

Lithium Pnictidoaluminates $(\text{Et}_2\text{O})_2\text{Li}[\mu\text{-E}(\text{SiMe}_3)_2]_2\text{AlH}_2$ (E = P, As): New Mixed-Metal Pnictogen-Bridged Four-Membered Ring Compounds

Jerzy F. Janik[†] and Richard L. Wells*

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University,
Durham, North Carolina 27708-0346

Peter S. White

Department of Chemistry, University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27514

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The lithium pnictidoaluminates $(\text{Et}_2\text{O})_2\text{Li}[\mu\text{-E}(\text{SiMe}_3)_2]_2\text{AlH}_2$, E = P (**1**) and As (**2**), were obtained from the reactions between LiAlH_4 and $\text{E}(\text{SiMe}_3)_3$ in diethyl ether by following dehydrosilylation chemistry described earlier by us for related gallium derivatives. No reaction was detected for E = N. Single-crystal X-ray diffraction studies for **1** and **2** provided the isomorphous structural solutions featuring the planar four-membered $\{\text{Li}[\mu\text{-E}]_2\text{Al}\}$ cores.

Introduction

Trimethylsilane elimination or dehydrosilylation has been confirmed in several cases to be an advantageous route for forming group 13–15 element bonds.¹ For example, in certain favorable dehydrosilylation systems, the rare representatives of phosphinogallanes and arsinogallanes containing the GaH_2 moiety, $[\text{H}_2\text{Ga-E}(\text{SiMe}_3)_2]_3$, E = P and As, were successfully synthesized and structurally characterized, as recently reported from this laboratory.^{2a} Apparently, the only other authenticated compound of this type is $(\text{H}_2\text{-GaPCy}_2)_3$ made via salt elimination from the combination of $\text{H}_2(\text{Cl})\text{Ga}\cdot\text{PCy}_3$ and $\text{LiPCy}_2\cdot n\text{THF}$.^{2b} In addition to these fundamental observations, practical aspects of efficient elimination–condensation chemistry for amenable precursors, i.e., their conversion to ceramic and/or semiconducting group 13–15 materials, still constitute a strong underlying motivation in research endeavors of our as well as several other laboratories.^{2–4}

We have recently reported the high yield synthesis of a structurally interesting group of compounds, $(\text{Et}_2\text{O})_2\text{-Li}[\mu\text{-E}(\text{SiMe}_3)_2]_2\text{GaH}_2$, E = P and As, featuring the mixed-metal pnictogen-bridged four-membered rings of $\{\text{Li}[\mu\text{-E}]_2\text{Ga}\}$.⁵ These compounds were obtained from the combinations of LiGaH_4 and $\text{E}(\text{SiMe}_3)_3$ in diethyl ether and were the major isolated products for a range of the reagents' ratios. A synthetic appeal of these derivatives relies on expectations that they may serve as starting materials for other potential mixed-metal precursors, for instance, those containing two different group 13 metals, and, consequently, lead to ternary group 13–15 materials. Regarding that chemistry, a preliminary report on the reactivity of $(\text{Et}_2\text{O})_2\text{Li}[\mu\text{-P}(\text{SiMe}_3)_2]_2\text{GaH}_2$ will soon be submitted for publication.⁶

There seems to be relatively few data on the reactions between lithium tetrahydridometalates and pnictines. For example, in a few favorable cases, the reactions between LiGaH_4 and PR_3 were reported to result in base displacement and in the formation of adducts $\text{H}_3\text{Ga}\cdot\text{PR}_3$ and LiH^7 while the reactions of LiAlH_4 and NR_3 yielded $\text{H}_3\text{Al}\cdot\text{NR}_3$ and Li_3AlH_6 .⁸ However, if conditions for accompanying elimination exist in the system, other products have been observed. Thus, reactions of LiAlH_4

* To whom correspondence should be addressed.

[†] On leave from the University of Mining and Metallurgy, Krakow, Poland.

(1) For example, see: (a) Wood, G. L.; Dou, D.; Narula, C. K.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Chem. Ber.* **1990**, *123*, 1455 and references therein. (b) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1987**, *26*, 4341. (c) Janik, J. F.; Duesler, E. N.; McNamara, W. F.; Westerhausen, M.; Paine, R. T. *Organometallics* **1989**, *8*, 506.

