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<td><strong>Abstract:</strong> Reactions between AlX3 (X = Cl, Br) and P(SiMe3)3 afforded the adducts X3Al?P(SiMe3)3. Et2AlP(SiMe3)2Al(EO)2As(SiMe3)2 was obtained from the equilibration of [Et2AlP(SiMe3)2][EO] and [Et2AlAs(SiMe3)2]. Reactions of Me3Al with Ph2AsH and Ph(Me3SiCH2)2AsH afforded [Me2AlAsPh2]3+(C7H8)2 and [Me2AlAs(Si2H2SiMe3)2]Ph3. Reactions of Ph3Al with E(SiMe3)3 (E = P or As) afforded Ph3Al•E(SiMe3)3 [E = P, As, respectively] and Ph2AlCl with E(SiMe3)3 (E = P, As) yielded Ph2(Cl)Al•E(SiMe3)3 [E = P, As]. Ph(Cl)2Al•P(SiMe3)3 was obtained from PhAlCl2 and P(SiMe3)3. and reactions of Et3Ga and (Me3SiCH2)2In with Sb(SiMe3)3 yielded Et3GaSb(SiMe3)3, and (Me3SiCH2)3InSb(SiMe3)3, respectively. Reaction of Me3CCH22GaCl or (Me3SiCH2)2InCl with Sb(SiMe3)3 afforded [(Me3CCH2)2GaSb(SiMe3)2]2 and [(Me3SiCH2)2InSb(SiMe3)2]2, respectively. Reaction of GaCl3 with Sb(SiMe3)3 affords an intermediate material which, upon thermolysis, yields nanocrystalline GaSb with an approximate average particle size of 12 nm. Reaction of (Me3SiCH2)3Al with E(SiMe3)3 (E = P, As) gave (Me3SiCH2)2AlP(SiMe3)3 and (Me3Sch2)3AlAs(SiMe3)3), and reaction of (Me3CCH2)3Al with E(SiMe3)3 (E = P, As) gave (Me3CCH2)2AlP(Me3SiCH2)3 and (Me3CCH2)3AlAs(SiMe3)3. (Me3SiCH2)2(Br)P(SiMe3)3 was obtained from the reaction of (Me3SiCH2)2AlBr with P(SiMe3)3. [(Me3SiCH2)2(Br)AlP(SiMe3)3]2 and [(Me3SiCH2)2AlAs(SiMe3)2]2 were isolated as rearrangement products of the 1:1 lithium halide elimination reactions of (Me3SiCH2)3AlBr with Li(SiMe3)2 (E = P, As). This metalated system also led to the isolation of [(Me3SiCH2)2AlP(SiMe3)3]2 and [(Me3SiCH2)2AlAs(SiMe3)2]2.</td>
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<td><strong>Subject Terms:</strong> aluminum, gallium, indium, phosphorus, arsenic, antimony, synthesis, structure, adduct, four-membered ring, six-membered ring, nanocrystalline</td>
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SYNTHESIS AND STUDIES OF ALUMINUM-NITROGEN, -PHOSPHORUS AND ARSENIC CYCLES AND CLUSTERS

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04 November 1996
SYNTHESIS AND STUDIES OF
ALUMINUM-NITROGEN, -PHOSPHORUS AND ARSENIC
CYCLES AND CLUSTERS

1.0 Summary

The attempted dehalosilylation reactions between AlX₃ (X = Cl, Br) and P(SiMe₃)₃ in toluene in 1:1 mole ratios afforded only the adducts Cl₃Al·P(SiMe₃)₃ (1) and Br₃Al·P(SiMe₃)₃ (2), respectively. Compounds 1 and 2 were characterized by ¹H, ¹³C, ²⁷Al, and ³¹P solution NMR spectroscopy, as well as partial elemental analysis. In addition, the solid state structures of the toluene solvates of 1 and 2 were determined by single-crystal X-ray analysis. Characterization revealed that the solid solvated adducts 1 and 2 are isostructural and their crystals are isomorphous. In each compound, the Al and the P atoms reside in tetrahedral environments, with each X₃Al·P(SiMe₃)₃ (X = Cl, Br) molecule associated with one interstitial toluene molecule in the crystals. These adducts are noteworthy in that they possess extremely short, essentially equal Al-P bond lengths [for 1: Al—P = 2.392(4) Å, and for 2: Al—P = 2.391(6) Å], which are the shortest found to date in aluminum-phosphorus molecular species.

