

Synthesis and characterization of a series of aminogallanes, $[\text{Me}_2\text{GaR}]_2$ The crystal structures of $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ and $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$

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Abstract

Me_3Ga was allowed to react with a series of ten amines at 110°C in toluene to give 75 to 90% yields of the corresponding aminogallanes, $[\text{Me}_2\text{GaR}]_2$ [$\text{R} = \text{NMe}_2, \text{NEt}_2, \text{NPr}_2^{\text{n}}, \text{NPr}_2^{\text{i}}, \text{NBu}_2^{\text{n}}, \text{NBu}_2^{\text{i}}, \text{N}(\text{c-C}_6\text{H}_{11})_2, \text{NC}_4\text{H}_8, \text{NC}_5\text{H}_{10}, \text{NC}_6\text{H}_{12}, \text{and N}(\text{CH}_2\text{CH}_2)_2\text{NMe}$], via a 1,2-elimination of CH_4 . Similarly, $[\text{Me}_2\text{AlNBu}_2]_2$ and $[\text{Me}_2\text{AlN}(\text{c-C}_6\text{H}_{11})_2]_2$ were prepared by an analogous thermolysis reaction. On the other hand, synthesis of $[\text{Me}_2\text{GaNPr}_2]_2$, $[\text{Me}_2\text{GaNBu}_2]_2$, and $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ was achieved by the reaction of Me_2GaCl with the respective lithium amide. A comparison of the ^1H and ^{13}C NMR chemical shifts for the aminogallanes with those previously obtained for the analogous series of aminoalanes indicates a similar sensitivity to the influence of the amide moiety. X-ray crystal structures were determined for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$, which has a slightly puckered four-membered Ga_2N_2 core, and $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$, which has a planar four-membered Ga_2N_2 core. © 1997 Elsevier Science S.A.

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1. Introduction

Although $[\text{Me}_2\text{GaNMe}_2]_2$ [1] was prepared almost 50 years ago from the reaction of Me_3Ga and HNMe_2 , recently there has been considerable interest in aminogallanes owing to their potential use as single-source precursors for the preparation of gallium nitride [2,3]. Several aminogallanes of the type $[\text{R}_2\text{GaNR}'\text{R}'']_2$ have been synthesized by either hydrocarbon or salt elimination reactions. Thermolysis of R_3Ga [4–11] with a primary or secondary amine results in methane elimination and the formation of the corresponding aminogallane, whereas salt elimination typically involves the reaction of R_2GaCl [12–16] with lithium amides. Recently, alternative methods for the preparation of aminogallanes have been reported. The reactions of $\text{Me}_2\text{GaC}_5\text{H}_5$ [17] with amines and $\text{Et}_2\text{GaC}_5\text{H}_5$ [18]

with amines, phosphines, or thiols at or below room temperature results in the formation of the corresponding gallane. Additionally, the reaction of Me_3Ga or Et_3Ga [19] with bulky $\text{Me}_3\text{SnNRR}'$ derivatives under mild thermolysis conditions ($< 60^\circ\text{C}$) produces the corresponding aminogallane with elimination of Me_4Sn or Me_3SnEt respectively.

Our laboratory has reported the synthesis of two homologous series of dimeric aminoalanes, $[\text{Me}_2\text{AlR}]_2$ [20] and $[\text{Bu}_2\text{AlR}]_2$ [21] which were obtained from the thermolysis of Me_3Al or Bu_2AlH with the respective amine, with the exception of $[\text{Bu}_2\text{AlNBu}_2]_2$, which was synthesized by salt elimination. As a continuation of these studies, the thermolysis of Me_3Ga with these amines was investigated to determine the effectiveness of this method toward the synthesis of aminogallanes. Herein we report the synthesis and characterization of a homologous series of aminogallanes, $[\text{Me}_2\text{GaR}]_2$ ($\text{R} = \text{NMe}_2, \text{NEt}_2, \text{NPr}_2^{\text{n}}, \text{NPr}_2^{\text{i}}, \text{NBu}_2^{\text{n}}, \text{NBu}_2^{\text{i}}, \text{NBu}_2^{\text{s}}, \text{N}(\text{CH}_2\text{Ph})_2, \text{N}(\text{c-C}_6\text{H}_{11})_2, \text{NC}_4\text{H}_8, \text{NC}_5\text{H}_{10}, \text{NC}_6\text{H}_{12}$,

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and $\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$), which were synthesized primarily by the thermolysis of Me_3Ga with the respective amine or by the reaction of Me_2GaCl with the respective lithium amide derivative, LiNR_2 . Although several compounds in this series have been reported, they were resynthesized for comparative purposes. The aminoalanes $[\text{Me}_2\text{AlNBu}_2]_2$ and $[\text{Me}_2\text{AlN}(c\text{-C}_6\text{H}_{11})_2]_2$ [22] were synthesized in order to complete the previously reported $[\text{Me}_2\text{AlR}]_2$ [20] series. ^1H and ^{13}C NMR chemical shift data are reported for all compounds and are compared to those of the corresponding $[\text{Me}_2\text{AlR}]_2$. Melting points, IR, MS or cryoscopic molecular weights, and elemental analyses are reported for all new compounds. X-ray structural data have been obtained for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ and $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$ and are compared with literature values for aminoalanes.

