the largest values ever reported for artificial adenine receptors.[1]

Taking account of the wide variety of functions of porphyrin complexes, the present new 1:2 complex of **1Zn** with adenine derivatives is expected to offer unique applications both for nucleoside recognition and for its reactions. The detailed characteristics of the present nucleobase recognition are now being investigated in our laboratory.

Tertiary Amine Stabilized Dialane

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Tertiary amine adducts of alane are of interest as hydride sources for hydroalumination of unsaturated substrates,[2] for formation of derivatives of other metal complexes,[3] and as precursors for chemical vapor deposition of aluminum metal.[4,5] Despite this there are only a few structural studies, notably on monomeric H_3AlNMe_3 (**1**) (gas phase),[6] $H_3AlN^nBu_3$ (**2**),[7] and $H_3Al(NMe_3)_2$ (**3**),[8] polymeric $H_3Al(TMEDA)$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) (**4**),[9] and ionic species $[H_2Al($*N,N,N',N'',N''*-pentamethyldiethylenetriamine$)]^+[AlH_4]^-$ and *trans*-$[H_2Al($*N,N',N'',N'''*-tetramethylcyclam$)]^+[AlH_4]^-$.[10]

Using X-ray diffraction data we have shown that dimeric species possessing two bridging hydrides are a common solid-state structural unit for a variety of alane adducts with unidentate tertiary amines, including the well-known compound **1**, and we report a high-level theoretical study on the model compound H_3AlNH_3. A dimeric structure for **1** alone has implications regarding (i) conflicting molecular weight determinations for this compound in solution, monomer versus some association; (ii) the higher vapor pressure of compound **3** compared to compound **1**;[11] and (iii) the generally accepted view that **1** is monomeric,[4] as in the solid-state structure of the corresponding gallium compound, H_3GaNMe_3.[12] In addition, the dimeric structures can be considered as tertiary amine adducts of the elusive dialane, $[H_2Al(\mu\text{-}H)]_2$, for which theory predicts a binding energy comparable to that of the ubiquitous diborane, $[H_2B(\mu\text{-}H)]_2$.[13]

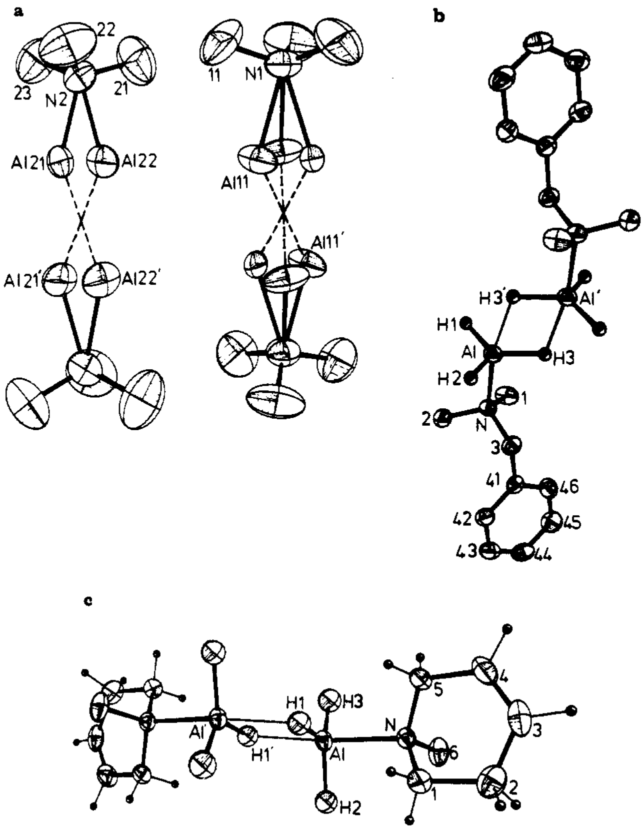
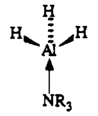
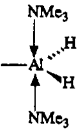


Figure 1. Projections of (a) $[\{H_3AlNMe_3\}_2]$ (**1**), (b) $[\{H_3Al(NMe_2CH_2Ph)\}_2]$ (**5**), and (c) $[\{H_3Al(\overline{NMeCH_2CH_2CH{=}CHCH_2})\}_2]$ (**6**) with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms where shown. Molecules of **1** are disordered across 2 and $\bar{3}$ symmetry sites, Al(21,22) and Al(11).



