Organometallics **1993,** *12,* 17-18

Monomeric Base-Stabilized Phosphino- and Arsinoalanes

David A. Atwood, Leopoldo Contreras, Alan H. Cowley,* Richard A. Jones,* and
Miguel A. Mardones

*Department of Chemistry and Biochemistry, The University of Texas at Austin,
Austin, Texas 78712*

Received June 26, 1992

Summary: The first base-stabilized phosphino- and arsinoalane monomers, $H_2AlEMes_2{\cdot}NMe_3$ (Mes = mesityl; 1, E = P; 2, E = As) have been prepared. Thermolysis at 95 °C converts 1 to the trimer $[H_2AlPMes_2]_3$ (3); further heating at 125 °C results in the formation of Mes_2PH and aluminum metal.

In comparison with the aminoboranes $(R_2NBR'_2)_n$ relatively little information is available regarding the chemistry of the heavier group 13/15 analogues such as the phosphinoalanes $(R_2PAlR'_2)_n$[1] and arsinoalanes $(R_2AsAlR'_2)_n$.[2] The few compounds that are known exist as dimers ($n = 2$) or trimers ($n = 3$) depending on the steric demands of the substituents. In part, our interest in such compounds stems from the possibility that, like the analogous arsinogallanes,[3] they might serve as single-source precursors to group 13/15 electronic materials. However, one of the drawbacks with the currently available single-source precursors is low volatility. Two obvious approaches to enhanced volatility are (i) to decrease the degree of oligomerization and (ii) to use less bulky substituents. Herein we report the isolation of the base-stabilized monomers $H_2AlEMes_2{\cdot}NMe_3$ (Mes = mesityl; **1**, E = P; **2**, E = As). The structure of the phosphorus compound **1** has been determined by X-ray analysis. To our knowledge, this represents the first structural information on a monomeric base-stabilized phosphinoalane. Another noteworthy feature is that **1** undergoes thermal decomposition to afford metallic aluminum rather than aluminum phosphide. This represents an unprecedented mode of thermolysis for compounds of this general type.

Monomers **1** and **2** were prepared in yields of 75–80% via the metathetical reaction of $H_2AlCl{\cdot}NMe_3$ with $LiE(Mes)_2$ in Et_2O solution at low temperature.[4] Both compounds are colorless, crystalline solids. In the case of **2**, the proposed molecular formula was established by the presence of a CI–MS peak at m/z 402,[7] which corresponds to $M + H^+$. For **1**, the highest m/z peak was detected at 299, thus indicating a loss of Me_3N. However, the presence of coordinated Me_3N in solutions of both **1** and **2** was demonstrated by ^1H and ^{13}C NMR spectroscopy.[7] There was no evidence for Me_3N dissociation at ambient temperature. Equal abundances of mesityl and hydride ligands were also clear from ^1H and ^{13}C NMR spectroscopic data. Only crystals of **1** proved suitable for X-ray analysis.[8] The solid state of **1** comprises individual molecules (Figure 1), and there are no short intermolecular contacts. A donor molecule of Me_3N is attached to the aluminum atom of each $H_2AlPMes_2$ unit, and the Al–N bond distance in **1** (2.009 (8) Å) is slightly shorter than that in $H_3Al{\cdot}NMe_3$ (2.063 (8) Å).[9] The P–Al bond order in **1** is unity as indicated by the fact that this bond distance (2.409 (3) Å) is only slightly shorter than those observed in Al_2P_2 dimers (range 2.433 (4)–2.475 (1) Å)[1] and virtually identical to

---

(1) As examples, see the following references and prior literature cited therein: (a) Janik, J. F.; Duesler, E. N.; McNamara, W. F.; Westerhausen, M.; Paine, R. T. *Organometallics* **1989**, *8*, 506. (b) Beachley, O. T.; Tessier-Youngs, C. *Organometallics* **1983**, *2*, 796. (c) Fritz, G.; Trenczek, G. *Z. Anorg. Chem.* **1964**, *331*, 206. (d) Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H.; Hrncir, D. C. *J. Organomet. Chem.* **1990**, *385*, 23.

