Stable Tertiary Phosphine Adducts of Alane

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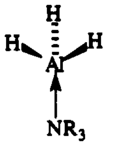
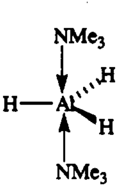
Summary: Treatment of $LiAlH_4/OEt_2$ solutions with bulky trialkylphosphine hydrochloride salts or phosphine and then ethereal HCl yields thermally stable phosphine–alane adducts, viz. $[H_3Al{\cdot}P(C_6H_{11})_3]$ (**10**), $(H_3Al)_n{\cdot}(PPr^i{}_2CH_2)_2$ (n = 1 (**11**), 2 (**12**)), and $[(H_3Al)_2{\cdot}\{P(C_6H_{11})_2CH_2\}_2]$ (**13**), which have been shown to be four-coordinate (**10** and **13**, Al–P = 2.467 (1), 2.460 (2) Å) or polymeric (**13**) with trigonal-bipyramidal aluminum centers (P apical) with exceptionally long Al–P bonds (2.732 Å (mean)). Ab initio calculations on the model species $H_3Al{\cdot}PH_3$ (Al–P = 2.605 Å) give a stabilization energy of 13.2 kcal/mol relative to AlH_3 and PH_3, and dimerization to dialane, $H_2Al(\mu\text{-}H)_2AlH_2$, and PH_3 is favored by 5.84 kcal/mol.

Alane, AlH_3, is a polymeric, nonvolatile solid, capable of forming adducts with a variety of Lewis bases. These include tertiary amines which yield stable, volatile compounds such as the 1:1 and 2:1 trimethylamine–alane adducts $H_3Al{\cdot}NMe_3$ (1) and $H_3Al{\cdot}2NMe_3$ (2).[2] These compounds have applications in (i) hydroalumination of unsaturated substrates,[3] (ii) formation of hydride derivatives of other metal complexes,[4] including SiH_4 from SiF_4,[5] (iii) electroless plating of aluminum,[6] and (iv) conventional thermal and laser-induced chemical vapor deposition (CVD) technology.[7-9] Overall, tertiary amine–alane chemistry is well developed, with a diverse range of structural types having been established. Compound 1 is monomeric in the gas phase,[10] whereas it is weakly associated in the solid state via unsymmetrical bridging hydrides,[11] as is $[\{LH_2Al(\mu\text{-}H)\}_2]$ (**3a**,**b**), but $H_3Al{\cdot}NBu^n{}_3$ (4) is monomeric in the solid state.[12] The polymeric five-coordinate species 2[13] and $H_3Al{\cdot}$(TMEDA) (5; TMEDA = *N,N,N′,N′*-tetramethylethylenediamine)[14] and ionic species for higher polydentate tertiary amines $[H_2Al(N,N,N',N'',N''\text{-pentamethyldiethylenetriamine})]^+[AlH_4]^-$ (6) and *trans*-$[H_2Al(N,N',N'',N'''\text{-tetramethylcyclam})]^+[AlH_4]^-$ (7)[15] are also found.



1, R = Me (gas phase)
4, R = Bu^n



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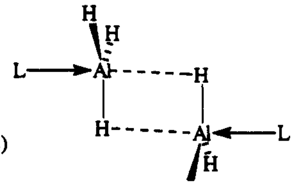
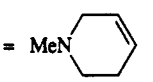
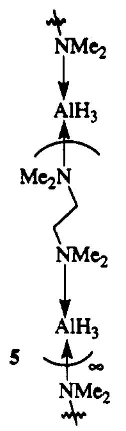


1, L = NMe_3 (solid)
3a, L = NMe_2CH_2Ph

3b, L =





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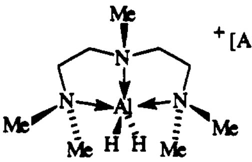
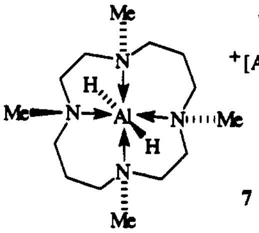


