Et_2O$), 3.25 (q, $^3J_{H\text{-}H}$ = 7.0 Hz; $CH_2$ in $Et_2O$), 4.4 (broad; Ga-H). $^{13}C\{^1H\}$ NMR: $\delta$ 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)($M^*$- $SiMe_3$ - Me), 191 (13)($M^*$- $SiMe_3$ - 2Me), 74 (5)($Et_2O$ or $SiMe_3$ + H), 73 (61)($SiMe_3$), 59 (9)($SiMe_2$). IR: $\nu$(Ga-H) 1834 $cm^{-1}$.

## Results and Discussion

The high yield syntheses of $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2GaH_2$, 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:

$$LiGaH_4 + 2E(SiMe_3)_3 \xrightarrow{Et_2O} (Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2GaH_2 + 2HSiMe_3 \qquad (1)$$

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 towards the formation of such products with the Ga to E ratio of 1 to 2 irrespective of utilized ratios of the reagents. For example, compound **(1)** was isolated as a 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, compound **(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, compound **(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 compound **(2)** was mostly decomposed after one day yielding $As(SiMe_3)_3$, $HSiMe_3$, and $H_2$.

The most striking feature of compound **(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 $Et_2O$, 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 two minutes by exposure in the dry-box 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 a half $Et_2O$ molecule per core molecule (see: Experimental Section). Apparently, a 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 $^1H$ 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 $^1H$ and $^{13}C\{^1H\}$ NMR spectra. This implied a symmetrical and planar, four-membered ring containing two virtually coupled phosphorus atoms. A single resonance in the $^{31}P\{^1H\}$ 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] Lastly, 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 $[H_2GaP(SiMe_3)_2]$, as well as their fragmentation ions, and they all could be the possible decomposition by-products of **(1)** under heat and electron impact conditions of the MS probe.

The characterization data for compound **(2)** paralleled in many cases those for **(1)**. The notable example was the unsatisfactory match between the calculated and determined element contents. However, the 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 $^1H$

NMR signals for freshly made solutions indicated two $Et_2O$ 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 $^1H$ and $^{13}C\{^1H\}$ 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 $\delta$ 0.58, 0.50, and 0.29 integrated with the approximate 1:2:1 ratio while the carbon resonances at $\delta$ 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 $Et_2O$ 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 $Et_2O$ 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 compound **(1)**. Apparently, compound **(2)** was either losing its symmetry or it formed a mixture of closely related, oligomeric species in the toluene solution. In this regard, 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 $As(SiMe_3)_3$, 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 $As(SiMe_3)_3$ ion and its logical fragmentation ions. It was apparent that although isolated compound **(1)** was losing the ether much easier than its isolated As analog **(2)**, it was decomposing in the solution much slowlier than **(2)**.

Unfortunately, all the data did not unambiguously provide the atomic connectivities for compounds **(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 $LiAlH_4$ and two equivalents of $HN(SiMe_3)_2$ via dihydrogen elimination,

$(Et_2O)_2Li[\mu\text{-}H]_2Al[N(SiMe_3)_2]_2$, consisted of the hydrogen-bridged four-membered $\{Li[\mu\text{-}H]_2Al\}$ core and two terminal $N(SiMe_3)_2$ 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, compounds **(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 $\{Li[\mu\text{-}E]_2Ga\}$ core with two bridging pnicogen atoms which can be contrasted with the hydrogen bridged ring of $\{Li[\mu\text{-}H]_2Al\}$ in $(Et_2O)_2Li[\mu\text{-}H]_2Al[N(SiMe_3)_2]_2$.[19] Each molecule possesses crystallographically imposed two-fold rotational symmetry, the two-fold axis passing through Ga and Li in the ring. A 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[20a, b] 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) °, respectively, supports more tightly bound $Et_2O$ molecules in **(2)**. The Ga-H bond lengths in **(1)**, 1.58(4) Å, and **(2)**, 1.51(5) Å, are in the typical range for terminal Ga-H distances (both in Lewis acid-base adducts of $\{GaH_3\}$ and in derivatives containing the $GaH_2$ moiety) as exemplified by structural studies of the following compounds: $Ga_2H_6$ (gas phase),[18a] 1.519(35) Å for the terminal hydrogens (but 1.710(38) Å for the bridging hydrogens); $[Me_2NGaH_2]_2$ (gas phase),[18c] 1.487(36) Å; a solid product from the reaction between $H_3Ga{\bullet}NMe_3$ and 1,4-di-t-butyl-1,4-diazabutadiene[17b] containing a terminal $GaH_2$ group, 1.57(8) Å and 1.54(12) Å; $H_3Ga{\bullet}P(C_6H_{11})_3$,[6a] 1.35 Å, 1.55 Å, and 1.54 Å (mean 1.48 Å).