(2) (a) Janik, J. F.; Wells, R. L.; Young, V. G., Jr.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 532. (b) Elms, F. M.; Koutsantonis, G. A.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1669. In ref 2a, we stated that $[\text{H}_2\text{GaP}(\text{SiMe}_3)_2]_3$ was the first authenticated phosphinogallane with the GaH_2 moiety. However, $(\text{H}_2\text{GaPCy}_2)_3$ was reported earlier (see ref 2b).

(3) For example, see reviews: (a) Wells, R. L.; Gladfelter, W. L. *J. Cluster Sci.* **1997**, *8*, 217. (b) Wells, R. L. *Coord. Chem. Rev.* **1992**, *112*, 273.

(4) For example, see: (a) Healy, M. D.; Laibinis, P. E.; Stupik, P. D.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1989**, 359. (b) Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438. (c) Butler, L.; Redmond, G.; Fitzmaurice, D. *J. Phys. Chem.* **1993**, *97*, 10750. (d) Laurich, B. K.; Smith, D. C.; Healy, M. D. *Mater. Res. Soc. Symp. Proc.* **1994**, *351*, 49. (e) Micic, O. I.; Sprague,

J. R.; Curtis, C. J.; Jones, K. M.; Machol, J. L.; Nozik, A. J.; Giessen, H.; Fluegel, B.; Mohs, G.; Peyghambarian, N. *J. Phys. Chem.* **1995**, *99*, 7754. (f) Guzelian, A. A.; Katari, J. E. B.; Kadavanich, A. V.; Banin, U.; Hamad, K.; Juban, E.; Alivisatos, A. P.; Wolters, R. H.; Arnold, C. C.; Heath, J. R. *J. Phys. Chem.* **1996**, *100*, 7212.

(5) Janik, J. F.; Wells, R. L.; Young, V. G., Jr.; Halfen, J. A. *Organometallics* **1997**, *16*, 3022.

(6) Wells, R. L.; Jouette, J. R.; Janik, J. F.; White, P. S.; Rheingold, A. L.; Guzei, I. A. To be submitted for publication.

(7) (a) Atwood, J. L.; Robinson, K. D.; Bennett, F. R.; Elms, F. M.; Koutsantonis, G. A.; Raston, C. L.; Young, D. *J. Inorg. Chem.* **1992**, *31*, 2673. (b) Elms, F. M.; Gardiner, M. G.; Koutsantonis, G. A.; Raston, C. L.; Atwood, J. L.; Robinson, K. D. *J. Organomet. Chem.* **1993**, *449*, 45.

(8) (a) Marlett, E. M.; Park, W. S. *J. Org. Chem.* **1990**, *55*, 2968. (b) Jones, C. J.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12*, 1829 and references therein.

and $\text{HN}(\text{SiMe}_3)_2$, known to yield $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ and $\text{LiN}(\text{SiMe}_3)_2$ as final products via dihydrogen elimination,⁹ were later shown to proceed through complex intermediates containing hydrogen-bridged $\{\text{Li}-\text{H}-\text{Al}\}$ cores.^{10a} Similarly, reactions of LiAlH_4 with $\text{HN}(t\text{-Bu})\text{CH}(t\text{-Bu})\text{CH}_2\text{N}(\text{H})(t\text{-Bu})$ afforded initially a simple adduct featuring the $\{\text{Li}-\text{H}-\text{Al}\}$ linkages which, upon elimination of dihydrogen, was converted to a compound with both the $\{\text{Li}-\text{H}-\text{Al}\}$ and $\{\text{Li}-\text{N}-\text{Al}\}$ bridges.^{10b} In another case, an apparently high driving force behind dihydrogen elimination in the system $\text{LiAlH}_4/\text{NH}_3$ resulted in $\text{LiAl}(\text{NH}_2)_4$,^{11a} with a complex structure featuring Li atoms coordinated to four N atoms and, in this case, forming $\{\text{Li}-\text{N}-\text{Al}\}$ connectivities.^{11b} Less understood reactions of LiAlH_4 with PH_3 and AsH_3 appeared to be slower and more complex than with NH_3 and, under specific conditions, lead to the proposed $\text{LiAl}(\text{PH}_2)_4$ ^{11a,c} and $\text{LiAl}(\text{AsH}_2)_4$,^{11d,e} respectively. Interestingly, the combination of LiAlH_4 and $\text{H}_2\text{AsR}/\text{DME}$, $\text{R} = \text{Me}_2\text{C}(i\text{-Pr})\text{SiMe}_2$, afforded via dihydrogen elimination the anionic lithium arsanylalanate fragment, $[(\text{DME})\text{-Li}(\mu\text{-H})_3(\text{HAlAsR})_3]^{2-}$. The cyclotriarsalanate core, $(\text{HAlAsR})_3$, of this compound is coordinated in a tripodal fashion to the DME-solvated Li atom through $\{\text{Li}-\text{H}-\text{Al}\}$ bridges.^{11e}