R = Me, **1** (vapor)
R = Bu^n, **2**



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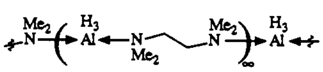

4

The new adducts of alane, $[\{H_3Al(NMe_2CH_2Ph)\}_2]$ (**5**) and $[\{H_3Al(\overline{NMeCH_2CH_2CH{=}CHCH_2})\}_2]$ (**6**), were prepared by treating $LiAlH_4$ with the hydrochloride salt of the amine, eq 1, and purified by sublimation in vacuo at 100 °C (0.1 mmHg) (for **5**) or recrystallization (for **6**).[14] They decompose, yielding alu-

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(14) Compound **5**: To a slurry of $LiAlH_4$ (1.0 g, 26.2 mmol) in diethyl ether (50 mL) at −78 °C was added the anhydrous hydrochloride salt of *N*-benzyldimethylamine (4.5 g, 26.2 mmol) over 30 min. After 1 h at ca. 20 °C, volatiles were removed in vacuo and the product sublimed as colorless prisms (1.43 g, 33% yield): mp 75–76 °C dec >150 °C; ^1H NMR (250 MHz, C_6D_6, 25 °C, TMS) δ 2.09 (s, 6 H, Me), 3.82 (s, 4 H, CH_2), 4.19 (br s, AlH), (m, 5 H, Ph); ^{13}C NMR δ 42.6 (NMe), 61.0 (NCH_2), 128.4, 131.1, 132.1 (Ph); IR ν (cm^{-1}) 1770 (br, AlH); UV λ_{max} (nm) 219, 253. Found: C, 64.32; H, 9.41; N, 8.5. Calcd: C, 66.20; H, 8.58; N, 8.58. Compound **6**: To a slurry of $LiAlH_4$ (1.0 g, 26.2 mmol) in diethyl ether (20 mL) at 0 °C was added the anhydrous hydrochloride salt of 1-methyltetrahydropyridine (3.6 g, 26.9 mmol) over 10 min. After 1 h at ca. 20 °C, volatiles the mixture was filtered, concentrated in vacuo to ca. 10 mL, and cooled to −30 °C, yielding massive prisms (2.43 g, 70% yield): mp 68–71 °C dec >120 °C; ^1H NMR (250 MHz, C_6D_6, 25 °C, TMS) δ 1.53 (m, 2 H, H_2C5), 2.01 (s, 3 H, CH_3) 2.46 (t, 2 H, H_2C6, ^3J = 4.4 Hz), 2.88 (m, 2 H, H_2C2), 4.09 (br s, AlH), 4.97, 5.27 (2 m, 2 H, HC3,4); ^{13}C NMR δ 20.5 (C5), 41.8 (CH_3), 49.9 (C6), 52.5 (C2), 121.5, 124.4 (C3,4); IR ν (cm^{-1}) 1720 (br, AlH); UV λ_{max} (nm) 218. Found: C, 55.85; H, 10.95; N, 10.79. Calcd: C 56.67; H, 11.10; N, 11.02.

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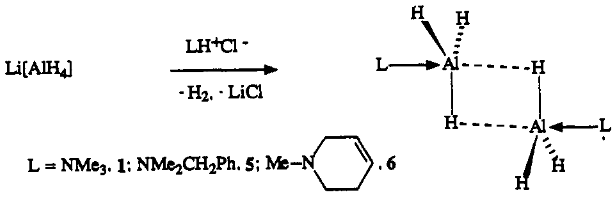
Table I. Experimental Geometries for the Metal Cores in $[\{H_3Al(NMe_2CH_2Ph)\}_2]$ (**5**) and $[\{H_3Al(\overline{NMeCH_2CH_2CH{=}CHCH_2})\}_2]$, (**6**) and Computed Geometries for $[(H_3AlNH_3)_2]$[a]