$^+[AlH_4]^-$

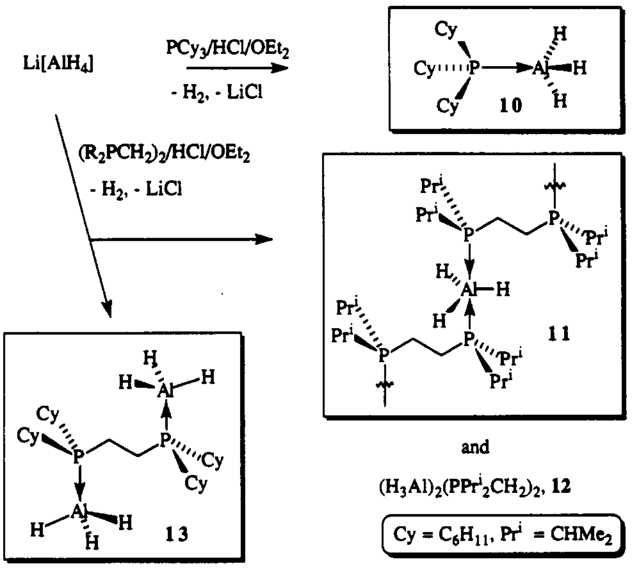
6



$^+[AlH_4]^-$

7

Scheme I



Tertiary phosphine–alane adducts, however, have been poorly characterized and the few compounds studied readily decompose under mild conditions; e.g., $H_3Al{\cdot}PEt_3$ decomposes above −20 °C.[16] Herein we report the synthesis of tertiary phosphine adducts of alane with remarkable stability. The first structure determinations of such derivatives shows that both four- and five-coordinate species are accessible. We also report the theoretical in-

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vestigation of the model species $H_3Al{\cdot}PH_3$, which is energetically less favored than dialane, $H_2Al(\mu\text{-}H)_2AlH_2$, and phosphine.

The new compounds feature bulky mono- or bidentate tertiary phosphines, $[H_3Al{\cdot}P(C_6H_{11})_3]$ (**10**), $(H_3Al)_n{\cdot}(PPr^i{}_2CH_2)_2$ (n = 1 (**11**), 2 (**12**)) and $[(H_3Al)_2{\cdot}\{P(C_6H_{11})_2CH_2\}_2]$ (**13**), the last two being alane-rich diphosphine species. Syntheses involved treating $LiAlH_4$ in diethyl ether with a phosphine hydrochloride (**10**) or treating $LiAlH_4$/phosphine mixtures with an HCl/OEt_2 solution (**11**–**13**) (Scheme I).[17] Attempts to prepare the 1:1 adduct of $\{P(C_6H_{11})_2CH_2\}_2$ with alane were unsuccessful, affording a mixture of phosphine and **13**, and less hindered phosphines such as $PMe_2(CH_2Ph)$ yielded polymeric alane, as was found for arylphosphines, including the potentially bidentate ligand $(PPh_2CH_2)_2$. Similarly, treating compound **1** with phosphines with a view to inducing ligand displacement was mostly unsuccessful, although $(PMe_2CH_2)_2$ yields the novel addition compound $\{Me_3N{\cdot}AlH_3{\cdot}PMe_2CH_2\}_2$.[18] In contrast, similar reactions involving gallane yield the displacement products, e.g. $(H_3Ga{\cdot}PMe_2CH_2)_2$[19,20] and $H_3Ga{\cdot}PCy_3$,[20] reflecting greater P-donor interaction toward gallium compared to that toward aluminum. The new compounds **10**–**13** have remarkable thermal stability relative to polymeric alane and phosphine (cf. $H_3Al{\cdot}PEt_3$, dec pt >−20 °C),[16] presumably because of the steric hindrance in either the four- or five-coordinate species blocking association via hydride bridges en route to $(AlH_3)_n$ (see the theroretical considerations below). Indeed, the decomposition pathway in the solid is formation of metal, hydrogen, and free ligand (>163 °C, **10**; >160 °C, **11**; >150 °C, **12**; >165 °C, **13**), with the decomposition temperatures comparable to those for the tertiary amine adducts of alane.[11,21]

