

Inorganica Chimica Acta 259 (1997) 249-255



Structural aspects of tertiary amine adducts of alane and gallane

Philip C. Andrews, Michael G. Gardiner, Colin L. Raston *, Vicki-Anne Tolhurst

Department of Chemistry, Monash University, Clayton, Vic. 3168, Australia

Received 12 September 1996; revised 27 November 1996; accepted 30 December 1996

Abstract

Structures of N-bound alane (AlH₃) and gallane (GaH₃) are reported: the dimethylbenzylamine adduct of gallane, [(PhCH₂(Me)₂NGaH₃], which is monomeric with four-coordinate Ga, and the first chlorine containing amino complex of alane, [ClCH₂CH₂(He)₂NAlH₃]₂, revealing that hydride bridging is favoured over Al-Cl interaction in Al obtaining a five-coordination environment. Also presented is a reinvestigation of the previously poorly defined structural determination of the trimethylamine adduct of gallane, [Me₃NGaH₃].

Keywords: Crystal structures; Alane adducts; Gallane adducts; Amine adducts

1. Introduction

Volatile Lewis base adducts of alane (AlH₃) and gallane (GaH₃) find application in chemical vapour deposition technology (CVD) [1]. The presence of M-H rather than M-C bonds in these compounds reduces the degree of carbonaceous contaminant in the deposited material which can ensure greater reproducibility and more consistent electronic properties [2]. Such Lewis base adducts are also already known to have important applications in organic synthesis as selective reducing agents [3] and in the preparation of transition metal aluminum and gallium hydrides [4,5].

In the solid state a number of structural varieties have been described for tertiary amine and phosphine adducts of alane and gallane. For alane several structural types of these adducts have been identified: (a) four-coordinate species, e.g. [(Quinuclidine)AlH₃] [6], [R₃PAlH₃], R = Bu^t or cyclohexyl, and related bidentate phosphines [7-9]; (b) five-coordinate species, as monomers, e.g. [(Me₃N)₂AlH₃], and polymers, e.g. [(L)AlH₃]_w, L=TMEDA (=tetramethylethylenediamine) [10] and related ligands [11]; (c) hydride bridging species, e.g. [LAIH₃]₂, L = NMe₃, NMe₂CH₂Ph, for which O-donor analogues are also known [12,13]; (d) ionic complexes, e.g. [LAIH₂] + [AIH₄] - [14]. Examples for gallane are much more rare, as a result of their greater thermal instability, but prefer four-coordinate species, e.g. the gallane-rich bridging TMEDA complex [(TMEDA)(GaH₃)₂] and [(Quinuclidine)GaH₃] [15]. The only exception is the polymeric structure of $[LGaH_3]$, L=N,N'-tetramethylpropylenediamine, which is only stable at low temperatures [16].

As part of our on-going interest in such complexes we herein present the crystal structures of a dimethylbenzylamine adduct of gallane, $[(PhCH_2(Me)_2MGaH_3]$ (3), a novel chlorine containing amino complex of alane, $[ClCH_2CH_2CH_2(Me)_2NAH_3]_2$ (1), and a reinvestigation of the previously poorly defined structural determination of the trimethylamine adduct of gallane, $[Me_3NGaH_3]$ (2).

2. Experimental

All manipulations were performed using standard Schlenk techniques in a dried argon gas atmosphere. All solvents were pre-dried over sodium wire prior to reflux over Na-K amalgam under nitrogen gas. Dimethylbenzylamine was distilled and dried over molecular sieves 4 Å. Both Me₃N·HCl and N,N-PhCH₂(Me)₂N were purchased from Sigma-Aldrich Co. PhCH₂(Me)₂N·HCl was prepared from the reaction of the amine and HCl gas in Et₂O. The hydrochloride salts were dried in vacuo prior to use.

2.1. Synthesis of [ClCH2CH2CH2(Me)2NAIH3]2(1)

LiAlH₄ (0.45 g, 11.8 mmol) was dissolved in 60 ml of Et₂O and cooled to -80° C. Solid ClCH₂CH₂CH₂(Me)₂-N·HCl (1.78 g, 12 mmol) was added slowly. On complete addition the reaction mixture was allowed to warm slowly to ambient temperature over 3 h. Gas evolution was visible.

