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Dr. Harold E. Guard

6. AUTHOR(S)
J, F. Janik, R. L. Wells
P. S. White

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
Duke University
Durham, NC 27708-0346

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Jerzy F. Janik, Richard L. Wells

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

Peter S. White

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

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Duke University
Department of Chemistry,
P. M. Gross Chemical Laboratory
Box 90346
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Jerzy F. Janik,‡ Richard L. Wells*

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University

Durham, NC 27708-0346

Peter S. White

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

Chapel Hill, NC 27514

Summary: The lithium pnictidoaluminates, $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2AlH_2$, E = P **(1)**, As **(2)**, were obtained from the reactions between $LiAlH_4$ and $E(SiMe_3)_3$ in diethyl ether 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 $\{Li[\mu\text{-}E]_2Al\}$ cores.

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* To whom correspondence should be addressed.

‡ On leave from the University of Mining and Metallurgy, Krakow, Poland.

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, $[H_2GaE(SiMe_3)_2]_3$, E = P, As, were successfully synthesized and structurally characterized, as recently reported from this laboratory.[2a] Apparently, the only other authenticated compound of this type is $(H_2GaPCy_2)_3$ made *via* salt elimination from the combination of $H_2(Cl)Ga{\bullet}PCy_3$ and $LiPCy_2{\bullet}nTHF$.[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, $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2GaH_2$, E = P, As, featuring the mixed-metal pnicogen-bridged four-membered rings of $\{Li[\mu\text{-}E]_2Ga\}$.[5] These compounds were obtained from the combinations of $LiGaH_4$ and $E(SiMe_3)_3$ 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 $(Et_2O)_2Li[\mu\text{-}P(SiMe_3)_2]_2GaH_2$ will soon be submitted for publication.[6]

There seems to be relatively few data on the reactions between lithium tetrahydridometallates 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 $H_3Ga{\bullet}PR_3$ and LiH[7] while the reactions of $LiAlH_4$ and NR_3 yielded $H_3Al{\bullet}NR_3$

and Li_3AlH_6.[8] However, if conditions for accompanying elimination exist in the system, other products have been observed. Thus, reactions of $LiAlH_4$ and $HN(SiMe_3)_2$, known to yield $Al[N(SiMe_3)_2]_3$ and $LiN(SiMe_3)_2$ as final products *via* dihydrogen elimination,[9] were later shown to proceed through complex intermediates containing hydrogen-bridged {Li–H–Al} cores.[10a] Similarly, reactions of $LiAlH_4$ with HN(t-Bu)CH(t-Bu)CH_2N(H)(t-Bu) afforded initially a simple adduct featuring the {Li–H–Al} linkages which, upon elimination of dihydrogen, was converted to a compound with both the {Li–H–Al} and {Li–N–Al} bridges.[10b] In another case, an apparently high driving force behind dihydrogen elimination in the system $LiAlH_4/NH_3$ resulted in $LiAl(NH_2)_4$,[11a] with a complex structure featuring Li atoms coordinated to four N atoms and, in this case, forming {Li–N–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 $LiAl(PH_2)_4$[11a, c] and $LiAl(AsH_2)_4$,[11d, e] respectively. Interestingly, the combination of $LiAlH_4$ and H_2AsR/DME, R = Me_2C(i-Pr)$SiMe_2$, afforded *via* dihydrogen elimination the anionic lithium arsanylalanate fragment, $[(DME)Li(\mu\text{-}H)_3(HAlAsR)_3]^{2-}$. The cyclotriarsaalanate core, $(HAlAsR)_3$, of this compound is coordinated in a tripodal fashion to the DME-solvated Li atom through {Li–H–Al} bridges.[11e]