There are no structurally characterized phosphidogallanes and only a few gallane organophosphine adducts of the $H_3Ga{\bullet}PR_3$ type have been structurally authenticated. For these and for some calculated cases, the following relevant Ga-P bond lengths have been derived: $H_3Ga{\bullet}P(C_6H_{11})_3$,[6a] 2.460(2) Å; $(H_3Ga)_2{\bullet}(PMe_2CH_2)_2$,[6a] 2.399(4) Å; $H_3Ga{\bullet}PH_3$ (calculated),[6a] 2.576 Å and 2.731 Å; $H_3Ga{\bullet}P(t\text{-}Bu)_3$,[6b] 2.444(6) Å; $H_3Ga{\bullet}PMe_3$ (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 $[Cl_2GaP(SiMe_3)_2]_2$[21] (2.379(2) Å), $[Br_2GaP(SiMe_3)_2]_2$[2b] (2.386(2) Å), and $[I_2GaP(SiMe_3)_2]_2$[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 $\{Li[\mu\text{-}P]_2Ga\}$ 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 in: $[LiP(SiMe_3)_2]_6$[22a] - solvent-free ladder, 2.38(1) to 2.63(1) Å; $[Li(Et_2O)PPh_2]_n$[20a] - polymeric chain, 2.483(10) to 2.496(10) Å; $[Li(THF)_2P(SiMe_3)_2]_2$[22b] - planar dimer, 2.62(2) Å; $[Li(DME)P(SiMe_3)_2]_2$[22c] - planar dimer, 2.559(4) Å; $[Li(DME)PH_2]_n$[22c] - polymeric chain, 2.537(5) to 2,596(5) Å; $[Li_2(\mu_3\text{-}t\text{-}Bu_2\text{-}P)(\mu_3\text{-}t\text{-}Bu_2\text{-}P)(THF)]_2$[22d] - ladder, 2.498(9) to 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: $[Li(THF)_2As(SiMe_3)_2]_2$[23a] - distorted planar dimer, 2.67(1) Å to 2.70(1) Å; $\{Li[\mu_2\text{-}As(SiMe_3)_2][\mu_3\text{-}As(SiMe_3)_2](THF)\}_2$[23a] - ladder, 2.53 Å (average for 4-coordinate Li) to 2.63 Å (average for 5-coordinate Li); $[Li(Et_2O)_2AsPh_2]_2$[20b] - planar dimer, 2.708(9) Å and 2.757(9) Å; $Li(1,4\text{-dioxane})_3AsPh_2$[20b] - monomer, 2.660(10) Å;

$[Li(DME)As(SiMe_3)_2]_2$[23b] - planar dimer, 2.59(2) Å; $[Li(THF)\{As(t\text{-}Bu)As(t\text{-}Bu)_2\}]_2$[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) Å 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 4-coordinate Ga and As centers such as found, for example, in the relevant dimeric structures of $[I_2GaAs(SiMe_3)_2]_2$[24a] (average 2.471(4) Å), $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$[24b] (average Ga-As ring distance, 2.517(1) Å) or $[(Me_3SiCH_2)_2GaAs(SiMe_3)_2]_2$[24c] (average 2.567(1) Å).

