cyclopentadienide when complexed to a transition metal.[11] However, quantitative data on the electronic effect of the trialkylsilyl moiety on systems such as 1 and 2 are not available.

With utilization of X-ray photoelectron spectroscopy,[9] a series of derivatives of 3 (n = 1–3; M = Zr, Hf) and of ferrocene were studied. Table I lists the binding energies for these compounds and for appropriate reference compounds. Examination of the series of zirconocene derivatives showed that the binding energies of the $3d_{5/2}$ electrons decreased by an average of 0.1 eV/trimethylsilyl group. Two, four, and six trimethylsilyl groups gave an orderly decrease in binding energy. The electronic impact of six trimethylsilyl groups on hafnocene dichloride and on ferrocene again averaged −0.1 eV/trimethylsilyl group.

Investigation of a large variety of transition-metal complexes of methylated cyclopentadienides showed that the methyl substituent averaged an electron donation of 0.08 eV to the complexed metal.[9,12] In comparison, the trimethylsilyl group is ca. 1.25 times more electron donating than the methyl moiety. Thus, in systems such as 1 and 2, we can confidently predict that the silyl substituent will be more electron donating than hydrogen to the complexed zirconium atom and that the zirconium atoms of 1 and 2 will be electron rich relative to zirconocene dichloride.

Experimental Section

X-ray photoelectron spectra were recorded on a Physical Electronics Model 555 ESCA–Auger–SIMS spectrometer, equipped with a retarding-grid cylindrical mirror analyzer operating at a pass energy of 25 eV. Samples were irradiated with Mg Kα X-rays. Samples[13-15] were finely dispersed on the surface of a polyethylene film, and all data were calibrated against the C(1s) signal of polyethylene.

Peak positions reported are the centroids of Gaussian + Lorentzian functions obtained via a standard nonlinear least-squares regression technique. Binding energies are corrected for sample charging by adjusting the C(1s) signal of polyethylene to 284.6 eV. While the C(1s) signal arose mainly from polyethylene, we observed small, unresolved shoulders on the low binding energy side of the signals, which we believe to have resulted from carbon atoms directly attached to the electropositive silicon atoms in the complexes studied. This interference was subtracted from the spectra as follows. The intensity of the shoulder signal arising from silicon-bound carbon atoms was calculated from the integrated area of the metal core electron signal using published tables of atomic sensitivities.[16] The shoulder binding energy was determined from spectra of heavily loaded samples, in which polyethylene was completely obscured and in which silicon-bound carbon atoms dominated the sample. After subtraction of the shoulder, the remaining C(1s) signal had a fwhm of less than 1.7 eV and was used as the internal charging standard.

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Registry No. 3 (M = Zr, n = 1), 60938-59-2; 3 (M = Zr, n = 2), 137964-45-5; 3 (M = Zr, n = 3), 137917-28-3; 3 (M = Hf, n = 3), 137917-29-4; $[(Me_3Si)_3C_2H_5]_2Fe$, 137917-30-7.

---

(11) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988,** *110,* 6130.

(12) Gassman, P. G.; Winter, C. H.; Macomber, D. W. Unpublished results.

(13) Tolstikov, G. A.; Miftakhov, M. S.; Monakhov, Y. B. *Zh. Obshch. Khim.* **1976,** *46,* 1778.

(14) Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* **1991,** *403,* 145.

(15) Okuda, J.; Herdtweck, E. *Chem. Ber.* **1988,** *121,* 1899. Miftakhov, M. S.; Tolstikov, G. A. *Zh. Obshch. Khim.* **1976,** *46,* 930.

(16) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Eden Prairie, MN, 1979; p 188.

