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Synthesis of Substituted Aminogallanes by Alkyltrimethyltin Elimination

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Alkyltrimethyltin elimination reactions of R_3Ga (R = Me, Et) with $R''R'NSnMe_3$ (R'' = *i*-Bu, $SnMe_3$, C_6H_{11} and R' = *i*-Bu, *i*-Pr, C_6H_{11}) have been investigated. The aminogallanes $[Me_2GaN(i\text{-}Bu)_2]_2$, $[Et_2GaN(i\text{-}Bu)_2]_2$, $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$, $[Me_2GaN(C_6H_{11})_2]_2$, and $[Et_2GaN(C_6H_{11})_2]_2$ were isolated in 88.6, 68.6, 69.1, 81.0, and 80.4% yields, respectively. X-ray crystallographic studies of $[Et_2GaN(i\text{-}Bu)_2]_2$, $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$, $[Me_2GaN(C_6H_{11})_2]_2$, and $[Et_2GaN(C_6H_{11})_2]_2$ indicate that the four aminogallanes are dimeric in the solid state. The four-membered $(Ga-N)_2$ rings in $[Et_2GaN(i\text{-}Bu)_2]_2$ and $[Et_2GaN(C_6H_{11})_2]_2$ (molecules 1 and 2) are nonplanar with fold angles on the Ga···Ga diagonals of 148.7(3) and 146.3(3), 147.7 (3)°. All five aminogallanes exist as dimers in benzene solutions. The ^1H and ^{13}C NMR spectra are reported and discussed.

Introduction

Traditionally, the alkane elimination (eq 1) reaction has been utilized to prepare the substituted aminogallanes $R_2GaNR'R''$ (R and R'' = alkyl or aryl and R' = H, alkyl, or aryl). Elimination reactions between Me_3-

$$R_3Ga + HNR'R'' \rightarrow R_2GaNR'R'' + RH \qquad (1)$$

Ga and 10 different primary amines have been reported.[2a−f] Typically, toluene solutions of the reactants, the reactants in sealed tubes, or the Lewis acid−base adducts of the reactants were heated at temperatures from 100 to 160 °C for periods of 7−24 h and the resulting aminogallanes were isolated in yields that varied from 67 to 100%. Reactions of Me_3Ga with secondary[2f,g] or heterocyclic[2h] amines also have been found to proceed under similar reaction conditions with comparable yields. Examples of elimination reactions that have involved trialkylgallium compounds other than Me_3Ga include those of Et_3Ga with ethyleneimine,[2g] $(PhMe_2CCH_2)_3Ga$ with H_2NPr,[2i] Et_3Ga or $(i\text{-}Bu)_3Ga$ with piperidine,[2j] Bu_3Ga with $HNEt_2$,[2k] $(c\text{-}C_3H_5)_3Ga$ with ethyleneimine,[2l] and $(i\text{-}Pr)_3Ga{\cdot}OEt_2$ with $HN(i\text{-}Pr)_2$.[2m] The first three reactions required temperatures of 120 °C or above for a period of several days or until gas evolution had ceased. The product $[(PhMe_2CCH_2)_2GaN(H)Pr]_2$ was obtained in 83% yield. In the case of the $Bu_3Ga/HNEt_2$ reaction, the reactants were heated to boiling for 1.5 h. Interestingly, the reactions of $(c\text{-}C_3H_5)_3Ga$ with ethyleneimine and $(i\text{-}Pr)_3Ga{\cdot}OEt_2$ with $HN(i\text{-}Pr)_2$ in benzene proceeded at or below room temperature and the aminogallanes were isolated in 85 and 90% yields. Also, $Me_2Ga\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}(OEt_2)$ was obtained in 73% yield from the reaction of Me_3Ga (prepared *in situ*) with 2-(benzylamino)pyridine in diethyl ether at room temperature.[2n] The alkane elimination reaction offers a simple, single-step synthetic route to aminogallanes. Generally, this synthetic procedure does not require a solvent and the yields are high. However, in most cases temperatures above 100 °C are needed to effect the formation of the aminogallane.

A number of monomeric[3ab] and dimeric[3c−g] aminogallanes have been prepared by LiCl elimination (eqs 2 and 3). In these examples hexane, diethyl ether, or hexane/

$$R_2GaCl + LiNR'R'' \rightarrow R_2GaNR'R'' + LiCl \qquad (2)$$

$$Cl_2GaNR'_2 + 2LiMe \rightarrow Me_2GaNR'_2 + 2LiCl \qquad (3)$$

diethyl ether solutions of the reactants were mixed at or below 0 °C and the resulting mixtures were stirred at room temperature or heated for a period of 4−18 h. The yields varied from 52 to 86%. This synthetic method offers the advantage of a facile, low-temperature pathway to the preparation of aminogallanes with bulky

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substituents on both the gallium and nitrogen atoms. The monomeric aminogallanes ($(t\text{-Bu})_2GaN(1\text{-Ad})SiPh_3$ and $Trip_2GaNPh_2$ (1-Ad = 1-adamantyl; Trip = 2,4,6-triisopropylphenyl) were isolated in 67 and 62% yields.[3a] However, the procedure requires several steps, the yields are usually lower than the yields in alkane elimination reactions, and solvents are needed.

