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Reaction of Me_3Ga and Me_3Al with the tertiary-tetraaza analog of adamantane, hexamethylenetetramine ($\text{N}_4\text{-Ada}$). Syntheses and molecular structures of $[(\text{Me}_3\text{M})_n \cdot \text{N}_4\text{-Ada}]$ ($n = 1\text{--}4$, $\text{M} = \text{Ga}$ or Al)

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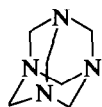
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Abstract

Reaction of Me_3Al or Me_3Ga with hexamethylenetetramine, $\text{N}_4\text{-Ada}$ (Ada = adamantane), in toluene affords the crystalline addition products $[(\text{Me}_3\text{M})_n \cdot \text{N}_4\text{-Ada}]$ ($n = 4$, $\text{M} = \text{Ga}$ (I); $n = 3$, $\text{M} = \text{Ga}$ (II); $n = 3$, $\text{M} = \text{Al}$ (III); $n = 2$, $\text{M} = \text{Ga}$ (IV); $n = 2$, $\text{M} = \text{Al}$ (V); $n = 1$, $\text{M} = \text{Ga}$ (VI)). Compound I crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with unit cell parameters $a = 10.365(3)$, $b = 11.814(6)$, $c = 11.991(6)$ Å, $\alpha = 94.16(4)$, $\beta = 92.56(3)$, $\gamma = 92.44(3)^\circ$, $V = 1461(1)$ Å³, and $D_{\text{calc.}} = 1.36$ g cm⁻³ for $Z = 2$. Least-squares refinement based on 2600 observed reflections converged at $R = 0.075$, $R_w = 0.089$. Compound III crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with unit cell parameters $a = 7.416(2)$, $b = 16.687(6)$, $c = 19.143(6)$ Å, $\beta = 91.71(2)^\circ$, $V = 2368(1)$ Å³, and $D_{\text{calc.}} = 1.00$ g cm⁻³ for $Z = 4$. Least-squares refinement based on 2235 observed reflections converged at $R = 0.085$, $R_w = 0.102$. The mean Ga–N bond distance in I is 2.29 (3) Å, while the corresponding Al–N distance is 2.11 (1) Å. The Ga–N distance of 2.318 (9) Å in I is the longest such distance reported. A molecular mechanics study was used to show that the sequential addition of Me_3M ($\text{M} = \text{Al}$ or Ga) units to $\text{N}_4\text{-Ada}$ significantly affects the relative Lewis basicities of the nitrogen atoms of the amine.

1. Introduction

Adamantane is a uniquely beautiful molecule. The symmetrical fusing of the three chair conformers of cyclohexane, affording the smallest repeating unit of the diamond lattice, results in an unusually rigid system. Moreover, principally due to the virtually perfect fit of the cyclohexane units, adamantane is generally considered to be a strain free molecule [1]. The substitution of nitrogen for carbon at the four tertiary positions in the hydrocarbon skeleton affords the tetraaza-adamantane derivative, hexamethylenetetramine, or $\text{N}_4\text{-Ada}$:

(N₄-Ada)

Importantly, the four nitrogen atoms of $\text{N}_4\text{-Ada}$ reside in exceedingly close proximity to each other as each

given Lewis base site is separated from either of the remaining three by only one $-\text{CH}_2-$ fragment. This spacial arrangement of the four nitrogen atoms affords a unique mechanism by which their comparative Lewis basicities may be examined relative to the sequential approach of Lewis acid units.

Herein we report the syntheses and molecular structures of $[(\text{Me}_3\text{M})_n \cdot \text{N}_4\text{-Ada}]$ ($n = 4$, $\text{M} = \text{Ga}$ (I); $n = 3$, $\text{M} = \text{Ga}$ (II); $n = 3$, $\text{M} = \text{Al}$ (III); $n = 2$, $\text{M} = \text{Ga}$ (IV); $n = 2$, $\text{M} = \text{Al}$ (V); $n = 1$, $\text{M} = \text{Ga}$ (VI)) isolated from reaction of $\text{N}_4\text{-Ada}$ with stoichiometric quantities of Me_3Ga or Me_3Al in toluene. Compounds I and III have been structurally characterized by single crystal X-ray diffraction techniques. Compound I represents the first report of $\text{N}_4\text{-Ada}$ accommodating four Lewis acid units while III is the first organoaluminum derivative of $\text{N}_4\text{-Ada}$ to be structurally characterized.

2. Experimental details

2.1. General

Standard Schlenk technique was employed in conjunction with an inert atmosphere dry box (Vacuum

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Atmospheres HE-43 Dri-Lab). Hexamethylenetetramine (Aldrich Chemical Co.) was used as received. Trimethylaluminum and trimethylgallium (Ethyl Corp.) were used without further purification. ^1H data were recorded on a Bruker AC-300-P NMR spectrometer. X-Ray intensity data for both compounds were collected on a Nicolet R3m/V diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystallographic calculations for **I** and **III** were performed using the SHELXTL [2] system of computer programs. Molecular mechanics and computational studies were performed using the CAChe WorkSystem for the Macintosh computer [3]. Elemental analyses were performed by E + R Microanalytical Laboratories, Corona, NY, USA.

2.2. Syntheses

The same synthetic procedure used for **I** was employed for compounds **II**–**VI**, namely stoichiometric quantities of Me_3Al or Me_3Ga were allowed to react with N_4 -Ada in toluene. Thus, only the procedure for **I** is presented in detail. All compounds were isolated in near quantitative yield (based on the amine).