Synthesis and Characterization of Novel Aluminum–Arsenic Compounds. Crystal Structure of $[Et_2AlAs(SiMe_3)_2]_2$

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Summary: The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type Al–As–Al–As and Al–As–Al–Cl was investigated. The second fully characterized aluminum–arsenic dimer, $[Et_2AlAs(SiMe_3)_2]_2$ (**1**), was isolated from a coupling reaction between Et_2AlCl and $LiAs(SiMe_3)_3$ carried out at −78 °C. Reactions between Et_2AlCl and $As(SiMe_3)_3$ in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected dehalosilylation products, instead yielding the adduct $Et_2(Cl)Al\cdot As(SiMe_3)_3$ (**2**). As evidenced by ^1H NMR spectra, an NMR tube sample of **2** in benzene-d_6 did undergo internal dehalosilylation to give **1** when heated to 87 °C in an oil bath. X-ray crystallographic analysis of **1** confirms its dimeric solid-state structure and shows the Al–As–Al–As ring to be planar. Compound **1** crystallizes in the monoclinic system, space group $C2/c$ (C_{2h}^6), with four molecules in a unit cell of dimensions a = 18.214 (2) Å, b = 9.542 (1) Å, c = 20.453 (2) Å, and β = 99.89 (1)°.

Of late, there has been heightened interest in the preparation of compounds that may serve as single-source precursors to group 13–15 semiconductor materials.[1,2] Two methods have been developed in our laboratories to fabricate compounds that may prove useful to this end: (a) dehalosilylation between tris(trimethylsilyl)arsine and a group 13 halide and (b) coupling reactions involving lithium bis(trimethylsilyl)arsenide and a group 13 halide. These methodologies have been applied to systems involving the heavier group 13 elements to prepare com-

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(1) Cowley, A. H.; Jones, R. A. *Angew. Chem., Intl. Ed. Engl.* **1989,** *28,* 1208.

(2) Cole-Hamilton, D. J. *Chem. Brit.* **1991,** 852.

0276-7333/92/2311-0960$03.00/0

pounds with core rings of the type $\overline{\mathrm{M{-}As{-}M{-}As}}$ and $\overline{\mathrm{M{-}As{-}M{-}Cl}}$, where M = Ga and In.[3-7] In an attempt to utilize these tactics to prepare analogous aluminum–arsenic species, reaction of Et_2AlCl with tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide was undertaken. While proving useful in the cases of Ga and In, room-temperature dehalosilylation reactions failed in this work instead yielding the adduct $Et_2(Cl)Al{\cdot}As(SiMe_3)_3$ (2). The novel dimer $[Et_2AlAs(SiMe_3)_2]_2$ (1) was prepared by a coupling reaction and is only the second Al–As dimer fully characterized by single-crystal X-ray analysis.

Experimental Section

General Considerations. All reactions and manipulations were carried out by utilizing standard Schlenk techniques, under an Ar atmosphere in a Vacuum/Atmospheres HE-493 Dri-Lab or under vacuum. Pentane and hexane were dried over $LiAlH_4$, while all other solvents were dried over, and distilled from, sodium benzophenone ketyl. Tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide were prepared by the methods of Becker et al.[8] Diethylaluminum chloride was purchased from Strem Chemicals, Inc., and used without further purification. ^1H, $^{13}C\{^1H\}$, and $^{27}Al\{^1H\}$ NMR spectra were obtained at 299.943, 75.4, and 78.2 MHz, respectively, on a Varian XL-300 spectrometer in 5-mm tubes. $^{13}\{^1H\}$ and ^1H NMR spectra were referenced to TMS using the carbons or residual protons of benzene-d_6 at δ 128 ppm and δ 7.15 ppm, respectively. $^{27}Al\{^1H\}$ spectra were referenced externally to $Al(NO_3)_3$ at δ 0.00 ppm. All spectra were run in benzene-d_6, and NMR tubes were flame-sealed under vacuum. Melting points were obtained on a Hoover Uni-Melt in sealed capillaries and are uncorrected. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Crystals used in X-ray analyses were flame-sealed under argon in 0.7-mm thin-walled glass capillaries. Volatile reaction products were analyzed for Me_3SiCl content by hydrolysis with deionized water followed by titration of the resulting HCl solution with standard NaOH to a phenolphthalein endpoint. NaOH was standardized against potassium hydrogen phthalate to a phenolphthalein endpoint.