atoms[b]	**5**	**6**	$[(H_3AlNH_3)_2]$[c]
Al–N	2.088 (2)	2.082 (4)	2.162
Al–μ-H	1.56 (2)	1.59 (4)	1.638
Al–H	1.54 (3), 1.57 (3)	1.64 (4), 1.61 (5)	1.590
Al···μ-H	2.07 (2)	2.01 (4)	2.068
Al···Al	2.883 (2)	2.862 (3)	2.900
N–Al–H	96.4 (9), 95.0 (9)	94 (1), 97 (2)	94.0
N–Al–μ-H	92.2 (8)	92 (1)	90.6
N–Al···μ-H	167.5 (9)	167 (1)	168.2
H–Al–H	122 (1)	121 (2)	123.6
H–Al–μ-H	120 (1), 116 (1)	117 (2), 120 (2)	117.9
μ-H–Al···μ-H	75 (1)	75 (2)	77.7
H–Al···μ-H	89 (1), 92 (1)	94 (2), 88 (2)	91.0
Al–μ-H···Al	104.7 (5)	105 (1)	102.4

[a] Distances, Å; angles, deg. [b] For compound **1**, Al(11)–N(1), 2.09 (2); Al (21,22)–N(2), 2.02 (2), 2.03 (2); Al(11)···Al(11), 2.88 (4); Al(21)···Al(22)′, 2.94 (4); Al(22)···Al(21)′, 2.88 (4) (see Figure 1). [c] N–H, 1.005 Å; Al–N–H, 111°.

minum mirrors, at >130 °C (**5**) and >120 °C (**6**), which are higher decomposition temperatures than those of other monodentate tertiary amine derivatives of alane, including **1** (dec >100 °C).[3] Polydentate tertiary amines such as TMEDA impart higher thermal stability to their alane derivatives (compound **4**, dec >200 °C). However, such amines destabilize gallane relative to monodentate tertiary amines.[15]



(1)

Results of the X-ray structure determinations of **1**, **5**, and **6**[16] are presented in Figure 1 and Table I. The structure of **1** is severely disordered, but when compared to the well-behaved dimeric structures of **5** and **6**, where even the hydrides were refined in x,y,z,U_{iso}, it is consistent with the formulation as dimers (see below). In both **5** and **6** half the molecule comprises the asymmetric unit, the other half being generated by an inversion center; aluminum centers have three primary hydrides in equatorial positions of a trigonal bipyramid ($\sum$(H–Al–H), 358° for **5** and **6**) with a N center and a weak secondary Al–H interaction in apical positions. The Al–N distances, 2.088 (2) Å (**5**) and 2.082 (4) Å (**6**), are significantly longer than in **1**, 2.063 (8) Å (gas phase),[6] as expected for a lower coordination number. In **1** two crystallographically independent dimers are disordered over D_{3h} and C_2 symmetry sites. The aluminum centers for each set of dimers are shown in Figure 1 by broken lines and come from a consideration of Al···Al distances and N–Al···Al′ angles; in **5** and **6** they are respectively 2.883 (2) Å, 136.2 (2)°, 2.862(3) Å, 134.7 (2)°, compared with two sets for Al21,22, 2.94 (4) Å, 146 (1)°, 2.88 (4) Å, 143 (1)°, and one set for Al11, 2.94 (4) Å, 133 (1)°.

