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

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Introduction

We have recently embarked on exploring a promising but rarely exploited elimination-condensation pathway for making group 13(M)−15(E) element bonds, through trimethylsilane elimination or dehydrohalogenation. In this regard, we rest our expectations on the results of our, as well as those of others, extensive studies on the related trimethylsilane elimination or dehaloelimination that has proven to be successful and led to a range of binary semiconducting materials such as nanocrystalline GaE (E = P, As, Sb) and InE' (E' = P, As, Sb) as well as AlAs. We also expected the frailty of group 13 metal−hydrogen bonds 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. However, the preparation of group 13 mixed-metal precursors of this type has not been widely investigated. We report herein the synthesis and characterization, including X-ray single-crystal structure determinations, of two novel lithium derivatives of pnicodigallates, (Et$_2$O)$_2$Li[$\mu$-E(SiMe$_3$)$_2$]$_2$GaH$_2$ (E = P, As, Sb), 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$_3$)$_2$ 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$_3$ and LiAlH$_4$ with NR$_3$. In a few favorable cases, base displacement reactions took place, resulting in the formation of the relevant adducts, H$_3$GaE and...
H₃Al–NR₃, and the precipitation of LiH and Li₂AlH₆, respectively.

**Experimental Section**

**General Techniques.** All experiments were carried out using standard vacuum/Schlenk techniques. Solvents were dried and distilled from sodium benzophenone ketyl or Na/K alloy prior to use. LiGaH₄, P(SiMe₃)₂, and As(SiMe₃)₃ were prepared according to the literature methods. H, ¹³C(H), and ³¹P NMR spectra were acquired on the Varian Unity 400 spectrometer at 25 °C from toluene-δ (3.0 mmol) sample of freshly prepared LiGaH₄ was dissolved in the structures were solved by direct methods. Mass spectra were collected on a J EOL J MS-SX 102A spectrometer operating in the EI mode at 20 eV. IR spectra were obtained from KBr pellets on a Brucker 66 FT-IR spectrometer. Electron diffraction 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 and 173 K for 2. All calculations were carried out using the SHELXTL V5.0 suite of programs;¹³ the structures were solved by direct methods.

**Synthesis of (Et₂O)₂Li[Li₃-P(SiMe₃)₂]GaH₄ (1).** A 0.24 g (3.0 mmol) sample of freshly prepared LiGaH₄ was dissolved in 10 mL of Et₂O, resulting in a slightly turbid solution. To this was added 1.50 g (6.0 mmol) of P(SiMe₃)₂ in 20 mL of Et₂O 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 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 LiGaH₄ to P(SiMe₃)₂ 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 Et₂O molecules and was converted into an insoluble, polycrystalline white solid. Further details for X-ray 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 Et₂O, i.e., Ca₂H₅GaLiO₂P₂Si₄ or with 1/2 coordinated Et₂O, i.e., 1–½ Et₂O): 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 = 1/1.0. ¹H NMR: δ 0.45 (t, J₉=6.5 Hz = 2.4 Hz; SiMe₃), 1.05 (t, J₉=6.5 Hz = 7.1 Hz; CH₃ in Et₂O), 2.93 (q, J₉=6.5 Hz = 7.1 Hz; CH₂ in Et₂O), 4.7 (broad; Ga-H). ¹³C(H) NMR: δ 4.3 (t, J₉=6.5 Hz = 5.0 Hz; SiMe₃), 15.0 (s; CH₃ in Et₂O), 65.9 (s; CH₃ in Et₂O). ³¹P(H) NMR: δ −277.7. MS [m/e (intensity, ion)]: peak clusters around 568 (8) (trimer [H₂Ga(P₂Si₄)₂SiMe₃] –2SiMe₃ –2Me –2H), 496 (65) (M–SiMe₃ –2Me –H) (silim [H₂Ga(P₂Si₄)₂SiMe₃] –2H –2Me), 424 (37) (M–SiMe₃ –H), 400 (9) (M–SiMe₃ –Me –H), 320 (23) (M–SiMe₃ –Me –2H –2H), and 247 (100) (monomer [H₂Ga(P₂Si₄)₂SiMe₃] –2H; also contribution from P(SiMe₃)₂ at 250, 178 (33) (P(SiMe₃)₂ + H), 163 (17) (P(SiMe₃)₂ –Me + H), 147 (14) (P(SiMe₃)₂ –2Me), and 73 (46) (SiMe₃). IR: v(Ga–H) 1838 cm⁻¹.