In this paper, we describe the reactions in diethyl ether of LiAlH_4 with selected tris(trimethylsilyl)pnictines, $\text{N}(\text{SiMe}_3)_3$, $\text{P}(\text{SiMe}_3)_3$, and $\text{As}(\text{SiMe}_3)_3$, and structural characterizations of the resulting two new lithium pnictidoaluminates, $(\text{Et}_2\text{O})_2\text{Li}[\mu\text{-E}(\text{SiMe}_3)_2]_2\text{AlH}_2$, $\text{E} = \text{P}$ and As . This work is an extension of our previously reported study on the gallium analogues;⁵ it confirms a general character of the dehydrosilylation chemistry in both metal systems and extends the pool of potential precursors for ternary (and higher) mixed-metal group 13–15 materials.

Experimental Section

General Techniques. All experiments were carried out using standard vacuum/Schlenk techniques.¹² Solvents were dried and distilled from Na benzophenone ketyl or Na/K alloy prior to use. LiAlH_4 was purchased from Aldrich; before use, it was extracted with Et_2O , filtered, and evacuated overnight. $\text{N}(\text{SiMe}_3)_3$ was purchased from Aldrich and used as received. $\text{P}(\text{SiMe}_3)_3$ ¹³ and $\text{As}(\text{SiMe}_3)_3$ ¹⁴ were prepared by the literature methods. ¹H, ¹³C{¹H}, and ³¹P NMR spectra were acquired on a 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; the CI mode

(isobutane) yielded comparable results. IR spectra were obtained from KBr pellets or from toluene and hexane solutions 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 for **1** and **2** were performed at the University of North Carolina at Chapel Hill, Chapel Hill, NC, on a Siemens SMART Platform CCD system using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K.¹⁵ All calculations were carried out with the help of NRCVAX programs;¹⁶ the structures were solved by direct methods.

Preparation of $(\text{Et}_2\text{O})_2\text{Li}[\mu\text{-P}(\text{SiMe}_3)_2]_2\text{AlH}_2$ (1**).** A sample of freshly purified LiAlH_4 , 0.11 g (3.0 mmol), was dissolved in 20 mL of Et_2O , and a solution of $\text{P}(\text{SiMe}_3)_3$, 1.50 g (6.0 mmol), in 10 mL of Et_2O was added to it at room temperature. The mixture was stirred overnight, concentrated by evacuation to a few milliliters, and diluted with a several drops of toluene, and the resulting solution was stored at $-30 \text{ }^\circ\text{C}$ in the freezer. After 6–8 weeks, an abundant colorless crystalline solid appeared which was cold-separated from the mother liquor and dried in the drybox atmosphere, 0.65 g or 40% yield of **1** based on eq 1 (vide infra). More crystalline material was obtained upon further concentration and storage of the solution in the freezer. Alternatively, a 1:2 ratio reaction in Et_2O (as above) was carried out in a partially evacuated and closed flask maintained at a 40 °C bath temperature for 3 days. Subsequent concentration of the mixture to a few milliliter volume and storage for 2 days at $-30 \text{ }^\circ\text{C}$ afforded a high yield of **1**. A 1:1 ratio reaction was also performed. In this case, the volatiles were removed after a 4 week storage at $-30 \text{ }^\circ\text{C}$, and a ¹H NMR check for the resulting solid did not show any presence of **1**. The solid was redissolved in 10 mL of Et_2O and refluxed under argon for 40 h. Some white solid formed, which was separated with a fine filter, and the brief evacuation of the filtrate afforded a foamy solid. Another NMR check showed the presence of **1** in the foamy product; however, the yield of **1** was not optimized in this case. Dry compound **1** appeared to be pyrophoric in air. Upon prolonged contact with hexane, it turned to a white, powdery slurry. Freshly isolated (not desolvated) compound **1** was soluble in toluene and Et_2O . X-ray-quality crystals were obtained at $-30 \text{ }^\circ\text{C}$ from the $\text{Et}_2\text{O}/$ toluene mixture. The crystals were coated with a protective oil at room temperature before determinations. For other characterization purposes, the crystals were cold-decanted from mother liquor and dried in the drybox atmosphere; a several minute evacuation at ambient temperatures resulted

