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Synthesis and Characterization of Unassociated Aluminum Monophosphides

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Monomeric main group 3–5 compounds of formula R_2MER_2' (M = B–Tl; E = N–Bi; R or R′ = alkyl or aryl group) have the potential for π-bonding between the pnictide lone pair and the empty p-orbital of the main group 3 element. For a long time, such bonding was confined to the B–N combination,[1] and its unequivocal establishment in the corresponding B–P[2] or B–As[3] species has occurred only within the last few years. Recent developments have indicated that weak π-bonding may also be possible in certain Ga–P compounds such as t-$Bu_2GaP(Mes^*)SiPh_3$[4a,b] or $MesP(GaTrip_2)_2$ (Mes, Trip, and Mes* = 2,4,6-$R_3C_6H_2$ where R = Me (Mes), i-Pr (Trip) and t-Bu (Mes*)).[4c] Yet, there has been no detailed information on molecular species that have bonding between three-coordinate aluminum and phosphino or arsino groups.[5] The first well-characterized examples of such compounds, the aluminum phosphides $Trip_2AlP(R)SiPh_3$ (R = Mes or 1-Ad), are now described.[6]

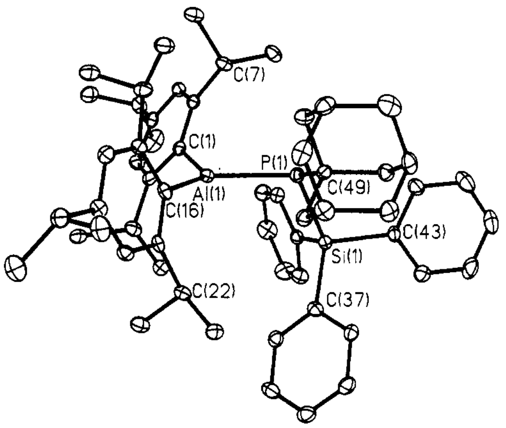

Figure 1. Thermal ellipsoidal plot of one of the molecules in the asymmetric unit of **2**. Selected bond distances (Å) and angles (deg), with corresponding parameters from the second molecule in braces, are as follows: Al(1)–P(1) = 2.342(2) {2.342(2)}, Al(1)–C(1) = 1.974(4) {1.985(4)}, Al(1)–C(16) = 1.988(4) (1.992(4)}, P(1)–Si(1) = 2.249(2), {2.245(2)}, P(1)–C(49) = 1.900(4) {1.894(4)}, C(1)–Al–C(16) = 125.3(2) {125.8(2)}, P(1)–Al(1)–C(1) = 123.27(14) {121.90(14)}, P(1)–Al(1)–C(16) = 110.53(13) {110.97)(13)}, Al(1)–P(1)–Si(1) = 111.70(6) {111.06(6)}, Al(1)–P(1)–C(49) = 106.36(14) {108.46(14)}, Si(1)–P(1)–C(49) = 112.17(14) {109.68(14)}.

The compounds $Trip_2AlP(R)SiPh_3$ (R = Mes, **1**; R = 1-Ad, **2**·0.5hexane) were prepared in moderate yield by the reaction of $Trip_2AlBr$[7] with $LiP(R)SiPh_3$.[8] Crystals of **2**·0.5 hexane were in found to be suitable for X-ray diffraction studies and the resultant structure is illustrated in Figure 1.[9] The structure consists of two well-separated, crystallographically independent, monomers of formula $Trip_2AlP(1\text{-}Ad)SiPh_3$, and a noninteractive hexane molecule per asymmetric unit. The structures of the two molecules are almost identical with the same Al–P bond length of 2.342(2) Å being observed in each. The aluminum centers have almost planar coordination with slight deviations of the aluminum atoms

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(4) (a) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1992**, *31*, 4038. (b) Petrie, M. A.; Power, P. P. *J. Chem. Soc. Dalton Trans.* **1993**, 1737. (c) Petrie, M. A.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1309. (d) A number of cyclic species involving bonding between three-coordinate gallium and phosphorus centers have been structurally characterized. These molecules are not thought to involve significant π-bonding, however. See the following references for further discussion: Atwood, D. A.; Cowley, A. H.; Jones, R. H.; Mardones, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 7050. Hope, H.; Pestana, D. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 691.