Recently, $Me_2Ga(C_5H_5)$ has been found to undergo a cyclopentadiene elimination reaction (eq 4) with several primary and secondary amines.[4] These elimination

$$Me_2Ga(C_5H_5) + HNR'R'' \rightarrow Me_2GaNR'R'' + C_5H_6 \tag{4}$$

reactions occurred overnight at or below room temperature in benzene or pentane solutions, and the resulting aminogallanes were obtained in yields of 63−90%. Like the alkane elimination reaction, the cyclopentadiene elimination reaction provides a simple, single-step synthetic route to aminogallanes. Unlike the alkane elimination reaction, however, reaction temperatures above 100 °C are not required. However, the elimination of cyclopentadiene appears to be inhibited when the amine has bulky substituents. No reaction was observed between $Me_2Ga(C_5H_5)$ and dicyclohexylamine, 2,4,6-tri-*tert*-butylaniline, or 2,2,4,4-tetramethylpiperidine.

As an extension of our studies of metathetical reactions between substituted gallanes and substituted aminosilanes,[5] the alkyltrimethyltin elimination reactions of Me_3Ga or Et_3Ga with $R''R'NSnMe_3$ were investigated. Exothermic reactions of $(n\text{-Bu})_3B$, Ph_3B, or Et_3Al with Me_2NSnMe_3 in diethyl ether, light petroleum ether, or benzene solvents have been reported, and the products $(n\text{-Bu})_2BNMe_2$, Ph_2BNMe_2, and $(Et_2AlNMe_2)_2$ were isolated in 86, 59, and 50% yields.[6] In addition, $t\text{-Bu(H)NSi(Me}_2)N(t\text{-Bu})GaMe_2$ was prepared in 94% yield by allowing $GaMe_3$ to react with $t\text{-Bu(H)NSi(Me}_2)N(t\text{-Bu})SnMe_3$ in benzene at 40 °C.[7] These results suggest that the alkyltrimethyltin elimination reaction may afford a simple, single-step, low-temperature pathway to substituted aminogallanes.

Experimental Section

Materials and General Procedures. Trimethylgallium, triethylgallium, and trimethyltin chloride were purchased from Strem Chemicals and used without further purification. Diisobutylamine, isopropylamine, and dicyclohexylamine (Aldrich Chemical Co.) were distilled from calcium hydride prior to use. The compounds $(i\text{-Bu})_2NSnMe_3$, $i\text{-PrN(SnMe}_3)_2$, and $(C_6H_{11})_2NSnMe_3$ were prepared by published procedures.[8] *Note*: trimethyltin compounds are toxic.[9] The solvents diethyl ether, benzene, and pentane were refluxed over sodium/benzophenone, calcium hydride, and sodium, respectively, and distilled into storage flasks. Toluene-d_8 (Aldrich Chemical Co.) was refluxed over calcium hydride and distilled into a storage flask. All experiments were performed under an oxygen-free, dry nitrogen or argon atmosphere by using Schlenk and glovebox techniques.[10]

The ^1H and ^{13}C NMR spectra were obtained from toluene-d_8 solutions with a Bruker AC-300 or AM-500 spectrometer. The ^1H and ^{13}C chemical shifts are reported in parts per million (ppm) with respect to Me_4Si at 0.0 ppm. The ^1H chemical shifts were referenced to the ^1H resonance of the residual $CHD_2C_6D_5$ (δ 2.09) solvent impurity, and the chemical shifts in the ^{13}C spectra were referenced to the methyl ^{13}C resonance of toluene-d_8 (δ 20.4). The molecular weights were determined cryoscopically in benzene with an apparatus similar to that described by Dilts and Shriver.[11] Melting points were obtained in sealed tubes on an Electrothermal IA 6304 melting point apparatus and are uncorrected. All elemental analyses were performed by E + R Microanalytical Laboratory, Corona, NY.

Reactions of Me_3Ga or Et_3Ga with $R''R'NSnMe_3$. $R''R'NSnMe_3$ was syringed into a 25 mL ampule that was equipped with a Teflon valve. The Me_3Ga or Et_3Ga was trap-to-trap distilled onto the aminostannane, and the ampule was allowed to stand at room temperature or was heated. Subsequently the volatile components were trap-to-trap distilled from the reaction solution or mixture and a solid remained. The composition of the distillate (Me_4Sn or $EtSnMe_3$ and unreacted trialkylgallium) was characterized by ^1H NMR.

$[Me_2GaN(i\text{-Bu})_2]_2$. A solution of Me_3Ga (1.40 g, 12.2 mmol) and $(i\text{-Bu})_2NSnMe_3$ (1.91 g, 6.53 mmol) was heated at 55−56 °C for 6 h. Recrystallization of the solid from pentane gave $[Me_2GaN(i\text{-Bu})_2]_2$ (1.32 g, 88.6% yield): mp 72−74 °C; ^1H NMR (500.138 MHz) δ 2.78 (d, NCH_2, 4.0H), 1.95 (m, $NCH_2CH(CH_3)_2$, 2.0H), 0.86 (d, $NCH_2CH(CH_3)_2$, 12.0H), −0.02 (s, $(CH_3)_2Ga$, 5.5H); ^{13}C NMR (125.759 MHz) δ 58.1 (NCH_2), 27.1 ($NCH_2CH(CH_3)_2$), 22.5 ($NCH_2CH(CH_3)_2$), −4.8 ($(CH_3)_2Ga$). Anal. Calcd for $C_{20}H_{48}Ga_2N_2$: C, 52.67; H, 10.61; N, 6.14. Found: C, 52.89; H, 10.81; N, 6.21. Molecular weight for $C_{20}H_{48}Ga_2N_2$: calcd, 456; found, 4.5×10^2 (calculated molality 0.0346).