(15) Crystallographic data for **1**: $\text{C}_{20}\text{H}_{58}\text{O}_2\text{LiAlP}_2\text{Si}_4$, $M = 538.88$, monoclinic, space group $C2/c$, $a = 9.8123(5) \text{ \AA}$, $b = 18.3553(11) \text{ \AA}$, $c = 20.3949(5) \text{ \AA}$, $\beta = 94.480(1)^\circ$, $V = 3662.1(3) \text{ \AA}^3$, $F(000) = 1186.74$, $Z = 4$, $D_c = 0.977 \text{ g/cm}^3$, $\mu = 0.29 \text{ mm}^{-1}$, specimen size (mm) $0.25 \times 0.25 \times 0.30$; 9598 reflections collected, 3227 unique reflections, 2295 reflections with $I > 3.0\sigma(I)$; 2θ range for data collection $3.00\text{--}50.0^\circ$. The final residuals were for $I > 3\sigma(I) = 2280$ $R = 0.056$ and $R_w = 0.070$, and for all data $R = 0.076$ and $R_w = 0.075$. A thermal ellipsoid diagram of **1** is available in the Supporting Information. Crystallographic data for **2**: $\text{C}_{20}\text{H}_{58}\text{O}_2\text{LiAlAs}_2\text{Si}_4$, $M = 626.78$, monoclinic, space group $C2/c$, $a = 9.8556(4) \text{ \AA}$, $b = 18.1859(8) \text{ \AA}$, $c = 20.4311(9) \text{ \AA}$, $\beta = 95.255(1)^\circ$, $V = 3646.5(3) \text{ \AA}^3$, $F(000) = 1330.80$, $Z = 4$, $D_c = 1.142 \text{ g/cm}^3$, $\mu = 2.00 \text{ mm}^{-1}$, specimen size (mm) $0.35 \times 0.35 \times 0.35$; 49 180 reflections collected, 5335 unique reflections, 4878 reflections with $I > 3.0\sigma(I)$; 2θ range for data collection $3.00\text{--}60.00^\circ$. The final residuals were for $I > 3\sigma(I) = 4716$ $R = 0.042$ and $R_w = 0.058$, and for all data $R = 0.052$ and $R_w = 0.062$. A thermal ellipsoid diagram of **2** is shown in Figure 1. Note: for both **1** and **2**, all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in ideal positions and refined isotropically using a standard riding model; the Al hydrogens could not be refined, and the Al–H bond length was assumed at 1.50 Å. Weights based on counting-statistics were used. Some equations of interest: $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w(F_o - F_c)^2 / \sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$.

(16) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(9) (a) Pump, J.; Rochow, E. G.; Wannagat, U. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 264. (b) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1969**, 2279.

(10) (a) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854. (b) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 1349.

(11) (a) Finholt, A. E.; Helling, C.; Imhof, V.; Nielsen, L.; Jacobson, E. *Inorg. Chem.* **1963**, *2*, 504. (b) Jacobs, H.; Jänichen, K.; Hadenfeldt, C.; Juza, R. Z. *Anorg. Allg. Chem.* **1985**, *531*, 125. (c) Norman, A. D.; Wingleth, D. C.; Heil, C. A. *Inorg. Synth.* **1974**, *15*, 177. (d) Anderson, J. W.; Drake, J. E. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 887. (e) Driess, M.; Merz, K.; Pritzkow, H.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2501.

(12) Shriver, D. F.; Drezzdon, M. A. *The Manipulation of Air Sensitive Compounds*; Wiley-Interscience: New York, 1986.

(13) Becker, G.; Hölderich, W. *Chem. Ber.* **1975**, *108*, 2484.

(14) (a) Becker, G.; Gutenkunst, G.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1980**, *462*, 113. (b) Wells, R. L.; Self, M. S.; Johansen, J. D.; Laske, J. A.; Aubuchon, S. R.; Jones, L. J. *Inorg. Synth.* **1997**, *31*, 150.

