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Mixed-Donor and Monomeric N-Donor Adducts of Alane

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Reaction of $H_3Al{\cdot}NMe_3$ with 1,2-bis(dimethylphosphino)ethane (=dmpe) affords the novel mixed-donor aluminum hydride complex $2(Me_3N{\cdot}AlH_3){\cdot}$dmpe (**1**) with the N- and P-donor groups in apical trigonal bipyramidal positions (structurally authenticated) which has been modeled by *ab initio* calculations on $H_3N{\cdot}AlH_3{\cdot}PMe_3$ and $H_3Al{\cdot}PMe_3$. The complexes $[H_3Al{\cdot}MeMorph]_\infty$ (**2**) (MeMorph = *N*-methylmorpholine) and $H_3Al{\cdot}$quin (**3**) (quin = quinuclidine) are prepared from $LiAlH_4$ and hydrochloride salts of the appropriate amines. Complex **2** is polymeric in the solid state, displaying donation from the N- and O-centers of successive ligands, unlike **3**, which is a monomer with four-coordinate metal centers and displays no reactivity toward dmpe. Crystal data (Mo Kα, $\lambda = 0.710\ 69$ Å): **1**, monoclinic, space group $P2_1/n$, $a = 6.694(2)$ Å, $b = 24.775(6)$ Å, $c = 7.044(2)$ Å, $V = 1168(6)$ Å^3, $Z = 2$, $R = 0.097$; **2**, orthorhombic, space group $P2_12_12_1$, $a = 13.504(4)$ Å, $b = 9.799(3)$ Å, $c = 5.965(2)$ Å, $V = 789$ Å^3, $Z = 4$, $R = 0.093$; **3**, monoclinic, space group $P2_1/m$, $a = 6.138(1)$ Å, $b = 9.066(2)$ Å, $c = 8.213(2)$ Å, $V = 453.0(2)$ Å^3, $Z = 2$, $R = 0.056$.

Introduction

Thin-film deposition and microelectronic device fabrication have been the driving forces for the recent resurgence of synthetic[1,2] and theoretical[3] interest in the donor adducts of aluminum and gallium hydrides. This is directly attributable to their utility as low-temperature, relatively stable precursors for both conventional and laser-assisted chemical vapor deposition,[4,5] with the latter evolving in recent years mainly in relation to the application of volatile Lewis base adducts in chemical vapor deposition (CVD) technology.[6–11] Herein, we report the syntheses, characterizations, and X-ray structure determinations of the first mixed-donor adducts of alane, $2(Me_3N{\cdot}AlH_3){\cdot}$dmpe (**1**) [dmpe = 1,2-bis(dimethylphosphino)ethane] and polymeric $[H_3Al{\cdot}MeMorph]_\infty$ (**2**) (MeMorph = *N*-methylmorpholine). Also presented are the X-ray structure determination of monomeric, four-coordinate $H_3Al{\cdot}$quin (**3**) (quin = quinuclidine) and theoretical studies on $H_3Al{\cdot}PMe_3$ and $H_3N{\cdot}AlH_3{\cdot}PMe_3$, as model systems for compound **1**.

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques and glass apparatus that was flame-dried prior to use. THF and diethyl ether were dried over sodium–potassium alloy and distilled under a purified nitrogen atmosphere. All solvents were freshly distilled and deoxygenated by freeze–thaw degassing, prior to use. ^1H and ^{13}C NMR spectra were recorded at 250 MHz using a Bruker WM-250 spectrometer and at 300 MHz using a Bruker CXP-300 spectrometer. All spectra were referenced relative to partially deuterated solvent signals and carbon signals, respectively. ^{27}Al spectra were recorded on a Bruker CXP-300 spectrometer operating at 78.2 MHz and were measured relative to 1 M $[Al(H_2O)_6]^{3+}$. The infrared spectra were recorded in the range 4000–400 cm^{-1} using a Perkin-Elmer 1725X Fourier transformed infrared spectrometer. Spectra were recorded as Nujol mulls on CsI plates. Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, Canada. Melting points were determined in sealed glass capillaries containing an atmosphere of argon when appropriate and are uncorrected.

$H_3Al{\cdot}NMe_3$[12] and dmpe[13] were prepared according to literature procedures. Commercially obtained quinuclidine (quin) and *N*-methylmorpholine (Aldrich) were sublimed and distilled under argon before use, respectively. Quinuclidine hydrochloride (quin·HCl) and *N*-methylmorpholine hydrochloride (MeMorph·HCl) were prepared by dissolution of the amine in a 3 M aqueous solution of HCl and subsequently dried under reduced pressure.