**Synthesis of (Et₂O)₂Li[Li₃-As(SiMe₃)₃]GaH₄ (2).** The preparation of 2 was carried out similarly, and on the same scale (0.24 g or 3.0 mmol of LiGaH₄ and 1.77 g or 6.0 mmol of As(SiMe₃)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 Et₂O. 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 Et₂O, i.e., Ca₂H₅GaLiO₂P₂Si₄ or with 1/2 coordinated Et₂O, i.e., 1–½ Et₂O): C, 34.85 (38.85 or 38.76); H, 9.12 (7.73 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 = 1/1.0. Freshly isolated 2, as opposed to 1, appeared not to lose its coordinated Et₂O molecules easily on evacuation. For example, ³¹H NMR of a sample evacuated for 20 min at room temperature and run immediately showed the coordinated ethereal was intact and integrated with both the Ga–H and SiMe₃ proton resonances as expected (see Results and Discussion). ¹³C(H) NMR: δ 0.58 (intensity 50), 0.50 (intensity 100), 0.29 (intensity 25–50) (s; SiMe₃), 1.07 (t, J₉=6.5 Hz = 7.0 Hz; CH₃ in Et₂O), 3.25 (q, J₉=6.5 Hz = 7.0 Hz; CH₂ in Et₂O), 4.4 (broad; Ga-H). ¹³C(H) NMR: δ 4.4 (intensity 100), 3.7 (intensity 25), 2.9 (intensity 50) (s; SiMe₃), 15.1 (s; CH₃ in Et₂O), 66.0 (s; CH₃ in Et₂O). MS [m/e (intensity, ion)]: peak clusters around 294 (100) (AsSiMe₃)₃, 279 (15) (M–Me), 221 (2) (M–SiMe₃), 206 (52) (M–

(13) Two small-intensity doublet resonances were also observed in the ³¹H NMR spectrum of the raw decanted crystals of 1 (less than 10–15% of the main triplet), 0.54 (d, J=4.3 Hz) and 0.54 (d, J=4.3 Hz) = 5.0 Hz. These were accompanied by the multiplet resonances in the ³¹P(H) NMR spectrum: δ = 247.1 (t, J=1.1 Hz), δ = 280.6 (second-order sextet).
SiMe₃ – Me), 191 (13) (M* – SiMe₃ – 2Me), 74 (5) (Et₂O or SiMe₃ + H), 73 (61) (SiMe₃), and 59 (9) (SiMe₃). IR: ν(Ga=H) 1834 cm⁻¹.

Results and Discussion

The high-yield syntheses of (Et₂O)₂Li[μ-E(SiMe₃)₂]₂GaH₂ (E = P (1), As (2)), were accomplished by combination of LiGaH₄ and E(SiMe₃)₃ in diethyl ether at ambient temperatures according to the following idealized equation:

\[ (\text{Et}_2\text{O})_2\text{Li[μ-E(SiMe}_3\text{)₂]₂GaH}_2 + 2\text{HSiMe}_3 \rightarrow \text{LiGaH}_4 + 2\text{E(SiMe}_3\text{)₃} \]

No reaction of any type occurred between LiGaH₄ and N(SiMe₃)₃ under comparable conditions. In the case of E = P, As, there appeared to be a large driving force forward 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 LiGaH₄ and P(SiMe₃)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 LiGaH₄ to As(SiMe₃)₃ ratios of 1:1 and 1:2. No significant reactions took place between LiGaH₄ and P(SiMe₃)₃ in toluene, and most of the unreacted phospine could be recovered. Both 1 and 2 were stable for weeks and days, respectively, when stored as ethereal or toluene solutions at −30°C. However, the room temperature stored toluene-d₈ 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(SiMe₃)₃, some HSiMe₃, and H₂, while 2 was mostly decomposed after 1 day, yielding As(SiMe₃)₃, HSiMe₃, and H₂.