2. Experimental

2.1. General procedures

Standard inert atmosphere techniques were used for the synthesis and manipulation of all compounds by use of a high vacuum-line in conjunction with an inert-atmosphere drybox (Vacuum Atmospheres HE-43 Dri-Lab). Hexane and toluene were distilled under an atmosphere of nitrogen over calcium hydride. All the amines (Aldrich) were dried over sodium or KOH and distilled prior to use. Me_3Ga was obtained as a gift from Morton Advanced Materials, Danvers, MA, GaCl_3 from Strem, and butyllithium from Aldrich. Benzene- d_6 (Isotec) was stored over molecular sieves. Me_2GaCl was synthesized by ligand redistribution from the reaction of GaCl_3 with two equivalents of Me_3Ga . $[\text{Me}_2\text{AlN}(c\text{-C}_6\text{H}_{11})_2]_2$ [22], $[\text{Me}_2\text{GaNMe}_2]_2$ [1], $[\text{Me}_2\text{GaNEt}_2]_2$ [17], $[\text{Me}_2\text{GaNPr}^i]_2$ [12], $[\text{Me}_2\text{GaN}^n\text{Bu}_2]_2$ [19], $[\text{Me}_2\text{GaN}(c\text{-C}_6\text{H}_{11})_2]_2$ [19], $[\text{Me}_2\text{GaN}^n\text{C}_4\text{H}_8]_2$ [7], and $[\text{Me}_2\text{GaN}^n\text{C}_5\text{H}_{10}]_2$ [6,7] were prepared as described below.

^1H and ^{13}C NMR spectral data were collected for 0.2 M C_6D_6 solutions using Bruker ARX 300 and DRX 400 NMR spectrometers. Chemical shifts for ^1H and ^{13}C NMR data were measured with respect to the solvent. FTIR data were collected using a Bruker Vector 22 FT spectrometer. Samples were prepared as Kel-F (halocarbon) and Nujol mulls on KBr plates. Low-resolution EI-MS data were obtained using the direct insertion probe on a Finnigan MAT95Q spectrometer at 70 eV. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. Melting points were obtained with a Thomas-Hoover melting point apparatus using sealed capillaries and are uncorrected.

2.2. General synthesis of $[\text{Me}_2\text{GaR}]_2$ dimers

2.2.1. Method A. from Me_3Ga

In a typical synthesis, 1.50 g (13.1 mmol) of Me_3Ga , 13.1 mmol of the respective amine (HNMe_2 , HNEt_2 , HNPr^n , HNBu^n , HNBu^i , $\text{HN}(c\text{-C}_6\text{H}_{11})_2$, HNC_4H_8 , $\text{HNC}_5\text{H}_{10}$, $\text{HNC}_6\text{H}_{11}$, and $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NMe}$), and 30 ml of toluene were mixed at room temperature. The mixture was heated to reflux and the progress of the reaction was monitored by using ^1H and ^{13}C NMR spectroscopy. Products were isolated by recrystallization from the toluene solutions which were cooled to -15°C . Product yields were typically 75–90%.

$[\text{Me}_2\text{GaNMe}_2]_2$ (**1b**): m.p. 34°C (33°C [1]). ^1H NMR: δ -0.24 (s, 12 H, GaCH_3), 2.15 (s, 12 H, NCH_3). ^{13}C NMR: δ -10.28 (GaCH_3), 43.64 (NCH_3).

$[\text{Me}_2\text{GaN}^n\text{Et}_2]_2$ (**2b**): m.p. $39\text{--}40^\circ\text{C}$ ($39\text{--}40.5^\circ\text{C}$ [17]). ^1H NMR: δ -0.18 (s, 12 H, GaCH_3), 0.74 (t, 12 H, NCH_2CH_3), 2.68 (q, 8 H, NCH_2). ^{13}C NMR: δ -8.38 (GaCH_3), 12.05 (NCH_2CH_3), 41.84 (NCH_2).

$[\text{Me}_2\text{GaNPr}^i]_2$ (**3b**): m.p. $53\text{--}55^\circ\text{C}$. ^1H NMR: δ -0.12 (s, 12 H, GaCH_3), 0.74 (t, 12 H, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.25 (m, 8 H, NCH_2CH_2), 2.70 (m, 8 H, NCH_2). ^{13}C NMR: δ -8.63 (GaCH_3), 11.67 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 20.60 (NCH_2CH_2), 51.38 (NCH_2). IR: (cm^{-1}) 2962 (s), 2933 (s), 2906 (w), 2877 (m), 1203 (s), 1142 (m), 1116 (m), 1077 (m), 955 (s), 898 (w), 858 (w), 727 (vs), 679 (w), 587 (s), 561 (m), 531 (w). MS: m/z 383, 385, 387 ($\text{M}^+ - 15$). Anal. Calcd. (found) for $\text{C}_{16}\text{H}_{40}\text{Ga}_2\text{N}_2$: C, 48.05 (48.11); H, 10.08 (9.99); N, 7.00 (7.00).

$[\text{Me}_2\text{GaN}^n\text{Bu}_2]_2$ (**5b**): m.p. $85\text{--}87^\circ\text{C}$. ^1H NMR: δ -0.07 (s, 12 H, GaCH_3), 0.86 (t, 12 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.18 (sext., 8 H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.33 (m, 8 H, NCH_2CH_2), 2.82 (m, 8 H, NCH_2). ^{13}C NMR: δ -8.36 (GaCH_3), 14.30 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 21.03 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 29.62 (NCH_2CH_2), 49.29 (NCH_2). IR: (cm^{-1}) 2959 (s), 2931 (vs), 2859 (m), 1204 (s), 1171 (w), 1144 (w), 1124 (m), 1078 (w), 1026 (w), 904 (w sh), 885 (s), 726 (vs), 678 (w), 596 (w sh), 585 (s), 565 (m), 528 (m). MS: m/z 439, 441, 443 ($\text{M}^+ - 15$). Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{48}\text{Ga}_2\text{N}_2$: C, 52.67 (52.92); H, 10.61 (10.66); N, 6.14 (6.18).