in a complete removal of Et₂O and formation of a toluene-insoluble polymeric solid. Melting behavior: change of color to yellow at around 200 °C and to yellow/orange at 300 °C with no melting. Anal. Found (calcd for C₂₀H₅₈AlLiO₂P₂Si₄): Al, 5.49 (5.01); P, 11.89 (11.50); Li, 1.69 (1.29); P/Al = 1.9. ¹H NMR: δ 0.48 (t, ³J_{P-H} = 2.3 Hz, SiMe₃), 1.08 (t, ³J_{H-H} = 7.1 Hz; CH₃ in Et₂O), 3.24 (q, ³J_{H-H} = 7.1 Hz; CH₂ in Et₂O); δ 4.3 (s, br; AlH). ¹³C{¹H} NMR: δ 4.7 (t, ²J_{P-C} = approximately 5 Hz; SiMe₃; the triplet was not well resolved, broad, and with shoulders), 15.4 (s; CH₃ in Et₂O), 66.1 (s; CH₂ in Et₂O). ³¹P{¹H} NMR: δ -282, broadened; note, the positions of all NMR resonances were somewhat concentration dependent and, for example, the ³¹P{¹H} signal varied from approximately δ -281 at lower concentrations to δ -283 at higher concentrations of **1**. MS [*m/e* (intensity) (ion)]: 250 (100) (P(SiMe₃)₃, M*), 235 (44) (M* - Me), 178 (35) (M* - SiMe₃ + H or HP-(SiMe₃)₂), 163 (24) (HP(SiMe₃)₂ - Me), 149 (19) (HP(SiMe₃)₂ - 2Me - H), 73 (78) (SiMe₃). IR (KBr; cm⁻¹): ν(Al-H) 1752 (w/m, br), 1672 (m), 1629 (sh). IR (toluene; cm⁻¹): ν(Al-H) 1761 (m).

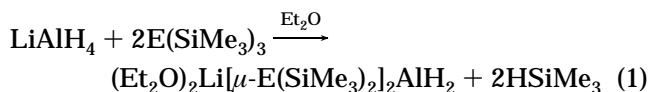
Preparation of (Et₂O)₂Li[μ-As(SiMe₃)₂]₂AlH₂ (2**).** Compound **2** was synthesized in a similar way as compound **1** above. The colorless crystalline solid isolated from the reaction mixture after several weeks of storage at -30 °C amounted to 55% yield of **2** based on eq 1 (vide infra); additional quantities of **2** were obtained after further concentrating and low-temperature storage of the solution. Alternatively, maintaining the mixture at room temperature for 2-3 days followed by storage at -30 °C also resulted in crystallization of **2** in high yield. Compound **2** seemed to be more soluble in hydrocarbons and aromatic solvents than **1**, and any washing of the crystals (to remove redundant oily As(SiMe₃)₃) could only be done with a brief exposure to cold pentane. Dry compound **2** seemed to be pyrophoric when exposed to air. X-ray-quality crystals were obtained at -30 °C from the Et₂O/toluene mixture and oil coated before determinations. For other characterization purposes, the compound, which was stored at -30 °C in mother liquor, was first isolated and then evacuated at ambient conditions for up to 5 min. A 15 min evacuation of **2** resulted in surface desolvation but the bulk of big crystals survived the treatment as evidenced by a NMR check in toluene-*d*₆; however, the resulting mixture was milky. Melting behavior for crystals: evacuated for 1 min, 84-86 °C; evacuated for 15 min, 93-96 °C. Anal. Found (calcd for C₂₀H₅₈AlLiO₂As₂Si₄): Al, 4.57 (4.30); As, 23.86 (23.91); C, 38.18 (38.33); H, 9.28 (9.33); As/Al = 2.0. ¹H NMR:¹⁷ δ 0.58 (s; SiMe₃), 1.08 (t, ³J_{H-H} = 7.0 Hz; CH₃ in Et₂O), 3.32 (q, ³J_{H-H} = 7.0 Hz; CH₂ in Et₂O), 4.15 (s, br; AlH). ¹³C{¹H} NMR: δ 5.3 (s; SiMe₃), 15.1 (s; CH₃ in Et₂O), 66.0 (s; CH₂ in Et₂O). MS [*m/e* (intensity) (ion)]: 442 (1) (As₂(SiMe₃)₄, M*), 370 (6) (M* - SiMe₃ + H), 294 (100) (As(SiMe₃)₃, M**), 279 (16) (M** - Me), 222 (49) (M** - SiMe₃ + H), 206 (91) (M** - SiMe₃ - Me), 191 (4) (M** - SiMe₃ - 2Me), 134 (4) (M** - 2SiMe₃ - Me + H), 73 (2) (SiMe₃). IR (KBr; cm⁻¹): ν(Al-H) 1754 (m, br), 1663 (w). IR (toluene; cm⁻¹): ν(Al-H) 1760 (m). IR (hexane; cm⁻¹): ν(Al-H) 1783 (m).