2.3. $[(\text{Me}_3\text{Ga})_4 \cdot \text{N}_4\text{-Ada}]$ (**I**)

Inside the dry box a reaction vessel was charged with N_4 -Ada (0.700 g, 4.99 mmol) and toluene (20 cm^3). Trimethylgallium (2.00 cm^3 , 20.0 mmol) was

slowly added via syringe. Reaction was immediate affording an abundance of amorphous material. Heating of the reaction vessel in an oil bath (100°C, 24 h) resulted in a homogeneous solution. Cooling to room temperature afforded a multitude of colorless, needle-like crystals. Compound **I** was obtained in quantitative yield (based on the amine) ^1H NMR (CDCl_3): δ 4.41 (s, 12H, $-\text{CH}_2-$); -0.39 (s, 36H, GaCH_3). Anal. Found: C, 35.90; H, 7.69. $\text{C}_{18}\text{H}_{48}\text{Ga}_4\text{N}_4$ calc.: C, 36.06; H, 8.07%. M.p. = 162–164°C (dec).

2.4. $[(\text{Me}_3\text{Ga})_3 \cdot \text{N}_4\text{-Ada}]$ (**II**)

^1H NMR (CDCl_3): δ 4.63 (s, 12H, $-\text{CH}_2-$); -0.90 (s, 27H, GaCH_3). Anal. Found: C, 37.25; H, 7.79. $\text{C}_{15}\text{H}_{39}\text{Ga}_3\text{N}_4$ calc.: C, 37.17; H, 8.11%. M.p. = 128°C (dec).

2.5. $[(\text{Me}_3\text{Al})_3 \cdot \text{N}_4\text{-Ada}]$ (**III**)

^1H NMR (CDCl_3): δ 4.61 (s, 12H, $-\text{CH}_2-$); -0.90 (s, 27H, AlCH_3). Anal. Found: C, 50.83; H, 10.85. $\text{C}_{15}\text{H}_{39}\text{Al}_3\text{N}_4$ calc.: C, 50.54; H, 11.03%. M.p. = 219°C (dec).

2.6. $[(\text{Me}_3\text{Ga})_2 \cdot \text{N}_4\text{-Ada}]$ (**IV**)

^1H NMR (CDCl_3): δ 4.50 (s, 12H, $-\text{CH}_2-$); -0.57 (s, 18H, GaCH_3). M.p. = 116°C.

TABLE 1. Summary of the crystallographic data for $[(\text{Me}_3\text{Ga})_4 \cdot \text{N}_4\text{-Ada}]$ (**I**) and $[(\text{Me}_3\text{Al})_3 \cdot \text{N}_4\text{-Ada}]$ (**III**)

	I	III
Empirical formula	$\text{C}_{18}\text{H}_{48}\text{Ga}_4\text{N}_4$	$\text{C}_{15}\text{H}_{39}\text{Al}_3\text{N}_4$
Color; habit	Colorless; parallelepiped	
Space group	Triclinic, $P\bar{1}$ (no. 2)	Monoclinic, $P2_1/c$ (no. 14)
Unit cell dimensions		
a (\AA)	11.814(6)	7.416(2)
b (\AA)	10.814(6)	16.687(6)
c (\AA)	11.991(6)	19.143(6)
α ($^\circ$)	95.16(4)	
β ($^\circ$)	92.56(3)	91.71(2)
γ ($^\circ$)	92.44(3)	
V (\AA^3)	1461(1)	2368(1)
Molecules per cell	2	4
Molecular weight (g mol^{-1})	599.50	356.44
$D_{\text{calc.}}$ (g cm^{-3})	1.36	1.00
Diffractometer	Nicolet R3m/V	
Radiation	Mo-K α ($\lambda = 0.71073 \text{ \AA}$)	
Temperature ($^\circ\text{C}$)	21	
2θ range ($^\circ$)	3.5–45.0	
Reflections collected	4077	3499
Reflections observed	2600	2235
GOF	2.55	3.50
R	0.075	0.080
R_w	0.089	0.102

2.7. $[(\text{Me}_3\text{Al})_2 \cdot \text{N}_4\text{-Ada}]$ (V)

^1H NMR (CDCl_3): δ 4.63 (s, 12H, $-\text{CH}_2-$); -0.90 (s, 18H, AlCH_3). M.p. = 143°C .

2.8. $[(\text{Me}_3\text{Ga}) \cdot \text{N}_4\text{-Ada}]$ (VI)

^1H NMR (CDCl_3): δ 4.58 (s, 12H, $-\text{CH}_2-$), -0.57 (s, 9H, GaCH_3). M.p. = 128°C .