$[\text{Me}_2\text{GaN}^i\text{Bu}_2]_2$ (**6b**): m.p. $72\text{--}73^\circ\text{C}$ ($72\text{--}74^\circ\text{C}$ [19]). ^1H NMR: δ 0.03 (s, 12 H, GaCH_3), 0.85 (d, 24 H, $\text{NCH}_2\text{CH}(\text{CH}_3)_2$), 1.95 (sept., 4 H, NCH_2CH), 2.79 (d, 8 H, NCH_3). ^{13}C NMR: δ -4.80 (GaCH_3), 22.51 ($\text{NCH}_2\text{CH}(\text{CH}_3)_2$), 27.04 (NCH_2CH), 58.02 (NCH_2).

$[\text{Me}_2\text{GaN}(c\text{-C}_6\text{H}_{11})_2]_2$ (**9b**): m.p. $190\text{--}191^\circ\text{C}$ ($190\text{--}191^\circ\text{C}$ [19]). ^1H NMR: δ 0.06 (s, 12 H, GaCH_3), 1.04 (qt, 4 H, $\text{NCHCH}_2\text{CH}_2\text{CH}_{a,v}$), 1.25 (qt, 8 H, $\text{NCHCH}_2\text{CH}_{a,v}$), 1.47 (qd, 8 H, $\text{NCHCH}_{a,v}$), 1.56 (br-d, 4 H, $\text{NCHCH}_2\text{CH}_2\text{CH}_{e,q}$), 1.73 (br-d, 8 H, $\text{NCHCH}_2\text{CH}_{e,q}$), 1.96 (br-d, 8 H, $\text{NCHCH}_{e,q}$), 3.10

(tt, 4 H, NCH_{ax}). ^{13}C NMR: δ -1.81 (GaCH_3), 26.63 ($\text{NCHCH}_2\text{CH}_2\text{CH}_2$), 28.40 ($\text{NCHCH}_2\text{CH}_2$), 38.20 (NCHCH_2), 64.86 (NCH).

$[\text{Me}_2\text{GaNC}_4\text{H}_8]_2$ (**10b**): m.p. 74–75 °C. (64–67 °C [7]). ^1H NMR: δ -0.25 (s, 12 H, GaCH_3), 1.31 (m, 8 H, NCH_2CH_2), 2.62 (t, 8 H, NCH_2). ^{13}C NMR: δ -10.17 (GaCH_3), 24.81 (NCH_2CH_2), 51.19 (NCH_2).

$[\text{Me}_2\text{GaNC}_5\text{H}_{10}]_2$ (**11b**): m.p. 99–101 °C (99–100 °C [7]). ^1H NMR: δ -0.16 (s, 12 H, GaCH_3), 1.25 (br s, 12 H, NCH_2CH_2 and $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.62 (br s, 8 H, NCH_2). ^{13}C NMR: δ -9.17 (GaCH_3), 24.63 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 27.06 (NCH_2CH_2), 51.91 (NCH_2).

$[\text{Me}_2\text{GaNC}_6\text{H}_{12}]_2$ (**12b**): m.p. 76–78 °C. ^1H NMR: δ -0.14 (s, 12 H, GaCH_3), 1.38 (br s, 16 H, NCH_2CH_2 and $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.84 (br s, 8 H, NCH_2). ^{13}C NMR: δ -8.03 (GaCH_3), 27.79 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 28.92 (NCH_2CH_2), 54.34 (NCH_2). IR: (cm^{-1}) 2933 (vs), 2856 (s), 1269 (w), 1203 (s), 1170 (w), 1121 (m), 1092 (w), 1031 (w), 1009 (m), 963 (w), 846 (s), 739 (m), 727 (s), 677 (w), 633 (w), 566 (m), 531 (m). MS: m/z 379, 381, 383 ($\text{M}^+ - 15$). Anal. Calcd. (found) for $\text{C}_{16}\text{H}_{36}\text{Ga}_2\text{N}_2$: C, 48.54 (48.60); H, 9.17 (9.36); N, 7.08 (6.93).

$[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$ (**13b**): m.p. 138–139 °C. ^1H NMR: δ -0.18 (s, 12 H, GaCH_3), 2.00 (s, 6 H, NCH_3), 2.06 (br s, 8 H, $\text{GaNCH}_2\text{CH}_2$), 2.78 (t, 8 H, GaNCH_2). ^{13}C NMR: δ -8.97 (GaCH_3), 46.69 (NCH_3), 50.79 ($\text{GaNCH}_2\text{CH}_2$), 56.30 (GaNCH_2). IR: (cm^{-1}) 2949 (s), 2938 (m), 2904 (s), 2852 (m), 2790 (s), 2764 (w), 2683 (w), 1288 (s), 1205 (m), 1151 (m), 1138 (w), 1117 (m), 1088 (w), 1049 (w), 1005 (s), 912 (w), 877 (s), 776 (w), 727 (vs), 680 (m), 567 (m), 531 (m), 521 (w), 472 (m). MS: m/z 381, 383, 385 ($\text{M}^+ - 15$). Anal. Calcd. (found) for $\text{C}_{14}\text{H}_{34}\text{Ga}_2\text{N}_4$: C, 42.26 (42.57); H, 8.61 (8.72); N, 14.08 (14.36).

2.2.2. Method B, from Me_2GaCl

A solution of Me_2GaCl (2.00 g, 14.8 mmol) in hexane (20 ml) was slowly added to a 50 ml hexane solution of LiNR_2 (14.8 mmol, previously prepared from the reaction of the respective amine and LiBu^n) at -40 °C. LiCl precipitated from the solution upon warming the mixture to room temperature. After stirring overnight at room temperature, the solution was decanted and the remaining solids were washed with hexane. The hexane was then removed in vacuo, leaving a white solid, which was purified by recrystallization from toluene at -15 °C.