$2(H_3Al{\cdot}NMe_3){\cdot}$dmpe (1). To a solution of $H_3Al{\cdot}NMe_3$ (0.45 g, 5.1 mmol) was added dmpe (0.50 mL, 3.0 mmol) and the slightly turbid solution allowed to stir for 2 d. The mixture was filtered and the solvent removed *in vacuo* to give a pure white solid of **1** (0.42 g, 79%): mp 35–36 °C; ν(Al–H) 1780 (br) cm^{-1}; ^1H NMR (C_6D_6, 250.12 MHz, 25 °C) δ 0.79 (12H, s, CH_3P), 1.29 (4H, vir t, $J = 3.5$ Hz, PCH_2), 1.95 (18H, s, NCH_3), 3.94 (br s, AlH); ^{13}C NMR (C_6D_6, 62.8 MHz, 25 °C) δ 13.5 (t, $^1J_{PC} = 6.5$ Hz, PCH_3), 27.5 (s, PCH_2), 47.2 (s, NCH_3); ^{31}P NMR (C_6D_6, 101.27 MHz, 25 °C) δ −47.9 (s, CH_3PCH_2); ^{27}Al NMR ($C_6H_5Me/C_6D_5CD_3$, 78.2 MHz, 25 °C) δ 120.1 (br s, line width at half peak height 2033 Hz).

$[AlH_3{\cdot}MeMorph]_\infty$ (2). MeMorph·HCl (1.81 g, 13.1 mmol) was added over 30 min to a stirred solution of $LiAlH_4$ (0.50 g, 13.2 mmol) in Et_2O (50 mL) at −80 °C. After gas evolution had ceased, the resulting suspension was warmed to room temperature and filtered. The filtrate was reduced to *ca.* 20 mL under vacuum and placed at −20 °C, yielding colorless prisms of **2** (1.31 g, 81% yield): mp 123–125 °C (dec 145 °C); ^1H NMR (250 MHz, C_6D_6) δ 1.86 (3H, s, NMe), 2.09 (4H, m, NCH_2), 3.44 (4H, t, $^3J_{HH} = 4.4$ Hz, OCH_2), 4.12 (3H, br s, AlH); ^{13}C NMR (62.8 MHz, C_6D_6) δ 42.9 (NMe), 54.7 (NCH_2), 62.6 (OCH_2); ^{27}Al NMR (78.2 MHz, C_6D_6) δ 142.2 (br s, line width at half peak height 1320 Hz); ν(Al–H) 1745 cm^{-1}; MW 145 ± 13 (association 1.11 ± 0.10). Anal. Calc for $C_5H_{14}NAlO$: C, 45.79; H, 10.76; N, 10.68. Found: C, 45.02; H, 10.51; N, 10.50.

$H_3Al{\cdot}$quin (3). To a suspension of $LiAlH_4$ (0.4 g, 10.5 mmol) in diethyl ether (50 mL) at 0 °C was added solid quinuclidine hydrochloride (1.5 g, 10.2 mmol) over 10 min. After gas evolution had ceased, the white suspension was stirred for 4 h and filtered to give a colorless solution.

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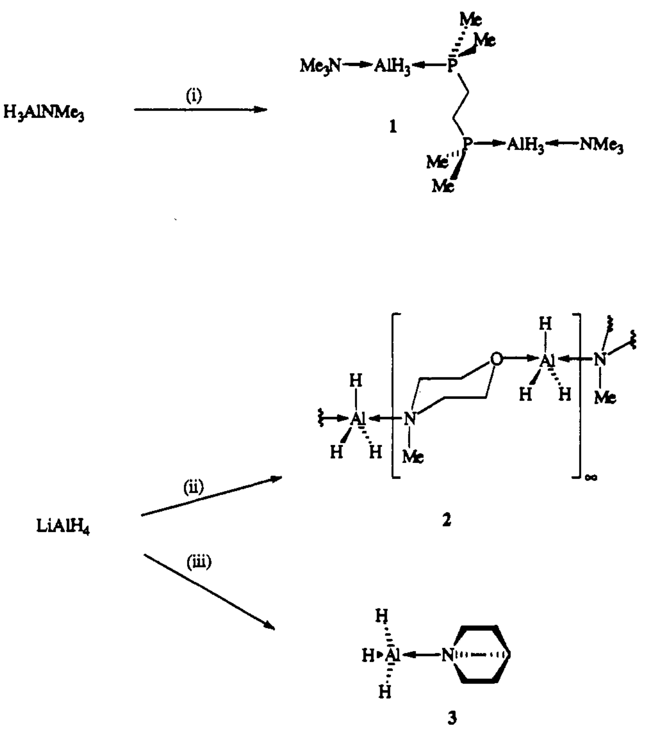
Table I. Summary of the Crystal Data and Details of Intensity Collection and Refinement for $2(H_3Al{\cdot}NMe_3){\cdot}dmpe$ (**1**), $[AlH_3{\cdot}MeMorph]_\infty$ (**2**), and $H_3Al{\cdot}quin$ (**3**)