^{*} Corresponding author. Tel.: +61 3 9905 4593; fax: +61 (0)3 9905 9143; e-mail: C.Raston@sci.monash.edu.au

^{0020-1693/97/\$17.00 © 1997} Elsevier Science S.A. All rights reserved Pll \$0020-1693(97)05465-0

Filtration and reduction of the majority of the solvent in vacuo left a clear solution. Colourless plate-like crystals were obtained at -25° C over 24 h. Yield 1.26 g, 83%. Slow decomposition at > 10°C. ¹H NMR (200 MHz, C₂D₅, 288 K): δ 4.10 (broad, s, Al-H), 2.77 (2H, t, CH₂Cl), 2.24 (2H, m, NCH₂), 1.81 (6H, s, NMe), 1.60 (2H, m, CH₂). ¹³C NMR (50.3 MHz, C₆D₆, 283 K): δ 57.4 (CCl), 44.9 (NCH₃), 42.4 (NCH₂), 7.71 (CH₂). Satisfactory elemental analysis was not obtained due to sample decomposition.

2.2. Synthesis of [Me3NGaH3] (2)

This was prepared by a variation of the literature procedure [17]. GaCl₃ (2.70 g, 15.3 mmol) was dissolved in 10 ml of Et₂O and cooled to - 80°C. This was added slowly to an Et₂O (45 ml) suspension of LiH (1.95 g, 278.6 mmol) at - 80°C. The reaction mixture was then allowed to stir and warm slowly to ambient temperature over a period of 12 h. Filtration gave a clear solution of LiGaH4 which was again cooled to - 80°C prior to the slow addition of solid (Me)₃N·HCl (1.34 g, 14.0 mmol) which was accompanied by gas evolution. This was then allowed to warm slowly to ambient temperature where it was stirred for a further 2 h. Filtration and in vacuo removal of Et₂O resulted in a white powder. Crystals suitable for X-ray diffraction were obtained via sublimation over a 3 week period at -25°C. Yield of crystals not optimised. M.p. 70-71°C. ¹H NMR (200 MHz, C₇D₈, 243 K): δ4.65 (broad, s, Ga-H), 1.82 (s, NMe). ¹³C NMR (50.3 MHz, C₇D₈, 243 K): δ45.0 (CH₃). Satisfactory elemental analysis was unable to be obtained due to sample decomposition.

2.3. Synthesis of [(PhCH2(Me)2NGaH3] (3)

LiGaH₄ was prepared as described above. To the solution of LiGaH₄ in Et₂O (80 ml) at -80° C was added slowly solid (PhCH₂(Me)₂N·HCl (2.41 g, 14.1 mmol). The reaction mixture was allowed to warm to ambient temperature at which point it was stirred for a further 2 h. On warming gas evolution was visible. The suspension was filtered and the majority of the Et₂O removed in vacuo. Crystals were obtained over 24 h at -25° C. Yield 1.57 g. M.p. 39–41°C. ¹H NMR (200 MHz, C₈D₆, 298 K): δ 7.05 (3H, m, Ph), 6.84 (2H, m, Ph), 5.07 (2H, broad, s, CH₂), 3.48 (broad, s, Ga-H), 1.93 (6H, s, NMe). ¹³C NMR (50.3 MHz, C₈D₆, 298 K): δ 132.9 (C), 131.5 (o-C), 128.4 (m-C), 128.3 (p-C), 63.5 (CH₂), 45.0 (CH₃). IR (Nujol mull): ν (Ga-H) 1835 cm⁻¹.

Anal. Calc.: C, 51.98; H, 7.76; N, 6.74. Found: C, 51.79; H, 7.66; N, 6.89%.

2.4. X-ray structural determination of [ClCH₂CH₂CH₂(Me)₂NAlH₃]₂(1)

A single crystal was suspended in oil cooled to -30° C in a stream of cold N₂ and mounted on a glass fibre. Intensity measurements were made on a Nicolet R3m/V diffractometer. $C_3H_{15}NCIAI, M = 151.61, T = -100^{\circ}C, monoclinic, space group P2, /a (No. 14), a = 10.221(6), b = 8.629(5), c = 11.186(6) Å, <math>\beta = 114.64^{\circ}, V = 896.8(9) Å^3, F(000) = 328, Z = 4, D_c = 1.123 g cm^{-3}, Mo K\alpha, \lambda = 0.71069 Å, \mu = 4.43 cm^{-1}. A total of 1764 reflections was measured of which 1677 were unique; 1170 with <math>I > 3\sigma(I)$ were used in the refinement, $2\theta_{max} = 50^{\circ}, R = 0.102, R' = 0.085$. The structure was solved using direct methods (SIR92) [18] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms in AlH₃ were refined isotropically, the rest were included in fixed positions. While the accuracy of the structure is low it nevertheless established the atom connectivity and the hydride bridge. All calculations were performed using the teXsan crystallographic software [19].