Preparation of $[Et_2AlAs(SiMe_3)_2]_2$ (1). $LiAs(SiMe_3)_2$ (0.373 g, 1.63 mmol) was dissolved in 25 mL of pentane and 10 mL of THF in the top bulb of a two-bulb reaction flask. Et_2AlCl (0.1969 g, 1.633 mmol) was washed into the bottom bulb with 35 mL of pentane. The lower bulb was cooled to −78 °C in an acetone/dry ice bath, and the upper bulb was cooled with a liquid-nitrogen wand. Upon mixing, a white precipitate formed (presumably LiCl, 0.0588 g, 87% yield) and the solution remained clear. After being stirred for 18 h at −78 °C, the reaction mixture was allowed to warm slowly to room temperature and volatiles were removed in vacuo to leave an off-white semisolid that was recrystallized at −15 °C from pentane to give 1 (0.651 g, 65.2% yield), mp 201 °C. No Me_3SiCl was eliminated over the course of the reaction. Anal. Calcd (found) for $C_{20}H_{56}Al_2As_2Si_4$: C, 39.20 (39.40); H, 9.15 (9.16). ^1H NMR: δ 0.42 [s, $Si(CH_3)_3$, 18 H], 0.51 (q, CH_2, 4 H), 1.38 (t, CH_3, 6 H). $^{13}C\{^1H\}$ NMR: δ 4.65 [s, $Si(CH_3)_3$], 9.68 (s, CH_3), CH_2 not observed. $^{27}Al\{^1H\}$ NMR: δ 181.87 (br s).

Preparation of $Et_2(Cl)Al{\cdot}As(SiMe_3)_3$ (2). (a) Reaction of Et_2AlCl with $As(SiMe_3)_3$ (1:1 Mole Ratio). Et_2AlCl (0.2058 g, 1.670 mmol) in 25 mL of pentane was added to $As(SiMe_3)_3$ (0.492 g, 1.67 mmol) in 25 mL of pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was noted upon mixing. Following stirring at room temperature for 3 days, volatiles were removed in vacuo, leaving an off-white solid that was recrystallized from pentane at −15 °C to give 2 (0.684 g, 98.7% yield), mp 138 °C. No Me_3SiCl was eliminated over the course of the reaction. Anal. Calcd (found) for $C_{13}H_{37}AlAsClSi_3$: C, 37.62 (37.37); H, 8.99 (8.89); Cl, 8.54 (8.12). ^1H NMR: δ 0.28 [s, $Si(CH_3)_3$, 27 H], 0.46 (q, CH_2, 4 H), 1.52 (t, CH_3, 6 H). $^{13}C\{^1H\}$ NMR: δ 3.09 [s, $Si(CH_3)_3$], 9.77 (s, CH_3), CH_2 not observed. $^{27}Al\{^1H\}$ NMR: δ 165.32 (br s).

Table I. Crystallographic Data[a] for $[Et_2AlAs(SiMe_3)_2]_2$ (1)

molecular formula	$C_{20}H_{56}Al_2As_2Si_4$
fw	612.82
cryst system	monoclinic
space group	$C2/c$ (C_{2h}^6)-No. 15
a, Å	18.214 (2)
b, Å	9.542 (1)
c, Å	20.453 (2)
β, deg	99.89 (1)
no. of orientation refls; θ range, deg	25; 40–45
V, Å^3	3502 (1)
Z	4
D_{calcd}, g cm^{-3}	1.162
μ(Cu Kα), cm^{-1} (radiation λ = 1.5418 Å)	42.5
temp, °C	23
cryst dimens, mm	0.15 × 0.25 × 0.32
T_{max}:T_{min}	1.00:0.65
scan type	ω–2θ
scan width, deg	0.70 + 0.14 tan θ
θ_{max}, deg	75
intensity control refls; variation; repeat time, h	312, 222, 13$\bar{1}$, 22$\bar{4}$; <2%; 2
tot. no. of refls (+h,+k,±l) recorded	3705
no. of nonequiv refls recorded	3118
R_{merge}(on I)	0.023
no. of refls retained [$I > 3.0\sigma(I)$]	1968
no. of params refined	128
extinction corr	3.7 (1) × 10^{-6}
R (R_w)[b]	0.039 (0.053)
goodness-of-fit[c]	1.11
max shift/esd in final least-squares cycle	0.02
final $\Delta\rho$, e/Å^3	0.32, −0.58

[a] An Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator was used for all measurements. Crystallographic calculations were performed on PDP11/4 and MicroVAX computer by use of the Enraf-Nonius Structure Determination Package (SDP). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$; $\sum\omega\Delta^2$ [$\omega = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. [c] Goodness-of-fit $[\sum\omega\Delta^2/(N_{observns} - N_{params})]^{1/2}$.