The structures of compounds **10**, **11**, and **13** are shown in Figure 1.[22,23] Both **10** and **13** are monomeric with respectively, one molecule and half a molecule (the other half being generated by an inversion center) as the asymmetric unit. Here the metal atoms are four-coordinate with Al–P distances of 2.467 (1) Å (**10**) and 2.460(2) Å (**13**) (cf. 2.53 (4) Å for the trimethylphosphine adduct of trimethylaluminum).[24] Analogous distances in related gallane derivatives $H_3Ga{\cdot}P(C_6H_{11})_3$[20] and $(H_3Ga)_2{\cdot}(PMe_2CH_2)_2$[19] are shorter at 2.460 (2) and 2.403 (1) Å, respectively, which is in accordance with weaker binding of phosphines with alane relative to that with gallane, noting aluminum and gallium have the same covalent radii. Compound **11** is polymeric with AlH_3 and the bridging diphosphine as the asymmetric unit. In this case the metal center is trigonal bipyramidal with the hydrides in the equatorial plane,[21] and the Al–P distances are exceptionally long (2.755 (3)–2.708 (3) Å), ca. 0.5 Å longer than in bis(tertiary amine) adducts of alane.[21] This reflects very weak solvation of alane by P-donors and the tendency for unhindered phosphine adducts of alane to decompose to polymeric alane under mild conditions (see above). In contrast, gallane appears to give only four-coordinate species with phosphines. The metal–H distances in **10**, **11**, and **13** are within the range established for a variety of amine derivatives of alane.[11,21]

Ab initio molecular orbital calculations have been carried out on the model species $H_3Al{\cdot}PH_3$ and have been used to investigate the potential energy hypersurface of the dimer $[H_3Al{\cdot}PH_3]_2$. All calculations were performed using the Gaussian 88[25] suite of programs with the standard 6-31G* split valence and double-ζ plus polarization (DZP) basis sets. The effects of electron correlation were con-

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(17) Syntheses were as follows. Compound **10**: Tricyclohexylphosphine (0.56 g, 2.0 mmol) was treated with hydrochloric acid (1.0 mL, 10 M) at ca. 20 °C for 10 min. The resulting clear solution was dried in vacuo, yielding a viscous oil which solidified as a white solid on the addition of acetone (2 mL) followed by drying in vacuo at 60 °C for 1 h. $LiAlH_4$ (0.114 g, 3.0 mmol) was then added and the mixture cooled to −65 °C, whereupon OEt_2 (50 mL) was added. After it was warmed to room temperature, the mixture was stirred overnight and then filtered to remove a white precipitate. Solvent was removed in vacuo and the residue recrystallized from OEt_2 (45 mL) at −26 *C*, affording colorless prisms: yield 0.31 g, 50%; mp 161–163 °C dec; ^1H NMR (250 MHz, C_6D_6) δ 4.25 (br s, AlH), 1.80, 1.60, 1.35, 1.02 (3 H, 3 H, 2 H, 3 H, m, C_6H_{11}); ^{13}C NMR (62.8 MHz, C_6D_6) δ 31.0 (d, CH, $^1J_{C\text{-}P}$ = 14.5 Hz), 29.2 (s, CH_2), 27.2 (d, CH_2, $^2J_{C\text{-}P}$ = 10.5 Hz), 26.0 (s, CH_2); ^{31}P NMR (121.47 Hz, OEt_2) δ 8.30 (cf. 11.1 for free ligand); IR ν(Al–H) 1750 br cm^{-1}. Compound **11**: 0.5 mL of 1,2-bis(diisopropylphosphino)ethane (0.47 g, 1.79 mmol) and ethereal hydrochloric acid (2 mL, 0.864 M) were added, in succession, to a solution of $LiAlH_4$ (0.084 g, 2.2 mmol) in OEt_2 at 0 °C. The mixture was stirred for 2 h at 0 °C. After it was warmed to room temperature, the mixture was filtered, to remove a white precipitate, and the filtrate was concentrated to yield colorless cubic crystals at −26 °C: yield 0.33 g, 64%; mp 46–48 °C; dec pt >160 °C; ^1H NMR (250 MHz, C_6D_6) δ 4.70 (br s, AlH), 2.57 (d, 4 H), 2.45 (m, 4 H), 2.04 (m, 24 H); ^{13}C NMR (62.8 MHz, C_6D_6) δ 22.8 (s, CH_3), 19.2 (t, CH_2, $^{A\text{-}B}J_{C\text{-}P}$ = 5.41 Hz), 18.3 (br, t, CH); ^{31}P NMR (121.47 MHz, C_6D_6) δ 9.7 (cf. 9.4 for free ligand); IR ν(Al–H) 1777 cm^{-1} br. Compound **12**: 0.37 mL of 1,2-bis(diisopropylphosphino)ethane (0.35 g, 1.18 mmol) and hydrochloric acid in OEt_2 (3 mL, 0.91 M) were added, in succession, to a solution of $LiAlH_4$ (0.1 g, 2.48 mmol, 20% excess) in OEt_2 at 0 °C. After 2 h at room temperature the solvent was removed in vacuo, to give an oily solid which was extracted into OEt_2 and recrystallized from hexane: yield 0.3 g, 79%; mp 83–85 °C; dec pt >150 °C; ^1H NMR (250 MHz, C_6D_6) δ 4.10 (br s, AlH), 1.89 (d, 4 H), 1.49 (m, 4 H), 0.93 (m, 24 H); ^{13}C NMR (62.8 MHz, C_6D_6) δ 22.2 (t, CH_2, $^{A\text{-}B}J_{C\text{-}P}$ = 6.2 Hz), 18.3 (br, CH), 17.6 (s, CH_3); ^{31}P NMR (121.47 MHz, C_6D_6) δ 10.2 (cf. 9.4 for free ligand); IR ν(Al–H) 1785 cm^{-1} br. Compound **13**: Solid 1,2-bis(dicyclohexylphosphino)ethane (0.5 g, 1.18 mmol) and hydrochloric acid in OEt_2 (3 mL, 0.91 M) were added to a solution of $LiAlH_4$ (0.1 g, 2.48 mmol) in OEt_2 at 0 °C. After it was warmed to room temperature (2 h), the mixture was filtered and the filtrate concentrated to yield colorless needles: yield 0.47 g, 83%; dec pt >165 °C; ^1H NMR (250 MHz, C_6D_6) δ 4.77 (br s, AlH), 2.90 (s), 2.57 (m), 2.04 (m); ^{13}C NMR (62.8 MHz, C_6D_6) δ 33.0 (s, CH_2), 29.8 (t, CH, $^{A\text{-}B}J_{C\text{-}P}$ = 4.71 Hz), 28.9 (s, CH_2), 27.2 (t, CH_2, $^{A\text{-}B}J_{C\text{-}P}$ = 5.45 Hz). 26.3 (s, CH_2); ^{31}P NMR (121.47 MHz, C_6D_6) δ 1.8 (cf. 1.3 for free ligand); IR ν(Al–H) 1757 cm^{-1} br. Anal. Calcd for $C_{26}H_{51}AlP_2$: C, 64.73; H, 11.2; P, 12.86. Found: C, 64.09; H, 11.02; P, 11.46. Analyses for **10**–**12** were unreliable, typically a few percent low in carbon.