2.5. X-ray structural determination of [(Me)3NGaH3] (2)

A single crystal was mounted in a glass capillary and stored at -78° C. Data were collected on an Enraf-Nonius CAD4 diffractometer. Crystal size $0.2 \times 0.32 \times 0.3$ mm. C₃H₁₂NGa, M = 131.02, $T = -100^{\circ}$ C, trigonal, hexagonal settings, space group R3m (No. 160), a = 9.3841(8), c = 6.6756(4) Å, $a = \beta = 90^{\circ}$, $\gamma = 114.64^{\circ}$, V = 509.1(1) Å³, F(000) = 204, $Z = 3 D_c = 1.290$ g cm⁻³, Mo Ka, $\lambda = 0.71069$ Å, $\mu = 39.3$ cm⁻¹. $J > 2.5\sigma(J)$, $2\theta_{max} = 50^{\circ}$, R = 0.043, R' = 0.035. The structure was solved using direct methods (XTAL 3.0) [20]. The positions of the methyl H atoms were calculated and constrained in x, y, z, U_{iso} with the unique hydride located and similarly constrained.

2.6. X-ray structural determination of [(PhCH₂(Me)₂NGaH₃] (3)

A single crystal of unknown dimensions was mounted on a glass fibre in oil. Intensity measurements were made on a Nicolet R3m/V diffractometer. C₉H₁₆NGa, M=207.95, $T=-100^{\circ}$ C, orthorhombic, space group *Pbca* (No. 61), a=10.678(7), b=10.699(6), c=18.649(9) Å, V=2130(1) Å³, F(000)=864, Z=8, $D_c=1.297$ g cm⁻³, Mo Ka, $\lambda=0.71069$ Å, $\mu=25.28$ cm⁻¹. A total of 2158 reflections was measured; 1189 with $I>3\sigma(I)$ were used in the refinement, $2\theta_{max}=50^{\circ}$, R=0.020, R'=0.035. The structure was solved using direct methods (SIR92) and expanded using Fourier techniques. The non-hydrogen atoms were refined non-isotropically. All H atoms were performed using the teXsan crystallographic software.

3. Results and discussion

The synthesis and structural determination of the trimethylamine adduct of gallane, [Me₃NGaH₃] (2), first appeared simultaneously from two independent groups in 1963 [21,22]. It was proposed from X-ray powder diffraction

Table

studies and from an imprecise X-ray crystal structure determination that the complex was monomeric with $C_{3\nu}$ symmetry. Since the crystals of 2 decompose above 0°C and that data collection was hindered by decomposition it is understandable that the structure was poorly defined. In an attempt to improve the structural information we grew needle-like crystals of 2 very slowly over 3 weeks in a cold box maintained at -25°C. The crystals were mounted and stored at -78°C before diffraction data were collected at -100°C. This allowed us to refine the structure down to R = 0.035. Fig. 1 reveals that the structure is indeed monomeric with C_{3y} symmetry. We have determined the Ga-N distance to be 2.07(1) Å as opposed to the previously reported distance of 1.97(9) Å. The average N-C distance which was reported as 1.47(6) Å is determined to be 1.456(8) Å, the C-N-C angle being 109.1(6)° which is a great improvement on the rather imprecise 105(10)°. The H1-Ga-N angle is 109.3° while the Ga-N-C angles are found to average 109.8(5)°. Therefore the four-coordinate Ga centre and nitrogen are in almost ideal tetrahedral environments. The Ga-H1 distance is determined to be 1.60 Å. Gallane is known to form a five-coordinate species with Me₃N but only at temperatures below -20°C giving at slightly higher temperatures the mono-adduct and free amine [23]. Bond distances and angles are given in Table 1, and atomic parameters in Table 2.