The aluminum mixed-nicogen compound Et₂AlP(SiMe₃)₂Al(ET)₂As(SiMe₃)₂ (3) is the first structurally-characterized compound to contain a four-membered ring with two aluminum centers bridged by two different heavier group 15 atoms. Compound 3 was synthesized by the equilibration of [Et₂AlP(SiMe₃)₂]₂ (4) and [Et₂AlAs(SiMe₃)₂]₂ (5) in a 1:1 mole ratio under ultrasonic conditions. Low-temperature X-ray crystallographic analysis revealed that crystals of 3 belong to the monoclinic space group C2/c (C₂h⁶), with unit cell dimensions of a = 17.960(4), b = 9.328(1), c = 20.194(5) Å, and β = 100.33(2)° for Z = 4, and isomorphous with those of 4 and 5. The electron ionization (20 eV) mass spectrum of 3 shows a fragmentation pattern consistent with this compound and no peaks above m/z 400 consistent with either 4 or 5.

The reactions of trimethylaluminum with diphenylarsine, Ph₂AsH, and phenyl(trimethylsilylmethyl)arsine, Ph(Me₃SiCH₂)₂AsH, in 1:1 mole ratios afford the trimeric compounds [Me₂AlAsPh₂]₃(C₇H₈)₂ (6) and [Me₂AlAs(CH₂SiMe₃)Ph₃] (7), respectively. Compounds 6 and 7 are the first Al-As six-membered ring compounds to be structurally characterized by single-crystal X-ray crystallography, as well as ¹H and ¹³C solution NMR spectroscopy. X-ray crystallographic analysis revealed that trimer 6 is a toulclimate which crystallizes in the monoclinic space group P 2₁/n, with a = 14.549(6) Å, b = 22.838(7) Å, c = 16.891(4) Å, and β = 105.12(5)° for Z = 4. Trimer 7 crystallizes in the triclinic space group P 2₁, and has two unique molecules in a unit cell with dimensions of a = 15.619(7) Å, b = 17.487(6) Å, c = 19.863(6) Å, α = 94.86(3)°, β = 101.41(3)°, and γ = 113.34(3)° for Z = 4. The six-membered Al-As rings in both 6 and 7 occupy chair conformations, furnishing both trimers with structural characteristics similar to cyclohexane. The Al and As centers of both 6 and 7 reside in pseudotetrahedral environments, with the Al—As bond lengths ranging from 2.512(3) Å to 2.542(3) Å in 6, and from 2.504(5) Å to 2.526(5) Å in 7.

The independent reactions of Ph₃Al with E(SiMe₃)₃ (E = P or As) in 1:1 mole ratios afforded the adducts Ph₃Al·E(SiMe₃)₃ [E = P (8) and As (9), respectively]. The attempted dehalosilylation reactions between Ph₂AlCl and E(SiMe₃)₃ (E = P or As) in 1:1 mole ratios yielded only the adducts Ph₂(Cl)Al·E(SiMe₃)₃ [E = P (10) and As (11)]. The adduct Ph(Cl)₂Al·P(SiMe₃)₃ (12)
was isolated from the reaction of equimolar amounts of PhAlCl₂ and P(SiMe₃)₃. Compounds 8-12 were characterized by NMR spectroscopy and partial elemental analysis. In addition, the solid-state structures of 8-10 were determined by single-crystal X-ray analysis. Compound 8 crystallizes in the monoclinic space group P 2₁/n (C₂h), while 9 crystallizes in the triclinic space group P ̅1 (C₁̅), each with two discrete molecules per asymmetric unit. Crystals of compound 10 belong to the orthorhombic space group P 2₁2₁2₁ (D₂), and compounds 8-10 are the first structurally-characterized compounds to contain phenyl-substituted Al centres bonded to heavier pnictogen atoms.