	1	**2**	**3**
Crystal Data			
color	colorless	colorless	colorless
size, mm^3	0.40 × 0.40 × 0.30	0.40 × 0.25 × 0.05	0.35 × 0.35 × 0.25
formula	$C_{12}H_{40}Al_2N_2P_2$	$C_6H_{11}AlNO$	$C_{17}H_{16}AlN$
fw	324.35	140.05	261.31
Z	2	4	2
ρ_{calc}, g·cm^{-3}	0.93	1.18	1.035
a, Å	6.694(2)	13.504(4)	6.138(1)
b, Å	24.775(6)	9.799(3)	9.066(2)
c, Å	7.044(2)	5.965(2)	8.213(2)
α, deg	90	90	90
β, deg	90.06(1)	90	97.61(1)
γ, deg	90	90	90
V, Å^3	1168(6)	789	453.0(2)
F(000)	364		156
Data Collection			
radiation	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.7106 93	0.7106 93	0.7106 93
T, K	297	297	297
sets of setting angles refined	25	25	25
max counting time, s	60	60	60
$2\theta_{max}$, deg	50	50	50
no. of stds	3	3	3
no. of unique data	2047	765	852
no. of data with $I \geq 2.5\sigma(I)$	992	305	720
μ, cm^{-1}	2.55	1.75	1.55
Structure Solution and Refinement			
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/m$
final no. of variables	109	38	65
data/variable ratio	9	8	11
R	0.097	0.093	0.056
R_w	0.097	0.098	0.056
GOF	1.417	2.23	0.520
weighting scheme	unit weights		unit weights

Concentration and cooling at −30 °C gave large colorless blocks of **3**, in two crops (1.4 g, 95%): mp 110–112 °C (lit.[14] 108 °C); ν(Al–H) 1720 (br) cm^{-1} (lit.[14] 1760 cm^{-1}); ^{1}H NMR (C_6D_6, 250 MHz, 25 °C) δ 0.99 (6H, m, CH_2), 1.25 (1H, m, CH), 2.78 (6H, t, $^3J_{HH}$ = 8 Hz, NCH_2), 3.87 (br s, AlH); ^{13}C NMR (C_6D_6, 62.8 MHz, 25 °C) δ 20.2 (s, CH), 24.4 (s, CH_2), 46.9 (s, NCH_2); ^{27}Al NMR (C_6D_6, 78.2 MHz, 25 °C) δ 129.9 (br s, line width at half peak height 1560 Hz). Anal. Calc for $C_7H_{16}NAl$: C, 59.55; H, 11.42; N, 9.92. Found: C, 58.91; H, 10.48; N, 9.95.

Structure Determinations of $2(H_3Al{\cdot}NMe_3){\cdot}dmpe$ (1), $[AlH_3{\cdot}MeMorph]_\infty$ (2), and $H_3Al{\cdot}quin$ (3). Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with crystals mounted in capillaries. Details of the crystal data, intensity collection, and refinement are summarized in Table I. The structures were solved by direct methods and refined by full-matrix least-squares techniques with non-hydrogen atoms anisotropic, for **1** and **3**. In **1** the populations of disordered NMe_3 carbons were initially refined with isotropic temperature factors and later refined with anisotropically invariant site occupancy factors of 0.72 (C1–C3) and 0.28 (C1a–C3a). The methylene carbon C6 was refined with high thermal motion, as attempts to model disorder for the atom were unsuccessful. For **2** no hydrides were located and only the aluminum was refined with anisotropic thermal parameters. For **3** hydrogen atoms were calculated (C–H) or located (Al–H) from difference maps and included as invariants or refined isotropically (Al–H). Unit weights were used, and the final residuals were R = 0.097, 0.093, and 0.056 for **1**–**3**, respectively. The structures of **1** and **3** were solved suing the XTAL 3.0[15] programs while the structure of **2** was solved using SHELX.[16]

Scheme I [a]



[a] Reagents and conditions: (i) dmpe, OEt_2, 20 °C; (ii) *N*-methylmorpholine hydrochloride, OEt_2, −80 °C; (iii) quinuclidine hydrochloride, OEt_2, −30 °C.

***Ab Initio* molecular orbital calculations** were carried out on $H_3N{\cdot}AlH_3{\cdot}PMe_3$ and $H_3Al{\cdot}PMe_3$ using Gaussian 90[17] on IBM RISC 6000 and Sun SPARCstation 2 computers with C_{3v} symmetry imposed. Structures were found initially using the 3-21G* basis set. These geometries were than refined using an all electron doublet zeta plus polarization basis set (D95*) and finally a second order Møller-Plesset correction was made on all electrons ($H_3Al{\cdot}PMe_3$) or valence electrons ($H_3N{\cdot}AlH_3{\cdot}PMe_3$).