Fig. 1. Molecular structure of [(Me)₃NGaH₃] (2). Thermal ellipsoids 20%.

Table 1						
Bond lengths	(Å)	and	bond	angles	(°)	in 2

Bond distances (Å)	
Ga-N	2.07(1)
N-C	1.456(8)
Ga-H(1)	1.60
C-H(2)	1.012
Bond angles (°)	
Ga-N-C	109.8(5)
C-N-C	109.1(6)
H(1)-Ga-N	109.3
N-C-H(2)	109.4

Table 2					
Atomic	positional and	l isotropic (displacement	parameters	for 2

Atom	x/a	y/b	zlc	U
Ga	2/3	1/3	0.66666	+0.0612(7)
N	2/3	1/3	0.976(2)	+0.024(3)
С	0.7510(6)	-X + 1	1.050(1)	+0.050(5)
H(1)	0.5741	0.4266	0.5875	0.038
H(2)	0.8678	0.3062	0.9973	0.072
H(3)	0.7519	-X+1	1.1973	0.072

-			•	
- 1.4	sn.	10	•	
	-			

Bond lengths (Å) and bond angles (°) in 3

Ga(1)-N(1)	2.071(3)	C(3)-H(3a)	1.25
Ga(1)-H(1)	1.44(4)	C(3)-H(3b)	0.91
Ga(1)-H(2)	1.55(4)	C(11)-C(12)	1.367(5)
Ga(1)-H(3)	1.58(4)	C(11)-C(16)	1.362(5)
N(1)-C(1)	1.485(5)	C(12)-C(13)	1.407(5)
N(1)-C(2)	1.501(4)	C(12)-H(12)	0.86
N(1)-C(3)	1.481(5)	C(13)-C(14)	1.358(6)
C(1)-C(11)	1.515(5)	C(13)-H(13)	0.95
C(1)-H(1a)	0.84	C(14)-C(15)	1.361(5)
C(1)-H(1b)	1.20	C(14)-H(14)	1.10
C(2)–H(2a)	1.26	C(15)-C(16)	1.405(5)
C(2)–H(2b)	0.94	C(15)-H(15)	1.10
C(2)-H(2c)	1.02	C(16)-H(16)	0.85
C(3)-H(3c)	1.07		
N(1)-Ga(1)-H(1)	105(1)	N(1)-C(3)-H(3c)	106.25
N(1)-Ga(1)-H(2)	97(1)	N(1)-C(3)-H(3a)	115.42
N(1)-Ga(1)-H(3)	102(1)	N(1)-C(3)-H(3b)	110.67
H(1)-Ga(1)-H(2)	113(2)	H(3c)-C(3)-H(3a)	115.10
H(1)-Ga(1)-H(3)	131(2)	H(3c)-C(3)-H(3b)	110.09
H(2)-Ga(1)-H(3)	103(2)	H(3a)-C(3)-H(3b)	99.19
Ga(1)-N(1)-C(1)	108.2(2)	C(1)-C(11)-C(12)	121.2(4)
Ga(1)-N(1)-C(2)	107.4(2)	C(1)-C(11)-C(16)	120.5(4)
Ga(1)-N(1)-C(3)	108.0(2)	C(12)-C(11)-C(16)	118.3(4)
C(1)-N(1)-C(2)	110.8(3)	C(11)-C(12)-C(13)	120.4(4)
C(1)-N(1)-C(3)	110.7(3)	C(11)-C(12)-H(12)	122.59
C(2)-N(1)-C(3)	111.6(3)	C(13)-C(12)-H(12)	116.99
N(1)-C(1)-C(11)	115.0(3)	C(12)-C(13)-C(14)	120.5(4)
N(1)-C(1)-H(1a)	112.39	C(12)-C(13)-H(13)	108.55
N(1)-C(1)-H(1b)	116.45	C(14)-C(13)-H(13)	130.89
C(11)-C(1)-H(1a)	109.41	C(13)-C(14)-C(15)	119.7(4)
C(11)-C(1)-H(1b)	110.24	C(13)-C(14)-H(14)	117.91
H(la)-C(l)-H(lb)	90.71	C(15)-C(14)-H(14)	122.34
N(1)-C(2)-H(2a)	110.44	C(14)-C(15)-C(16)	119.5(4)
N(1)-C(2)-H(2b)	107.24	C(14)-C(15)-H(15)	128.59
N(1)-C(2)-H(2c)	106.87	C(16)-C(15)-H(15)	111.90
H(2a)-C(2)-H(2b)	100.67	C(11)-C(16)-C(15)	121.6(4)
H(2a)C(2)H(2c)	122.47	C(11)-C(16)-H(16)	121.80
H(2b)-C(2)-H(2c)	108.19	C(15)-C(16)-H(16)	115.69