(b) Reaction of Et_2AlCl with $As(SiMe_3)_3$ (2:1 Mole Ratio). Et_2AlCl (0.3934 g, 3.20 mmol) in 20 mL of pentane was added to $As(SiMe_3)_3$ (0.470 g, 1.60 mmol) in 30 mL of pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was seen upon addition. Following stirring for 3 days at room temperature, volatiles were removed in vacuo to leave an off-white solid which was recrystallized from pentane at −15 °C to give clear crystals (0.653 g, 98.3% yield); melting point and NMR spectra (^1H and $^{13}C\{^1H\}$) match those of an authentic sample of 2; vide supra. No Me_3SiCl was eliminated over the course of the reaction.

Intramolecular Dehalosilylation of 2 To Form 1. An NMR tube sample of 2 in benzene-d_6 was heated to 87 °C in an oil bath for 4 days. ^1H NMR spectra taken over this time showed peaks consistent with an authentic sample of 1 and one that may be attributed to Me_3SiCl at δ 0.165, indicating that internal dehalosilylation occurred.

Attempted Conversion of 1 to $Et_2\overline{AlAs(SiMe_3)_2Al(Et)_2Cl}$. Et_2AlCl (0.0376 g, 0.312 mmol) in 20 mL of pentane was added to 1 (0.0956 g, 0.156 mmol) in a one-necked, round-bottomed flask fitted with a Teflon valve and equipped with a magnetic stir bar. Following stirring for 2 days at room temperature, volatiles were removed in vacuo to leave an off white semisolid that was recrystallized from pentane at −15 °C; melting point and NMR

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[3] Purdy, A. P.; Wells, R. L.; McPhail, A. T.; Pitt, C. G. *Organometallics* **1987**, *6*, 2099.

[4] Holley, W. K.; Pasterczyk, J. W.; Pitt, C. G.; Wells, R. L. *Heteroatom Chem.* **1990**, *1*, 475.

[5] Wells, R. L.; Jones, L. J.; McPhail, A. T.; Alvanipour, A. *Organometallics* **1991**, *10*, 2345.

[6] Wells, R. L.; Purdy, A. P.; Higa, K. T.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* **1987**, *325*, C7.

[7] Wells, R. L.; Holley, W. K.; Shafieezad, S.; McPhail, A. T.; Pitt, C. G. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1989**, *41*, 15.

[8] Becker, G.; Gutekunst, G.; Wessely, H. J., *Z. Anorg. Allg. Chem.* **1980**, *462*, 113.

spectra (^{1}H and ^{13}C{^{1}H}) matched those of an authentic sample of 1, vide supra, indicating no reaction had occurred.

X-ray Crystal Structure Analysis of 1. Crystallographic data are summarized in Table I. Intensity data were corrected for the usual Lorentz and polarization effects. An empirical absorption correction, based on the ϕ dependency of the intensities of several reflections with ψ ca. 90°, was also applied. The crystal structure was solved by the heavy-atom approach. The systematically absent reflections, hkl when $h + k \neq 2n$ and $h0l$ when $l \neq 2n$, are compatible with two space groups, viz. Cc and $C2/c$. With only four formula units in the latter, dimeric molecules must either lie on a crystallographic center of symmetry or C_2 symmetry axis. Approximate coordinates for the As atoms, derived from a Patterson map, were related by a center of symmetry, and thus all further calculations were performed using equivalent positions appropriate to the centrosymmetric space group $C2/c$. The remaining non-hydrogen atoms were located in a series of weighted F_o and difference Fourier syntheses. Positional and thermal parameters of the non-hydrogen atoms (at first isotropic and then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. In the later iterations, hydrogen atoms were incorporated at their calculated positions (C–H = 1.05 Å) and an extinction correction was included as a variable. A final difference Fourier synthesis contained no unusual features. For all structure-factor calculations, neutral-atom scattering factors and their anomalous dispersion corrections were taken from ref 9.