$[Et_2GaN(i\text{-Bu})_2]_2$. A solution of Et_3Ga (1.81 g, 11.5 mmol) and $(i\text{- Bu})_2NSnMe_3$ (1.74 g, 5.96 mmol) was heated at 56−57 °C for 6 h. Recrystallization of the solid from pentane gave $[Et_2GaN(i\text{-Bu})_2]_2$ (1.05 g, 68.6% yield): mp 97−98 °C; ^1H NMR (500.138 MHz) δ 2.87 (d, NCH_2, 4.1H), 1.96 (m, $NCH_2CH(CH_3)_2$, 2.0H), 1.37 (t, $(CH_3CH_2)_2Ga$, 6.1H), 0.91 (d, $NCH_2CH(CH_3)_2$, 12.0H), 0.74 (q, $(CH_3CH_2)_2Ga$, 4.2H); ^{13}C NMR (125.759 MHz) δ 58.4 (NCH_2), 27.5 ($(NCH_2CH(CH_3)_2$), 22.7 ($NCH_2CH(CH_3)_2$), 11.2 ($(CH_3CH_2)_2Ga$), 5.0 ($(CH_3CH_2)_2Ga$). Anal. Calcd for $C_{24}H_{56}Ga_2N_2$: C, 56.28; H, 11.02; N, 5.47. Found: C, 56.27; H, 10.89; N, 5.47. Molecular weight for $C_{24}H_{56}Ga_2N_2$: calcd, 512; found, 5.3×10^2 (calculated molality 0.0311).

$[Me_2GaN(i\text{-Pr})SnMe_3]_2$. A solution of Me_3Ga (1.38 g, 12.0 mmol) and $i\text{-PrN(SnMe}_3)_2$ (2.04 g, 5.31 mmol) was heated at 44−45 °C for 15.5 h. Recrystallization of the solid from pentane (2.0 mL)/diethyl ether (1.5 mL) gave $[Me_2GaN(i\text{-Pr})SnMe_3]_2$ (1.18 g, 69.1% yield): mp 151−152 °C; ^1H NMR (300.133 MHz) δ 3.78 (sept, NCH, 1.1H), 1.02 (d, $NCH(CH_3)_2$, 6.8H), 0.38 (s, $(CH_3)_3Sn$, 8.7H, $^2J_{Sn-H} = 52.7$ Hz), −0.09 (s, $(CH_3)_2Ga$, 6.0H); ^{13}C NMR (75.469 MHz) δ 53.6 (NCH, $^2J_{Sn-C} = 19.5$ Hz), 29.3 ($NCH(CH_3)_2$, $^3J_{Sn-C} = 14.8$ Hz), 2.4 ($(CH_3)_3Sn$, $^1J_{Sn-C} = 365, 349$ Hz), −0.8 ($(CH_3)_2Ga$). Anal. Calcd for $C_{16}H_{44}Ga_2N_2Sn_2$: C, 29.96; H, 6.92; N, 4.37. Found: C, 30.13; H, 7.11; N, 4.44. Molecular weight for $C_{16}H_{44}Ga_2N_2Sn_2$: calcd, 641; found, 6.3×10^2 (calculated molality 0.0296).

$[Me_2GaN(C_6H_{11})_2]_2$. After the ampule had been warmed to room temperature, the solution of Me_3Ga (0.425 g, 3.70 mmol) and $(C_6H_{11})_2NSnMe_3$ (0.936 g, 2.72 mmol) slowly

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Table 1. Experimental Data from the X-ray Diffraction Study

	$[Et_2GaN(i\text{-}Bu)_2]_2$	$[Me_2Ga(i\text{-}Pr)SnMe_3]_2$	$[Me_2GaN(C_6H_{11})_2]_2$	$[Et_2GaN(C_6H_{11})_2]_2$
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
cell dimens[a]				
a, Å	10.252(4)	8.770(2)	11.560(6)	19.024(6)
b, Å	24.129(8)	15.124(3)	9.537(2)	19.325(8)
c, Å	12.086(5)	9.622(1)	13.509(7)	10.158(2)
α, deg				100.17(3)
β, deg	101.75(3)	94.82(1)	107.14(4)	102.25(2)
γ, deg				109.83(3)
V, Å^3	2927(21)	1271(2)	1423(19)	3305(61)
Z	4	2	2	4
mol wt	512.2	641.4	560.2	616.3
ρ(calcd), g cm^{-3}	1.16	1.68	1.31	1.24
radiation	Mo K$\bar{\alpha}$ (0.71069Å)			
monochromator	graphite			
2θ range, deg	4−46			
scan type	$\omega/2\theta$			
scan speed, deg min^{-1}	1−3 (in ω)			
scan width, deg	$0.8 + 0.35 \tan \theta$			
no. of unique data	4406	1768	2158	9179
no. of unique data with $F_0{}^2 > 3\sigma(F_0{}^2)$	3716		1840	
R[b]	0.0655	0.0326[d]	0.0613	0.0824[d]
R_w[c]	0.0574	0.0799[e]	0.0685	0.1495[e]

[a] Unit cell parameters were derived from a least-squares refinement of 25 reflections: 11.63° ≤ θ ≤ 13.78°, 9.31° ≤ θ ≤ 12.31°, 10.01° ≤ θ ≤ 13.99°, 9.47° ≤ θ ≤ 12.05°. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1,2}]$. [d] R1 for all reflection data in SHELXL-93. [e] $wR2 = [\sum w(F_o{}^2 - F_c{}^2)/\sum w(F_o{}^2)^2]^{1/2}$ for all reflection data in SHELXL-93.