In this paper, we describe the reactions in diethyl ether of $LiAlH_4$ with selected tris(trimethylsilyl)pnictines, $N(SiMe_3)_3$, $P(SiMe_3)_3$, and $As(SiMe_3)_3$ and structural characterizations of the resulting two new lithium pnictidoaluminates, $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2AlH_2$, E = P, As. This work is an extension of our previously reported study on the gallium analogs;[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. $N(SiMe_3)_3$ was purchased from Aldrich and used as received. $P(SiMe_3)_3$,[13] $As(SiMe_3)_3$[14] 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; 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 (λ = 0.71073 Å) 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 $(Et_2O)_2Li[\mu\text{-}P(SiMe_3)_2]_2AlH_2$ (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 $P(SiMe_3)_3$, 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, diluted with a several drops of toluene, and the resulting solution stored at −30 °C in the freezer. After 6 to 8 weeks, abundant colorless crystalline solid appeared which was cold-separated from the mother liquor and dried in the dry-box 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 three days. Subsequent concentration of the mixture to a few milliliter volume and storage for two days at –30 °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 °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 hours. 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 °C from the Et_2O/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 dry-box atmosphere; a several minute evacuation at ambient temperatures resulted in a complete removal of Et_2O 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 $C_{20}H_{58}AlLiO_2P_2Si_4$): 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, $SiMe_3$), 1.08 (t, $^3J_{H-H}$ = 7.1 Hz; CH_3 in Et_2O), 3.24 (q, $^3J_{H-H}$ = 7.1 Hz; CH_2 in Et_2O); δ 4.3 (s, br; AlH). $^{13}C\{^1H\}$ NMR: δ 4.7 (t, $^2J_{P-C}$ = approximately 5 Hz; $SiMe_3$; the triplet was not well resolved, broad, and with shoulders), 15.4 (s; CH_3 in Et_2O), 66.1 (s; CH_2 in Et_2O). $^{31}P\{^1H\}$ NMR: δ –282, broadened; note, the positions of all NMR resonances were somewhat concentration dependent and, for example for the $^{31}P\{^1H\}$ signal, varied from approximately δ –281 at lower concentrations to δ –283 at

higher concentrations of **1**. MS [*m/e* (intensity) (ion)]: 250 (100) ($P(SiMe_3)_3$, M^*), 235 (44) ($M^* - Me$), 178 (35) ($M^* - SiMe_3 + H$ or $HP(SiMe_3)_2$), 163 (24) ($HP(SiMe_3)_2 - Me$), 149 (19) ($HP(SiMe_3)_2 - 2Me - H$), 73 (78) ($SiMe_3$). 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 $(Et_2O)_2Li[\mu\text{-}As(SiMe_3)_2]_2AlH_2$ (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 $As(SiMe_3)_3$) 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 Et_2O/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 minutes. A 15 minute 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_8; however, the resulting mixture was milky. Melting behavior for crystals evacuated for one minute, 84-86 °C, and evacuated for fifteen minutes, 93-96 °C. Anal. Found (calcd for $C_{20}H_{58}AlLiO_2As_2Si_4$): 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; $SiMe_3$), 1.08 (t, $^3J_{H-H}$ = 7.0 Hz; CH_3 in Et_2O), 3.32 (q, $^3J_{H-H}$ = 7.0 Hz; CH_2 in Et_2O), 4.15 (s, br; AlH). $^{13}C\{^1H\}$ NMR: δ 5.3 (s; $SiMe_3$), 15.1 (s; CH_3 in Et_2O), 66.0 (s; CH_2 in Et_2O). MS [*m/e* (intensity) (ion)]: 442 (1) ($As_2(SiMe_3)_4$, M^*), 370 (6) ($M^* - SiMe_3 + H$), 294 (100) ($As(SiMe_3)_3$, M^{**}), 279 (16) ($M^{**} - Me$), 222 (49)

(M^{**} – $SiMe_3$ + H), 206 (91) (M^{**} – $SiMe_3$ – Me), 191 (4) (M^{**} – $SiMe_3$ – 2Me), 134 (4) (M^{**} – 2$SiMe_3$ – Me + H), 73 (2) ($SiMe_3$). 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 $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2AlH_2$, E = P (**1**), As (**2**), were carried out by reacting $LiAlH_4$ with $E(SiMe_3)_3$ in diethyl ether and could be described, similarly as for the analogous $LiGaH_4/E(SiMe_3)_3$ system,[5] by the following idealized equation:

$$LiAlH_4 + 2E(SiMe_3)_3 \xrightarrow{Et_2O} (Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2AlH_2 + 2HSiMe_3 \qquad (1)$$