$[\text{Me}_2\text{GaNPr}^i]_2$ (**4b**): 71% yield. M.p. 123–124 °C (124 °C [12]). ^1H NMR: δ 0.10 (s, 12 H, GaCH_3), 1.14 (d, 24 H, $\text{NCH}(\text{CH}_3)_2$), 3.54 (sept., 4 H, NCH). ^{13}C NMR: δ -1.64 (GaCH_3), 26.83 ($\text{NCH}(\text{CH}_3)_2$), 52.65 (NCH).

$[\text{Me}_2\text{GaNBu}^i]_2$ (**7b**): 63% yield. M.p. 65–66 °C. ^1H NMR: δ 0.01 (m, 12 H, GaCH_3), 0.82 (t, 12 H, $\text{NCHCH}_2\text{CH}_3$), 1.16 (m, 12 H, NCHCH_3), 1.55 (m, 8

H, NCHCH_2), 3.19 (m, 4 H, NCH). ^{13}C NMR: δ -2.42 (avg., 5 peaks, GaCH_3), 13.43 (avg., 5 peaks, $\text{NCHCH}_2\text{CH}_3$), 23.70 (avg., 6 peaks, NCHCH_3), 34.66 (avg., 4 peaks, NCHCH_2), 60.74 (avg., 6 peaks, NCH). IR: (cm^{-1}) 2969 (s), 2938 (m), 2877 (w), 1203 (m), 1170 (w), 1151 (w), 1129 (m), 1022 (w), 977 (w), 920 (w), 891 (m), 732 (vs), 675 (w), 630 (m), 553 (w), 526 (w). Cryoscopic molecular weight: calcd. mol. wt., 456.05. Observed mol. wt. (molality); 452 (0.097). Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{48}\text{Ga}_2\text{N}_2$: C, 52.67 (53.15); H, 10.61 (11.17); N, 6.14 (5.93).

$[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ (**8b**): 78% yield. M.p. 135–137 °C [23]. ^1H NMR: δ 0.21 (s, 12 H, GaCH_3), 4.15 (s, 8 H, NCH_2), 6.94 (m, 8H, H-2), 7.01 (m, 4H, H-4), 7.03 (m, 8H, H-3) ($\text{NCH}_2\text{C}_6\text{H}_5$). ^{13}C NMR: δ -5.91 (GaCH_3), 54.35 (NCH_2), 127.03, C-4; 128.06, C-3; 129.14, C-2; 137.64, C-1 ($\text{NCH}_2\text{C}_6\text{H}_5$).

2.3. Synthesis of $[\text{Me}_2\text{AlNBu}^i]_2$ and $[\text{Me}_2\text{AlN}(c\text{-C}_6\text{H}_{11})_2]_2$

General procedure: in a typical synthesis, 1.00 g (13.9 mmol) of Me_3Al , 13.9 mmol of the respective amine (HNBu^i , $\text{HN}(c\text{-C}_6\text{H}_{11})_2$), and 20 ml of toluene were mixed at room temperature and the reaction mixture was heated to reflux for 3 days. The resulting solution was concentrated by removal of volatiles under vacuum and then cooled in the freezer to -15 °C, to yield a colorless crystalline product.

$[\text{Me}_2\text{AlNBu}^i]_2$ (**7a**): 85% yield. M.p. 69–71 °C. ^1H NMR: δ -0.26 (m, 12 H, AlCH_3), 0.80 (t, 12 H, $\text{NCHCH}_2\text{CH}_3$), 1.22 (m, 12 H, NCHCH_3), 1.62 (m, 8 H, NCHCH_2), 3.28 (m, 4 H, NCH). ^{13}C NMR: δ -4.9 (AlCH_3), 13.52 (avg., 4 peaks, $\text{NCHCH}_2\text{CH}_3$), 23.73 (avg., 2 peaks, NCHCH_3), 34.89 (NCHCH_2), 59.04 (avg., 5 peaks, NCH). IR: (cm^{-1}) 2970 (s), 2936 (m), 2880 (w), 1201 (s), 1171 (w), 1154 (w), 1119 (s), 1020 (w), 981 (m), 919 (w), 891 (m), 743 (vs), 697 (m), 682 (vs), 667 (m), 566 (w). MS: m/z 355 ($\text{M}^+ - 15$). Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{48}\text{Al}_2\text{N}_2$: C, 64.82 (64.67); H, 13.06 (13.20); N, 7.56 (7.48).

$[\text{Me}_2\text{AlN}(c\text{-C}_6\text{H}_{11})_2]_2$ (**9a**): 75% yield. M.p. 235–236 °C (239 °C [22]). ^1H NMR: δ -0.25 (s, 12 H, AlCH_3), 1.00 (qt, 4 H, $\text{NCHCH}_2\text{CH}_2\text{CHH}_{ax}$), 1.25 (qt, 8 H, $\text{NCHCH}_2\text{CHH}_{ax}$), 1.51 (qd, 8 H, NCHCHH_{ax}), 1.53 (br-d, 8 H, $\text{NCHCH}_2\text{CH}_2\text{CHH}_{eq}$), 1.72 (br-d, 8 H, $\text{NCHCH}_2\text{CHH}_{eq}$), 2.08 (br-d, 8 H, NCHCH_{eq}), 3.22 (tt, 4 H, NCH_{ax}). ^{13}C NMR: δ -4.09 (AlCH_3), 26.47 ($\text{NCHCH}_2\text{CH}_2\text{CH}_2$), 28.46 ($\text{NCHCH}_2\text{CH}_2$), 38.25 (NCHCH_2), 62.97 (NCH).