2.9. Structural solution and refinement

Single crystals of **I** and **III** were mounted in thin-walled glass capillaries under an atmosphere of argon. The structures of both compounds were solved by direct methods. The methyl groups bound to the gallium and aluminum atoms in **I** and **III**, respectively, were found to be disordered over two equivalent sets of positions related by rotation (approximately 15%) about the M–N bonds. The non-hydrogen atoms, other than the half-occupancy carbon atoms modeling the disorder, were refined using anisotropic thermal parameters; the half carbon atoms were refined using isotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions ($d_{\text{C-H}} = 0.96 \text{ \AA}$), and were allowed to ride on the atom to which they were bonded. Isotropic group thermal parameters for **I** were refined for the methylene hydrogen atoms of $\text{N}_4\text{-Ada}$, $U_{\text{iso}} = 0.043$ (8) \AA^2 , and for the half occupancy hydrogen atoms bonded to the disordered methyl carbons, $U_{\text{iso}} = 0.12$ (1) \AA^2 . Similarly, isotropic group thermal parameters for **III** were refined for the methylene hydrogen atoms ($U_{\text{iso}} = 0.042$ (4) \AA^2) and for the half-hydrogen atoms associated with the disordered methyl groups ($U_{\text{iso}} = 0.113$ (7) \AA^2). For **I**, the final cycle of full-matrix least-squares refinement, based on 2600 observed reflections ($I > 3\sigma(I)$), converged at $R = 0.075$, $R_w = 0.089$. The final cycle of full-matrix least-squares refinement for **III**, based on 2235 observed reflections ($I > 3\sigma(I)$), converged at $R = 0.085$, $R_w = 0.102$. Relevant crystallographic data for **I** and **III** are given in Table 1. Final atomic coordinates are given in Tables 2 and 4. Selected bond distances and angles are provided in Tables 3 and 5. Thermal ellipsoid plots of **I** and **III** are given in Fig. 1 and 2, respectively.

3. Results and discussion

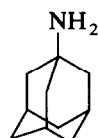
Principally due to their unique capacity to sterically inhibit decomposition pathways by saturating the coordination sphere of the metal, the use of sterically demanding ligands has long been an important feature of organometallic chemistry research. In the context of main group chemistry, sterically demanding amines have provided insight into the extent of π -bonding in organoaluminum compounds [4]. The primary amine

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $[(\text{Me}_3\text{Ga})_4 \cdot \text{N}_4\text{-Ada}]$ (I)

Atoms	x	y	z	U_{eq}^a
Ga(1)	-3930(1)	-1017(1)	2451(1)	70(1)
Ga(2)	-1057(1)	2497(2)	5867(1)	77(1)
Ga(3)	47(1)	2534(1)	851(1)	62(1)
Ga(4)	-5168(1)	4045(1)	2466(1)	66(1)
N(1)	-3098(8)	831(8)	2694(7)	49(3)
N(2)	-1961(8)	2208(9)	4060(7)	52(3)
N(3)	-1526(8)	2209(8)	2069(7)	49(4)
N(4)	-3591(8)	2807(9)	2714(8)	53(3)
C(1)	-2495(11)	1056(11)	3841(10)	56(4)
C(2)	-2069(10)	1039(10)	1900(9)	51(4)
C(3)	-4092(10)	1646(10)	2562(10)	52(4)
C(4)	-971(10)	2378(11)	3213(9)	56(4)
C(5)	-2564(10)	2991(10)	1933(9)	52(4)
C(6)	-2994(11)	2991(11)	3893(9)	56(4)
C(7)	-4628(30)	-1194(26)	3898(23)	71(8)
C(8)	-5191(32)	-920(30)	1051(29)	87(10)
C(9)	-2266(31)	-1791(29)	1982(28)	65(9)
C(7A)	-4010(31)	-1357(27)	4107(24)	74(8)
C(8A)	-5507(30)	-914(28)	1598(27)	81(9)
C(9A)	-2588(39)	-1697(39)	1667(35)	103(15)
C(10)	-2116(36)	3542(35)	6509(34)	104(12)
C(11)	-1199(34)	752(29)	6259(28)	82(9)
C(12)	742(40)	2863(43)	5479(37)	140(15)
C(10A)	-2592(30)	3177(28)	6658(27)	75(8)
C(11A)	-630(36)	1060(32)	6166(31)	93(11)
C(12A)	364(31)	3719(30)	5731(28)	92(9)
C(13)	-1163(35)	2490(34)	-648(30)	85(12)
C(14)	1044(37)	1289(33)	1097(31)	74(12)
C(15)	590(34)	4149(30)	1495(30)	58(9)
C(13A)	-890(27)	2151(27)	-532(24)	56(8)
C(14A)	1317(36)	1393(33)	1391(32)	72(11)
C(15A)	463(47)	3998(41)	1168(37)	97(16)
C(16)	-6248(28)	3709(26)	3682(24)	59(8)
C(17)	-5572(41)	3566(37)	790(36)	69(12)
C(18)	-4044(32)	5547(30)	2545(30)	77(10)
C(16A)	-6497(35)	3285(34)	3426(31)	91(11)
C(17A)	-5725(50)	3701(48)	1037(42)	99(20)
C(18A)	-4236(37)	5383(35)	2949(35)	96(13)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. Atoms C(7)–C(18A) represent equivalent sets ($m = 0.5$) of disordered methyl groups.

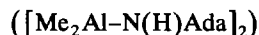
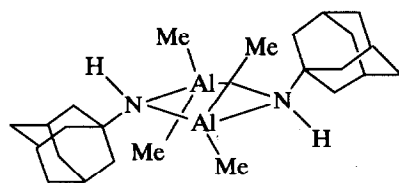
derivative of adamantane, 1-adamantamine, $\text{H}_2\text{N-Ada}$, has recently been brought to the fore of organoaluminum chemistry in a series of studies.

(H₂N-Ada)

Reaction of $\text{H}_2\text{N-Ada}$ with Me_3Al has been shown to afford the organoaluminum dimeric product $[\text{Me}_2\text{Al-N(H)Ada}]_2$ [5].