converted to a waxy, white solid over a period of 1.2 h. The ampule was allowed to stand at room temperature for 20.3 h, and a powdery, white solid along with a liquid formed. Recrystallization of the solid from pentane gave $[Me_2GaN(C_6H_{11})_2]_2$ (0.617 g, 81.0% yield): mp 190−191 °C; ^1H NMR (500.138 MHz) δ 3.08 (triplet of triplets, $^3J_{ax-ax} = 11.6$ Hz, $^3J_{ax-eq} = 2.1$ Hz, $NCHCH_2CH_2CH_2CH_2CH_2$, 2.0H), 1.95 (d, $^2J_{ax-eq} \approx 12.1$ Hz, $NCHC(H_{eq})HCH_2CH_2CH_2C(H_{eq})H$, 4.2H), 1.74 (d, $^2J_{ax-eq} \approx 12.8$ Hz, $NCHCH_2C(H_{eq})HCH_2C(H_{eq})HCH_2$, 4.2H), 1.57 (d, $^2J_{ax-eq} \approx 13.0$ Hz, $NCHCH_2CH_2C(H_{eq})HCH_2CH_2$, 2.3H), 1.47 (quartet of doublets, $^2J_{ax-eq} \approx {}^3J_{ax-ax} \approx 12.0$ Hz, $^3J_{ax-eq} = 2.7$ Hz, $NCHC(H_{ax})HCH_2CH_2CH_2C(H_{ax})H$, 3.7H), 1.25 (quartet of triplets, $^2J_{ax-eq} \approx {}^3J_{ax-ax} \approx 12.8$ Hz, $^3J_{ax-eq} = 3.1$ Hz, $NCHCH_2C(H_{ax})HCH_2C(H_{ax})HCH_2$, 4.0H), 1.04 (quartet of triplets, $^2J_{ax-eq} \approx {}^3J_{ax-ax} \approx 13.0$ Hz, $^3J_{ax-eq} = 4.1$ Hz, $NCHCH_2CH_2C(H_{ax})HCH_2CH_2$, 1.9H), 0.01 (s, $(CH_3)_2Ga$, 6.1H); ^{13}C NMR (75.469 MHz) δ 64.9 ($NCHCH_2CH_2CH_2CH_2CH_2$), 38.3 ($NCHCH_2CH_2CH_2CH_2CH_2$), 28.5 ($NCHCH_2CH_2CH_2CH_2CH_2$), 26.7 ($NCHCH_2CH_2CH_2CH_2CH_2$), −1.9 ($(CH_3)_2Ga$). Anal. Calcd for $C_{28}H_{56}Ga_2N_2$: C, 60.03; H, 10.08; N, 5.00. Found: C, 60.13; H, 10.19, N, 5.06. Molecular weight for $C_{28}H_{56}Ga_2N_2$: calcd, 560; found, 5.5 × 10^2 (calculated molality 0.0267).

$[Et_2GaN(C_6H_{11})_2]_2$. A solution of Et_3Ga (1.51 g, 9.64 mmol) and $(C_6H_{11})_2NSnMe_3$ (3.24 g, 9.40 mmol) was heated at 52−53 °C for 10.9 days. Clear, colorless crystals slowly precipitated during this period. The crystalline $[Et_2GaN(C_6H_{11})_2]_2$ (2.33 g, 80.4% yield) was washed four times with pentane: mp 142−143 °C; ^1H NMR (500.138 MHz) δ 3.03 (triplet of triplets, $^3J_{ax-ax} = 11.7$ Hz, $^3J_{ax-eq} = 2.1$ Hz, $NCHCH_2CH_2CH_2CH_2CH_2$, 2.0H), 1.94 (d, $^2J_{ax-eq} \approx 12.1$ Hz, $NCHC(H_{eq})HCH_2CH_2CH_2C(H_{eq})H$, 4.2H), 1.76 (d, $^2J_{ax-eq} \approx 12.8$ Hz, $NCHCH_2C(H_{eq})HCH_2C(H_{eq})HCH_2$, 4.2H), 1.57 (d, $^2J_{ax-eq} \approx 12.9$ Hz, $NCHCH_2CH_2C(H_{eq})HCH_2CH_2$, 2.3H), 1.52 (quartet of doublets, $^2J_{ax-eq} \approx {}^3J_{ax-ax} \approx 12.0$ Hz, $^3J_{ax-eq} = 2.7$ Hz, $NCHC(H_{ax})HCH_2CH_2CH_2C(H_{ax})H$, 4.0H), 1.37 (t, $^3J_{H-H} = 8.0$ Hz, $(CH_3CH_2)_2Ga$, 6.2H), 1.26 (quartet of triplets, $^2J_{ax-eq} \approx {}^3J_{ax-ax} \approx 12.9$ Hz, $^3J_{ax-eq} = 3.0$ Hz, $NCHCH_2C(H_{ax})HCH_2C(H_{ax})HCH_2$, 4.2H), 1.04 (quartet of triplets, $^2J_{ax-eq} \approx {}^3J_{ax-ax} \approx 13.0$ Hz, $^3J_{ax-eq} = 4.0$ Hz, $NCHCH_2CH_2C(H_{ax})HCH_2CH_2$, 2.0H), 0.72 (q, $^3J_{H-H} = 8.0$ Hz, $(CH_3CH_2)_2Ga$, 4.0H); ^{13}C NMR (75.469 MHz) δ 64.4 ($NCHCH_2CH_2CH_2CH_2CH_2$), 38.2 ($NCHCH_2CH_2CH_2CH_2CH_2$), 28.5 ($NCHCH_2CH_2CH_2CH_2CH_2$), 26.6 ($NCHCH_2CH_2CH_2CH_2CH_2$), 11.1 ($(CH_3CH_2)_2Ga$), 7.2 ($(CH_3CH_2)_2Ga$). Anal. Calcd for $C_{32}H_{64}Ga_2N_2$: C, 62.36; H, 10.47; N, 4.54. Found: C, 62.48; H, 10.74; N, 4.67. Molecular weight for $C_{32}H_{64}Ga_2N_2$: calcd, 616; found, 5.9 × 10^2 (calculated molality 0.0277).