2.4. Collection of X-ray diffraction data and structure solution.

2.4.1. General considerations

In each of the structural studies an X-ray quality crystal was sealed into a thin-walled glass capillary

under strictly anaerobic conditions. The crystal was then mounted and accurately aligned on an Enraf Nonius CAD4 diffractometer. Intensity data (MoK α , $\lambda = 0.71073 \text{ \AA}$) were collected at room temperature using graphite-monochromatized radiation. All data were corrected for Lorentz and polarization effects as well as for absorption.

All crystallographic calculations were carried out on an IBM-PC, with the use of the Siemens SHELXTL-PC program package [24]. All positional and anisotropic thermal parameters for all non-hydrogen atoms were refined. Refinement continued until convergence was reached with $\Delta/\sigma < 0.001$; the structural solution was then verified by means of a final difference-Fourier synthesis in which no chemically meaningful residuals were found.

2.4.2. $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$

A crystal with the dimensions $0.40 \times 0.30 \times 0.15 \text{ mm}^3$ was chosen for the study. The crystal belongs to the orthorhombic crystal system with the systematic absences hkl for $h+k=2n+1$, $0kl$ for $k=2n+1$ and $h0l$ for $h, l=2n+1$ defining either the centrosymmetric space group $Cmcm$ or one of the non-centrosymmetric space groups $Cm2_1$ or $Ama2$. Intensity statistics favored one of the non-centrosymmetric space groups with the final choice being $Cmc2_1$ (No. 36). This choice was later verified by successful solution and refinement of the crystal structure. All hydrogen atoms were placed in calculated positions in the appropriate staggered geometry and with $d(\text{C-H}) = 0.96 \text{ \AA}$ [25]. The isotropic thermal parameter for each hydrogen atom was set equal to the U_{eq} of the carbon atom to which it was bound. The structure refined to convergence with $R = 3.74\%$ and $R_w = 4.19\%$ for those 922 reflections with $|F_o| > 6\sigma(|F_o|)$ and $R = 4.18\%$ for all data. The absolute structure was determined by the η -refinement procedure [26]. A final difference-Fourier map showed features in the range of $+0.52$ to $-0.38 \text{ e}^- \text{ \AA}^{-3}$.

2.4.3. $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$

A crystal with the dimensions $0.30 \times 0.30 \times 0.20 \text{ mm}^3$ was chosen for the structural study. The crystal belongs to the triclinic crystal system with the possible space groups being the non-centrosymmetric $P1$ (No. 1) or the centrosymmetric $P\bar{1}$ (No. 2). Intensity statistics favored the centrosymmetric case, which was later verified by successful solution and refinement of the crystal structure. The positional and isotropic thermal parameters for all hydrogen atoms were refined. The structure refined to convergence with $R = 2.75\%$ and $R_w = 2.93\%$ for those 1135 unique reflections with $|F_o| > 6\sigma(|F_o|)$ and $R = 2.91\%$ for all data. A difference-Fourier map showed residual electron density in the range of $+0.50$ to $-0.38 \text{ e}^- \text{ \AA}^{-3}$.

3. Results and discussion

The reactions of Me_3Ga with the amines HNMe_2 , HNEt_2 , HNPr_2^{n} , HNBu_2^{n} , HNBu_2^{i} , $\text{HN}(c\text{-C}_6\text{H}_{11})_2$, HNC_4H_8 , $\text{HNC}_5\text{H}_{10}$, $\text{HNC}_6\text{H}_{12}$, and $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NMe}$ at 110°C in toluene were monitored by ^1H and ^{13}C NMR spectroscopy. These resulted in the formation of the corresponding aminogallanes, $[\text{Me}_2\text{GaR}]_2$ in yields ranging from 75–90% via 1,2-elimination of CH_4 . The aminoalanes $[\text{Me}_2\text{AlNBU}_2]_2$ and $[\text{Me}_2\text{AlN}(c\text{-C}_6\text{H}_{11})_2]_2$ were also synthesized by this route. For the reaction of Me_3Ga with $\text{HN}(\text{CH}_2\text{Ph})_2$, peaks assigned to the desired aminogallane, $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$, were observed in the ^1H and ^{13}C NMR spectra while monitoring the progress of the reaction. However, additional spectral peaks suggested that this dimer eliminated one CH_4 molecule per monomer unit and that orthometallation of one phenyl group bound to each nitrogen occurred to yield $[\text{Me}_2\text{GaN}(\text{CH}_2\text{C}_6\text{H}_4)(\text{CH}_2\text{Ph})]_2$ [23]. $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ was then synthesized by the reaction of Me_2GaCl with $\text{LiN}(\text{CH}_2\text{Ph})_2$. The thermolysis of Me_3Ga with the more sterically demanding amines HNPr_2^{i} and HNBu_2^{i} resulted in complicated reactions forming a mixture of products, from which no dimeric aminogallane could be isolated. Thus, $[\text{Me}_2\text{GaNPr}_2^{\text{i}}]_2$ and $[\text{Me}_2\text{GaNBU}_2^{\text{i}}]_2$ were synthesized by the reaction of Me_2GaCl with $\text{LiNPr}_2^{\text{i}}$ and $\text{LiNBU}_2^{\text{i}}$ respectively. This requirement to use salt elimination reactions to prepare these three aminogallanes is in contrast to the preparation of the corresponding aminoalanes, which were synthesized by the thermolysis of the respective $\text{Me}_2\text{Al}/\text{secondary amine}$ adducts [20]. Thus, the thermolysis of mixtures of Me_3Ga with less sterically demanding secondary amines represents an efficient synthetic route to aminogallanes of the type $[\text{Me}_2\text{GaR}]_2$.