TABLE 3. Selected bond distances (Å) and angles (°) for [(Me₃Ga)₄·N₄-Ada] (I)

Ga(1)–N(1)	2.306(9)	Ga(1)–C(7)	1.932(29)
Ga(1)–C(8)	2.094(34)	Ga(1)–C(9)	2.067(34)
Ga(1)–C(7A)	2.059(29)	Ga(1)–C(8A)	1.903(31)
Ga(1)–C(9A)	1.888(43)	Ga(2)–N(2)	2.318(9)
Ga(2)–C(10)	1.837(40)	Ga(2)–C(11)	2.147(34)
Ga(2)–C(12)	1.979(42)	Ga(2)–C(10A)	2.051(32)
Ga(2)–C(11A)	1.828(38)	Ga(2)–C(12A)	2.039(33)
Ga(3)–N(3)	2.275(9)	Ga(3)–C(13)	2.141(36)
Ga(3)–C(14)	1.866(40)	Ga(3)–C(15)	2.052(34)
Ga(3)–C(13A)	1.899(28)	Ga(3)–C(14A)	2.043(39)
Ga(3)–C(15A)	1.774(47)	Ga(4)–N(4)	2.263(10)
Ga(4)–C(16)	1.931(30)	Ga(4)–C(17)	2.067(42)
Ga(4)–C(18)	2.074(34)	Ga(4)–C(16A)	2.053(38)
Ga(4)–C(17A)	1.795(49)	Ga(4)–C(18A)	1.858(38)
N(1)–C(1)	1.486(14)	N(1)–C(2)	1.486(14)
N(1)–C(3)	1.452(15)	N(2)–C(1)	1.448(16)
N(2)–C(4)	1.495(14)	N(2)–C(6)	1.461(16)
N(3)–C(2)	1.467(15)	N(3)–C(4)	1.460(14)
N(3)–C(5)	1.459(15)	N(4)–C(3)	1.441(15)
N(4)–C(5)	1.468(14)	N(4)–C(6)	1.515(14)
N(1)–Ga(1)–C(7)	100.7(9)	N(1)–Ga(1)–C(8)	100.8(10)
N(1)–Ga(1)–C(9)	98.4(9)	N(1)–Ga(1)–C(7A)	98.8(9)
N(1)–Ga(1)–C(8A)	104.2(10)	N(1)–Ga(1)–C(9A)	99.9(14)
C(7)–Ga(1)–C(8)	119.5(13)	C(7)–Ga(1)–C(9)	121.5(13)
C(8)–Ga(1)–C(9)	110.1(13)	C(7A)–Ga(1)–C(8A)	118.6(13)
C(7A)–Ga(1)–C(9A)	115.5(16)	C(8A)–Ga(1)–C(9A)	115.2(16)
N(2)–Ga(2)–C(10)	102.0(13)	N(2)–Ga(2)–C(11)	96.5(9)
N(2)–Ga(2)–C(12)	97.8(13)	N(2)–Ga(2)–C(10A)	99.6(9)
N(2)–Ga(2)–C(11A)	101.9(12)	N(2)–Ga(2)–C(12A)	103.2(10)
C(10)–Ga(2)–C(11)	120.6(16)	C(10)–Ga(2)–C(12)	123.7(19)
C(11)–Ga(2)–C(12)	108.5(17)	C(10A)–Ga(2)–C(11A)	117.9(15)
C(10A)–Ga(2)–C(12A)	110.3(13)	C(11A)–Ga(2)–C(12A)	119.9(15)
N(3)–Ga(3)–C(13)	98.0(10)	N(3)–Ga(3)–C(14)	98.9(12)
N(3)–Ga(3)–C(15)	96.7(10)	N(3)–Ga(3)–C(13A)	100.2(9)
N(3)–Ga(3)–C(14A)	97.8(11)	N(3)–Ga(3)–C(15A)	102.3(15)
C(13)–Ga(3)–C(14)	118.6(15)	C(13)–Ga(3)–C(15)	113.4(15)
C(14)–Ga(3)–C(15)	122.3(15)	C(13A)–Ga(3)–C(14A)	117.4(14)
C(13A)–Ga(3)–C(15A)	116.1(18)	C(14A)–Ga(3)–C(15A)	117.4(19)
N(4)–Ga(4)–C(16)	100.3(9)	N(4)–Ga(4)–C(17)	96.0(12)
N(4)–Ga(4)–C(18)	99.4(10)	N(4)–Ga(4)–C(16A)	96.7(11)
N(4)–Ga(4)–C(17A)	102.8(18)	N(4)–Ga(4)–C(18A)	98.7(13)
C(16)–Ga(4)–C(17)	126.0(14)	C(16)–Ga(4)–C(18)	120.3(13)
C(17)–Ga(4)–C(18)	107.0(16)	C(16A)–Ga(4)–C(17A)	105.9(2)
C(16A)–Ga(4)–C(18A)	122.7(16)	C(17A)–Ga(4)–C(18A)	123.4(22)
Ga(1)–N(1)–C(1)	109.9(7)	Ga(1)–N(1)–C(2)	111.2(6)
C(1)–N(1)–C(2)	106.9(8)	Ga(1)–N(1)–C(3)	112.0(6)
C(1)–N(1)–C(3)	107.4(4)	C(2)–N(1)–C(3)	109.3(9)
Ga(2)–N(2)–C(1)	111.1(7)	Ga(2)–N(2)–C(4)	111.3(6)
C(1)–N(2)–C(4)	106.6(9)	Ga(2)–N(2)–C(6)	110.3(6)
C(1)–N(2)–C(6)	108.6(8)	C(4)–N(2)–C(6)	108.9(9)
Ga(3)–N(3)–C(2)	111.3(6)	Ga(3)–N(3)–C(4)	109.2(6)
C(2)–N(3)–C(4)	107.9(9)	Ga(3)–N(3)–C(5)	110.6(7)
C(2)–N(3)–C(5)	109.0(8)	C(4)–N(3)–C(5)	108.9(9)
Ga(4)–N(4)–C(3)	111.5(6)	Ga(4)–N(4)–C(5)	110.2(7)
C(3)–N(4)–C(5)	109.8(9)	Ga(4)–N(4)–C(6)	110.0(7)
C(3)–N(4)–C(6)	107.4(9)	C(5)–N(4)–C(6)	107.8(8)
N(1)–C(1)–N(2)	113.1(10)	N(1)–C(2)–N(3)	111.1(9)
N(1)–C(3)–N(4)	112.8(8)	N(2)–C(4)–N(3)	112.0(8)
N(3)–C(5)–N(4)	111.9(9)	N(2)–C(6)–N(4)	110.6(9)