Results and Discussion

Syntheses and Properties. Complexes **1**–**3** were prepared according to Scheme I. Complexes **2** and **3** gave satisfactory microanalyses while compound **1** proved to be too thermally sensitive over a period for satisfactory microanalysis. Complex **1** is a low-melting solid that sublimes *in vacuo* at 50 °C without decomposition. This is unexpected, given that the related compound $H_3Al{\cdot}2NMe_3$ readily loses one amine *in vacuo*[18] and that phosphine adducts of alane such as $H_3Al{\cdot}PEt_3$ decompose above *ca.* −20 °C to polymeric alane and free ligand,[19,20] except for bulky phosphines, where decomposition occurs at greater than *ca.* 160 °C, yielding aluminum metal.[21] Complex **1** could not be formed in hexane solvent, possibly because of the persistence of the hydride bridge dimer of $H_3Al{\cdot}NMe_3$ found in the solid.[1] The ^{31}P NMR spectrum of **1** was particularly informative. It comprised a singlet at δ −47.9, a value which differs little from

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that for the free ligand (δ –47.5). Barron[22,23] found that the most important factor affecting chemical shifts in the ^{13}C and ^{31}P NMR spectra of a large series of phosphine adducts of trimethylaluminum was steric repulsion between the aluminum methyl groups and the phosphine ligands, although definitive statements on the correlation of adduct stability and reactivity with chemical shift can only be made when donor ability and steric congestion of a series of phosphine ligands coincide.[22,23] For **1** the coordination chemical shift, Δ (=δ(complex) – δ(free phosphine)) is –0.4 ppm and suggests that there is very little steric interation between the AlH_3 moiety and the dmpe ligand. Bulkier ligands force $AlMe_3$ to become distorted from planarity in phosphine adducts of trimethylaluminum.[22,23] In contrast, the phosphine resonance in the ^{31}P NMR spectrum of $2H_3Ga{\cdot}dmpe$[24] (δ –29.5) is shifted considerably downfield with respect to that of the free ligand and has been shown to have a tetrahedral Ga in the solid state.[24,25]

The structure of the alane adduct of the nitrogen analogue of dmpe, $[H_3Al{\cdot}Me_2N(CH_2)_nNMe_2]_\infty$ ($n = 2$), has been published[26] and established the polymeric nature of the complex in the solid state. Davidson and Wartik[27] had previously reported the preparation of the N analogue by the reaction of $H_3Al{\cdot}2NMe_3$ with *N,N,N′,N′*-tetramethylethylenediamine (=tmeda). The product had a high vapor pressure, and a dimeric structure was proposed for the gas phase in which tmeda was thought to adopt a bidentate coordination mode. Structurally characterized $[H_3Al{\cdot}Me_2N(CH_2)_nNMe_2]_\infty$ (n = 2,[26] 3,[28] 4[29]) are all polymeric in the solid state with the metal centers five-coordinate; thus it seems unlikely that tmeda would adopt a bidentate mode of bonding with octahedral Al as previously suggested.[27] More likely is a gas-phase cyclic dimer[30] in which the Al atoms are five-coordinate with N atoms in apical positions, as suggested for the solution-state structure of $[H_3Al{\cdot}Me_2N(CH_2)_3NMe_2]_\infty$.[28]

The product $[AlH_3{\cdot}MeMorph]_\infty$ (**2**) was isolated as a moderately soluble, white powder which was purified in good yield by recrystallization from Et_2O. In an early preparation of **2**, a greater than stoichiometric addition of MeMorph·HCl resulted in a product with partial chloride contamination (17%) of the total hydride content, as determined by X-ray crystallography.[31] This problem was alleviated by careful attention to stoichiometries in later reactions. Attempts to prepare **2** by displacement of NMe_3 from $H_3Al{\cdot}NMe_3$ with the bifunctional ligand were unsuccessful. This is likely a result of the poor donating properties of each ligand (pK_a: MeMorph, 7.38[32]), thus precluding the displacement of NMe_3 (pK_a 9.81[33]) from $H_3Al{\cdot}NMe_3$. However, an equilibrium involving the formation of five-coordinate species $Me_3N{\cdot}AlH_3{\cdot}2MeMorph$ cannot be ruled out. Such a species presumably would have *N*-methylmorpholine bound through the N-center, in accordance with the precedence for alane to bind to N-donors over O-donors, given the lower basicity of the latter. In an endeavor to prepare the bis(ligand)–alane adduct $AlH_3{\cdot}2MeMorph$, **2** was treated with an excess of MeMorph. Subsequent purification by crystallization from Et_2O yielded only starting materials.

Previously briefly reported[14] complex **3** is remarkably thermally robust, subliming with no appreciable decomposition at 120 °C (0.1 mmHg), in 95% yield, and only decomposing at temperatures >165 °C, yielding aluminum metal.