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 evaporated, likely polymeric powdery product was practically insoluble in toluene, slightly soluble in Et₂O, 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 between the integrated signals due to the other molecules relative to the SiMe₃ 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 SiMe₃ protons and carbons showed as triplets in the respective ¹H and ¹³C(¹H) NMR spectra. This implied a symmetrical and planar four-membered ring containing two virtually coupled phosphorus atoms. A single resonance in the ³¹P(¹H) NMR spectrum at −27.7 ppm complied well with such a notion. Second, the broad proton resonance at 4.7 ppm suggested the presence of terminal GaH₂ moieties in the structure. 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 H₂) symmetrical and antisymmetrical stretches. 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(SiMe₃)₃ and the trimeric, dimeric, and monomeric units of [H₂GaP(SiMe₃)₂]₃, 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 ¹H NMR signals for freshly made solutions indicated two Et₂O molecules per one GaH₂ moiety. In this regard, the symmetrical, broad proton resonance at 4.4 ppm was consistent with the presence of the terminal GaH₂ group in the molecule, as was the IR Ga–H stretching band at 1834 cm⁻¹. But, surprisingly, both ¹H and ¹³C(¹H) NMR spectra obtained for the freshly prepared toluene-d₈ solutions of 2 consistently showed three major peaks in the SiMe₃ region. The proton resonances at 1.05, 0.50, and 0.29 integrated with an approximately 1:2:1 ratio, while the carbon resonances at 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 Et₂O resonances, and this implied two ether molecules per combined SiMe₃ protons (assuming two As(SiMe₃)₂ groups per one GaH₂ group). Since a similar ratio was obtained for the relative quantities of the Ga hydrides and Et₂O protons, we concluded that one GaH₂ group was correlated with all three SiMe₃ 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 (¹³P(¹H) NMR: δ = 265.8); this new compound, [H₂GaP(SiMe₃)₂]₃, was also synthesized in our laboratory from an independent reaction between H₃Ga–NMe₃ and P(SiMe₃)₃. Similarly, [H₂GaAs(SiMe₃)₂]₃ was obtained from the combination of H₃Ga–NMe₃ and As(SiMe₃)₃. Research to be published.


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. 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. 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),18b 1.487(36) Å; a solid product from the reaction between H3Ga-NMe2 and 1,4-di-t-tert-butyl-1,4-diazabutadiene containing a terminal GaH2 group, 1.57(8) and 1.54(12) Å; and H3Ga-P(C6H11)3,6b 1.35, 1.55, and 1.54 Å (mean 1.48 Å).

There are no structurally characterized phosphido-gallanes, and only a few gallane organophosphine adducts of the H3Ga-P(NMe3)3 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)3,6b 2.460(2) Å; (H3Ga)2(PMe2-CH2)2,5a 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, 2.412(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 [C2GaP(SiMe3)2]2 (2.379(2) Å), [Br2GaP(SiMe3)2]2 (2.386(2) Å), and [I2GaP(SiMe3)2]2 (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]220 solvent-free ladder, 2.38(1)–2.63(1) Å; [Li(Et2O)PPh2]221a polymeric chain, 2.483(10)–2.496(10) Å; [Li(THF)P(SiMe3)2]222 planar dimer, 2.62(2) Å; [Li(DME)P(SiMe3)2]223 planar


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

<table>
<thead>
<tr>
<th>Bond</th>
<th>1 (E = P)</th>
<th>2 (E = As)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga–H</td>
<td>1.58(4)</td>
<td>1.51(5)</td>
</tr>
<tr>
<td>E–Ga</td>
<td>2.412(12)</td>
<td>2.494(5)</td>
</tr>
<tr>
<td>E–Li</td>
<td>2.716(8)</td>
<td>2.736(6)</td>
</tr>
<tr>
<td>E–Si(av)</td>
<td>2.236(2)</td>
<td>2.336(11)</td>
</tr>
<tr>
<td>Li–O</td>
<td>1.967(8)</td>
<td>1.937(6)</td>
</tr>
</tbody>
</table>


dimer, 2.559(4) Å; [Li(DME)PH2]22c polymeric chain, 2.537(5)–2.596(5) Å; and [Li(µ3-t-Bu2-P)µ3-t-Bu2-P]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)2As(SiMe3)2]22a distorted planar dimer, 2.67(1)–2.70(1) Å; [Li(µ2-As(SiMe3)2)[µ3-As(SiMe3)2](THF)]22b ladder, 2.53 (average for four-coordinate Li)–2.63 Å (average for five-coordinate Li); [Li(Et2O)2AsPh2]220b planar dimer, 2.708(9) and 2.757(9) Å; Li(1,4-dioxane)3AsPh220b monomer, 2.660–(10) Å; [Li(DME)As(SiMe3)2]22c planar dimer, 2.59(2) Å; and [Li(THF)2(As-t-Bu)As(t-Bu)2]22d 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 [I2GaAs(SiMe3)2]224a (average 2.471(4) Å), [[(Me3SiCH2)2As]2GaBr]224b (average Ga–As ring distance, 2.517(1) Å), and [[(Me3SiCH2)2GaAs(SiMe3)2]22c (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 dehydroxylation 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 RnMX3–n (R = H, alkyl, aryl, SiMe3; X = halogen; n = 0, 1, 2).

Acknowledgment. We thank the Office of Naval Research for its financial support.

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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