The Ga-N bond distance in 2 is directly comparable with that of 2.071(3) Å found in [PhCH₂(Me)₂NGaH₃] (3), which is also a monomeric tertiary amine adduct as shown in Fig. 2. Important bond distances and angles are given in Table 3, and atomic parameters are given in Table 4. The N-C distances are slightly longer, ranging from 1.481(5) to 1.501(4) Å, with the N-C-N angles being slighter more obtuse, averaging 111.03(30)°. Concomitantly the Ga-N-C angles become more acute, averaging 107.8(2). Fortunately



Fig. 2. Molecular structure of [PhCH₂(Me)₂NGaH₃] (3).

in this structure the hydrides were located and found to have Ga-H distances of 1.44(4), 1.55(4) and 1.58(4) Å which are comparable with all other reported distances.

As stated in Section 1, due to a high degree of thermal instability, in comparison with alane, there are very few gallane complexes which have been structurally authenticated. However further comparisons can be made with the monomeric quinuclidine adduct and the gallane-rich bridged TMEDA complex, [GaH₃N(Me)₂CH₂CH₂(Me)₂NGaH₃] [15,16]. As a result of the greater basicity of quinuclidine over that of TMEDA the quinuclidine adduct is thermally very stable, only decomposing at temperatures >100°C, while the TMEDA adduct decomposes at ~20°C. An analysis of the Ga-N bond lengths illustrates this fact in that in the quinuclidine adduct the bond distance is 2.063(4) Å and in the TMEDA adduct it is 2.094(4) Å. Given the Ga-N bond distances of 2.07(1) and 2.071(3) Å in 2 and 3, respectively, it is then possible to understand their relative stability in solution and in the solid state. The only structurally characterised stable five-coordinate gallane complex is that of [(Me₃)₂N(CH₂)₃N(Me)₂GaH₃]₂ which is polymeric with the ligand bridging the GaH3 units similar to that found in the TMEDA analogue. The greater saturation of the metal centre accounts for the much longer Ga-N bond distances which average 2.36 Å. As is common in related polymeric alane systems, such as in the analogous aluminum compound [15], the hydrides and metal centre become planar in a fivecoordinate trigonal bipyramidal environment.

In comparison to the predominance of four-coordinate species in the solid state for gallane, alane shows a greater degree of structural variety. Two important aspects of this are complexes with five-coordinate bonding environments for Al: (a) from Al:ligand ratios of 1:1 for polydentate ligands and 1:2 for monodentate ligands and also (b) from the existence of hydride bridging which allows for a greater degree of association and has not yet been observed for gallane adducts, but is found in digallane, $H_2Ga(\mu-H)_2GaH_2$ [24]. Thus the analogous alane complex of 2 exists at ambient temperature, i.e. with one Me₃N unit bound to Al but so also does the bis ligated complex, thus giving respectively four- and five-coordinate monomers, while the analogous complex to 3 reveals hydride bridging allowing Al in the 1:1 complex to become five-coordinate.

Such hydride bridging also forms an integral part of the dimeric alane complex $[ClCH_2CH_2CH_2(Me)_2NAIH_3]_2(1)$, the crystal structure of which is shown in Fig. 3. Bond angles and bond lengths are given in Table 5, and atomic parameters in Table 6.

It was of interest to us, given that alane will act as a Lewis acid towards N, P and to a lesser degree O donors, whether it was possible to form a dative bond between Al and Cl. One aspect which appeared to mitigate in our favour was precisely