The molecular weight of complex **3** was determined in benzene at room temperature using the Signer method.[34] Results show it is minimally associated in solution—1.21—consistent with the solid-state structure, although theoretical calculations on the model compound $H_3Al{\cdot}NH_3$ yield comparable energies for the dimer relative to two monomers, which are certainly within the realms of crystal packing forces.[1]

Structural Commentary. Results of the X-ray structure determinations of monomeric **1–3** are presented in Figure 1 (Tables II and III). In the determinations of **1–3**, no intramolecular hydride bridging was evident. Compound **1** crystallizes in the monoclinic space group $P2_1/n$, with two molecules in the unit cell, and possesses an inversion center. The structure of **1** is severely disordered, and the hydride atoms were not located; however, the molecular connectivity was unambiguously established. The P–Al–N arrangement is almost linear [178.0(3)°] with the Al–N distance [2.155(9) Å] similar to the analogous distances in the only other bis(donor) adducts of alane structurally authenticated: 2.18(1) Å in $H_3Al{\cdot}2NMe_3$[18] and 2.187(4), 2.188(4) Å in $H_3Al{\cdot}2$(1,3,5-trimethylhexahydro-1,3,5-triazine).[29] A distance of 2.688(5) Å for the Al–P bond in **1** is best compared with the Al–P distance [2.755(3) Å] in five-coordinate $[H_3Al{\cdot}dippe]_\infty$[21] [dippe = 1,2-bis(diisopropylphosphino)ethane], and as expected the Al–P distance in **1** is significantly longer than in monomeric $H_3Al{\cdot}P(C_6H_{11})_3$ [2.467(1) Å].[21]

Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The X-ray structure of **2** shows it to consist of polymeric strands, the asymmetric unit of **2** comprising AlH_3 and one MeMorph ligand. The hydride atoms were not located in **2** or in one monomeric unit of its chloride-substituted analogue.[31] The geometry of the aluminum center in the structure is assumed to be trigonal bipyramidal with a nitrogen and an oxygen atom in apical positions; N-Al-O angle = 175(1)°.

This is directly comparable with the polymeric bifunctional amine–alane complexes[29] and again highlights the tendency of alane to form five-coordinate species in a donor-rich environment. Interestingly, the partially chlorinated **3** shows a similar structural geometry yet crystallizes in a different space group.[31] This could be a result of the effect the more bulky chloride ligands have on the symmetry of the polymeric chains or a consequence of differing crystal packing effects arising from the variation in polarity between Al–H and Al–Cl bonds.

The Al–O interaction in **2** appears to be weak, having a bond length greater than that normally seen for dative Al–O bonds. It appears that in **2** the primary coordination is from the N-donor functionality with a weaker secondary coordination from the O-donor of the MeMorph ligand. This is in accordance with theoretical studies on the model compound $H_3Al{\cdot}NH_3{\cdot}OH_2$[35] with Al–N = 2.175 Å and Al–O = 2.344 Å (at the Hartree–Fock (HF) level of theory using double-ζ plus polarization (D95) basis sets). In comparison, the experimentally determined distances from the X-ray structure of **2** are comparable in the case of the Al–N1 distance (2.15 Å) but significantly shorter in the case of the Al–O interaction. The application of Møller–Plesset corrections to the *ab initio* calculations on model compounds containing phosphorus was found to cause significant improvement in agreement between calculated and experimental distances.

A precendent for MeMorph coordinating an aluminum center exists with the monomeric compound $2AlMe_3{\cdot}MeMorph$, in which

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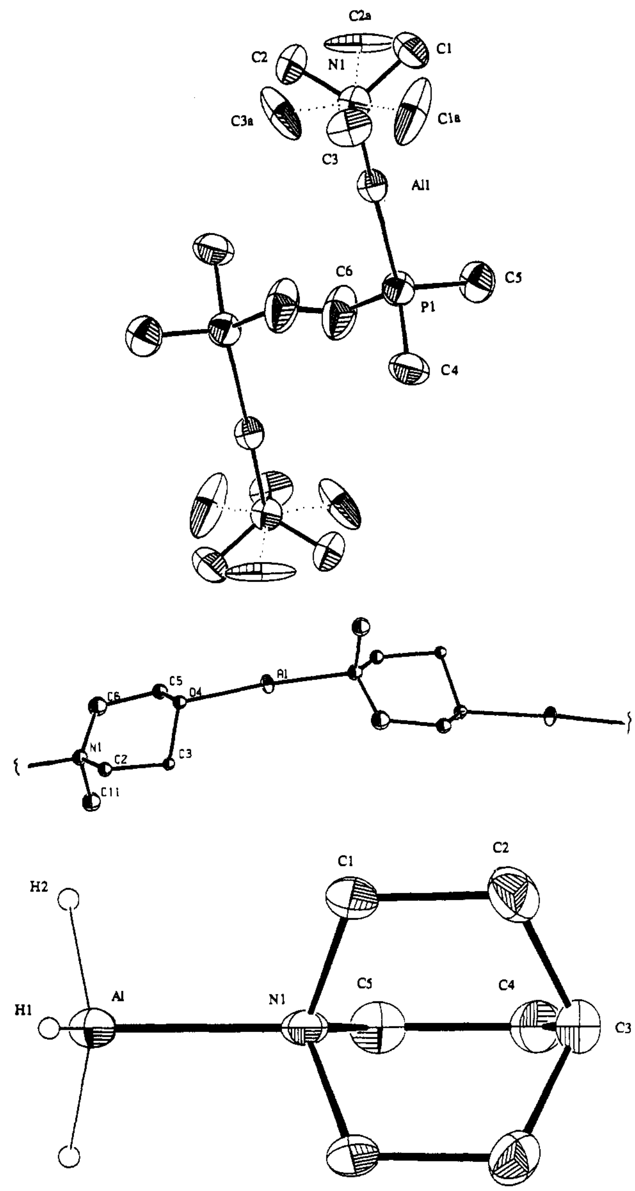