Results and Discussion

The preparations of the new pnictidoaluminates (Et₂O)₂Li[μ-E(SiMe₃)₂]₂AlH₂, E = P (**1**) and As (**2**), were carried out by reacting LiAlH₄ with E(SiMe₃)₃ in diethyl ether and could be described, similarly as for the analogous LiGaH₄/E(SiMe₃)₃ system,⁵ by the following

(17) The ¹H NMR spectra of numerous toluene-*d*₆ solutions of both evacuated and not evacuated compound **2** tenaciously showed an additional resonance in the SiMe₃ region at δ 0.51 (10-20% of the resonance for the SiMe₃ protons in **2**) plus a resonance at δ 0.34 due to free As(SiMe₃)₃ (from spontaneous decomposition of **2**; see Results and Discussion). The ¹H NMR resonance at δ 0.51 was related to an additional ¹³C{¹H} NMR signal at δ 7.6.

idealized equation:



The reactions afforded moderate to high yields of **1** and **2** from mixtures maintained at -30 °C for several weeks. Alternatively, for E = P, heating the 1:2 ratio reaction mixture at slightly elevated temperatures for several days also provided good yields of **1**. A 1:1 ratio reaction, upon a 2 day reflux in Et₂O, was also shown to give small quantities of **1** but provided mostly ether insoluble solids. In a parallel case of E = As, an alternative 1:2 ratio reaction showed the formation of compound **2** after 2-3 days at room temperature followed by several days at -30 °C. These observations could be compared with the related LiGaH₄/E(SiMe₃)₃ chemistry wherein the reactions were observed to progress significantly toward the expected products after only several hours at -30 °C. Finally, no reaction occurred between LiAlH₄ and N(SiMe₃)₃ under comparable conditions and the unreacted volatile amine was recovered from the system while evacuating the solvent. In regard to the dehydrosilylation chemistry involved in the syntheses of (Et₂O)₂Li[μ-E(SiMe₃)₂]₂AlH₂, it is interesting to note that the related compound Li[AlH₂(PEt₂)₂] was reported from yet different combinations, i.e., reactions between LiPEt₂ and either [H₂AlPEt₂]₃ or H₂AlCl; however, no structural studies were included.¹⁸

Compound **1** is reasonably stable at room temperature, at least in toluene solution; a toluene-*d*₈ sample of **1** maintained at ambient conditions showed by NMR spectroscopy almost no changes in the course of several weeks, except for the formation of very little HSiMe₃. Heating a fresh sample to 80 °C in a VT NMR experiment for a short period of time did not result in noticeable decomposition either. However, a facile loss of the coordinated Et₂O in the solid state, even upon a short evacuation, plagued the consistency of the compound's characterization. For example, the results of elemental analysis provided a satisfactory P/Al ratio of 1.9 while C and H determinations were erratic and low, and this could be linked to the loss of Et₂O. Second, the IR spectra in KBr showed in the Al-H stretching region the prevailing bands at 1672 and 1629 cm⁻¹ (shoulder) in the range typical for bridging rather than terminal Al hydrogens.¹⁹ These bands were routinely observed for both the evacuated and not evacuated samples, and they might represent a hypothetical polymeric species formed upon desolvation of **1** occurring during the preparation of KBr pellets. The weaker, broad band at approximately 1750 cm⁻¹, typical for terminal Al hydrogens, may thus be tentatively assigned to **1**. An IR spectrum for a toluene solution of **1** showed only one band in this region at 1761 cm⁻¹, consistent with the above. Finally, mass spectrometry did not show a parent ion for **1** but, instead, it displayed the prevailing *m/e* ion pattern due to P(SiMe₃)₃ and its fragments; the latter was in agreement with negligible

(18) Fritz, G.; Trenczek, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 482 and references therein.

(19) For example, see review: Cucinella, S.; Mazzei, A.; Marconi, W. *Inorg. Chim. Acta Rev.* **1970**, *4*, 51.

volatility and similar decomposition/fragmentation behavior for **1** and its gallium analogue. Eventually, it was mostly the NMR data such as the virtual triplets in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for the P–SiMe₃ groups that strongly supported the close analogy with the gallium counterpart and thus the planar, four-membered $\{\text{Li}[\mu\text{-P}]_2\text{Al}\}$ ring for compound **1**.