Table 4 Atomic positional and isotropic displacement parameters for 3

Atom	x	у	z	Beq
Ga(1)	0.94773(5)	-0.01776(4)	0.28683(2)	3.32(1)
N(1)	0.9389(3)	0.0192(3)	0.1780(1)	2.32(7)
C(1)	0.8397(4)	0.1140(4)	0.1658(2)	2.39(10)
C(2)	0.9072(4)	-0.1012(4)	0.1408(2)	3.7(1)
C(3)	1.0626(4)	0.0675(4)	0.1551(2)	3.6(1)
C(11)	0.8178(4)	0.1485(4)	0.0880(2)	2.14(10)
C(12)	0.7290(4)	0.0889(4)	0.0478(2)	3.7(1)
C(13)	0.7121(4)	0.1201(5)	-0.0248(2)	4.2(1)
C(14)	0.7819(4)	0.2117(4)	-0.0556(2)	3.3(1)
C(15)	0.8706(4)	0.2718(4)	-0.0162(2)	3.7(1)
C(16)	0.8875(4)	0.2396(4)	0.0562(2)	3.4(1)
H(la)	0.7709	0.0937	0.1849	5.0978
H(1b)	0.8446	0.2067	0.2022	5.0978
H(1)	1.058(4)	-0.094(3)	0.296(2)	5.9(10)
H(2a)	0.8085	-0.1472	0.1665	5.0978
H(2b)	0.9667	-0.1613	0.1557	5.0978
H(2c)	0.9189	-0.0863	0.0873	5.0978
H(2)	0.824(3)	-0.093(3)	0.292(2)	6(1)
H(3c)	1.0589	0.0751	0.0981	5.0978
H(3a)	1.0993	0.1637	0.1871	5.0978
H(3b)	1.1249	0.0139	0.1683	5.0978
H(3)	0.911(3)	0.113(3)	0.320(2)	5(1)
H(12)	0.6804	0.0319	0.0653	5.0978
H(13)	0.6457	0.0711	-0.0435	5.0978
H(14)	0.7671	0.2311	-0.1127	5.0978
H(15)	0.9356	0.3459	-0.0332	5.0978
H(16)	0.9336	0.2890	0.0805	5.0978

Table 5			
Bond lengths (Å)	and bond angles	(°) in 1	

		,	
Cl(1)-C(3)	1.73(1)	Al(1)-H(2)'	1.99(5)
Al(1)-Al(1)	2.881(4)	N(1)-C(1)	1.485(9)
Al(1)-N(1)	2.068(6)	N(1)-C(4)	1.43(1)
Al(1)-H(1)	1.20(7)	N(1)-C(5)	1.459(9)
AI(1)-H(2)	1.84(3)	C(1)-C(2)	1.47(1)
Al(1)-H(3)	1.40(6)	C(2)-C(3)	1.51(1)
Al(1)-Al(1)-N(1)	139.7(2)	H(2)-Al(1)-H(3)	94(2)
Al(1)-Al(1)-H(!)	105(3)	H(3)-Al(1)-H(3)	65(3)
AI(1)-AI(1)-H(2)	107(1)	Al(1)-H(3)-Al(1)'	116(3)
Al(1)-Al(1)-H(2)	38(2)	Al(1)-N(1)-C(1)	112.5(5)
Al(1)-Al(1)-H(2)'	26(2)	Al(1)-N(1)-C(4)	109.2(4)
N(1)-Al(1)-H(1)	97(3)	Al(1)-N(1)-C(5)	108.5(5)
N(1)-Al(1)-H(2)	95(1)	C(1)-N(1)-C(4)	111.9(6)
N(1)-Al(1)-H(3)	101(2)	C(1)-N(1)-C(5)	106.7(5)
N(1)-Al(1)-H(2)'	166(2)	C(4)-N(1)-C(5)	107.9(7)
H(1)-Al(1)-H(2)'	112(3)	N(1)-C(1)-C(2)	115.6(6)
H(1)-Al(1)-H(3)	123(4)	C(1)-C(2)-C(3)	113.2(6)
H(1)-Al(1)-H(2)	89(3)	Cl(1)-C(3)-C(2)	114.3(6)
H(2)-Al(1)-H(3)	120(3)		

the tendency of Al to become five-coordinate. Thus reactions were carried out with the chlorinated amino ligands $(Me)_2N(CH_2)_nC1$ (n=2 and 3) using the low temperature salt elimination reaction of LiAlH₄ with the hydrochloride salt of the ligand. When n=2 only an oil is formed even at temperatures below -25° C. However when n=3 plate-like crystals are obtainable overnight at -25° C. These crystals

Fig. 3. Molecular structure of [ClCH₂CH₂CH₂(Me)₂NAlH₃]₂ (1).