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 two day reflux in Et_2O, 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 $LiGaH_4/E(SiMe_3)_3$ 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 $LiAlH_4$ and $N(SiMe_3)_3$ 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 $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2AlH_2$, it is interesting to note that the related compound $Li[AlH_2(PEt_2)_2]$ was

reported from yet different combinations, i.e., reactions between $LiPEt_2$ and either $[H_2AlPEt_2]_3$ or H_2AlCl; 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 $HSiMe_3$. 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 Et_2O 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 Et_2O. Secondly, the IR spectra in KBr showed in the Al–H stretching region the prevailing bands at 1672 cm^{-1} 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 $P(SiMe_3)_3$ and its fragments; the latter was in agreement with negligible volatility and similar decomposition/fragmentation behavior for **1** and its gallium analog. Eventually, it was mostly the NMR data such as the virtual triplets in the ^1H and $^{13}C\{^1H\}$ NMR spectra for the P–$SiMe_3$ groups that strongly supported the close analogy with the gallium counterpart and thus the planar, four-membered $\{Li[\mu\text{-}P]_2Al\}$ 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 $As(SiMe_3)_3$ and $HSiMe_3$. For example, after 20 hrs 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 analog, $(Et_2O)_2Li[\mu\text{-}As(SiMe_3)_2]_2GaH_2$, but that compound decomposed almost entirely after one 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 $As(SiMe_3)_3$, thus supporting the compound's instability also under MS probe conditions. However, the aforementioned relatively tight coordination of the Et_2O 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 Et_2O 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 analogs. 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 twofold rotational symmetry is reflected by a twofold axis passing through Al and Li in the ring with two pnicogen atoms bridging the two metal atoms. The planar but "kite-shaped" ring of the $\{Li[\mu\text{-}E]_2Al\}$ 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 distances[20] when going from **1** to **2**, from 1.956(5) Å to 1.929(4) Å, respectively, similar with the relevant gallium analogs, $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2GaH_2$, 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 Et_2O molecules in compound **2**. These Et_2O 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 analog, $(Et_2O)_2Li[\mu\text{-}P(SiMe_3)_2]_2GaH_2$, 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 distance can be compared with some relevant short Al–P bond lengths such as found in aluminaphosphacubane $[i\text{-}BuAl(\mu_3\text{-}PSiPh_3)]_4$, 2.414(4) Å,[21a] and in the base stabilized adduct $[H_2AlPMes_2]\cdot NMe_3$, 2.409(3) Å.[21b] The recently published *ab initio* calculations of the structures of the dimer $[H_2AlPH_2]_2$ and cubic cluster $[HAlPH]_4$ has provided the Al–P distances of 2.451 Å 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 $\{Li[\mu\text{-}P]_2Al\}$ core.

However, we could not reconcile in a straightforward way such a conjecture with the equally short Al–P bond lengths in the trimer $[H_2AlP(SiMe_3)_2]_3$, av 2.398 Å.[23]

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 analogs. 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 analogs, makes these derivatives attractive starting materials for other mixed-metal rings and materials precursors. Some of the envisioned reaction systems to study include $(Et_2O)_2Li[\mu\text{-}E(SiMe_3)_2]_2AlH_2/R_nMX_{3-n}$, R = H, alkyl, aryl, $SiMe_3$; n = 0–2. This kind of derivatization chemistry is currently under scrutiny in our laboratory.

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Supporting Information Available. Thermal ellipsoid diagram for **1**; crystal packing diagrams for **1** and **2**; tables of bond distances, bond and torsion angles, anisotropic temperature factor parameters, and atomic parameters for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

References

(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.

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(15) Crystallographic data for **1**: $C_{20}H_{58}O_2LiAlP_2Si_4$, M = 538.88, monoclinic, space group C2/c, a = 9.8123(5) Å. b = 18.3553(11) Å, c = 20.3949(5) Å, β = 94.480(1)°, V = 3662.1(3) Å^3, F(000) = 1186.74, Z = 4, D_c = 0.977 g/cm^3, μ = 0.29 mm^{-1}, specimen size (mm): 0.25x0.25x0.30; 9598 reflections collected, 3227 unique reflections, 2295 reflections with I > 3.0σ (I); 2Θ range for data collection: 3.00 to 50.0°. The final residuals were for (I > 3σ(I) = 2280) R = 0.056, R_w = 0.070, and for all data R = 0.076, R_w = 0.075. A thermal ellipsoid diagram of **1** is available in the Supporting Information. Crystallographic data for **2**: $C_{20}H_{58}O_2LiAlAs_2Si_4$, M = 626.78, monoclinic, space group C2/c, a = 9.8556(4) Å. b = 18.1859(8) Å, c = 20.4311(9) Å, β = 95.255(1)°, V = 3646.5(3) Å^3, F(000) = 1330.80, Z = 4, D_c = 1.142 g/cm^3, μ = 2.00 mm^{-1}, specimen size (mm): 0.35x0.35x0.35; 49180 reflections collected, 5335 unique reflections, 4878 reflections with I > 3.0σ (I); ; 2Θ range for data collection: 3.00 to 60.00°. The final residuals were for (I > 3σ (I) = 4716) R = 0.042, R_w = 0.058, and for all data R = 0.052, 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 $w = 1/\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P$.