Compound **2** displayed somewhat opposite stability to that of **1**. On one hand, freshly isolated **2** appeared not to easily lose the coordinated ether molecules, but on the other hand, it was clearly not stable but subject to spontaneous extensive decomposition at room temperature. The latter process was followed in the course of several days by NMR spectroscopy for a room-temperature-stored toluene-*d*₈ sample of **2**. Generally, it showed decreasing resonances with time for **2** and a concurrent increase of signals for free As(SiMe₃)₃ and HSiMe₃. For example, after 20 h and 8 days past sample preparation, about 25% and 60% of **2**, respectively, had undergone decomposition. Interestingly, similar decomposition byproducts were detected earlier for the gallium analogue, (Et₂O)₂Li[μ-As(SiMe₃)₂]₂GaH₂, but that compound decomposed almost entirely after 1 day. Additionally, the formation of free dihydrogen was observed in the latter case possibly due to a higher thermal frailty of the Ga–H functionalities compared to the Al–H groups in **2**. Mass spectrometry under both EI and CI conditions showed the prevailing *m/e* ion fragments mostly associated with As(SiMe₃)₃, thus supporting the compound's instability also under MS probe conditions. However, the aforementioned relatively tight coordination of the Et₂O molecules and the overall integrity of the compound soon after isolation was reflected in a well-defined melting point that showed a relatively small change with its evacuation. Apparently, this property resulted also in quite coherent IR data for **2**. The prevailing band for the KBr pellet in the Al–H stretching region was at 1754 cm⁻¹ in the range for terminal Al hydrogens as expected for the presumed structure of **2**, and there was only a weak band at 1663 cm⁻¹, which could be linked to some loss of Et₂O as discussed earlier. Other characterization data such as rather simple NMR spectra and, especially, satisfactory elemental analysis further supported compound **2** as described by eq 1. The final proof of atomic connectivities and structural details for both **1** and **2** was provided by single-crystal X-ray structure determinations.

The single-crystal X-ray structural results provided the isostructural solutions for **1** and **2** which also happened to be isostructural with the relevant gallium analogues. This was consistent with similar elimination chemistry operating in these systems and close relationship within this new family of compounds. Selected bond lengths and angles for **1** and **2** are included in Table 1. A thermal ellipsoid diagram of **2** shown in Figure 1 exemplifies a general layout of atomic connectivities for both compounds. The C hydrogen atoms are removed for clarity, but the Al hydrogen atoms, nor refined though, are included to unambiguously describe the four-coordination of all ring atoms. A crystallographically imposed 2-fold rotational symmetry is reflected by a 2-fold axis passing through Al and Li in the ring with two pnictogen atoms bridging the two metal

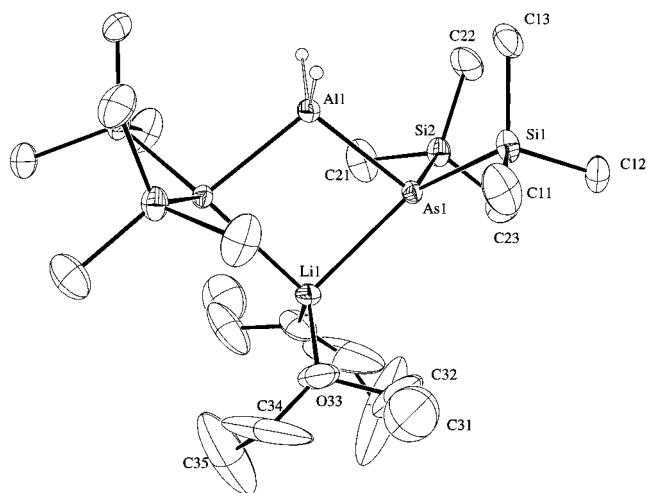


Figure 1. Thermal ellipsoid diagram (35% probability ellipsoids) showing the molecular structure of **2**. All C hydrogen atoms are omitted for clarity.

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		
E–Al	2.4001(13)	2.4934(7)
E–Li	2.692(6)	2.732(4)
E–Si(av)	2.228	2.329
Li–O	1.956(5)	1.929(4)
Bond Angles		
E–Al–H(av)	111.1	111.3
E–Al–E	102.90(6)	102.08(4)
E–Li–E	88.42(23)	90.43(18)
Al–E–Li	84.34(12)	83.74(9)
O–Li–O	109.9(4)	112.4(3)
O–Li–E(av)	114.3	113.1
Si(1)–E–Si(2)	105.77(5)	103.67(3)
Si(1)–E–Li	137.80(6)	142.01(3)
Si(2)–E–Li	112.74(5)	112.21(3)
Si–E–Al(av)	103.4	101.5