The independent 1:1 reactions of Et₃Ga and (Me₅SiCH₂)₃In with Sb(SiMe₃)₃ yield the simple Lewis acid-base adducts Et₃Ga·Sb(SiMe₃)₃ (13) and (Me₅SiCH₂)₃In·Sb(SiMe₃)₃ (14), respectively. Reaction of (Me₅CCH₂)₂GaCl or (Me₅CCH₂)₂InCl with Sb(SiMe₃)₃ in a 1:1 mole ratio affords the dehalosilylation products [(Me₅CCH₂)₂GaSb(SiMe₃)₂]ₓ (15) and [(Me₅CCH₂)₂InSb(SiMe₃)₂]₂ (16), respectively. These new compounds were characterized by multinuclear solution NMR (¹H and ¹³C), partial elemental analysis and for 13, 14, and 16, single crystal X-ray analysis.

The 1:1 reaction of GaCl₃ with Sb(SiMe₃)₃ in pentane solution affords an intermediate material which, upon thermolysis, yields nanocrystalline GaSb (17) with an approximate average particle size of 12 nm. The product was characterized through powder X-ray diffraction, elemental analysis, and HRTEM.

Reaction of (Me₅SiCH₂)₃Al with E(SiMe₃)₃ (E = P, As) in a 1:1 mole ratio affords the Lewis acid-base adducts (Me₅SiCH₂)₃AlP(SiMe₃)₃ (18) and (Me₅SiCH₂)₃AlAs(SiMe₃)₃ (19). Similarly, the 1:1 mole ratio reaction of Np₃Al with E(SiMe₃)₃ (E = P, As) leads to the isolation of (Me₅CCH₂)₃AlP(SiMe₃)₃ (20) and (Me₅CCH₂)₃AlAs(SiMe₃)₃ (21). The adduct (Me₅SiCH₂)₂(AlBr)AlP(SiMe₃)₃ (22) was obtained from the 1:1 mole ratio reaction of (Me₅SiCH₂)₂AlBr with P(SiMe₃)₃. The dimers [Me₅SiCH₂(AlBr)AlP(SiMe₃)₂]₂ (23) and [Me₅SiCH₂(AlBr)AlAs(SiMe₃)₂]₂ (24) were isolated as rearrangement products of the 1:1 lithium halide elimination reactions of (Me₅SiCH₂)₂AlBr with LiE(SiMe₃)₂ (E = P, As). This metathetical system also led to the isolation of [(Me₅SiCH₂)₂AlP(SiMe₃)₂]₂ (25) and [(Me₅SiCH₂)₂AlAs(SiMe₃)₂]₂ (26). Various physical and spectroscopic data, including a multinuclear variable temperature NMR study of 23 and 24, were obtained for the above compounds, along with the X-ray crystal structures of 19-24 and 26.

2.0 Publications and Presentations at Meetings Describing Results Obtained

2.1 Publications


4. J. A. Laske Cooke, H. Rahbarnoohi, A. T. McPhail, R. L. Wells, and P. S. White, “Reactions of Phenylaluminum Compounds with E(SiMe₃)₃ (E = P or As): X-ray Crystal Structures of Ph₃Al•E(SiMe₃)₃ (E = P or As) and Ph₂(Cl)Al•P(SiMe₃)₃”, *Polyhedron* **1996**, *15*, 3033.


3.0 Presentations at Meetings


2.2 Students Supported by the Grant