Table 6 Atomic positional and isotropic displacement parameters for 1

Atom	x	y	z	Beq
Cl (1)	0.7970(3)	0.9153(3)	0.4405(2)	6.18(7)
AI(1)	0.6211(3)	0.4449(3)	0.1143(2)	3.45(5)
N(1)	0.8391(6)	0.4864(6)	0.2166(5)	2.9(1)
C(1)	0.8691(8)	0.6299(9)	0.2968(7)	4.2(2)
C(2)	0.8006(9)	0.7720(9)	0.2247(7)	4.8(2)
C(3)	0.8444(9)	0.9158(9)	0.3086(8)	4.7(2)
C(4)	0.9050(9)	0.4892(10)	0.1266(8)	4.7(2)
C(5)	0.9023(10)	0.3586(10)	0.3081(8)	5.4(2)
H(1)	0.630(7)	0.309(8)	0.093(6)	4(1)
H(la)	0.9702	0.6458	0.3357	5.0849
H(1b)	0.8364	0.6144	0.3640	5.0849
H(2)	0.578(3)	0.474(4)	0.257(3)	-2.5(6)
H(2a)	0.6992	0.7607	0.1919	5.7348
H(2b)	0.8269	0.7844	0.1532	5.7348
H(3)	0.583(6)	0.558(7)	0.016(6)	3(1)
H(3a)	0.9460	0.9259	0.3420	5.6544
H(3b)	0.7998	1.0025	0.2546	5.6544
H(4a)	1.0059	0.5026	0.1737	5.6640
H(4b)	0.8665	0.5726	0.0666	5.6640
H(4c)	0.8863	0.3942	0.0794	5.6640
H(5a)	1.0028	0.3753	0.3551	6.4574
H(5b)	0.8863	0.2641	0.2606	6.4574
H(5c)	0.8587	0.3532	0.3683	6.4574

though are not stable above 0°C and will decompose with gas evolution. Therefore a single crystal was mounted with difficulty at -30° C using a low temperature device utilising a cold N₂ stream obtained by the resistive heating of liquid N₂. The crystal was covered in oil at this temperature, cut to size, cooled to -80° C, and mounted on the diffractometer, where data were collected at -100° C. One major difficulty proved to be in centring the crystal in the X-ray beam due to the opaque nature of the mineral oil at such low temperatures. However data were collected and refined to an R value of 0.105.

As is clear from the crystal structure there is no interaction between the Al centre and the Cl atom. In gaining a fivecoordination environment the Al centre will preferentially form the dimer via hydride bridges, which at first seems surprising given the availability of electrons on Cl as opposed to the weak electrostatic interaction offered by $H^{\delta-}$. One alternative outcome may have been chlorine-hydride exchange which was witnessed recently in the formation of a polymeric species from 2-chloroethylmorpholine hydrochloride and LiAlH₄ [12]. That this exchange occurs at all means that intimate contact between Al and Cl at some time is possible. This may also give a clue as to the elusiveness of the species where n = 2. If with a chloroethyl group exchange is favoured then the mother liquor most likely contains a mixture of compounds.

The structural features are in agreement with those found in other unsymmetrically bridged hydride complexes, i.e. $[{H_2Al(\mu-H)_2L}] L = NMe_3$, PhCH₂(Me)₂N and 1-methyltetrahydropyridine. The terminally bound hydrides have distances of 1.20(7) and 1.40(4) Å with the Al-bridging H distance extending to 1.84 Å. The distance from Al(1) to the bridging hydride intimately bound with the second Al centre (H3') becomes even greater, being 1.99(5) Å. The Al-N distance of 2.068(6) Å is comparable with the distance of 2.063(8) Å found in [Me₃NAIH₃]₂ although the thermal stabilities differ significantly. One explanation for this could be that a nucleophilic attack on the Al centre by Cl is thermally promoted. The free ligand is known to cyclise by this method at temperatures above 30°C.

Acknowledgements

We thank the Australian Research Council, and Karl Byriel and Colin Kennard at the University of Queensland for some data collection.