atoms. The planar but “kite-shaped” ring of the $\{\text{Li}[\mu\text{-E}]_2\text{Al}\}$ core underlines some ring stress as supported by the acute Al–E–Li angles of 84.34(12)° (**1**) and 83.74(9)° (**2**) or the opened E–Al–E angles of 102.90(6)° (**1**) and 102.08(4)° (**2**). There is a trend in shortening of rather typical Li–O distances²⁰ when going from **1** to **2**, from 1.956(5) to 1.929(4) Å, respectively, similar with the relevant gallium analogues, (Et₂O)₂Li[μ-E(SiMe₃)₂]₂GaH₂, from 1.967(8) Å (E = P) to 1.937(6) Å (E = As), that perhaps could be linked to the experimentally confirmed fact of more tightly coordinated Et₂O molecules in compound **2**. These Et₂O molecules are also characterized by an increased thermal motion disorder which is apparently more pronounced in **1** than **2**.

Of notable structural features for **1**, the Li–P bond length, 2.692(6) Å, is one of the longest distances of this type and similar to this distance in the structurally related gallium analogue, (Et₂O)₂Li[μ-P(SiMe₃)₂]₂GaH₂, 2.716(8) Å. Another interesting feature is the Al–P bond length, 2.4001(13) Å, one of the shortest distances among four-coordinated Al and P ring compounds. This

(20) (a) Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243. (b) Bartlett, R. A.; Dias, R. H. V.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6921.

distance can be compared with some relevant short Al–P bond lengths such as found in aluminaphosphacubane [*i*-BuAl(μ_3 -PSiPh₃)₄, 2.414(4) Å,^{21a} and in the base-stabilized adduct [H₂AlPMes₂] \cdot NMe₃, 2.409(3) Å.^{21b} The recently published ab initio calculations of the structures of the dimer [H₂AlPH₂]₂ and cubic cluster [HALPH]₄ have provided the Al–P distances of 2.451 and 2.434 Å, respectively.²² It would intuitively seem that the observed relative strengthening of the Al–P bonds coupled with lengthening of the Li–P bonds in compound **1** could be a manifestation of Al winning the competition with Li for electron density from the P centers in the {Li[μ -P]₂Al} core. However, we could not reconcile in a straightforward way such a conjecture with the equally short Al–P bond lengths in the trimer [H₂AlP(SiMe₃)₂]₃, average 2.398 Å.²³

(21) (a) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1409. (b) Atwood, D. A.; Contreras, L.; Cowley, A. H.; Jones, R. A.; Mardones, M. A. *Organometallics* **1993**, *12*, 17.

(22) Davy, R. D.; Schaefer, H. F., III *J. Phys. Chem. A* **1997**, *101*, 5707.

(23) The reaction system H₃Al \cdot NMe₃/E(SiMe₃)₃, E = P and As, recently under investigation in our laboratory, provided the trimer [H₂AlP(SiMe₃)₂]₃ and base-stabilized adduct [H₂AlAs(SiMe₃)₂] \cdot NMe₃, respectively: *Inorg. Chem.*, in press.

(24) (a) Heaton, D. E.; Jones, R. A.; Kidd, K. B.; Cowley, A. H.; Nunn, C. M. *Polyhedron* **1988**, *7*, 1901. (b) Wells, R. L.; McPhail, A. T.; Speer, T. M.; *Organometallics* **1992**, *11*, 960. (c) Laske-Cooke, J. A.; Purdy, A. P.; Wells, R. L.; White, P. S. *Organometallics* **1996**, *15*, 84.

The ring structure of **2** in comparison with **1** generally displays properties which show similar trends that were previously observed for the P/As pair of the related gallium analogues. Additionally, a rather long Li–As bond length of 2.732(4) Å appears to match the Li–As distance in the gallium counterpart, 2.736(6) Å. The Al–As bond length in **2**, 2.4934(7) Å, belongs to short bonds of this type among a few reported four-coordinated Al–As ring structures.²⁴

The relatively high stability of compounds **1** (especially) and **2** at ambient conditions, much higher than that of the related gallium analogues, makes these derivatives attractive starting materials for other mixed-metal rings and materials precursors. Some of the envisioned reaction systems to study include (Et₂O)₂-Li[μ -E(SiMe₃)₂]₂AlH₂/R_nMX_{3-n} (R = H, alkyl, aryl, SiMe₃; X = halide; *n* = 0–2). This kind of derivatization chemistry is currently under scrutiny in our laboratory.

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Supporting Information Available: A thermal ellipsoid diagram for **1** and tables of X-ray parameters, bond distances, bond and torsion angles, anisotropic temperature factor parameters, and atomic parameters for **1** and **2** (11 pages). Ordering information is given on any current masthead page.

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