X-ray Crystallographic Analysis. Colorless crystals of $[Et_2GaN(i\text{-}Bu)_2]_2$, $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$, $[Me_2GaN(C_6H_{11})_2]_2$, and $[Et_2GaN(C_6H_{11})_2]_2$ were mounted in capillary tubes under a nitrogen atmosphere. The determination of the unit cell and the collection of the intensity data were made on a CAD-4 diffractometer equipped with a graphite monochromator. Unit cell parameters and details of the data collection are given in Table 1. The positions of the C, N, Ga, and Sn atoms were taken from Patterson maps. After several cycles of a full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, the hydrogen atoms were generated at calculated positions (C−H = 0.96 Å; H−C−H = 109.5°) with rigid geometry. Additional cycles of refinement led to convergence. All calculations were performed on a DEC VAX 8530 or IBM PS/2 Model 90 computer using ORFFE4,[12] SHELXS-86,[13 a] and SHELX-76[13b] or SHELXL-93.[13c] Scattering factors for all atoms included real and imaginary anomalous dispersion components.[14] Selected bond lengths and angles are given in Tables 2−5.

Results and Discussion

The alkyltrimethyltin elimination reaction (eq 5) of R_3Ga (R = Me, Et) with $R''R'NSnMe_3$ (R'' = i-Bu, $SnMe_3$, C_6H_{11} and R' = i-Bu, i-Pr, C_6H_{11}) in the absence of a solvent gave $[Me_2GaN(i\text{-}Bu)_2]_2$, $[Et_2GaN(i\text{-}Bu)_2]_2$, $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$, $[Me_2GaN(C_6H_{11})_2]_2$, and $[Et_2GaN(C_6H_{11})_2]_2$ in 88.6, 68.6, 69.1, 81.0, and 80.4% yields.

$$2R_3Ga + 2R''R'NSnMe_3 \rightarrow [R_2GaNR'R'']_2 + 2RSnMe_3 \quad (5)$$

In all cases except one, the neat reactants were heated

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(12) Busing, W. R.; Martin, K. O.; Levy, H. A. ORFFE (revised by F. M. Brown, C. K. Johnson, and W. E. Thiessen); Oak Ridge National Laboratory: Oak Ridge, TN, 1985.

(13) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; Cambridge University Press: New York, 1975. (c) Sheldrick, G. M. SHELXL-93; University of Göttingen, Göttingen, Germany, 1993.

(14) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 2. Selected Intramolecular Distances (Å) and Bond Angles (deg) for $[Et_2GaN(i\text{-}Bu)_2]_2$

	Distances		
Ga(1)···Ga(2)	2.864(1)	N(1)···N(2)	2.837(9)
Ga(1)−N(1)	2.061(6)	Ga(1)−N(2)	2.068(6)
Ga(2)−N(1)	2.053(6)	Ga(2)−N(2)	2.035(6)
Ga(1)−C(1)	2.010(8)	Ga(1)−C(3)	1.983(9)
Ga(2)−C(5)	1.975(8)	Ga(2)−C(7)	1.993(9)
N(1)−C(9)	1.484(10)	N(1)−C(13)	1.495(10)
N(2)−C(17)	1.494(10)	N(2)−C(21)	1.489(10)
	Angles		
N(1)−Ga(1)−N(2)	86.8(2)	N(1)−Ga(2)−N(2)	87.9(2)
C(1)−Ga(1)−C(3)	123.2(4)	C(5)−Ga(2)−C(7)	112.7(4)
C(1)−Ga(1)−N(1)	110.2(3)	C(7)−Ga(2)−N(1)	107.4(3)
C(1)−Ga(1)−N(2)	109.4(3)	C(7)−Ga(2)−N(2)	109.4(3)
C(3)−Ga(1)−N(1)	111.2(4)	C(5)−Ga(2)−N(1)	120.4(4)
C(3)−Ga(1)−N(2)	110.0(4)	C(5)−Ga(2)−N(2)	116.3(3)
Ga(1)−N(1)−Ga(2)	88.2(2)	Ga(1)−N(2)−Ga(2)	88.5(2)
C(9)−N(1)−C(13)	112.1(7)	C(17)−N(2)−C(21)	111.5(7)
C(9)−N(1)−Ga(1)	118.5(5)	C(17)−N(2)−Ga(1)	118.3(4)
C(9)−N(1)−Ga(2)	110.3(5)	C(17)−N(2)−Ga(2)	109.8(5)
C(13)−N(1)−Ga(1)	111.1(5)	C(21)−N(2)−Ga(1)	110.3(5)
C(13)−N(1)−Ga(2)	114.7(5)	C(21)−N(2)−Ga(2)	116.9(5)

Table 3. Selected Intramolecular Distances (Å) and Bond Angles (deg) for $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$