(2) (a) Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233. (b) Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241. (c) Heaton, D. E.; Jones, R. A.; Kidd, K. B.; Cowley, A. H.; Nunn, C. M. *Polyhedron* **1988**, *7*, 1901. (d) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *New J. Chem.* **1988**, *12*, 553. (e) Wells, R. L.; McPhail, A. T.; Speer, T. M. *Organometallics* **1992**, *11*, 960.

(3) For reviews see: (a) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* 1988, *28*, 1208. (b) Wells, R. L. *Coord. Chem. Rev.* **1992**, *112*, 273.

(4) **1**: A solution of Mes_2PH[5] (540 mg, 2.0 mmol) in Et_2O (45 mL) was treated with *n*-BuLi (1.25 mL, 1.6 M, 2.0 mmol) at −78 °C. The resulting yellow solution was allowed to warm to 25 °C, and stirring was continued for an additional 1 h at this temperature. After being cooled to −78 °C, the $LiP(Mes)_2$ solution was added dropwise to a solution of $H_2AlCl{\cdot}NMe_3$[6] (250 mg, 2.0 mmol) in Et_2O (30 mL) at −78 °C. The solvent and volatiles were removed under reduced pressure, and the colorless residue was extracted with hexane (50 mL). After filtration and concentration of the filtrate, colorless crystals of **1** formed in 75% yield (mp 122 °C dec). **2**: The procedure was similar to that described for **1** except that toluene was used for extraction and recrystallization. Yield: 80%. Mp: 115–118 °C dec. **3**: A mixture of $LiAlH_4$ (115 mg, 3.0 mmol) and $AlCl_3$ (400 mg, 3.0 mmol) in Et_2O (50 mL) was allowed to warm from −78 to 25 °C, and stirring was continued for an additional 48 h at the latter temperature. The white, cloudy suspension was cooled to −78 °C and treated with 3.0 mmol of $LiP(Mes)_2$ (see above). After the solution was warmed to 25 °C, the solvent and volatiles were removed under reduced pressure. The resulting colorless residue was extracted with toluene (30 mL). After filtration, attempts were made to grow crystals of **3** by storage of concentrated solutions at −40 °C. These attempts were not successful, and **3** was isolated as a colorless powder (mp 80 °C dec) in 50% yield by complete removal of the solvent.

(5) Schmidbaur, H.; Schnatterer, S. *Chem. Ber.* **1983**, *116*, 1947. For Mes_2AsH, see: Pitt, C. G.; Purdy, A. P.; Higa, K. T.; Wells, R. L. *Organometallics* **1986**, *5*, 1266.

(6) Ruff, J. K. *Inorg. Synth.* **1967**, *9*, 30.