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

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.

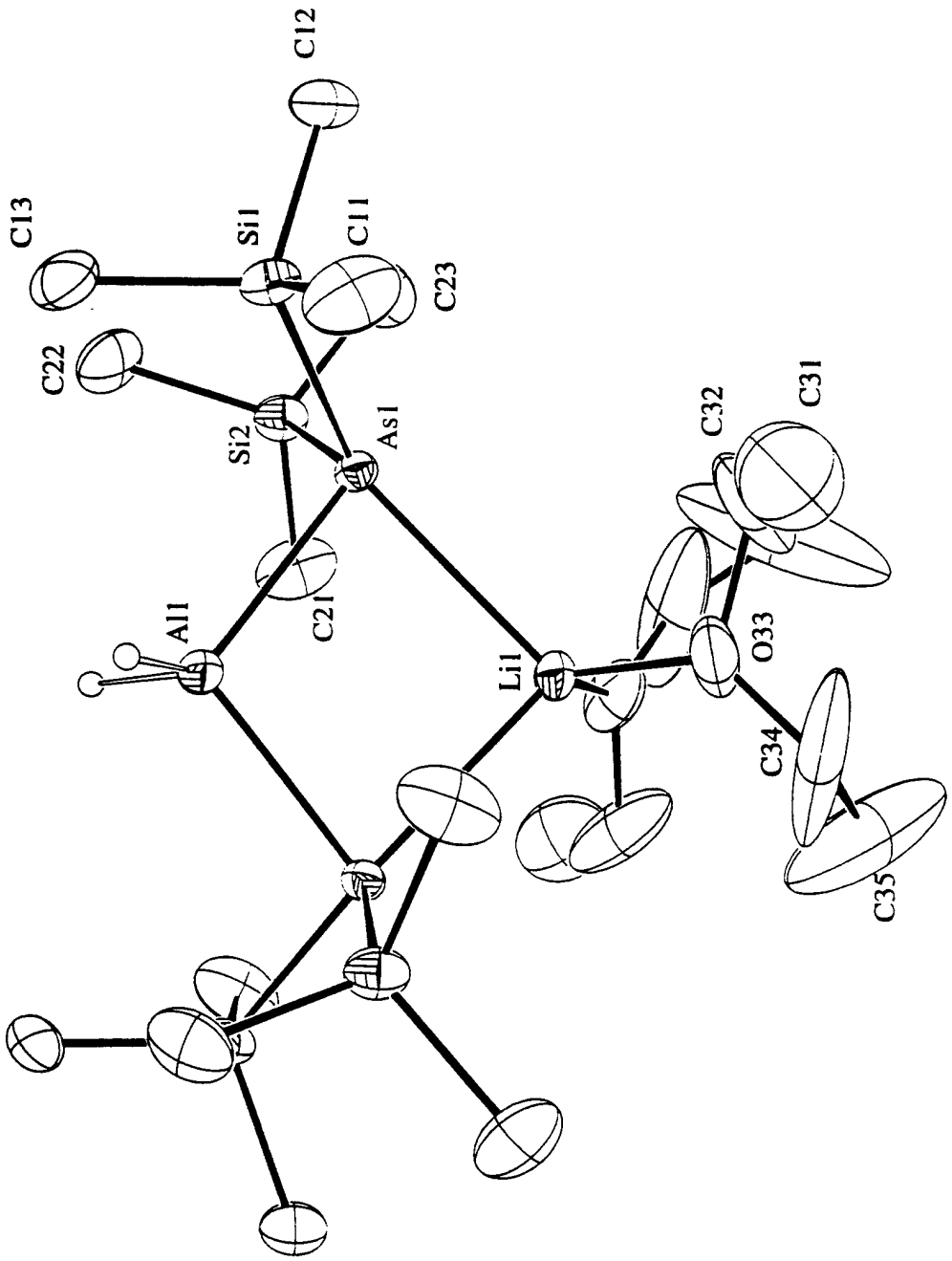

Fig 1

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