Figure 1. Molecular projections of (top) $2(Me_3N\cdot AlH_3)\cdot dmpe$ (**1**), disordered methyl carbons denoted by dashed lines, (middle) $[AlH_3\cdot MeMorph]_\infty$ (**2**), and (bottom) $H_3Al\cdot quin$ (**3**), showing the labeling schemes. Thermal ellipsoids are drawn at the 20% probability level, and only the hydride hydrogens of **3** are shown with arbitrary radii. Selected bond distances (Å) and angles (deg): compound **1**, Al–N1 2.155(9), Al1–P1 2.688(5), P1–C4,5,6 1.85(1), 1.85(1), 1.88(2), N1–C1,2,3 1.50(3), 1.49(2), 1.46(2), N1–C1a,2a,3a 1.48(9), 1.4(1), 1.51(8), P1–Al1–N1 178.0(3), Al–P1–C4,5,6 112.3(4), 115(2), 122.8(5), C4–P1–C5,6 102.7(6), 102.9(8), Al1–N1–C1,2,3 111(1), 111(1), 111(1), Al1–N1–C1a,2a,3a 100(3), 104(4), 102(3), C1–N1–C2,3 106(2), 107(2), C2–N1–C3 109(2), C1a–N1–C2a,3a 113(6), 126(6), C2a–N1–C3a 109(6); compound **2**, Al–N1 2.15(2), Al–O4′ 2.19(2), N1–C2 1.55(3), N1–C6 1.41(4), N1–C11 1.51(2), O4–C3 1.56(3), O4–C5 1.34(3), C2–C3 1.56(5), C5–C6 1.57(6), Al–N1–C2 103(3), Al–N1–C6 113(2), Al–N1–C11 108(1); compound **3**, Al1–N1 1.991(4), Al–H1,2 1.38(5), 1.56(3), N1–Al–H1,2 102(2), 101(1), H2–Al1–H1,2 123(1), 102(2).

Table II. Atomic Positional Parameters, Isotropic Equivalent Thermal Parameters, and Site Occupation Parameters for $2(Me_3N\cdot AlH_3)\cdot dmpe$ (**1**)

	x/a	*y/b*	*z/c*	*U*, Å²	PP
Al1	0.1360(4)	0.6312(1)	0.4395(5)	0.089(1)	
P1	0.3467(5)	0.5648(1)	0.6654(5)	0.109(1)	
N1	–0.040(1)	0.6851(4)	0.267(1)	0.094(4)	
C4	0.185(2)	0.5270(5)	0.832(2)	0.141(7)	
C5	0.526(2)	0.5986(5)	0.826(2)	0.141(6)	
C6	0.517(4)	0.5110(9)	0.570(2)	0.21(1)	
C1a	–0.15(2)	0.714(4)	0.416(8)	0.26(5)	0.2810
C2a	0.10(1)	0.718(4)	0.18(2)	0.23(6)	0.2810
C3a	–0.13(1)	0.647(2)	0.12(1)	0.24(4)	0.2810
C1	0.013(5)	0.7432(9)	0.305(4)	0.13(1)	0.7190
C2	–0.002(4)	0.676(1)	0.061(3)	0.12(1)	0.7190
C3	–0.253(2)	0.679(1)	0.305(4)	0.13(1)	0.7190

Table III. Atomic Positional Parameters and Isotropic or Isotropic Equivalent Thermal Parameters for $[AlH_3\cdot MeMorph]_\infty$ (**2**) and $H_3Al\cdot quin$ (**3**)

	x/a	*y/b*	*z/c*	*U*, Å²
Al	0.8528(4)	0.741(1)	0.132(1)	0.037(9)
C11	0.680(1)	0.771(3)	0.437(3)	0.048(6)
N1	0.696(1)	0.763(3)	0.187(2)	0.033(4)
C2	0.654(3)	0.632(3)	0.078(5)	0.027(7)
C3	0.539(2)	0.641(2)	0.088(4)	0.020(5)
O4	0.5117(7)	0.767(2)	–0.059(2)	0.025(3)
C5	0.544(2)	0.884(2)	0.036(4)	0.031(6)
C6	0.657(4)	0.883(3)	0.091(6)	0.054(10)
		Compound 3		
Al	0.1798(3)	$^1/_4$	–0.1470(2)	0.0568(6)^a
N1	0.2761(6)	$^1/_4$	0.0942(4)	0.042(1)^a
C1	0.1864(6)	0.3835(4)	0.1718(4)	0.060(1)^a
C2	0.2579(7)	0.3864(5)	0.3567(5)	0.071(1)^a
C3	0.3981(9)	$^1/_4$	0.4067(6)	0.058(2)^a
C4	0.5924(9)	$^1/_4$	0.3154(8)	0.063(2)^a
C5	0.5177(9)	$^1/_4$	0.1333(7)	0.059(2)^a
H1	–0.046(8)	$^1/_4$	–0.153(6)	0.071
H2	0.311(5)	0.117(4)	–0.203(4)	0.071