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(22) Data for crystal structure determinations (T = 297 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries, λ = 0.71069 Å) are as follows. Compound **10**: $C_{18}H_{36}AlP$, M = 310.4, triclinic, space group $P\bar{1}$, a = 8.026 (2) Å, b = 11.057 (2) Å, c = 11.544 (2) Å, α = 75.32 (2)°, β = 88.52 (2)°, γ = 82.06 (2)°, U = 981.4 Å^3, $F(000)$ = 344, Z = 2, D_c = 1.05 g·cm^{-3}, μ(Mo Kα) = 1.80 cm^{-1}, specimen 0.30 × 0.30 × 0.45 mm, 3447 unique reflections, 2612 with $I > 2.5\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°. Compound **11**: $C_{14}H_{35}AlP_2$, M = 292.4, monoclinic, space group $P2_1/m$, a = 7.969 (7) Å, b = 21.160 (4) Å, c = 11.626 (10) Å, β = 95.573 (4)°, U = 1951 Å^3, $F(000)$ = 712, Z = 4, D_c = 1.10 g·cm^{-3}, μ(Mo Kα) = 2.54 cm^{-1}, specimen 0.15 × 0.25 × 0.40 mm, 3432 unique reflections, 1468 with $I > 2.5\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°. Compound **13**: $C_{26}H_{54}Al_2P_2$, M = 482.60, monoclinic, space group $P2_1/n$, a = 7.068 (1) Å, b = 11.640 (1) Å, c = 18.681 (4) Å, β = 100.5 (9)°, U = 1510.9 Å^3, $F(000)$ = 532, Z = 2, D_c = 1.06 g.cm^{-3}, μ(Mo Kα) = 2.16 cm^{-1}, specimen 0.20 × 0.25 × 0.35 mm, 2810 unique reflections, 1285 with $I > 2.5\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°. The structures were solved by direct methods and refined by full-matrix least-squares refinement with non-hydrogen atoms anisotropic. H atom details: located and refined in x, y, z, U_{iso}, **10**; calculated, C–H, or located, Al–H, from difference maps and included as invariants, **11**; located and refined in x, y, z, U_{iso}, Al–H, or calculated and included as invariants, C–H, **13**. Unit weights were used, and the final residuals were R = 0.034, 0.042, and 0.042 for **10**, **11**, and **13**, respectively.