As determined by single crystal X-ray diffraction, $[\text{Me}_2\text{Al}-\text{N}(\text{H})\text{Ada}]_2$ was shown to assume an accommodating *trans*-conformation while residing about a planar, and slightly asymmetric, Al_2N_2 four-membered ring (Al–N distances: 1.968(2) and 1.958(2) Å). The coordination of the Al atoms was described as distorted tetrahedral as bond angles ranged from 85° to 119°. The mean Al–N bond distance was determined to be 1.962 (3) Å while the mean Al–C bond distance was shown to be 1.958 (1) Å. The Me_3Ga analog was found to be isostructural with $[\text{Me}_2\text{Al}-\text{N}(\text{H})\text{Ada}]_2$. Interestingly, the corresponding product isolated from reaction of the sterically demanding aluminum alkyl trineopentylaluminum with this amine, $[\text{NeO}_2\text{Al}-$

$\text{N}(\text{H})\text{Ada}]_2$, assumed an unexpected *cis*-conformation [6].

The pronounced rigidity of the adamantane skeleton, coupled with the close proximity of the four nitrogen atoms, makes hexamethylenetetramine, $\text{N}_4\text{-Ada}$, an attractive Lewis base. The initial examination of the organoaluminum chemistry of $\text{N}_4\text{-Ada}$ was performed by Krause *et al.* a decade ago [7] in which Me_3M (M = Al, Ga, In, and Tl) was allowed to react with $\text{N}_4\text{-Ada}$ in a variety of solvents. Only the 1:1 and 2:1 Me_3Ga derivatives of $\text{N}_4\text{-Ada}$, $[(\text{Me}_3\text{Ga}) \cdot \text{N}_4\text{-Ada}]$ and $[(\text{Me}_3\text{Ga})_2 \cdot \text{N}_4\text{-Ada}]$, were structurally characterized in this study. The Ga–N distance was determined to be 2.14(2) Å for $[(\text{Me}_3\text{Ga}) \cdot \text{N}_4\text{-Ada}]$ while a value of 2.138(9) Å was found for $[(\text{Me}_3\text{Ga})_2 \cdot \text{N}_4\text{-Ada}]$. It is interesting that regardless of the stoichiometric quantities of Me_3M employed, these workers were unable to isolate a 4:1 addition product, $[(\text{Me}_3\text{M})_4 \cdot \text{N}_4\text{-Ada}]$. This point, in particular, piqued our interest regarding the interaction of Group 13 metal alkyls with $\text{N}_4\text{-Ada}$ and the associated factors affecting product formation.

TABLE 4. Atomic coordinates (10^4) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for $[(\text{Me}_3\text{Al})_3 \cdot \text{N}_4\text{-Ada}]$ (III)

Atoms	x	y	z	U_{eq}^a
Al(1)	1829(3)	5038(1)	1072(1)	54(1)
Al(2)	1872(3)	7148(1)	3505(1)	52(1)
Al(3)	2054(3)	3700(1)	3960(1)	51(1)
N(1)	2907(5)	5169(2)	2108(2)	34(1)
N(2)	2905(5)	6069(3)	3116(2)	35(1)
N(3)	2977(5)	4615(3)	3299(2)	36(1)
N(4)	5606(6)	5309(3)	2849(3)	45(2)
C(1)	2234(7)	5929(3)	2392(3)	38(2)
C(2)	2325(7)	5396(3)	3555(3)	38(2)
C(3)	2304(7)	4508(3)	2564(3)	37(2)
C(4)	4918(7)	5185(4)	2150(3)	48(2)
C(5)	4937(7)	6058(3)	3114(3)	45(2)
C(6)	4998(7)	4656(3)	3297(3)	48(2)
C(7)	2372(24)	3960(11)	805(10)	76(5)
C(8)	–771(24)	5257(11)	1220(10)	72(5)
C(9)	3215(22)	5871(10)	595(9)	71(5)
C(7A)	3125(25)	4047(11)	784(10)	78(5)
C(8A)	–737(22)	4919(11)	1251(9)	67(5)
C(9A)	2435(21)	6056(9)	637(8)	64(4)
C(10)	–699(21)	6976(10)	3368(9)	61(5)
C(11)	2972(29)	7939(14)	2861(12)	80(7)
C(12)	2977(24)	7129(10)	4470(9)	76(5)
C(10A)	–706(23)	7088(10)	3107(10)	70(5)
C(11A)	3338(24)	7933(11)	3034(9)	54(5)
C(12A)	2128(22)	7053(10)	4500(8)	67(4)
C(13)	3012(29)	2710(14)	3590(13)	91(8)
C(14)	3078(26)	4014(12)	4843(10)	72(6)
C(15)	–626(20)	3870(10)	3834(8)	57(4)
C(13A)	3581(27)	2776(12)	3672(10)	67(6)
C(14A)	2594(24)	4193(10)	4919(9)	59(5)
C(15A)	–473(22)	3604(10)	3663(9)	70(5)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. Atoms C(7)–C(15A) represent equivalent sets ($m = 0.5$) of disordered methyl groups.