	Distances		
Ga···Ga′	2.892(1)	N···N′	2.859(7)
Ga−N	2.039(4)	Ga−N′	2.028(4)
Ga−C(1)	1.984(5)	Ga−C(2)	1.975(5)
N−C(3)	1.513(6)	N−Sn	2.112(4)
Sn−C(6)	2.135(6)	Sn−C(7)	2.143(7)
Sn−C(8)	2.148(6)		
	Angles		
N−Ga−N′	89.3(2)	Ga−N−Ga′	90.7(2)
C(1)−Ga−C(2)	110.0(3)	C(1)−Ga···Ga′	125.6(2)
C(2)−Ga···Ga′	124.4(2)	C(1)−Ga−N	113.4(2)
C(2)−Ga−N	114.4(2)	C(1)−Ga−N′	115.6(2)
C(2)−Ga−N′	113.0(2)	C(3)−N−Sn	114.0(3)
C(3)−N···N′	122.4(3)	Sn−N···N′	123.6(2)
C(3)−N−Ga	111.9(3)	C(3)−N−Ga′	112.4(3)
Sn−N−Ga	112.6(2)	Sn−N−Ga′	113.2(2)

Table 4. Selected Intramolecular Distances (Å) and Bond Angles (deg) for $[Me_2GaN(C_6H_{11})_2]_2$

	Distances		
Ga···Ga′	2.911 (2)	N···N′	2.938 (9)
Ga−N	2.070 (5)	Ga−N′	2.066 (4)
Ga-C(1)	1.981 (9)	Ga-C(2)	1.978 (8)
N-C(3)	1.499 (7)	N−C(9)	1.498 (9)
	Angles		
N−Ga−N′	90.5 (2)	Ga−N−Ga′	89.5 (2)
C(1)−Ga−C(2)	116.1 (5)	C(1)−Ga···Ga′	121.9 (4)
C(2)−Ga···Ga′	122.0 (3)	C(1)−Ga−N	111.7 (4)
C(2)−Ga−N	112.2 (3)	C(1)−Ga−N′	111.9 (3)
C(2)−Ga−N′	111.7 (3)	C(3)−N−C(9)	118.3 (5)
C(3)−N···N′	121.0 (4)	C(9)−N···N′	120.7 (4)
C(3)−N−Ga	112.3 (3)	C(3)−N−Ga′	110.7 (4)
C(9)−N−Ga	110.3 (4)	C(9)−N−Ga′	112.2 (3)

at temperatures between 44 and 57 °C for periods of 6 h to 10.9 days. The exception is the reaction of Me_3Ga with $(C_6H_{11})_2NSnMe_3$, in which the reaction mixture was allowed to stand at room temperature for 20.3 h. All five aminogallanes are colorless crystalline solids at room temperature.

The X-ray crystallographic study of $[Et_2GaN(i\text{-}Bu)_2]_2$, $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$, $[Me_2GaN(C_6H_{11})_2]_2$, and $[Et_2GaN(C_6H_{11})_2]_2$ reveals that the four aminogallanes are dimeric in the solid state (Figures 1−4). The narrow melting point range for $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$ indicates that only one isomer is present in the solid state, and it is the trans isomer (Figure 2). The four-membered $(Ga-N)_2$ rings in $[Et_2GaN(i\text{-}Bu)_2]_2$ and $[Et_2GaN(C_6H_{11})_2]_2$ (molecules 1 and 2) are nonplanar with fold angles on the Ga···Ga diagonals of 148.7(3) and 146.3(3), 147.7(3)°. These angles are smaller than the fold angles of 154.2 and 171.8(2)° that were observed in the only other reported aminogallanes $[Me_2GaN(H)Dipp]_2$ (Dipp = 2,6-i-$Pr_2C_6H_3$)[2a] and $[(2,3\text{-}Me_2C_4H_4)GaNEt_2]_2$[3g] with nonplanar $(Ga-N)_2$ rings. The Ga-methylated aminogallanes and all other substituted dimeric aminogallanes[2a,i,3−f] for which structural data are known contain planar $(Ga-N)_2$ rings. Steric overcrowding between substituents on neighboring atoms in the $(Ga-N)_2$ ring and packing forces are probably responsible for the distortion of the $(Ga-N)_2$ rings in the Ga-ethylated aminogallanes.

The C−Ga bond lengths (Tables 4 and 5) in $[Et_2GaN(C_6H_{11})_2]_2$ (average 1.996(7), 1.996(7) Å) are slightly longer than the corresponding bond lengths in $[Me_2GaN(C_6H_{11})_2]_2$ (average 1.980(9) Å). The longer C−Ga bonds in the former aminogallane probably result from an increase in substitution on the carbon atoms bonded to the gallium atoms. A similar trend is found in the C−Ga bond distances for $[(t\text{-}Bu)_2GaN(H)Ph]_2$ (2.006(9) and 2.18(2) Å)[3e] and $[Me_2GaN(H)Ph]_2$ (1.954(6) and 1.936(6) Å).[2a] Despite significant variations in the N−Ga bond lengths in molecule 1 of $[Et_2GaN(C_6H_{11})_2]_2$, the average N−Ga bond distances in molecules 1 and 2 (2.070(5), and 2.069(5) Å) are nearly identical with the average N−Ga bond length (2.068(5) Å) found in $[Me_2GaN(C_6H_{11})_2]_2$. By comparison, the average N−Ga distances in $[Et_2GaN(i\text{-}Bu)_2]_2$ (2.054(6) Å) and *trans*-$[Me_2GaN(i\text{-}Pr)SnMe_3]_2$ (2.034(4) Å) are shorter. The small decrease in the average N−Ga bond length within the series $[R_2GaN(C_6H_{11})_2]_2$, $[Et_2GaN(i\text{-}Bu)_2]_2$, and *trans*-$[Me_2GaN(i\text{-}Pr)SnMe_3]_2$ can be attributed to the decrease in the steric requirements of nitrogen substituents in the series.