Discussion

Dehalosilylation reactions between a group 13 halide and $As(SiMe_3)_3$ have been used to prepare dimeric and mixed-bridge species, $\overline{\mathrm{M{-}As{-}M{-}As}}$ and $\overline{\mathrm{M{-}As{-}M{-}Cl}}$, respectively, where M = Ga and In. It has been shown that, in the case of indium halides, dimers may be prepared if reaction is carried out in a 1:1 mole ratio and mixed bridges if a 2:1 stoichiometry of In to As reactants is employed.[5] However, no gallium–arsenic dimers have been isolated by utilizing such reactions. Instead, only mixed-bridge products have been obtained in reactions of either 1:1 or 2:1 stoichiometry of Ga to As reactants.[4,6,7] While this method has been shown to be of general utility in these systems, seminal investigations show it to fail as group 3 is ascended to aluminum. Thus, reaction of Et_2AlCl with $As(SiMe_3)_3$ at ambient temperature in either 1:1 or 2:1 stoichiometry (eq 1) gives only 2 with no evidence of silyl cleavage.

$$n\mathrm{Et_2AlCl} + \mathrm{As(SiMe_3)_3} \rightarrow \underset{\mathbf{2}}{\mathrm{Et_2(Cl)Al{\cdot}As(SiMe_3)_3}} + (n-1)\mathrm{Et_2AlCl} \quad (1)$$

$$n = 1,2$$

This behavior may be understood by consideration of the relative strengths of the group 13–Cl bonds. They are 420.7, 354.0, and 328.0 kJ mol^{-1} for Al, Ga, and In, respectively.[10] Since this bond is much stronger in the case of aluminum, its cleavage may be energetically unfavored, and hence, dehalosilylation is not observed. Instead, simple adducts are formed. To date, reaction conditions have not been varied to elucidate the effect of temperature upon such reactions. Such steps may provide a driving force that would enable dehalosilylation to occur.

Table II. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}, Å^2
As	0.18753 (3)	0.25453 (6)	−0.07961 (2)	4.06 (1)
Al	0.18075 (7)	0.3337 (2)	0.04040 (7)	4.25 (3)
Si(1)	0.10419 (8)	0.0731 (2)	−0.11613 (7)	5.27 (3)
Si(2)	0.17122 (9)	0.4338 (2)	−0.15669 (7)	5.68 (3)
C(1)	0.1045 (3)	0.2321 (6)	0.0788 (3)	5.7 (1)
C(2)	0.1042 (4)	0.2663 (7)	0.1520 (3)	7.5 (2)
C(3)	0.1774 (3)	0.5409 (6)	0.0486 (3)	6.7 (1)
C(4)	0.1042 (4)	0.6022 (8)	0.0471 (5)	11.8 (2)
C(11)	0.1094 (4)	−0.0631 (7)	−0.0520 (3)	7.8 (2)
C(12)	0.0072 (3)	0.1409 (8)	−0.1347 (4)	9.4 (2)
C(13)	0.1301 (4)	−0.0092 (8)	−0.1915 (3)	8.2 (2)
C(21)	0.0790 (4)	0.5213 (9)	−0.1594 (4)	10.0 (2)
C(22)	0.1754 (4)	0.3628 (9)	−0.2401 (3)	8.3 (2)
C(23)	0.2467 (4)	0.5662 (7)	−0.1334 (4)	8.8 (2)

While crystals of 2 suitable for single-crystal X-ray analysis have not been obtained, other data support the postulation of its structure as an adduct. Its ^{1}H, ^{13}C{^{1}H}, and ^{27}Al{^{1}H} NMR spectra suggest such a formulation in that the ^{1}H integration and splitting patterns are compliant, the ^{13}C{^{1}H} spectrum intensities are appropriate for those peaks observed, and only one type of aluminum is present as evidenced by a single peak in the ^{27}Al{^{1}H} spectrum. This, coupled with a partial elemental analysis (C, H, Cl), and the fact that no Me_3SiCl was found in reaction volatiles and that yield was nearly quantitative indicates that the structure of the product is correctly stated as 2.