(5) (a) Zintl species of formula $[Al_2P_4]^{6-}$ that feature a four-membered Al_2P_2 ring (Al–P = 2.339(6) Å) with each aluminum also bound to a terminal phosphorus (Al–P = 2.251(5) Å) have been reported in the following reference: Somer, M.; Thiery, D.; Peters, K.; Walz, L.; Hartwig, M.; Popp, T.; von Schnering, H. G. *Z. Naturforsch.* **1991**, *46B*, 789. (b) Three recent reviews have surveyed the large amount of information available for associated aluminum phosphides and related compounds: Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. Wells, R. L. *Coord. Chem. Rev.* **1992**, *112*, 273. Taylor, M. J.; Brothers, P. J. In *Chemistry of Aluminum Gallium, Indium and Thallium*: Downs, A. J., Ed.; Blackie-Chapman and Hall: London, 1993; Chapter 3.

(6) The compound $[\{(Me_3Si)CH_2\}_2AlPPh_2]$ was reported to exist as a monomer–dimer equilibrium mixture in dilute benzene solution in the following reference: Beachley, O. T.; Tessier-Youngs, C. *Organometallics* **1983**, *2*, 796.

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(0.08 Å for Al(1) and 0.10 Å for Al(2)) from the C_2P coordination planes. The phosphorus centers have pyramidal geometry with $\sum°P$ of *ca.* 330° in both molecules. There are, however, torsion angles of 49.2° and 45.7° between the perpendiculars to the averaged aluminum and PCSi coordination planes when observed along the Al–P axis. The thermal ellipsoidal plot shows that the 1-Ad group almost eclipses one of the Trip groups in each molecule (C(16)Al(1)P(1)C(49) and C(59)Al(2)P(2)C(107) torsion angles = 15.3 and 10°). In addition, the P–Al–C angles on this side of the molecule are considerably (11–13°) wider than those on the opposite side. The bond lengths to the aluminum and phosphorus substituents are unremarkable and similar to those observed in other related compounds.

The main inferences to be drawn from the structure are the following: (a) The Al–P bond length is very close to that expected from the sum of the covalent radii[10] of aluminum and phosphorus when corrected for ionic effects,[11] indicating that the Al–P bond is, for the most part, a single one. (b) In harmony with this view, the torsion angles between the perpendiculars to the coordination planes at aluminum and phosphorus suggest little overlap between phosphorus lone pair and the empty aluminum p-orbital. (c) The 1-Ad substituent on phosphorus is located so as to minimize steric interference from the *o*-*i*-Pr groups of one of the Trip substituents, and approximately eclipses the aromatic ring of the C(16) or C(59) Trip groups in each molecule. This is, in part, necessitated by the fact that the torsion angles between the plane at the aluminum and Trip ring planes are, for steric reasons, high and in the range 61.1–70.3°. This view of the structure implies that alignment between the phosphorus lone pair and the aluminum p-orbital would not be favored sterically while phosphorus retains a pyramidal geometry. (d) The retention of the pyramidal geometry at phosphorus implies the presence of a significant inversion barrier at this center. This is in spite of the fact that phosphorus is bound to two electropositive substituents ($Trip_2Al$– and –$SiPh_3$), one of which ($Trip_2Al$–) is probably capable of delocalizing the phosphorus lone pair in the transition state of the inversion process.[12]