Ab initio molecular orbital calculations were carried out using the HONDO-7 package;[17] all calculations were at the Hartree–Fock (HF) level using the DZP polarized basis set on the model compound H_3AlNH_3. The calculation for a monomer converged with C_{3v} symmetry, Al–N 2.067 Å, Al–H 1.600 Å, N–Al–H 99.5° (N–H 1.002 Å, Al–N–H 111.3°), which is close to the structure of **1** in the gas phase (Al–N 2.063 (8) Å, Al–H 1.56 (1) Å, N–Al–H 104 (1)°.[6] The minimum energy calculated for a dimer corresponds to a structure similar to that found in **5** and **6**, possessing C_{2h} symmetry as in **6**; calculated parameters are presented in Table I. Major differences between the two computed structures are the elongation of the Al–μ-H bond (2.4%) and the Al–N bond (4.6%) on association. The only significant difference between the computed dimer and **5** and **6** is for the Al–N distances, with the calculated distance ca. 3.7% longer. The energies of the monomer and the dimer obtained at the HF/DZP level are −299.87452 and −599.74967 hartrees, which represents a difference in energy between the two monomers and one dimer of only 0.40 kcal/mol in favor of the monomer. This difference is within the limits of crystal packing forces and is consistent with the finding of both dimers (**1**, **5**, and **6**) and monomers (**2**) in the solid.[7]

The trimethylamine adduct of gallane[12] is monomeric in the solid, yet the corresponding alane species, **1**, is dimeric. Like **1**, trimethylaluminum is monomeric in the vapor and dimeric in the solid,[18] although here the bridging is symmetrical and yields four coordinate species whereas in **1** it yields pseudo-five-coordinate species. The compound $HAlMe_2$, however, is dimeric in the gas phase,[19] and for both $AlMe_3$ and $HAlMe_2$ theoretical studies point to the importance of some Al···Al interaction in their dimers,[20] the associated distances being 2.60–2.62 Å[18] and 2.52 Å.[19] The present theoretical study on H_3AlNH_3 indicates that there is minimal Al···Al interaction with a bond index close to 0, in accordance with the much longer Al···Al separations found in **1**, and also **5** and **6**.

Acknowledgment. The financial support provided by the Australian Research Council and the Department of Industry, Technology and Commerce (Australia) is gratefully acknowledged.

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(16) Crystal structure determinations (T = 296 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries); compound **1**: $C_6H_{24}Al_2N_2$, M = 175.2, trigonal, space group $R\bar{3}c$, a = 14.084 (2) Å, α = 90.08 (1)°, U = 2793 Å^3, $F(000)$ = 774; Z = 8, D_{calcd} = 0.84 g·cm^{-3}, μ(Cu Kα) = 15.5 cm^{-1}, specimen 0.2 × 0.20 × 0.05 mm, 849 unique reflections, 322 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 110°. Compound **5**: $C_{18}H_{32}Al_2N_2$, M = 310.4, monoclinic, space group $P2_1/c$, a = 9.313 (1) Å, b = 10.588 (2) Å, c = 10.924 (2) Å, β = 91.09 (1)°, U = 1076.9 Å^3, $F(000)$ = 356; Z = 2, D_{calcd} = 1.02 g·cm^{-3}, μ(Cu Kα) = 11.8 cm^{-1}, specimen 0.25 × 0.30 × 0.30 mm, 1266 unique reflections, 1090 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 110°. Compound **6**: $C_{12}H_{28}Al_2N_2$, M = 127.2, triclinic, space group $P\bar{1}$, a = 6.768 (1) Å, b = 7.400 (1) Å, c = 8.949 (3) Å, α = 79.00 (2)°, β = 71.03 (2)°, γ = 76.95 (1).° U = 409.6 Å^3, $F(000)$ = 140; Z = 1, D_{calcd} = 1.03 g·cm^{-3}, μ(Cu Kα) = 14.3 cm^{-1}, specimen 0.40 × 0.40 × 0.50 mm, 1063 unique reflections, 1021 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 110°. The structures were solved by direct methods and refined by full-matrix least-squares refinement with non-hydrogen atoms anisotropic. Molecules in **1** lie across 2 and $\bar{3}$ symmetry elements with the aluminum atoms disordered with 50% and 33% occupancy sets as shown in Figure 1. For **5** and **6** 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, R' = 0.111, 0.095; 0.039, 0.038; and 0.057, 0.071, for **1**, **5**, and **6**, respectively. For **1** the structure was initially solved and refined in space group $R3c$ to similar agreement factors but with correlation problems.