References

- [1] L.H. Dubois, B.R. Zegarski, M.E. Gross and R.G. Nuzzo, Surf. Sci., 244 (1991) 89; P. Zanella, G. Rossetto, N. Brianese, F. Osoff, M. Porchia, Chem. Mater, 3 (1991) 225; A.A. Melas, US Patent No. 4740 606 (1988); W.L. Gladfelter, D.C. Boyd and K.F. Jensen, Chem. Mater, 1 (1989) 339; D. O'Hare, J.S. Foori, T.C. Page and T.J. Whitaker, J. Chem. Soc., Chem. Commun., (1991) 1445; M.J. Henderson, C.H.L. Kennard, C.L. Raston and G. Smith, J. Chem. Soc., Chem. Commun., (1990) 1203.
- [2] T.H. Baum, C.E. Larson and R.L. Jackson, Appl. Phys. Lett., 55 (1989) 1264; A.T.S. Wee, A.J. Murrell, N.K. Singh and J.S. Foord, J. Chem. Soc., Chem. Commun., (1990) 11.
- [3] E.M. Marlett and W.S. Park, J. Org Chem., 55 (1990) 2968; C.L. Raston, A.F.H. Sui, C.T. Tranter and D.J. Young, *Tetrahedron Lett.*, 32 (1994) 5915.
- [4] G.A. Koutsantonis, F.-C. Lee and C.L. Raston, J. Chem. Soc., Chem. Commun., (1994) 1975; R.A. Fischer, J. Behm, T. Priermeier and W. Sarcherer, Angew. Chem., Int. Ed. Engl., 32 (1993) 746.
- [5] K. Khan, C.L. Raston, B.W. Skelton and A.H. White, unpublished results.
- [6] J.L. Atwood, K.W. Butz, M.G. Gardiner, C. Jones, G.A. Koutsantonis, C.L. Raston and K.D. Robinson, *Inorg. Chem.*, 32 (1993) 3482.
- [7] F.R. Bennet, F.M. Elms, M.G. Gardiner, G.A. Koutsantonis, C.L. Raston and N.K. Roberts, Organometallics, 11 (1992) 1457.
- [8] F.M. Elms, M.G. Gardiner, G.A. Koutsantonis and C.L. Raston, J. Organomet, Chem., 449 (1993) 45.
- [9] M.R. Mason and A.R. Barron, Chemtracts Inorg. Chem., (1992) 179.
- [10] G.J. Palenik, Acta Crystallogr., 17 (1964) 1573.
- [11] J.L. Atwood, F.R. Bennett, C. Jones, G.A. Koutsantonis, C.L. Raston and K.D. Robinson, J. Chem. Soc., Chem. Commun., (1992) 541,
- [12] P.C. Andrews, C.L. Raston, B.W. Skelton and A.H. White, J. Chem. Soc., Chem. Commun., (1997) 245.
- [13] I.B. Gorrell, P.B. Hitchcock and J.D. Smith, J. Chem. Soc., Chem. Commun., (1989) 189.
- [14] J.L. Atwood, C. Jones, C.L. Raston and K.D. Robinson, J. Chem. Soc., Chem. Commun., (1991) 1697.
- [15] J.L. Atwood, S.G. Bott, F.M. Elms, C. Jones and C.L. Raston, *Inorg. Chem.*, 30 (1991) 3793.

- [16] J. Lorbeth, R. Dorn, S. Wocadlo, W. Massa, E.O. Gobel, T. Marschner, H. Protzmann, O. Zsebök and W. Stolz, Adv. Mater., 4 (1992) 576.
- [17] D.F. Shriver and A.F. Shirk, Inorg. Synth., 15 (1977) 43.
- [18] A. Altamore, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, J. Appl. Crystallogr., 26 (1994) 343.
- [19] teXsan, crystal structure analysis package, Molecular Structure Corporation, The Woodlands, TX, 1985 and 1992.
- [20] S.R. Hall and J.M. Stewart (eds.), XTAL User's Manual, Version 3.0, Universities of Western Australia and Maryland, 1990.
- [21] N.N. Greenwood, A. Storr and M.G.H. Wallbridge, Inorg. Chem., 2 (1963) 1036.
- [22] D.F. Shriver and R.W. Parry, Inorg. Chem., 2 (1963) 1039.
- [23] D.F. Shriver and C.E. Nordman, Inorg. Chem., 2 (1963) 1298.
- [24] C.R. Pulham, P.T. Brain, A.J. Downs, D.W.H. Rankin and H.E. Robertson, J. Chem. Soc., Chem. Commun., (1990) 177.