^{a} Isotropic equivalent thermal parameters.

a trimethylaluminum center is coordinated to both the N- and O-functionalities of the ligand. In the compound related to the present study, the monomeric 1:1 complex $AlMe_3\cdot MeMorph$, coordination to the $AlMe_3$ unit is only through the stronger N-donor.[36] Similarly, the solution-stable alane adduct $AlH_3\cdot NMe_3\cdot Et_2O$ readily loses the ether of coordination upon evaporation of the solvent.[37] Evidence to support the weakness of the Al–O interaction in **2** also comes from its infrared spectrum, which exhibits an Al–H stretching band in the lower end of the region normally associated with four-coordinate alane adducts. The high solubility of **2** in Et_2O also suggests that the Al–O bond is easily cleaved in the presence of O-donor coordinating solvents.

In **2** the Al–N distance [2.15(1) Å] compares well with those observed for the polymeric bifunctional tertiary amine–alane adducts described in the literature.[29] The Al–O distance in **2** is considerably longer than generally seen in related compounds {e.g. $AlCl_3\cdot 2thf$ [1.990(1) Å],[38] $[AlCl_3\cdot dioxane]_\infty$ [2.017(2) Å],[39] $2AlMe_3\cdot dioxane$ [2.02(2) Å],[40] and $AlH_3\cdot 2thf$ [2.070(3), 2.063(3) Å][41]} and is indicative of the weakness of this bond.

Compound **3** crystallizes in the monoclinic space group $P2_1/m$ with two molecules in the unit cell, each being a discrete monomer lying on a crystallographic mirror plane. It is noteworthy that we have recently described the unequivocal dimeric nature of $[H_3Al\cdot NMe_3]_2$[1] and other tertiary amine adducts of alane in the solid state, illustrating the propensity of alane adducts to form five-coordinate species. While the structure of $[H_3Al\cdot NMe_3]_2$ is dimeric, the X-ray crystal structure of **3** showed it to be monomeric in the solid state. The monomeric nature of **3** is surprising, considering that the steric limitations of the ligand in **3** are similar to those of the ligand in $[H_3Al\cdot NMe_3]_2$. One possible explanation for this discrepancy is the greater basicity (which can be considered a measure of electron donor strength) of quinuclidine compared

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Table IV. D95*//D95*-Optimized Energies and Geometries for Model Compounds

	molecule (symmetry)				
quantity[a]	NH_3 (C_{3v})	PMe_3 (C_{3v})	$H_3N{\cdot}AlH_3$ (C_{3v})	$AlH_3{\cdot}PMe_3$ (C_{3v})	$H_3N{\cdot}AlH_3{\cdot}PMe_3$ (C_{3v})
energy	−56.199 09	−459.578 23	−299.859 37	−703.228 47	−759.441 94
Al–N			2.095		2.198
Al–P				2.540	2.864
Al–H			1.600	1.602	1.610
P–C		1.866		1.844	1.853
N–H	1.003		1.007		1.005
C–H_a		1.086		1.085	1.086
C–H_b		1.086		1.084	1.085
Al–N–H			111.4		111.1
Al–P–C				114.5	116.3
N–Al–H			99.5		92.3
P–Al–H				99.7	87.7
C–P–C		99.8		104.0	101.8
H–N–H	107.7		107.5		107.8
P–C–H_a		112.5		111.5	112.2
P–C–H_b		109.7		109.5	109.4
H_a–C–H_b		108.6		109.2	109.0

[a] Units: energy, hartrees; bond lengths, angstroms; bond angles, degrees. H_a refers to the H atoms having a H–C–P–Al dihedral angle of 180°.

Table V. MP2/D95*//MP2/D95*-Optimized Energies and Geometries for Model Compounds

	molecule (symmetry)				
quantity[a]	NH_3 (C_{3v})	PMe_3 (C_{3v})	$H_3N{\cdot}AlH_3$ (C_{3v})	$AlH_3{\cdot}PMe_3$ (C_{3v})	$H_3N{\cdot}AlH_3{\cdot}PMe_3$ (C_{3v})
energy	−56.381 22	−460.190 73	−300.227 80	−704.026 45	−760.178 87
Al–N			2.091		2.187
Al–P				2.498	2.709
Al–H			1.602	1.603	1.615
P–C		1.865		1.843	1.853
N–H	1.020		1.027		1.024
C–H_a		1.099		1.098	1.010
C–H_b		1.098		1.097	1.098
Al–N–H			111.7		111.4
Al–P–C				115.0	116.7
N–Al–H			99.4		91.9
P–Al–H				99.2	88.1
C–P–C		98.5		103.4	101.4
H–N–H	107.1		107.2		107.5
P–C–H_a		112.0		111.1	111.8
P–C–H_b		109.5		109.2	109.1
H_a–C–H_b		109.0		109.5	109.4