The structure of **2** may also be compared with those of *t*-$Bu_2GaP(R)SiPh_3$ (R = Trip[4b] or Mes*[4a]) or the base-stabilized compounds $H_2AlPMes_2{\cdot}NMe_3$[13] or *t*-$Bu_2AlP(Trip)SiPh_3{\cdot}Et_2O$.[4b] In contrast to the structure of **2**, the structures of the base free gallium species[4a,b] do show alignment between the lone pair on phosphorus and the p-orbital on gallium. In addition, the phosphorus center has flattened geometry, consistent with a weak π-interaction in the Ga–P bond.[4d] It may be that these Ga–P species are able to achieve the requisite alignment for a π-interaction owing to the different steric requirements of the *t*-Bu groups on gallium vis-à-vis the Trip substituents in **1** and **2**. On the other hand, it is possible that Ga–P π-bonding is more efficient than Al–P π-bonding owing to a better match in size and electronegativity for the Ga–P moiety.[14] The Al–P distances observed in the base-stabilized species mentioned above are 2.409(3)[12] and 2.416(3) Å,[4b] which are *ca.* 0.06 Å longer than that observed in **2**. These longer distances are to be expected in view of the higher coordination number at aluminum, and the lengthening is not indicative of the presence of π-bonding in the corresponding three-coordinate species. The similarity of the Al–P bond lengths in the base-stabilized species indicate that, in these molecules and in **2**, steric factors do not strongly influence the Al–P bond lengths.

The NMR spectroscopy of compounds **1** and **2** is also of considerable interest. Variable-temperature (VT) ^1H NMR studies of **1** and **2** indicate significant dynamic behavior. The ^1H NMR spectrum of **2** was studied in the temperature range −100 to +105 °C and that of **1** in the temperature range −95 to +40 °C in C_7D_8. For **2**, time averaged (on the ^1H NMR time scale) spectra could only be observed at temperatures > 100 °C. Cooling the solution leads to a broadening of the *o*-CH (T_c = 303 K), *p*-CH (T_c = 273 K), and *o*- and *p*-CH_3 signals and their eventual separation. The use of an approximate formula[15] and maximum peak separations of 108 and 42 Hz leads to estimated barriers ($\Delta G^{\ddagger}$) of 14.4 and 13.4 kcal mol^{-1}, respectively. Cooling to *ca.*