It was previously shown by us that the adduct $Cl_3Al{\cdot}As(SiMe_3)_3$ undergoes intramolecular dehalosilylation to give AlAs when heated neat, under vacuum, in a cool flame.[11] With this in mind, attempted internal dehalosilylation of 2 was undertaken. Here, however, it was achieved at a much lower temperature. An NMR tube sample of 2 in benzene-d_6 was heated at 87 °C for 4 days. ^{1}H NMR spectra taken as early as 1 day after heating showed peaks that may be attributed to compound 1 and Me_3SiCl. Thus, dehalosilylation may be brought about under very mild conditions in the case of 2 (eq 2).

$$\underset{\mathbf{2}}{2\mathrm{Et_2(Cl)Al{\cdot}As(SiMe_3)_3}} \rightarrow \underset{\mathbf{1}}{[\mathrm{Et_2AlAs(SiMe_3)_2}]_2} + 2\mathrm{Me_3SiCl} \quad (2)$$

Compound 1 was prepared initially in relatively high yield (65%) by employing a coupling reaction between $LiAs(SiMe_3)_2$ and Et_2AlCl at −78 °C (eq 3). When the reaction was carried out at room temperature, product was obtained in very low yield with an uncharacterized viscous, orange liquid as the predominant product. It is noteworthy that, prior to this work, only four other arsinoalanes had ever been reported.[12-15] Three of them are dimers,[12,14,15] but only one was fully characterized by single-crystal X-ray analysis.[15]

$$2\mathrm{Et_2AlCl} + 2\mathrm{LiAs(SiMe_3)_2} \rightarrow \underset{\mathbf{1}}{[\mathrm{Et_2AlAs(SiMe_3)_2}]_2} + 2\mathrm{LiCl} \quad (3)$$

The conversion of sundry group 13–As dimers to mixed-bridge compounds by treatment with 2 mol equiv of a dialkyl group 13 halide has been shown to be applicable to such Ga- and In-containing species.[5,16,17] However, it

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[9] *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

[10] Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row Publishers: New York, 1983.

[11] Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 45.

[12] Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233.

[13] Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241.

[14] Arif, A. M.; Benac, B. L.; Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *New J. Chem.* **1988**, *12*, 253.

[15] Heaton, D. E.; Jones, R. A.; Kidd, K. B.; Cowley, A. H.; Nunn, C. M. *Polyhedron* **1988**, *7*, 1901.

[16] Holley, W. K.; Wells, R. L.; Shafieezad, S.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* **1990**, *381*, 15.

[17] Wells, R. L.; Pasterczyk, J. W.; McPhail, A. T.; Johansen, J. D.; Alvanipour, A. *J. Organomet. Chem.* **1991**, *407*, 17.

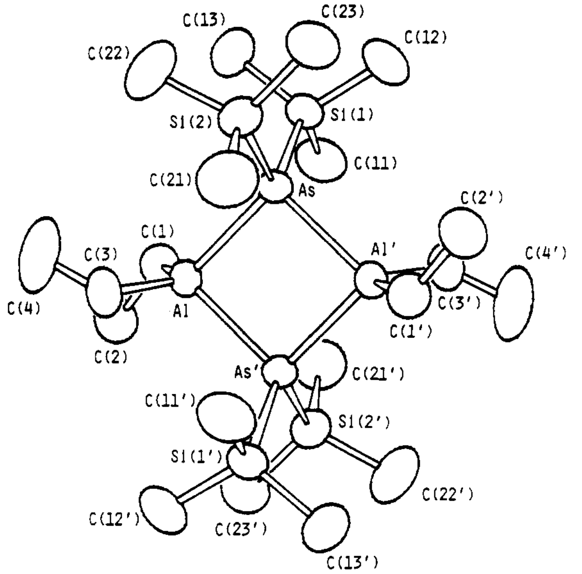

Figure 1. ORTEP diagram (40% probability ellipsoids) showing the solid-state conformation and atom-numbering scheme of $[Et_2AlAs(SiMe_3)_2]_2$ (1). Primed atoms are related to unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) for 1 with Estimated Standard Deviations in Parentheses