Currently, we are doing extensive work on the preparation of other lithium pnictido-Group 13 element derivatives of similar type to **(1)** and **(2)**, and on exploring alternative dehydrosilylation systems for the formation of Group 13-15 bonds. We also study a further conversion of **(1)** and **(2)** to appropriate mixed-metal compounds and precursors by reactions with $R_nMX_{3-n}$ (R = H, alkyl, aryl, $SiMe_3$; X = halogen; n = 0, 1, 2).

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**Supporting Information Available.** Thermal ellipsoid diagram for **(1)**; tables of bond distances, bond and torsion angles, anisotropic temperature factor parameters, atomic fractional coordinates, observed and calculated structure factors for **(1)** and **(2)** (29 pages). Ordering information is given on any current masthead page.

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(12) Crystallographic data for **(1)** (293K): $C_{20}H_{58}GaLiO_2P_2Si_4$, M = 581.62, monoclinic, space group C2/c, a = 9.8572(6) Å, b = 18.7154(11) Å, c = 20.7034(11) Å, $\beta$ = 93.762(1) °, V = 3811.2(4) Å$^3$, F(000) = 1256, Z = 4, $D_c$ = 1.014 Mg/m$^3$, $\mu$ = 9.44 cm$^{-1}$, specimen size (mm): 0.38x0.25x0.20, 9022 reflections collected, 3271 independent reflections ($R_{int}$ = 0.0316); $\Theta$ range for data collection: 1.97 to 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) R1 = 0.0613 %, wR2 = 0.1160 %, and for all data R1 = 0.1057, wR2 = 0.1317. Some equations of interest: $R_{int} = \Sigma|F_o^2 - \langle F_o\rangle^2|/\Sigma|F_o^2|$; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (a\cdot P)^2 + b\cdot P$. A thermal ellipsoid diagram of **(1)** is available in the Supplementary Material.

(13) Crystallographic data for **(2)** (173 K): $C_{20}H_{58}As_2GaLiO_2Si_4$, M = 669.52, monoclinic, space group C2/c, a = 9.8900(2) Å, b = 18.2158(4) Å, c = 20.4558(4) Å, $\beta$ = 95.282(1) °, V = 3669.55(13) Å$^3$, F(000) = 1400, Z = 4, $D_c$ = 1.212 Mg/m$^3$, $\mu$ = 26.83 cm$^{-1}$, specimen size (mm): 0.32x0.16x0.14, 9366 reflections collected, 3225 independent reflections ($R_{int}$ = 0.0277); $\Theta$ range for data collection: 2.00 to 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. 16 restraints in positional and anisotropic displacement parameters were applied to better model the disorder. The molecule sets on a crystallographic two-fold so one-half is in the asymmetric unit. The final residuals were for ($I > 2\sigma(I) = 2741$) $R1 = 0.0346$, $wR2 = 0.0829$ and for all data $R1 = 0.0434$, $wR2 = 0.0866$. For some equations of interest see reference (12). A thermal ellipsoid diagram of **(2)** is shown in Figure 1.

(14) SHELXTL-plus V5.0, Siemens Industrial Automation, Inc., Madison, WI.

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

(16) A very small amount of a toluene-soluble by-product was detected by NMR ($^{31}P\{^1H\}$ NMR: $\delta$ -265.8); this new compound, $[H_2GaP(SiMe_3)_2]_3$, was also synthesized in our laboratory from an independent reaction between $H_3Ga{\bullet}NMe_3$ and $P(SiMe_3)_3$. Similarly, $[H_2GaAs(SiMe_3)_2]_3$ was obtained from the combination of $H_3Ga{\bullet}NMe_3$ and $As(SiMe_3)_3$. To be published.