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(8) All syntheses were carried out under anaerobic and anhydrous conditions. $Trip_2AlP(Mes)SiPh_3$, **1**. A solution of 1.027 g (2.0 mmol) of $Trip_2AlBr$[7] in *n*-hexane (30 mL) was added to a slurry of 0.81 g (1.97 mmol) of $LiP(Mes)SiPh_3$[4b] in *n*-hexane (30 mL) with cooling in an ice bath. The mixture was stirred overnight and the fine colorless precipitate was allowed to settle. The pale yellow supernatant liquid was decanted and the solvent was evaporated under reduced pressure. The remaining solid was redissolved in *ca.* 30 mL of *n*-hexane and filtered. The filtrate was concentrated to incipient crystallization and cooled in a −20 °C freezer for 3 days after which pale yellow microcrystals of the product **1** were obtained. Yield: 0.65 g, 38.5%. Mp: 135–137 °C (softens at 118–120 °C). Anal. Calcd for **1**, $C_{57}H_{72}AlPSi$: C, 81.19; H, 8.61. Found: C, 81.01; H, 8.32. ^1H NMR (C_7D_8): δ 1.14 (d, $^3J_{HH}$ = 6.6 Hz, *o*-CH_3), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, *p*-CH_3), 1.97 (s, *p*-CH_3(Mes)), 2.32 (s, *o*-CH_3(Mes)), 2.74 (sept, *p*-CH), 3.18 (sept, *o*-CH), 6.52 (d, $^4J_{PH}$ = 2.7 Hz, *m*-H(Mes)), 6.93 (s, *m*-H); $SiPh_3$: 6.97 (t, *J* = 7.5 Hz), 7.07 (d, *J* = 7.2 Hz, *p*-H), 7.53 (d, *J* = 6.9 Hz). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 20.9 (*p*-CH_3(Mes)), 24.1 (*p*-CH_3), 25.4 (*o*-CH_3) 26.2 (d, $^3J_{PC}$ = 9.6 Hz, *o*-CH_3(Mes)), 34.7 (*p*-CH), 41.4 (*o*-CH), 120.9 (*m*-C), 156.3 (*o*-C), 127.5, 128.9, 129.0, 129.4, 135.7 (d, Δν = 12.2 Hz), 136.7 (d, Δν = 2.5 Hz), 137.1, 142.5 (d, Δν = 22.0 Hz), 146.4 (d, Δν = 7.3 Hz), 150.5 (aryl C's). ^{31}P NMR (C_7D_8): δ −157.1 (s). $Trip_2AlP(1\text{-}Ad)SiPh_3$, **2**. The phosphine $HP(1\text{-}Ad)SiPh_3$ was synthesized in a similar manner to the previously reported bulky phosphines in ref 4b, except that the reaction time was 40 h. The crude product was extracted with toluene and recrystallized from hexane/Et_2O (1:1, 40 mL) at −20 °C. Yield: 57%. Mp: 140–142 °C. ^1H NMR (C_6D_6): δ 1.44 (s, δ-CH_2), 1.64 (s, γ-CH), 1.80 (s, β-CH_2), 3.01 (d, $^1J_{PH}$ = 201.0 Hz), 7.14 (m, *p*,*m*-H), 7.85 (m, *o*-H). ^{31}P NMR: δ −96.7 (d). A solution of $HP(1\text{-}Ad)SiPh_3$ (0.55 g 1.3 mmol) in Et_2O (20 mL) was heated with *n*-BuLi (0.85 mL of a 1.6 M *n*-BuLi solution in hexanes). After 3 h of stirring, all the solvent was evaporated under reduced pressure, and the resulting pale yellow solid was suspended in hexane (20 mL). A solution of $Trip_2AlBr$ (0.67 g, 1.3 mmol) in *n*-hexane (20 mL) was added to the lithium phosphide slurry, and the resulting yellow mixture was stirred overnight. Filtration, concentration (to *ca.* 5–8 mL), and crystallization in a 20 °C freezer afforded pale yellow crystals of **2**. Concentration of the mother liquor and subsequent crystallization afforded another 0.13 g of product. Yield: 0.62 g (54%). Mp: 157–159 °C (changes color to slightly yellow-green at *ca.* 125 °C). Crystals suitable for X-ray diffraction were obtained by recrystallizing twice from the minimum amount of *n*-hexane (*ca.* 10 mL) at −20 °C. ^1H NMR (C_7D_8, 105 °C): $SiPh_3$, δ 7.80 (m), 7.06 (s, broad), 7.04 (s, broad); Trip, δ 6.95 (s, *m*-H), 3.26 (sept, *o*-CH), $^3J_{HH}$ = 6.3 Hz), 2.78 (sept, p-CH, $^3J_{HH}$ = 6.3 Hz), 1.21 (d, *o*- and *p*-CH_3); 1-Ad, δ 2.02 (m, β-CH_2), 1.59 (s, broad, γ-CH), 1.37 (m, δ-CH_2); hexane, δ 0.85 (m, CH_3, CH_2 groups obscured by Trip-CH_3). $^{13}C\ \{^1H\}$ NMR (C_6D_6): $SiPh_3$, δ 137.5 (d, *i*-C, $^2J_{PC}$ = 10.7 Hz), 136.6 (s, *o*-C), 129.2 (s, *p*-C), 128.0 (s, *m*-C); Trip, 156.0 (s, *o*-C), 150.8 (s, broad, p-C), 144.3 and 144.6 (two unresolved m, *i*-C), 121.1 (s, *m*-C), 36.4 (s, *o*-CH), 34.8 (s, *p*-CH), 25.0 (broad ~70 Hz unresolved signal, *o*-CH_3), 24.2 (s, *p*-CH_3); Ad, 47.9 (d, β-CH_2, $^2J_{PC}$ = 6.3 Hz), 41.0 (d, δ-CH_2, $^4J_{PC}$ = 1.9 Hz), 36.5 (d, α-C, $^1J_{PC}$ = 8.9 Hz), 30.1 (d, γ-C, $^3J_{PC}$ = 9.0 Hz); hexane, δ 14.3 (s, CH_3), 23.0 (s, β-CH_2), 31.9 (s, γ-CH_2). ^{31}P NMR (C_6D_6): δ = −93.8 (s). Anal. Calcd for **2**, $C_{58}H_{76}AlPSi$: C, 81.07; H, 8.92. Found: C, 80.45; H, 9.08.