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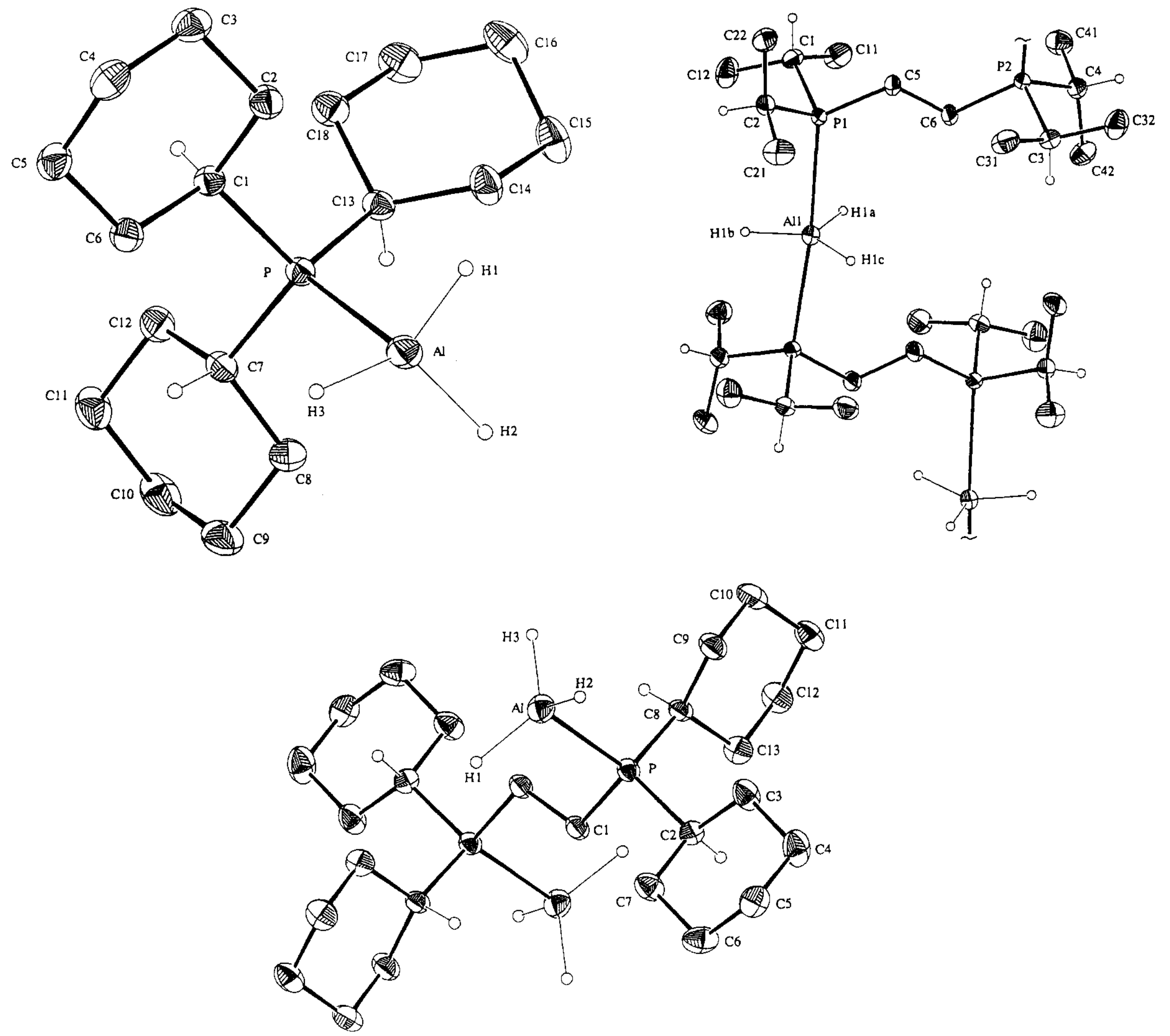