Herein, we report the syntheses and molecular structures of a series of [(Me₃M)_n · N₄-Ada] addition compounds prepared in high yield from reaction of stoichiometric quantities of Me₃Ga or Me₃Al with N₄-Ada in toluene: (*n* = 4, M = Ga (I); *n* = 3, M = Ga (II); *n* = 3, M = Al (III); *n* = 2, M = Ga (IV); *n* = 2, M = Al (V); *n* = 1, M = Ga (VI)). All of these compounds were readily isolated as crystalline solids.

A number of points are worthy of note concerning structure and bonding in I and III. These molecules are quite symmetrical approaching *T_d* and *C_{3v}* point symmetry (omitting the methyl groups on the metals) for I and III, respectively. The coordination of the metal atoms in these compounds may be described as distorted tetrahedral. Of particular significance, and surely a consequence of the associated steric demands,

TABLE 5. Selected bond distances (Å) and angles (°) for [(Me₃Al)₃ · N₄-Ada] (III)

Al(1)–N(1)	2.127(5)	Al(1)–C(7)	1.916(18)
Al(1)–C(8)	1.992(18)	Al(1)–C(9)	1.970(17)
Al(1)–C(7A)	1.997(19)	Al(1)–C(8A)	1.954(17)
Al(1)–C(9A)	1.951(15)	Al(2)–N(2)	2.101(5)
Al(2)–C(10)	1.938(16)	Al(2)–C(11)	1.997(23)
Al(2)–C(12)	1.998(17)	Al(2)–C(10A)	2.039(17)
Al(2)–C(11A)	1.942(18)	Al(2)–C(12A)	1.914(16)
Al(3)–N(3)	2.110(5)	Al(3)–C(13)	1.941(24)
Al(3)–C(14)	1.906(19)	Al(3)–C(15)	2.015(15)
Al(3)–C(13A)	2.001(20)	Al(3)–C(14A)	2.039(17)
Al(3)–C(15A)	1.949(17)	N(1)–C(1)	1.472(7)
N(1)–C(3)	1.485(7)	N(1)–C(4)	1.491(7)
N(2)–C(1)	1.478(7)	N(2)–C(2)	1.475(7)
N(2)–C(5)	1.507(6)	N(3)–C(2)	1.479(7)
N(3)–C(3)	1.490(7)	N(3)–C(6)	1.500(7)
N(4)–C(4)	1.432(8)	N(4)–C(5)	1.442(7)
N(4)–C(6)	1.467(8)		
N(1)–Al(1)–C(7)	105.6(6)	N(1)–Al(1)–C(8)	100.7(5)
N(1)–Al(1)–C(9)	100.0(5)	N(1)–Al(1)–C(7A)	99.9(5)
N(1)–Al(1)–C(8A)	100.8(5)	N(1)–Al(1)–C(9A)	102.9(5)
C(7)–Al(1)–C(8)	115.0(8)	C(7)–Al(1)–C(9)	115.0(7)
C(8)–Al(1)–C(9)	117.2(7)	C(7A)–Al(1)–C(8A)	116.3(7)
C(7A)–Al(1)–C(9A)	119.0(7)	C(8A)–Al(1)–C(9A)	113.6(7)
N(2)–Al(2)–C(10)	101.2(5)	N(2)–Al(2)–C(11)	100.8(7)
N(2)–Al(2)–C(12)	99.8(5)	N(2)–Al(2)–C(10A)	100.0(5)
N(2)–Al(2)–C(11A)	101.5(6)	N(2)–Al(2)–C(12A)	104.8(5)
C(10)–Al(2)–C(11)	115.6(8)	C(10)–Al(2)–C(12)	119.8(7)
C(11)–Al(2)–C(12)	114.6(8)	C(10A)–Al(2)–C(11A)	113.0(7)
C(10A)–Al(2)–C(12A)	115.6(7)	C(11A)–Al(2)–C(12A)	118.5(7)
N(3)–Al(3)–C(13)	105.5(7)	N(3)–Al(3)–C(14)	101.8(6)
N(3)–Al(3)–C(15)	99.3(5)	N(3)–Al(3)–C(13A)	101.3(6)
N(3)–Al(3)–C(14A)	100.9(5)	N(3)–Al(3)–C(15A)	102.2(5)
C(13)–Al(3)–C(14)	114.7(9)	C(13)–Al(3)–C(15)	116.5(8)
C(14)–Al(3)–C(15)	115.7(7)	C(13A)–Al(3)–C(14A)	117.5(8)
C(13A)–Al(3)–C(15A)	113.8(8)	C(14A)–Al(3)–C(15A)	117.2(7)
Al(1)–N(1)–C(1)	108.1(3)	Al(1)–N(1)–C(3)	111.1(3)
C(1)–N(1)–C(3)	108.2(4)	Al(1)–N(1)–C(4)	113.5(3)
C(1)–N(1)–C(4)	108.3(4)	C(3)–N(1)–C(4)	107.4(4)
Al(2)–N(2)–C(1)	110.6(3)	Al(2)–N(2)–C(2)	109.5(3)
C(1)–N(2)–C(2)	108.6(4)	Al(2)–N(2)–C(5)	112.7(3)
C(1)–N(2)–C(5)	107.7(4)	C(2)–N(2)–C(5)	107.5(4)
Al(3)–N(3)–C(2)	108.9(3)	Al(3)–N(3)–C(3)	112.0(3)
C(2)–N(3)–C(3)	108.3(4)	Al(3)–N(3)–C(6)	112.2(3)
C(2)–N(3)–C(6)	107.3(4)	C(3)–N(3)–C(6)	108.0(4)
C(4)–N(4)–C(5)	109.7(4)	C(4)–N(4)–C(6)	109.4(4)
C(5)–N(4)–C(6)	108.8(5)	N(1)–C(1)–N(2)	112.0(4)
N(2)–C(2)–N(3)	112.3(4)	N(1)–C(3)–N(3)	111.6(4)
N(1)–C(4)–N(4)	112.4(5)	N(1)–C(5)–N(4)	111.5(4)
N(3)–C(6)–N(4)	111.1(4)		