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Supplementary Material Available: Listing of final atomic parameters, anisotropic thermal parameters, and bond lengths and angles for **1**, **5**, and **6** (8 pages); listing of observed and calculated structure factor amplitudes for **1**, **5**, and **6** (15 pages). Ordering information is given on any current masthead page.

Novel Photochemical Route to the Mitomycin and FR-900482 Series

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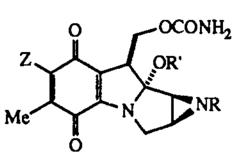
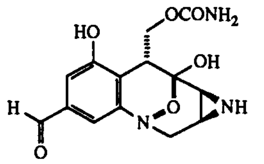
Organic chemists have long been fascinated by the mitomycins.[1,2] The novel structure of these compounds is clearly a contributing factor. Emerging descriptions of mechanisms for their bioactivation[3,4] and increasingly detailed insights into their interactions with nucleic acid receptors[5] continue to fuel interest in the field. The recent isolation of mitomycin variants from natural sources with synthetically challenging structural features[6,7] has served to promote new research in this series. Finally, the fact that mitomycin C is a clinically useful antineoplastic drug[8] provides incentives at the pharmaceutical level for fresh departures. Herein we disclose a new synthetic strategy which has potential for reaching either the mitomycins, the recently discovered FR-900482 (**1**),[9] or congeners of these drugs.

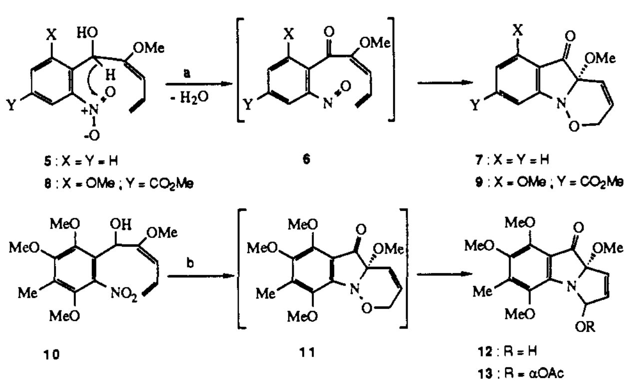


Mitomycins



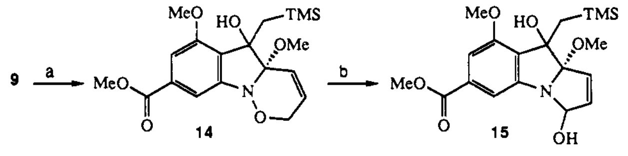
1 = FR-900482

Scheme I[a]



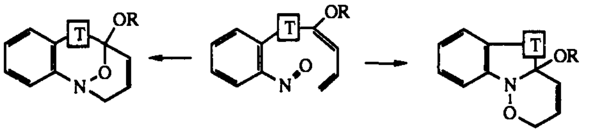
[a](a) 0.01 M in MeOH, hν (366 nm); (b) 0.01 M in MeOH, hν (350 nm).

Scheme II



(a) TMSCH$_2$MgCl, Et$_2$O/PhH.
(b) 0.01M in THF, hν (254nm).

We started with consideration of an intramolecular cycloaddition of a dienyl nitroso system (see generalized system **2**).[10] In principle, such a process could lead to a bridged oxazine derivative (cf. **3**) or to a fused version (cf. **4**). The nature of the outcome would, presumably, be strongly influenced by the nature of the diene and by the character and length of the T "tether".[11]



3 bridged mode **2** T = tether **4** fused mode

In order to address such questions, it would be necessary to develop a route to reach **2**. Our solution contemplated unveiling the nitroso function with the diene already present via a photochemically driven redox reaction of an *o*-nitrobenzyl alcohol prototype.[12] In our opening investigation of this possibility, we examined a system with a minimum C$_1$ tether on the grounds that candidate substrates of this type could be assembled rapidly. Below we demonstrate the feasibility of the photochemical redox route to produce nitroso dienes, and the rather interesting chemistry which ensues therefrom.

Reaction of *o*-nitrobenzaldehyde with 1-methoxy-1-lithiobutadiene[13] generates carbinol **5** (Scheme I). Photolysis of **5**

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