(9) Crystal data at 130 K with Cu Kα (λ = 1.54 178 Å): $C_{61}H_{83}AlPSi$, *M* = 902.31, *a* = 20.841(4) Å, *b* = 21.790(3) Å, *c* = 24.774(3) Å, β = 104.542(12)°, monoclinic, $P2_1/n$, *Z* = 8 (two unique monomers), 9106 unique observed ($I > 2\sigma\ I$)) data, *R* = 0.067.

(10) Radii of 1.3 Å and 1.10 Å were used for aluminum and phosphorus: Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 258.

(11) Covalent bonds with ionic character are normally shorter than the bond length predicted from the sum of the covalent radii. The Al–P bond length may be estimated by using the empirical formula of Schomaker and Stevenson which gives a value of 2.34 Å. For further discussion see the following references: Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37; Haaland, A. In *Coordination Chemistry of Aluminum*: Robinson, G. H., Ed.; VCH: New York, 1993; Chapter 1.

(12) For a survey of the major factors that influence inversion barriers see the following reference: Lambert, J. B. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1971; Vol. 6, p 19.

(13) Atwood, D. A.; Contreras, L.; Cowley, A. H.; Jones, R. A.; Mardones, M. *Organometallics* **1993**, *12*, 17.

(14) The Allred–Rochow EN scale gives an EN value of 1.47 for aluminum and 1.82 for gallium(III). In addition, the significantly smaller size of gallium in comparison to aluminum is supported by several recent structures of compounds with Al–Al and Ga–Ga bonds: Uhl, W. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1386; Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983.

(15) Kost, D.; Carlson, E. H.; Raban, M. J. *J. Chem. Soc., Chem. Commun.* **1971**, 656.

173 K leads to further splitting indicating a second dynamic process, (probably Trip ring flipping) with a ΔG^{*} barrier of <8 kcal mol^{-1}. Similar studies for **1** indicated coalescence of the *o*-CH and *p*-CH signals at 178 and 188 K which afforded a barrier of 8.9 kcal mol^{-1} for the dynamic process.[16] The observation of these barriers can be explained in terms of restricted rotation around the Al–P bonds. However, it is unlikely that this restriction is a consequence of π-bonding in view of the smaller barriers observed in the related gallium species where the phosphorus center has more planar geometry and the Ga–P, p-orbital–lone pair, alignment is favorable for π-bonding. It is more probable that the rotational barrier is a consequence of steric interference between the aluminum and phosphorus substituents as noted above in the X-ray crystal structure.

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Supplementary Material Available: Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (17 pages). Ordering information is given on any current masthead page.

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(16) The observation of a very low barrier in **1** is consistent with a monomeric formulation in solution. Association (i.e. dimerization) of **1** would lead to an extremely crowded species, which should give rise to different *o*-*i*-Pr signals for *both* cis- and trans-isomeric forms of the dimer. It is also notable that the ^{31}P NMR spectrum gives rise to one signal only over a variety of temperatures, suggesting the presence of only one species (a monomer) in solution.