All of the compounds in this study were characterized by ^1H and ^{13}C NMR spectroscopy. ^1H and ^{13}C NMR chemical shift data for the methyl groups bound to Al and Ga in the aminoalane and aminogallane series are listed in Table 1. Previous studies with $\text{Me}_3\text{M} \cdot \text{HR}$ [20,27] ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) and $[\text{Me}_2\text{AlR}]_2$ [20] have indicated correlations between the $\text{Me-M}^1\text{H}$ and ^{13}C NMR chemical shifts and the relative steric demands of the secondary amine or amide moieties respectively. This trend is also noted for the aminogallanes, indicating a similar sensitivity to the influence of the amide. There is a good correlation between the aminogallane and aminoalane series $\text{Me-M}^1\text{H}$ ($R = 0.986$) and ^{13}C ($R = 0.999$) NMR chemical shifts, which move downfield together with increasing steric demands of the amide moiety. The $\text{Me-M}^1\text{H}$ and ^{13}C NMR chemical shifts for the aminogallanes are also downfield from those of the corresponding aminoalanes by an average of 0.3 ppm and 1.7 ppm in the ^1H and ^{13}C NMR spectra respectively. The ^1H and ^{13}C NMR chemical shift data

Table 1
Me–M ^1H and ^{13}C NMR data for $[\text{Me}_2\text{AlR}]_2$ and $[\text{Me}_2\text{GaR}]_2$ compounds

R	Number	^1H		^{13}C	
		Al ^a	Ga	Al ^a	Ga
NMe ₂	1	-0.59	-0.24	-11.7	-10.28
NEt ₂	2	-0.50	-0.18	-9.9	-8.38
NPr ₂ ⁿ	3	-0.42	-0.12	-10.2	-8.63
NPr ₂ ⁱ	4	-0.27	0.10	-4.0	-1.64
NBu ₂ ⁿ	5	-0.38	-0.07	-10.0	-8.36
NBu ₂ ⁱ	6	-0.28	0.03	-6.6	-4.80
NBu ₂ ^z	7	-0.26 ^b	0.01	-5.0 ^b	-2.50
N(CH ₂ Ph) ₂	8	-0.08	0.21	-7.6	-5.91
N(<i>c</i> -C ₆ H ₁₁) ₂	9	-0.25 ^b	0.06	-4.1 ^b	-1.81
NC ₄ H ₈	10	-0.57	-0.25	-11.0	-10.17
NC ₅ H ₁₀	11	-0.48	-0.16	-10.5	-9.17
NC ₆ H ₁₂	12	-0.44	-0.14	-9.6	-8.03
N(CH ₂ CH ₂) ₂ NMe	13	-0.50	-0.18	-10.4	-8.97

^a Data obtained from Ref. [20] except where noted.

^b This work.

for the amide moiety in a given aminogallane is consistent with that reported for the corresponding aminoalane, with the ^{13}C NMR chemical shift of the carbon directly attached to nitrogen being on the average 2 ppm further downfield for the aminogallane.

The ^1H NMR spectra for $[\text{Me}_2\text{GaN}(\textit{c}\text{-C}_6\text{H}_{11})_2]_2$ [19] and $[\text{Me}_2\text{AlN}(\textit{c}\text{-C}_6\text{H}_{11})_2]_2$ suggest that the cyclohexyl rings are in a locked conformation. Separate ^1H NMR resonances are observed for the axial and equatorial protons on each carbon in the cyclohexyl ring. Assignments have been made based on the observations that (1) J_{HH} in cyclohexyl derivatives follow the order $^3J_{\text{ax-ax}} \approx ^2J_{\text{ax-eq}} > ^3J_{\text{ax-eq}} \approx ^3J_{\text{eq-eq}}$ and (2) $\delta_{\text{H}}(\text{axial}) < \delta_{\text{H}}(\text{equatorial})$ for protons on a given carbon [28].

The dimeric compound $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ crystallized with four discrete molecules in the unit cell. The labeling of the atoms is provided in Fig. 1. Selected bond distances and angles are collected in Table 2. The molecule possesses mirror symmetry, with the atoms Ga(1), Ga(2), C(1), C(2), C(3), C(4), H(1A), H(2A), H(3A), H(4A) lying on a crystallographic mirror plane. The four-membered Ga₂N₂ core is slightly puckered,

Table 2
Selected bond lengths (Å) and angles (deg) for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$

Ga(1)···Ga(2)	2.887(2)	Ga(1)–N(1)	2.045(6)
Ga(1)–C(1)	1.956(16)	Ga(1)–C(2)	1.968(12)
Ga(1)–N(1A)	2.045(6)	Ga(2)–N(1)	2.042(6)
Ga(2)–C(3)	1.937(13)	Ga(2)–C(4)	2.004(15)
Ga(2)–N(1A)	2.042(6)	N(1)–C(10)	1.494(11)
N(1)–C(20)	1.494(12)		
N(1)–Ga(1)–N(1A)	89.9(3)	Ga(1)–N(1)–Ga(2)	89.9(2)
N(1)–Ga(2)–N(1A)	90.1(3)	N(1)–Ga(1)–C(1)	109.4(4)
N(1)–Ga(1)–C(2)	111.0(4)	C(1)–Ga(1)–C(2)	121.6(7)
C(1)–Ga(1)–N(1A)	109.4(4)	C(2)–Ga(1)–N(1A)	111.0(4)
N(1)–Ga(2)–C(3)	109.9(4)	N(1)–Ga(2)–C(4)	111.5(4)
C(3)–Ga(2)–C(4)	119.9(8)	C(3)–Ga(2)–N(1A)	109.9(4)
C(4)–Ga(2)–N(1A)	111.5(4)	Ga(1)–N(1)–C(10)	114.0(5)
Ga(2)–N(1)–C(10)	112.4(4)	Ga(1)–N(1)–C(20)	112.9(4)
Ga(2)–N(1)–C(20)	114.7(5)	C(10)–N(1)–C(20)	111.3(5)
N(1)–C(10)–C(11)	116.5(6)	N(1)–C(20)–C(21)	115.9(6)