(7) CI–MS (CH_4): **1**, m/z 299 ($M + H^+ - Me_3N$); **2**, m/z 402 ($M + H^+$); **3**, m/z 596 (dimer$^+$). ^1H NMR (300.15 MHz, C_6D_6, 295 K): **1**, δ 1.76 (9H, s, NMe_3), 2.12 (6H, s, 4-Me), 2.63 (12H, s, 2,6-Me), 6.80 (4H, s, 3,5-H ring), 4.40 (2H, vbr, AlH_2); **2**, δ = 1.72 (9H, s, NMe_3), 2.12 (6H, s, 4-Me), 2.60 (12H, s, 2,6-Me), 6.78 (4H, s, 3,5-H ring), 4.55 (2H, vbr, AlH_2); **3**, δ = 1.97 (6H, s, 4-Me), 2.51 (12H, s, 2,6-Me), 6.60 (4H, s, 3,5-H ring), 5.20 (2H, vbr, AlH_2). $^{13}C\{^1H\}$ NMR (75.48 MHz, 295K, C_6D_6, TMD external standard): **1**, δ = 20.9 (s, 4-Me), 24.9 (d, J = 10.3 Hz, 2,6-Me), 47.5 (s, NMe_3), 129.4 (d, J = 2.4 Hz, 3,5-C ring), 135.5 (s, 4-C ring), 136.1 (d, J = 17.9 Hz, 1-C ring), 142.9 (d, J = 10.3 Hz, 2,6-C ring); **2**, δ 20.9 (s, 4-Me), 25.8 (s, 2,6-Me), 47.7 (s, NMe_3), 129.1 (s, 3,5-C ring), 135.6 (s, 4-C ring), 138.1 (s, 1-C ring), 142.9 (s, 2,6-C ring); **3**, δ 20.7 (s, 4-Me), 24.9 (t, J = 3.4 Hz, 2,6-Me), 130.4 (d, J = 3.4 Hz, 3,5-C ring), 139.2 (s, 4-C ring), 139.5 (m, 1-C ring), 144.3 (t, J = 4.0 Hz, 2,6-C ring). $^{31}P\{^1H\}$ NMR (121.5 MHz, 295 K, C_6D_6, 85% H_3PO_4 external standard): **1**, δ = −97.3 (s, br); **3**, δ = −84.9 (s, br). IR (Nujol mulls, NaCl, ν_{Al-H}, cm^{-1}): **1**, 1810 vs, 1785 vs; **2**, 1800 sh, 1790 s; **3**, 1840 sh, 1825 vs. Mp: **1**, 95 °C dec; **2**, 115–118 °C dec; **3**, 100 °C dec. Anal. Calcd for **1**: C, 70.56; H, 9.31. Found: C, 70.08; H, 9.17. **2**: C, 62.84; H, 8.29. Found: C, 62.62; H, 8.27. Calcd for **3**: C, 72.47; H, 8.11. Found: C, 72.84; H, 7.72.

(8) **1**: monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$; $a = 17.180$ (5), $b = 8.318$ (2), $c = 16.643$ (6) Å; $\beta = 114.53$ (2)°; $V = 2163$ (20) Å^3; $\rho_{calcd} = 1.10$ g cm^{-3}; $2 < 2\theta < 50°$ (Mo Kα, $\lambda = 0.710\,69$ Å, $\mu = 1.66$ cm^{-1}); $T = 24$ °C; 1726 reflections with $I > 6.0\sigma(I)$ were used to solve (direct methods) and refine (full-matrix, least squares) the structure of **1**, $R = 0.0616$ and $R_w = 0.0657$.

(9) This is a gas-phase electron diffraction value: Almenningen, A.; Gundersen, G.; Haugen, T.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3928. The solid-state structure consists of a severely distorted dimer: Atwood, J. L.; Bennett, F. R.; Elms, F. M.; Jones, C.; Raston, C. L.; Robinson, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 8183.