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

Bond Lengths

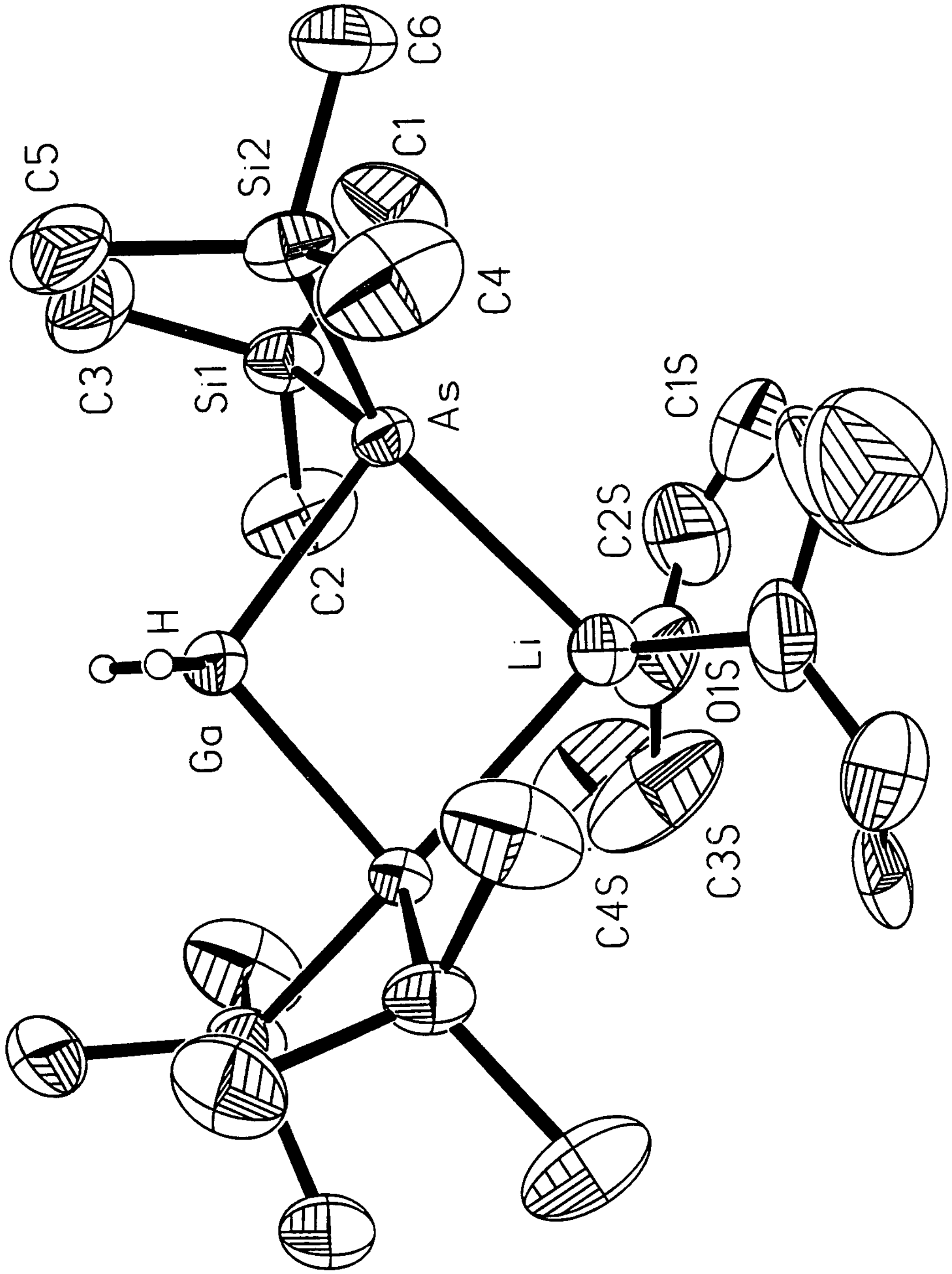
| | **1** (E = P) | **2** (E = As) |
|---|---|---|
| Ga - H | 1.58(4) | 1.51(5) |
| E - Ga | 2.4122(12) | 2.4941(5) |
| E - Li | 2.716(8) | 2.736(6) |
| E - Si (av.) | 2.236(2) | 2.3360(11) |
| Li - O | 1.967(8) | 1.937(6) |

Bond Angles

| | **1** (E = P) | **2** (E = As) |
|---|---|---|
| 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) |

## Caption to Figure 1

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


C6
C5
Si2
C1
C4
C3
Si1
As
C1S
C2S
C2
H
Ga
Li
O1S
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