Cryoscopic molecular weight measurements indicate that all five aminogallanes are dimers in benzene solutions. *trans*-$[Me_2GaN(i\text{-}Pr)SnMe_3]_2$ appears to be the only isomer present in a toluene solution at room temperature. The ^1H NMR spectrum of $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$ in toluene exhibited only one $Ga-CH_3$ resonance. Two additional $Ga-CH_3$ resonances of equal intensity would be expected if the cis isomer were also present in the solution.[2d,4]

The nonplanar $(Ga-N)_2$ rings in $[Et_2GaN(i\text{-}Bu)_2]_2$ and $[Et_2GaN(C_6H_{11})_2]_2$ render the two ethyl groups on a gallium atom and the two substituents on a nitrogen atom magnetically nonequivalent in the solid state. However, the ^1H NMR spectrum of each Ga-ethylated aminogallane in toluene solution exhibited only one signal for the methyl protons and one signal for the methylene protons in the ethyl group at room temperature. At −68 °C the width of the bands at half-height increased to 5 Hz—probably due to the increase in viscosity of the toluene solution—but only one quartet and one triplet were observed for the methyl and methylene protons in the spectra of $[Et_2GaN(i\text{-}Bu)_2]_2$ and $[Et_2GaN(C_6H_{11})_2]_2$. Either the rate of inversion of the $(Ga-N)_2$ rings in both aminogallanes is very fast in comparison to the NMR time scale or the rings are planar in solution.

The signals associated with the axial and equatorial protons on the cyclohexyl groups are well-resolved in the ^1H NMR spectra of $[Me_2GaN(C_6H_{11})_2]_2$ and $[Et_2GaN-$

Table 5. Selected Intramolecular Distances (Å) and Bond Angles (deg) for $[Et_2GaN(C_6H_{11})_2]_2$[a]

		Distances	
Ga(1)···Ga(2)	2.878(1), 2.872(1)	N(1)···N(2)	2.849(8), 2.862(9)
Ga(1)−N(1)	2.049(5), 2.069(5)	Ga(1)−N(2)	2.086(5), 2.064(5)
Ga(2)−N(1)	2.086(5), 2.072(5)	Ga(2)−N(2)	2.061(5), 2.072(5)
Ga(1)−C(1)	1.990(6), 1.992(7)	Ga(1)−C(3)	1.999(7), 2,002(7)
Ga(2)−C(5)	2.004(7), 1,994(8)	Ga(2)−C(7)	1.993(7), 1.996(7)
N(1)−C(9)	1.496(8), 1.531(8)	N(1)−C(15)	1.519(8), 1.491(8)
N(2)−C(21)	1.521(8), 1.518(8)	N(2)−C(27)	1.483(8), 1.534(8)
		Angles	
N(1)−Ga(1)−N(2)	87.1(2), 87.7(2)	N(1)−Ga(2)−N(2)	86.8(2), 87.4(2)
Ga(1)−N(1)−Ga(2)	88.2(2), 87.8(2)	Ga(1)−N(2)−Ga(2)	87.9(2), 88.0(2)
C(1)−Ga(1)−C(3)	110.4(3), 113.2(3)	C(5)−Ga(2)−C(7)	113.1(3), 112.6(4)
C(1)−Ga(1)−N(1)	114.6(2), 113.7(3)	C(5)−Ga(2)−N(1)	120.3(3), 118.2(3)
C(3)−Ga(1)−N(1)	112.9(3), 111.7(3)	C(7)−Ga(2)−N(1)	109.4(3), 108.9(3)
C(1)−Ga(1)−N(2)	121.1(3), 117.7(3)	C(5)−Ga(2)−N(2)	112.9(3), 115.6(3)
C(3)−Ga(1)−N(2)	108.9(3), 119.2(3)	C(7)−Ga(2)−N(2)	111.6(3), 111.7(3)
C(9)−N(1)−C(15)	117.7(5), 118.0(5)	C(21)−N(2)−C(27)	118.5(5), 116.5(5)
C(9)−N(1)−Ga(1)	113.4(4), 110.7(4)	C(21)−N(2)−Ga(1)	115.8(4), 116.6(4)
C(15)−N(1)−Ga(1)	108.9(4), 112.2(4)	C(27)−N(2)−Ga(1)	109.0(4), 109.0(4)
C(9)−N(1)−Ga(2)	109.8(4), 109.7(4)	C(21)−N(2)−Ga(2)	107.8(4), 112.4(4)
C(15)−N(1)−Ga(2)	115.1(4), 114.5(4)	C(27)−N(2)−Ga(2)	113.8(4), 111.0(4)

[a] Data are given the order molecule 1, molecule 2.

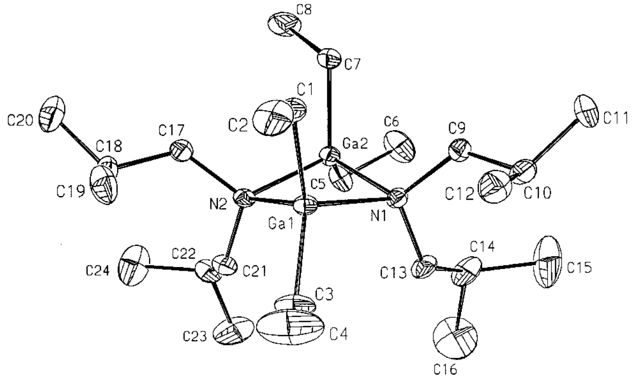

Figure 1. ORTEP diagram of $[Et_2GaN(i\text{-}Bu)_2]_2$.