Figure 1. Molecular projections of (a, top left) $[H_3AlP(C_6H_{11})_3]$ (**10**), (b, top right) $[(H_3Al)_2(PPr^i{}_2CH_2)_2]$ (**11**), and (c, bottom) $[(H_3Al)_2\cdot\{P(C_6H_{11})_2CH_2\}_2]$ (**13**), showing the labeling schemes. Thermal ellipsoids are drawn at the 20% probability level, and only key hydrogens with arbitrary radii are shown for clarity. Selected bond distances (Å) and angles (deg) are as follows. Compound **10**: Al – P, 2.467 (1); Al–H1,2,3, 1.51 (2), 1.73 (2), 1.55 (4); P–C1,7,13, 1.840 (2), 1.850 (2), 1,858 (3); P–Al–H1,2,3, 106 (1), 104.5 (6), 99 (1); Al–P–Cl,7,13, 110.90 (7), 110.90 (8), 113.53 (8); H1–Al–H2,3, 110 (1), 112 (1); H2–AlH3, 123 (1). Compound **11**: Al1–P,2, 2.755 (3), 2.708 (3); Al1–H1a,b,c, 1.61, 1.57, 1.60; P1–C1,2,5, 1.841 (6), 1.851 (6), 1.864 (6); P2–C3,4,6, 1.852 (6), 1.847 (5),1.855 (6); P1 – Al1–H1a,b,c, 92, 88, 89; P2–Al1–H1a,b,c, 91, 87, 93; P1–Al1–P2, 175.03 (7); H1a–Al1–H1b,c, 117, 114; H1b–Al1–H1c, 129; Al1–P1–C1,2,5, 114.4 (2), 110.3 (2), 120.8 (2); Al1–P2–C3,4,6, 115.3 (2), 111.9 (2), 117.0 (2). Compound **13**: Al–P, 2.406 (2); Al–H1,2,3, 1.56 (2), 1.55 (2), 1.55 (2); P–C, 1.840 (5), 1.846 (4), 1.841 (4); P–Al–H1,2,3, 98 (1), 107 (1), 102 (1); H1–Al–H2,3, 122 (2), 117 (2); H2–Al – H3, 108 (2), Al–P–C1,2,8, 108.8 (2), 114.6 (2), 115.1 (2).

sidered by the inclusion of fourth-order Møller–Plesset perturbation theory for DZP basis calculations. Calculated geometries for monomeric $H_3Al{\cdot}PH_3$ are Al–P = 2.605 Å, P–H = 1.424 Å, Al–H = 1.600 Å, P–Al–H = 119.2°, and Al–P–H = 96.8°; the Al–P distance is longer than that determined experimentally for **10** and **13** but is within 2 standard deviations of the Al–P distance in $Me_3Al{\cdot}PMe_3$.[24] The stabilization energy of $H_3Al{\cdot}PH_3$ relative to AlH_3 and PH_3 is 13.2 kcal/mol, ignoring zero point energy corrections. No minimum was found to exist on the surface for the C_{2h} symmetry $(H_3Al{\cdot}PH_3)_2$ dimer, unlike the case for the amine analogue.[11] Instead convergence was on dialane, $H_2Al(\mu\text{-}H)_2AlH_2$, and two phosphines as the thermodynamically favorable system, 5.84 kcal/mol more stable than two isolated $H_3Al{\cdot}PH_3$ species. This is consistent with the above instability of phosphine adducts relative to polymeric alane. The geometry of the dialane was close to that calculated by Duke and Schaefer,[26] Al···Al = 2.620 Å (cf. 2.616 Å in the present study). Optimized geometries for the corresponding monomeric gallane and borane monophosphine adducts $H_3Ga{\cdot}PH_3$[20] and $H_3B{\cdot}PH_3$[27] have already been established.

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Registry No. **10**, 139526-60-6; **11**, 139526-59-3; **13**, 139526-61-7; H_3AlPH_3, 126425-81-8; PCy_3, 2622-14-2; 1,2-bis(diisopropylphosphino)ethane, 87532-69-2; 1,2-bis(dicyclohexylphosphino)ethane, 23743-26-2.

Supplementary Material Available: Lists of U_{ij} values, hydrogen atom parameters and bond distances and angles for compounds **10**, **11**, and **13** and a table of ab initio derived geometries (10 pages). Ordering information is given on any current masthead page.

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