0276-7333/93/2312-0017$04.00/0

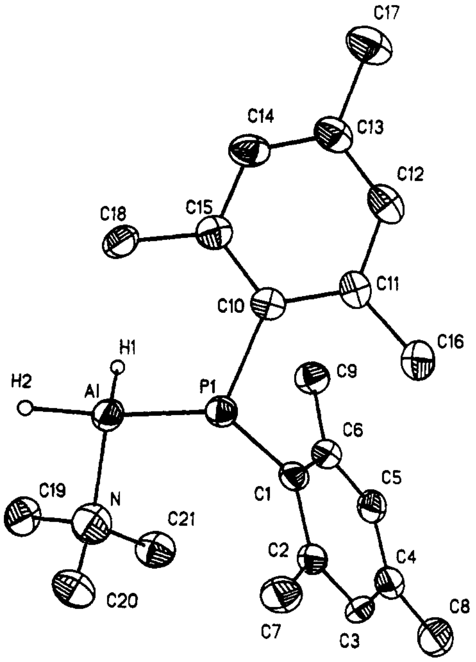

Figure 1. View of the crystal structure of $H_2AlPMes_2{\cdot}NMe_3$ (1). Important bond distances (Å) and angles (deg) (standard deviations in parentheses) are as follows: Al–P = 2.409 (3), P–C1 = 1.856 (7), P–C10 = 1.862 (7), Al–N = 2.009 (8), Al–H1 = 1.598 (7), Al–H2 = 1.53 (7); Al–P–C1 = 100.3 (2), Al–P–C10 = 110.3 (3), C1–P–C10 = 106.6 (3), P–Al–N = 111.3 (2), N–Al–H1 = 101 (3), N–Al–H2 = 97 (3), P–Al–H1 = 118 (3), P–Al–H2 = 110 (3), H1–Al–H2 = 115 (4).

that observed in an aluminum–phosphorus cubane.[10] Such a view is supported by the observed pyramidality at phosphorus (sum of angles = 317.2°). Like monomeric phosphinoboranes,[11] phosphino- and arsinoalanes are, in principle, capable of multiple bonding. Clearly, however, in the case of 1 such bonding is thwarted by the strong donor action of Me_3N and consequent rehybridization at aluminum.

When solid 1 was heated under vacuum at 95 °C for 0.5 h, Me_3N was eliminated and a colorless, microcrystalline compound of empirical composition $H_2AlPMes_2$ (3) was formed[7] together with Mes_2PH. Compound 3 can also be isolated (50% yield) from the reaction of H_2AlCl with $LiP(Mes)_2$.[4] The degree of oligomerization of 3 was not clear from mass spectroscopic data since the highest *m/z* peak that was detectable in CI or EI experiments corresponds to the dimer.[7]

Peralkylated derivatives of empirical composition $R_2MER'_2$ undergo thermolysis via alkene/alkane elimination. As such, they represent attractive single-source precursors to group 13/15 semiconductor materials, ME. Interestingly, compound 1 (and preliminary 2) undergo thermolysis by a completely different pathway. As pointed out above, heating 1 at 95 °C causes initial loss of Me_3N. Further heating at 125 °C (toluene solution) results in the formation of Mes_2PH as the sole phosphorus-containing product.

$$\underset{1}{H_2AlPMes_2{\cdot}NMe_3} \rightarrow {}^1/_3\underset{3}{(H_2AlPMes_2)_3} \rightarrow Al + Mes_2PH + {}^1/_2H_2$$

There is considerable current interest in new aluminum precursors for the microelectronics industry. To date, most of the emphasis has been placed on adducts of the type $base{\cdot}AlH_3$.[12] To our knowledge σ-bonded derivatives with Al–H functionalities have not been explored as potential aluminum sources. We have succeeded in growing films of aluminum from 3 on Si[100] substrates in a horizontal cold-wall OMCVD reactor. The temperatures of the saturator and deposition zones were 70 and 300 °C, respectively, and the reactor pressure was 1×10^{-3} Torr. The films were characterized by X-ray photoelectron spectroscopy (XPS) after etching with ionized argon. The XPS analysis also indicated traces (350 ppm) of phosphorus.

Acknowledgment. We are grateful to the National Science Foundation (Grants CHE-9007166, CHE-9108228), the Science and Technology Center Program (Grant CHE-08920120), the Robert A. Welch Foundation, and the Army Research Office for generous financial support.

Supplementary Material Available: Tables of positional and thermal parameters and selected bond distances, bond angles, and torsion angles and a figure showing the unit cell of 1 (8 pages). Ordering information is given on any current masthead page.

OM9203845

---

[10] Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G.; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1409.

[11] (a) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449. (b) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426.

[12] (a) Gladfelter, W. L.; Boyd, D. C.; Jensen, K. F. *Chem. Mater.* **1989**, *1*, 339. (b) Wee, A. T. S.; Murrell, A. J.; Singh, N. K.; O'Hare, D.; Ford, J. S. *J. Chem. Soc., Chem. Commun.* **1990**, 11.