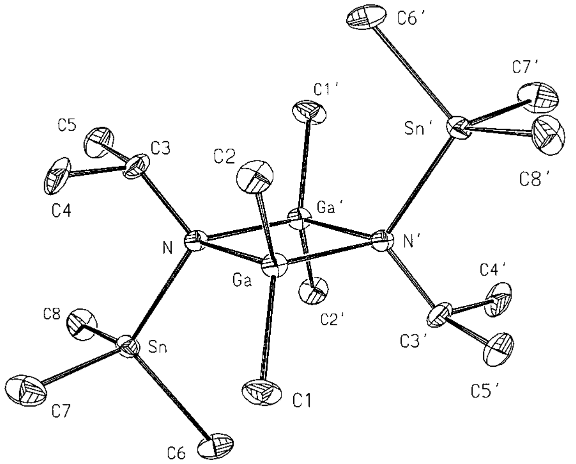

Figure 2. ORTEP diagram of $[Me_2Ga(i\text{-}Pr)SnMe_3]_2$.

$(C_6H_{11})_2]_2$. The three doublets in the region from 2.0 to 1.57 ppm were assigned to the equatorial protons on the β-, γ-, and δ-carbon atoms, and the three quartets of doublets or triplets in the region from 1.52 to 1.0 ppm were assigned to the axial protons on the β-, γ-, and δ-carbon atoms. These assignments are consistent with the COSY contour plots of the aminogallanes and spectral features distinctive to cyclohexyl groups.[15]

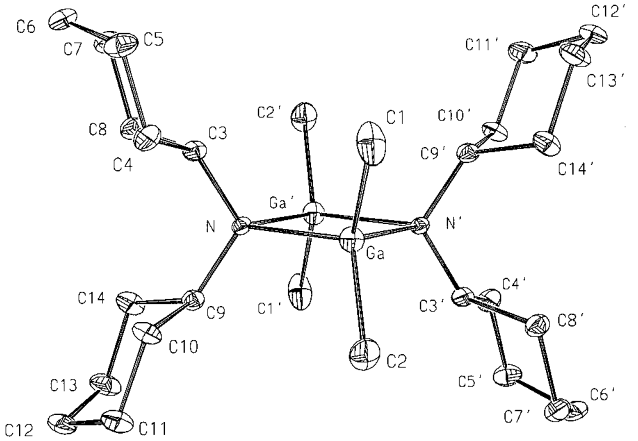

Figure 3. ORTEP diagram of $[Me_2GaN(C_6H_{11})_2]_2$.

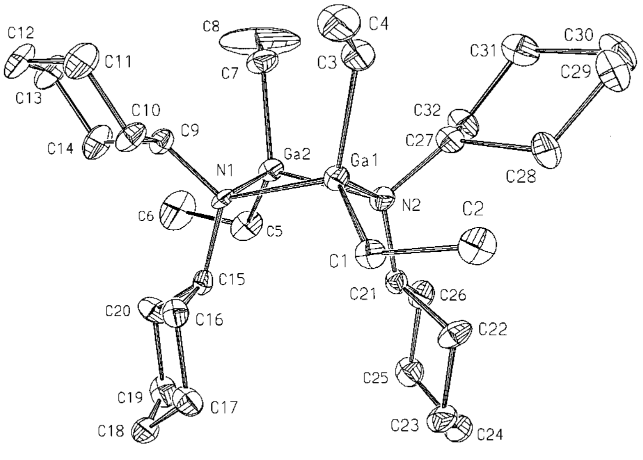

Figure 4. ORTEP diagram of $[Et_2GaN(C_6H_{11})_2]_2$ (molecule 1).

The alkyltrimethyltin elimination reaction (eq 5) affords a convenient, single-step, low-temperature pathway to substituted Ga-methylated or Ga-ethylated aminogallanes. With the exception of the reaction of Et_3Ga with $(C_6H_{11})_2NSnMe_3$, which required 10.9 days, the elimination reactions that were investigated proceeded readily in the absence of a solvent at or below 57 °C. Even when the substituents on the nitrogen atom were the bulky cyclohexyl groups, the aminogallanes $[Me_2GaN(C_6H_{11})_2]_2$ and $[Et_2GaN(C_6H_{11})_2]_2$ were obtained in

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[15] Morelle, N.; Gharbi-Benarous, J.; Acher, F.; Valle, G.; Crisma, M.; Toniolo, C.; Azerad, R.; Girault, J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 525.

good yields. Attempts to prepare $[Me_2GaN(C_6H_{11})_2]_2$ by cyclopentadiene elimination (eq 4) were unsuccessful,[4] and the adduct $Me_3Ga{\cdot}N(H)(C_6H_{11})_2$ has been found to be stable to methane elimination (eq 1) during sublimation at 40−60 °C and 0.01 Torr.[3c] It should be noted that, at least in the case of the reactions of Me_3Ga or Et_3Ga with $(C_6H_{11})_2NSnMe_3$, higher reaction temperatures and longer reaction times were required to effect the formation of $[Et_2GaN(C_6H_{11})_2]_2$ than $[Me_2GaN(C_6H_{11})_2]_2$.

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Supporting Information Available: Listings of bond lengths, bond angles, selected dihedral angles, hydrogen coordinates, anisotropic temperature factors, and final positional parameters for $[Et_2GaN(i\text{-}Bu)_2]_2$, $[Me_2GaN(i\text{-}Pr)SnMe_3]_2$, $[Me_2GaN(C_6H_{11})_2]_2$, and $[Et_2GaN(C_6H_{11})_2]_2$ and COSY plots for $[Me_2GaN(C_6H_{11})_2]_2$ and $[Et_2GaN(C_6H_{11})_2]_2$ (40 pages). Ordering information is given on any current masthead page.

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