	Bond Lengths		
As–Al	2.539 (2)	As–Si(1)	2.351 (2)
As–Si(2)	2.347 (2)	As–Al′	2.531 (1)
Al–C(1)	1.965 (6)	Al–C(3)	1.986 (6)
	Bond Angles		
Al–As–Si(1)	114.10 (6)	Al–As–Si(2)	114.79 (6)
Al–As–Al′	91.01 (5)	Si(1)–As–Si(2)	107.59 (6)
Si(1)–As–Al′	112.30 (6)	Si(2)–As–Al′	116.60 (6)
As–Al–C(1)	112.5 (2)	As–Al–C(3)	112.5 (2)
As–Al–As′	88.99 (5)	C(1)–Al–C(3)	115.0 (3)
C(1)–Al–As′	114.7 (2)	C(3)–Al–As′	110.3 (2)

was found that this methodology was not successful for 1. Upon treatment with 2 mol equiv of Et_2AlCl, no reaction was observed, as evidenced by ^1H and ^{13}C NMR spectra. This suggests that perhaps the dimer does not undergo dissociation in solution, thus not allowing for the monomeric unit to react with the aluminum halide.

Crystals of 1 suitable for X-ray analysis were grown from pentane. Crystallographic data are reported in Table I. An ORTEP diagram showing the atom-numbering scheme is presented in Figure 1. Table II lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters, while selected bond lengths and angles are given in Table III.

Compound 1 crystallizes in the monoclinic space group *C*2/*c* with the four discrete dimeric molecules in the unit cell lying on crystallographic centers of symmetry, and thus, the $\overline{\text{Al–As–Al–As}}$ ring is constrained to be exactly planar as is the case for the only other previously characterized aluminum–arsenic dimer, $[Et_2AlAs(t\text{-}Bu)_2]_2$ (3).[15] The mean Al–As distance of 2.535 Å in 1 is slightly shorter than that of 2.567 Å in 3. The mean of the Al–C(1) [1.965 (6) Å] and Al–C(3) [1.986 (6) Å] bond distances at 1.976 Å in 1 is also slightly less than the corresponding mean of 1.992 Å in 3. The geometry about the Al and As atoms in 1 is distorted tetrahedral with the endocyclic angle subtended at As [Al–As–Al′ = 91.01 (5)°] being slightly larger than that at Al [As–Al–As′ = 88.99 (5)°]; the difference between the Al–As–Al′ and As–Al–As′ angles in 3 [94.54 (4)° vs 85.64 (4)°] is much more pronounced. The Si–As–Si and C–Al–C angles at 107.59 (6) and 115.0 (3)° in 1 deviate from tetrahedral in the same sense as do the C–As–C and C–Al–C angles, 108.9 (3) and 111.5 (3)°, respectively, in 3.

Compound 1 is of particular interest because it may be useful as a single-source precursor for the facile formation of AlAs. There are several ways in which this molecule may be envisaged as being utilized for such purposes. The ethyl groups provide for the possibility of β-hydrogen transfer with concurrent evolution of ethene and subsequent elimination of trimethylsilane to give AlAs. A second possibility is alcoholysis. Douglas and Theopold showed that a Ga–As dimer, when treated with methanol, underwent internal elimination to give GaAs.[18] The third way in which AlAs might be obtained is to take advantage of the fact that covalent halides are known to cleave the silicon–arsenic bond.[19] Thus, treatment of 1 with HCl should afford Me_3SiCl and an AsH_2-containing species, which should readily eliminate ethane, or ethene and dihydrogen, to yield AlAs.

Conclusions

The work presented herein shows the viability of lithium chloride elimination reactions in the preparation of aluminum–arsenic dimers. While this methodology was successfully applied, dehalosilylation reactions were ineffective in that neither an aluminum–arsenic–chlorine mixed-bridge compound nor a dimer could be prepared directly by this route; albeit, evidence was obtained which indicated an adduct underwent dehalosilylation on heating to give a dimer. This study will be used as a starting point for further investigation of aluminum–arsenic systems. Through variation of temperature, substituents on aluminum, and other reaction conditions, a better understanding of the limitations and applications of lithium halide elimination and dehalosilylation reactions to the preparation of single-source precursors to AlAs may be developed.

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Supplementary Material Available: For 1 tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, complete interatomic distances and angles, including torsion angles, and equations of least-squares planes through groups of atoms (5 pages); a listing of observed and calculated structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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(18) Douglas, T.; Theopold, K. H. *Inorg. Chem.* **1991**, *30*, 596.
(19) Abel, E. W.; Illingworth, S. M. *J. Chem. Soc. A* **1969**, 1094.