with an angle of fold about the N(1)···N(1A) axis of 2.7° as defined by the intercept of the N(1)–Ga(1)–N(1A) and N(1)–Ga(2)–N(1A) planes. The distances associated with the molecular core are Ga(1)–N(1) = Ga(1)–N(1A) = 2.045(6) Å and Ga(2)–N(1) = Ga(2)–N(1A) = 2.042(6) Å. The cross-ring distances of Ga(1)···Ga(2) = 2.887(2) Å and N(1)···N(1A) = 2.890(2) Å suggest no bonding interactions. The internal angles of the Ga₂N₂ ring are N(1)–Ga(1)–N(1A) = 89.9(3)°, N(1)–Ga(2)–N(1A) = 90.1(3)° and Ga(1)–N(1)–Ga(2) = Ga(1)–N(1A)–Ga(2) = 89.9(2)°. These distances and angles indicate that the Ga₂N₂ core adopts a slightly folded square geometry.

The interligand angles about each gallium atom are C(1)–Ga(1)–C(2) = 121.6(7)° and C(3)–Ga(1)–C(4) = 119.9(8)°. Each nitrogen atom has two benzyl groups bound to it with the interligand angle C(10)–N(1)–C(20) = 111.3(5)°. These ligands are arranged in such a fashion that the plane formed by the atoms C(10)–N(1)–C(20) intersects the mean plane through the Ga₂N₂ core at 93.3°. The benzyl ligands adopt a staggered conformation with the torsion angle C(11)–C(10)–C(20)–C(21) = 76.4°. The planes defined by the

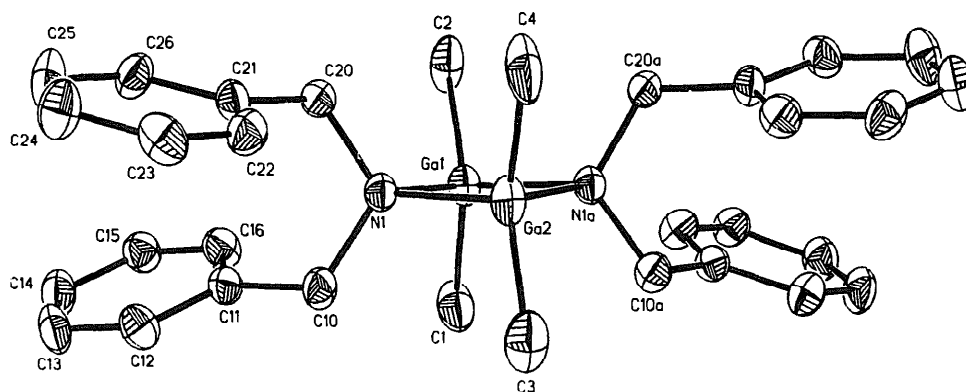


Fig. 1. Molecular structure and atom numbering scheme for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$.

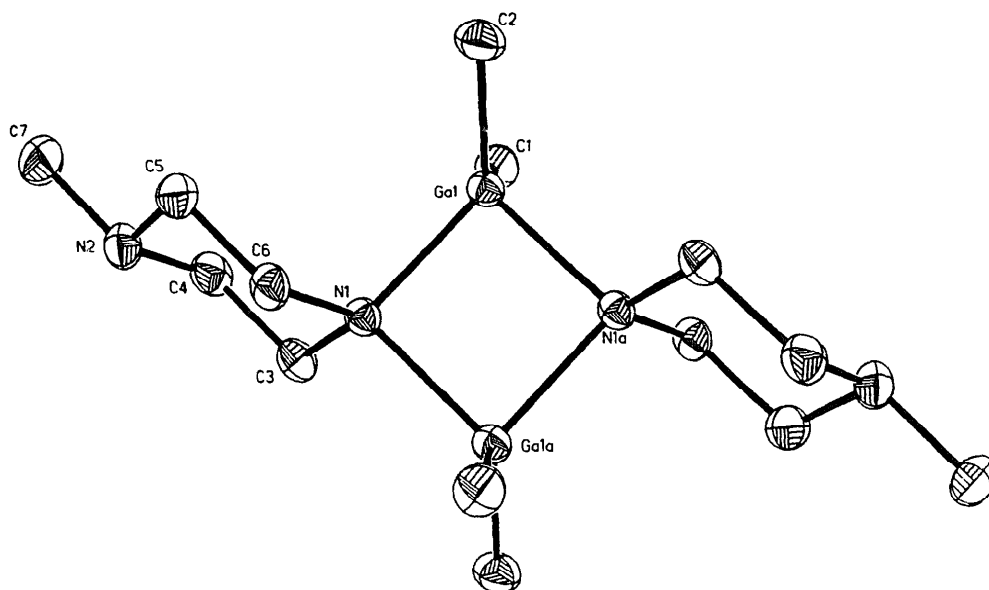


Fig. 2. Molecular structure and atom numbering scheme for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$.

phenyl units of the benzyl groups intercept at an angle of 24.9° . The overall arrangement of the benzyl ligands about the molecular core give this molecule a 'biplane-like' appearance.