[a] Units: energy, hartrees; bond lengths, angstroms; bond angles, degrees. H_a refers to the H atoms having a H–C–P–Al dihedral angle of 180°.

with NMe_3. However, there exist two reports of structural studies of monomeric alane adducts: (i) $Me_3N{\cdot}AlH_3$[42] in the vapor phase and (ii) the imprecise determination of $H_3Al{\cdot}NBu^n_3$.[43] These compounds have Al–N distances of 2.063(8) and 1.98(2) Å, respectively, which are, in the former case, significantly longer than but, in the latter case, strictly comparable to the Al–N distance in **3** [1.991(4) Å]. Hydride atoms in the structure of **3** were located, refined in *x*, *y*, and *z*, and found to contribute to a distorted tetrahedral geometry about the aluminum. The geometry of the quinuclidine ligand is similar to that determined for $Me_3Al{\cdot}quin$[44] and $H_3Ga{\cdot}quin$.[2]

Results of the theoretical work are given in Tables IV and V. Experimentally derived parameters compare favorably (Table VI) to those for $H_3Al{\cdot}P(C_6H_{11})_3$[21] and $2(Me_3N{\cdot}AlH_3){\cdot}dmpe$ (**1**). The stabilization energy, at D95*//D95*, of $H_3N{\cdot}AlH_3{\cdot}PMe_3$ relative to $H_3Al{\cdot}NH_3$ and PMe_3 is 2.72 kcal/mol and relative to NH_3 and $H_3Al{\cdot}PMe_3$ is 9.02 kcal/mol, ignoring zero point energy corrections. Attempts at calculating the effect of the interaction between model compounds $H_3Al{\cdot}NH_3$ and PH_3 resulted in the detection of no minima, reflecting the basicity of phosphine relative to trimethylphosphine. Attempts to obtain synthetically $H_3Al{\cdot}PMe_3$ *via* the reaction of PMe_3 with $[H_3Al{\cdot}NMe_3]_2$ were unsuccessful as were previously reported attempts *via* the same route and the reaction of lithium aluminum hydride and ethereal HCl in the presence of PMe_3.[45] However, the gas-phase structure of $Me_3Al{\cdot}PMe_3$ has been determined by electron diffraction and the value of 2.53(4) Å for the Al–P bond is similar to the theoretical distance calculated for $H_3Al{\cdot}PMe_3$.

Table VI. Comparison of Experimentally and Theoretically Determined Bond Distances and Angles

	molecule			
	experimental		theoretical	
quantity[a]	$H_3Al{\cdot}P(C_6H_{11})_3$[b]	$2(Me_3N{\cdot}AlH_3){\cdot}dmpe$[c]	$AlH_3{\cdot}PMe_3$[c]	$H_3N{\cdot}AlH_3{\cdot}PMe_3$[c]
Al–N		2.155(9)		2.187
Al–P	2.467(1)	2.688(5)	2.498	2.709
Al–H	1.583		1.603	1.615
P–C	1.849	1.860	1.843	1.853
Al–P–C	111.8	116.8	115.0	116.7

[a] Units: bond lengths, angstroms; bond angles, degrees. [b] Reference 21. [c] This work.

It is clear that electron saturation at the metal center is an important factor in determining whether aluminum adopts four- or five-coordinate geometry in alane adducts. Less basic amines have the ability to promote five-coordinate alane adducts through the formation of intermolecular hydride bridges[1] or through the

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formation of polymeric structures with bidentate amines,[29] thus saturating the aluminum center. A product analogous to **1** was not evident from the reaction of $H_3Al{\cdot}quin$ and dmpe under a variety of conditions. This probably relates to the more basic nature of quinuclidine (pK_a 10.95) versus trimethylamine, providing more electronic saturation. In the case of phosphine ligands, recent theoretical calculations[46] showed that the major contribution of the P substituents is due not to the σ-donor ability, which only varies 10% from PMe_3 to PF_3, but to the ability of the ligands to act as π-acceptors. These calculations have also shown that the σ-basicity and π-acidity of the ligands vary as a function of the metal. However, steric effects cannot be neglected. The loss of trimethylamine from the mixed-donor adduct $Me_3N{\cdot}H_3Al{\cdot}PBu^t_3$ *in vacuo* is unusual, given the relative donor strengths of the ligands toward alane[47] and the theoretical considerations above. Presumably this results from the exceptionally large steric demand of the phosphine ligand coupled with the volatility of the amine and supports the premise that bulkier ligands cause more distortion from planarity about the aluminum.[22]

We have shown that mixed-donor adducts of alane arise when a careful balance of steric and electronic factors is achieved. Theoretical calculations show that $H_3Al{\cdot}PMe_3$ should be accessible experimentally, but this has yet to be achieved.

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Supplementary Material Available: Tables listing thermal parameters and interatomic distances and angles (3 pages). Ordering information is given on any current masthead page.

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