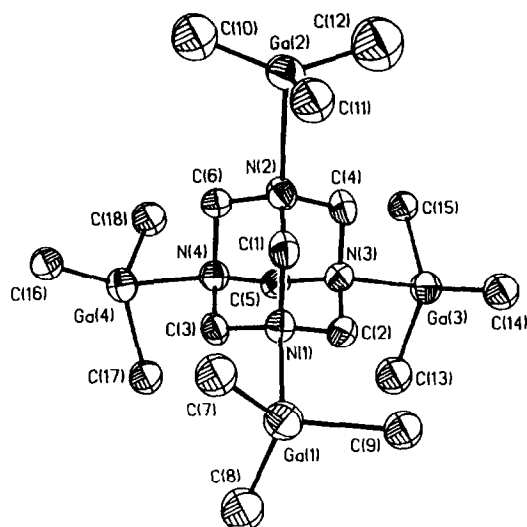


Fig. 1. A thermal ellipsoid plot of [(Me₃Ga)₄·N₄-Ada] (**I**) showing the atom labeling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

are the extremely long M–N bond distances: 2.306(9) Å, 2.318(9) Å, 2.275(9) Å, and 2.263(9) Å for **I** and 2.127(5) Å, 2.101(5) Å, and 2.110(5) Å for **III**. Certainly, the Ga–N bond distances determined for **I** are the longest reported [8*]. The sums of the three C–Ga–C angles in **I** are in the range 351.1–354.3° and 6–7° less for the C–Al–C angles in **III**. Table 6 provides a comparison of M–N (M = Al, Ga) bond distances in addition compounds. In addition, considering the fact that Me₃Al is a stronger Lewis acid than Me₃Ga, it is intriguing that only the 3:1 addition product, [(Me₃Al)₃·N₄-Ada], **III**, was isolated, even in cases where an eight-fold excess of Me₃Al was employed. Furthermore, this appears to be at odds with the fact that, as evidenced by the formation of **I**, the N₄-Ada moiety is readily capable of accommodating four Me₃M units.

It is interesting to consider the possibility that the interaction of a given nitrogen atom of N₄-Ada with a Lewis acid could affect the relative Lewis basicities of the remaining nitrogen atoms. In order to explore this assertion, a molecular mechanics examination of the [(Me₃M)_n·N₄-Ada] system was undertaken. The procedure entailed the construction and minimization of one N₄-Ada unit and four Me₃Al units using the CAChe WorkStation. An ideal Me₃Al unit was placed about each of the four tertiary nitrogen apexes of N₄-Ada at Al···N contacts of 10 Å. This system was then minimized using the PM3 and MOPAC programs.

* Reference number with asterisk indicates a note in the list of references.

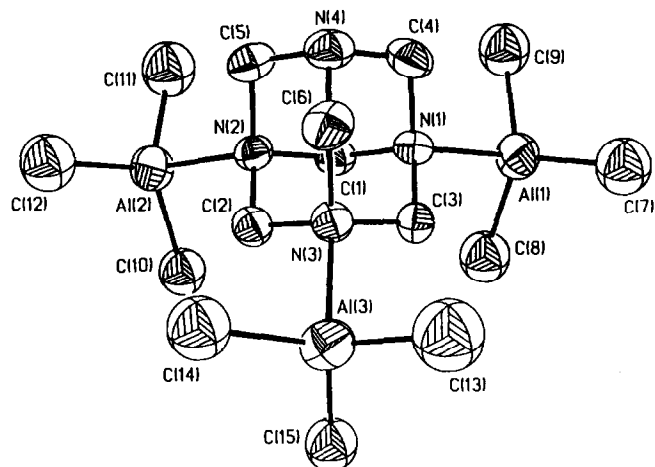


Fig. 2. A thermal ellipsoid plot of [(Me₃Al)₃·N₄-Ada] (**III**) showing the atom labeling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

The Al–N distance was then shortened to 2 Å for one of the Me₃Al–N fragments. This 1:1 complex was then minimized again using MOPAC. Subsequently, each of the remaining three Me₃Al–N bonds was shortened to ca. 2 Å and minimized affording the mono, bis, tris, and tetrakis Me₃Al addition products of N₄-Ada. For each complex the partial charge on both the bound and unbound nitrogen atoms was calculated. This procedure was repeated similarly for the Me₃Ga·N₄-Ada compounds. The resulting data are presented in Table 7.