The dimeric compound $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$, crystallized with one molecule per unit cell. This dimeric molecule possesses precise C_i symmetry with the four-membered Ga_2N_2 ring structure centered about the inversion center $(0,0,\frac{1}{2})$. This symmetry denotes that the four-membered molecular core must be strictly planar. Thus, the structure adopted, by the dimer, is isomorphous with the corresponding aluminum derivative, $[\text{Me}_2\text{AlN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$ [21]. The labeling of the atoms is provided in Fig. 2. Selected bond distances and angles are collected in Table 3. The interatomic distances within this four-membered core are $\text{Ga}(1)\text{--N}(1) = \text{Ga}(1\text{A})\text{--N}(1\text{A}) = 2.022(2) \text{ \AA}$ and $\text{Ga}(1\text{A})\text{--N}(1) = \text{Ga}(1)\text{--N}(1\text{A}) = 2.042(2) \text{ \AA}$, with the cross-ring distance $\text{Ga}(1) \cdots \text{Ga}(1\text{A}) = 2.932(2) \text{ \AA}$. The internal angles as-

sociated with the molecular core are $\text{Ga}(1)\text{--N}(1)\text{--Ga}(1\text{A}) = \text{Ga}(1)\text{--N}(1\text{A})\text{--Ga}(1\text{A}) = 92.4(1)^\circ$ and $\text{N}(1)\text{--Ga}(1)\text{--N}(1\text{A}) = \text{N}(1)\text{--Ga}(1\text{A})\text{--N}(1\text{A}) = 87.6(1)^\circ$. A structural comparison of $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$ with $[\text{Me}_2\text{AlN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$ indicates the two are very similar, with the exception of differences in bond distance and angles about gallium due to its increased size. For $[\text{Me}_2\text{AlN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$, the Al–N bond distances are $1.968(1) \text{ \AA}$ and $1.980(2) \text{ \AA}$, and the internal angles are $\text{N--Al--N} = 88.67(6)^\circ$ and $\text{Al--N--Al} = 91.33(6)^\circ$ [21]. The six-membered ring amide fragments, $\text{--N}(\text{CH}_2\text{CH}_2)_2\text{NMe}$, in the two structures are nearly identical.

A comparison of Ga–N and Ga–C bond distances for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ and $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$ with those of similar aminogallane derivatives indicates that they are well within the range of values reported for these types of compound [4,5,9,13,15,16,19,29]. Internal Ga_2N_2 ring angles for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{Ph})_2]_2$ are similar to those for $[\text{Me}_2\text{GaN}(c\text{-C}_6\text{H}_{11})_2]_2$ [19], $[\text{Me}_2\text{GaN}(\text{Pr}^i)\text{SnMe}_3]_2$ [19], and $[\text{MeGaN}(\text{CH}_2\text{C}_6\text{H}_4)(\text{CH}_2\text{Ph})_2]$ [23], with all Ga–N–Ga and N–Ga–N angles ranging from $89.3\text{--}90.7^\circ$. However, several compounds of the type $[\text{R}_2\text{GaN}(\text{H})\text{R}']_2$ [4,5,9,15] have Ga_2N_2 cores that are slightly elongated along the $\text{Ga} \cdots \text{Ga}$ axis, which produces Ga–N–Ga and N–Ga–N angles that range from $93.6\text{--}98.3^\circ$ and $81.7\text{--}86.7^\circ$ respectively. $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$ has internal Ga_2N_2 ring angles that lie between these ranges with Ga–N–Ga and N–Ga–N angles of $92.4(1)^\circ$ and $87.6(1)^\circ$ respectively. The structural data for related aminoalanes derived from secondary amines has been summarized recently [21,30]. An examination of structural and steric trends in these and other aminoalanes has been published [30].

Table 3
Selected bond lengths (\AA) and angles (deg) for $[\text{Me}_2\text{GaN}(\text{CH}_2\text{CH}_2)_2\text{NMe}]_2$

$\text{Ga}(1) \cdots \text{Ga}(1\text{A})$	2.932(1)	$\text{Ga}(1)\text{--N}(1)$	2.022(2)
$\text{Ga}(1)\text{--N}(1\text{A})$	2.042(2)	$\text{Ga}(1\text{A})\text{--N}(1)$	2.042(2)
$\text{Ga}(1\text{A})\text{--N}(1\text{A})$	2.022(2)	$\text{Ga}(1)\text{--C}(1)$	1.962(6)
$\text{Ga}(1)\text{--C}(2)$	1.964(6)	$\text{N}(1)\text{--C}(3)$	1.477(5)
$\text{N}(1)\text{--C}(6)$	1.485(5)		
$\text{Ga}(1)\text{--N}(1)\text{--Ga}(1\text{A})$	92.4(1)	$\text{N}(1)\text{--Ga}(1)\text{--N}(1\text{A})$	87.6(1)
$\text{N}(1)\text{--Ga}(1)\text{--C}(1)$	112.5(2)	$\text{N}(1)\text{--Ga}(1)\text{--C}(2)$	112.1(2)
$\text{C}(1)\text{--Ga}(1)\text{--C}(2)$	120.0(2)	$\text{C}(1)\text{--Ga}(1)\text{--N}(1\text{A})$	109.3(2)
$\text{C}(2)\text{--Ga}(1)\text{--N}(1\text{A})$	110.6(2)	$\text{Ga}(1)\text{--N}(1)\text{--C}(3)$	116.8(2)
$\text{Ga}(1)\text{--N}(1)\text{--C}(6)$	115.9(2)	$\text{C}(3)\text{--N}(1)\text{--C}(6)$	106.6(3)
$\text{C}(3)\text{--N}(1)\text{--Ga}(1\text{A})$	112.1(2)	$\text{C}(6)\text{--N}(1)\text{--Ga}(1\text{A})$	112.7(2)
$\text{N}(1)\text{--C}(3)\text{--C}(4)$	112.7(3)	$\text{N}(1)\text{--C}(6)\text{--C}(5)$	112.3(4)

4. Supplementary material

ORTEP drawings, X-ray data collection parameters, tables of atomic positions, thermal parameters, bond distances and angles, and structure factor tables are available.

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