As additional Me₃Al units are complexed by N₄-Ada, the calculated negative charge for the unbound nitrogen atoms (Table 7) decreases to a greater extent than that for the corresponding Me₃Ga complexes. Indeed, the partial charge on the bound nitrogen atoms actually becomes positive upon complexation of the first Me₃Al unit and increases still further as additional Me₃Al units are complexed. This factor is certainly destabilizing relative to Lewis acid–Lewis base

TABLE 6. Comparison of Me₃M:N (M = Al, Ga) bond distances

Compound	Ga–N (Å)	Al–N (Å)	Reference
[GaMe ₃] ₂ [14]aneN ₄	2.124(4)		[9]
[GaMe ₃] ₂ [14]aneN ₄ [GaMe ₃] ₂	2.126(5)		[10]
[GaMe ₃] ₄ [Me ₄ [14]aneN ₄] ₄	2.19(1)		[10]
[AlMe ₃] ₂ [14]aneN ₄		2.028(3)	[9]
[AlMe ₃] ₂ [14]aneN ₄ [AlMe ₃] ₂		2.042(4)	[11]
[AlMe ₃] ₄ [Me ₄ [14]aneN ₄] ₄		2.098(5)	[12]
[(Me ₃ Ga) ₄ ·N ₄ -Ada] (I)	2.29(2)		This study
[(Me ₃ Al) ₃ ·N ₄ -Ada] (III)		2.11(1)	This study

TABLE 7. Calculated partial charges of nitrogen atoms in N₄-Ada relative to Me₃M (M = Al, Ga) complexation

Number of Me ₃ M units complexed	Partial charge on unbound nitrogen	Partial charge on bound nitrogen
<i>M = Al</i>		
0	-0.135	-
1	-0.122	0.020
2	-0.109	0.024
3	-0.098	0.030
4	-	0.22
<i>M = Ga</i>		
0	-0.135	-
1	-0.112	-0.106
2	-0.112	-0.076
3	-0.111	-0.069
4	-	-0.060

adduct formation. The situation is quite the converse for the Me₃Ga case. The partial charge on the unbound nitrogen atoms decreased to a smaller extent compared to the aluminum case. Furthermore, the partial charge calculated for the bound nitrogen atoms are all negative. The unbound nitrogen in the 3:1 gallium complex has more negative charge than the nitrogen atom in the 3:1 corresponding aluminum complex. Moreover, the calculated partial charges of the bound nitrogens in the Me₃Ga system retain more of a negative charge.

It would thus appear that the capability of N₄-Ada to accommodate Me₃M units is inversely proportional to the relative Lewis acid strength of the metal alkyl; the stronger the Lewis acid the more substantial the M-N interaction. The M-N interaction would be sufficiently substantial in order to effect a decrease of the Lewis basicity of the remaining nitrogen atoms in N₄-Ada. Conversely, if the metal alkyl is a weaker Lewis acid, the M-N interaction would not be as extensive (relative to a stronger Lewis acid) leaving the remaining nitrogen atoms in N₄-Ada largely unaffected. These nitrogen atoms in N₄-Ada would thus retain greater Lewis base character.

4. Supplementary material available

Tables of bond distances and angles, final atomic coordinates, and thermal parameters (21 pages) and a listing of observed and calculated structure factors (26 pages) are available from the authors.

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References and notes

- 1 R. C. Ford and P. R. Schleyer, *Chem. Rev.*, **64** (1964) 277.
- 2 G. M. Sheldrick, *SHELXTL, Crystallographic Computing System, Revision 5.1*, Nicolet Instruments Division, Madison WI, 1986.
- 3 CAChe WorkStation (version 2.7) using MOPAC (version 6.0), 1991, CAChe Scientific, Inc., Beaverton, OR.
- 4 (a) K. M. Waggoner, H. Hope and P. P. Power, *Angew. Chem. Int. Ed. Engl.*, **27** (1988) 1699; (b) M. D. Healy, D. A. Wierda and A. R. Barron, *Organometallics*, **7** (1988) 2543; (c) M. D. Healy, J. W. Ziller and A. R. Barron, *Organometallics*, **10** (1991) 597.
- 5 (a) K. M. Waggoner and P. P. Power, *J. Am. Chem. Soc.*, **113** (1991) 3385; (b) B. Lee, W. T. Pennington and G. H. Robinson, *Inorg. Chim. Acta*, **190** (1991) 173.
- 6 S. J. Schauer, W. T. Pennington and G. H. Robinson, *Organometallics*, **11** (1992) 3287.
- 7 H. Krause, K. S. Stille, H. -D. Hausen and J. Weidlein, *J. Organomet. Chem.*, **235** (1982) 253.
- 8 For a representative discussion of Ga-N bond distances, see [5b] and refs. therein.
- 9 G. H. Robinson, W. T. Pennington, B. Lee, M. F. Self and D. C. Hrcir, *Inorg. Chem.*, **30** (1991) 809.
- 10 B. Lee, W. T. Pennington and G. H. Robinson, *J. Organomet. Chem.*, **396** (1990) 269.
- 11 G. H. Robinson, A. D. Rae, C. F. Campana, and S. K. Byram, *Organometallics*, **6** (1987) 1227.
- 12 G. H. Robinson, H. Zhang and J. L. Atwood, *J. Organomet. Chem.*, **331** (1987) 153.