1287-25-8; 1,1′-diphenylferrocene, 12098-13-4; cyclopentadiene, 542-92-7; iodobenzene, 591-50-4; ferrous chloride, 7758-94-3; 1-chloronaphtalene, 90-13-1; zinc chloride, 7646-85-7; bromoferrocene, 1273-73-0; 1,1-dilithioferrocene, 33272-09-2; 1-iodonaphthalene, 90-14-2.

Supplementary Material Available: Tables of (i) anisotropic thermal parameters, (ii) H atom positions, (iii) bond angles for cyclopentadienyl rings, and (iv) observed and calculated structure amplitudes (13 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Crystal and Molecular Structure of $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$

R. B. Hallock,[1a] W. E. Hunter,[1b] Jerry L. Atwood,[1b] and O. T. Beachley, Jr.*[1a]

Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and University of Alabama, University, Alabama 35486

Received June 18, 1984

The complex $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$, prepared from $Ga(CH_2SiMe_3)_3$, has been fully characterized by analysis, standard spectroscopic methods, cryoscopic molecular weight measurements, and an X-ray structural study. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 9.911$ (4) Å, $b = 16.427$ (6) Å, $c = 14.770$ (6) Å, $\beta = 90.43$ (4)°, and $Z = 2$ for $d_{calcd} = 1.08$ g cm^{-3}. Full-matrix least-squares refinement led to a final R value of 0.075 for 1598 observed reflections. The molecule lies on a crystallographic inversion center. The geometry about the gallium atom is distorted tetrahedral with a Ga–C(av) distance of 1.99 [1] Å and a Ga–N distance of 2.241 (9) Å.

Introduction

The (trimethylsilyl)methyl group is considered to be a bulky substituent with larger steric effects than those of a methyl group. Consequently, the (trimethylsilyl)methyl group 3 derivatives $M(CH_2SiMe_3)_3$ (M = Al, Ga, In) are considered to be weaker Lewis acids than the corresponding methyl derivatives. For example, diethyl ether can be readily removed from the gallium[2] and indium[3] derivatives, but the strong base NMe_3 forms stable complexes with all of these group 3 compounds. Diamines of the type $Me_2N(CH_2)_nNMe_2$ (n = 2, 3) react with MMe_3 (M = Al, Ga, In) to form 1:2 complexes[4] $Me_3M{\cdot}Me_2N(CH_2)_nNMe_2{\cdot}MMe_3$. Cryoscopic molecular weight measurements of these methyl complexes in benzene solution are consistent with monomeric behavior and little dissociation into 1:1 complexes and free Lewis acid. During the course of some of our investigations of the chemistry of $M(CH_2SiMe_3)_3$, $Ga(CH_2SiMe_3)_3$ was reacted with a large excess of $Me_2NC_2H_4NMe_2$. The isolated product $(Me_3SiCH_2)_3Ga{\cdot}Me_2NCH_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$ was fully characterized by analysis, standard spectroscopic methods, cryoscopic molecular weight measurements, and an X-ray structural study. This structural study represents only the second report of a structure of a neutral trialkylgallium–amine donor–acceptor complex and the first with an alkyl group other than methyl.

Experimental Section

The organogallium compounds described in this investigation were oxygen and moisture sensitive and were manipulated in a vacuum line or a purified argon atmosphere. The reagent $Ga(CH_2SiMe_3)_3$ was synthesized by the literature procedure.[2] The ligand $Me_2NC_2H_4NMe_2$ (TMED) was dried over P_2O_5 and was vacuum distilled immediately prior to reaction. Infrared spectra were recorded in the range 4000–250 cm^{-1} by means of a Perkin-Elmer 683 spectrometer. The spectra were recorded as Nujol mulls by using CsI plates. Bands due to mulling agents have been omitted. The ^1H NMR spectrum was recorded at 90 MHz and ambient temperature by using a Varian EM-390 spectrometer. Chemical shift data are reported in δ units (ppm) and are referenced to $SiMe_4$ as 0.00 and C_6H_6 as 7.13. Molecular weight measurements were obtained cryoscopically in benzene by using an instrument similar to that described by Shriver.[5]

Synthesis of $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$. The title compound was prepared by vacuum distilling a large (tenfold) excess of $Me_2NC_2H_4NMe_2$ onto 0.785 g (2.37 mmol) of $Ga(CH_2SiMe_3)_3$ in a reaction tube equipped with a Teflon valve. After being warmed to room temperature, the reaction mixture was stirred for 5 h. The excess ligand was removed by vacuum distillation at room temperature to leave a viscous yellow liquid. This liquid was then heated to 45 °C under high vacuum, and colorless crystals were sublimed to the cooler portions of the tube. The crystals were isolated and resublimed at 45 °C. The final product $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NNe_2{\cdot}Ga(CH_2SiMe_3)_3$ (0.71 g, 0.912 mmol, 77.3%) was isolated as colorless crystals: mp 89–91 °C, ^1H NMR (benzene, δ) +2.34 (s, 1.0, CH_2-TMED), +1.88 (s, 2.9, Me-TMED), +0.20 (s, 11.4, Me-CH_2SiMe_3), −0.30 (s, 3.0, CH_2-CH_2SiMe_3); IR (Nujol, cm^{-1}) 1288 (w), 1252 (m), 1240 (s), 1162 (vw), 1128 (w), 1095 (vw), 1012 (m, sh), 999 (m), 982 (s), 960 (m), 945 (m), 860 (s, sh), 850 (s), 822 (vs), 783 (w), 748 (m), 721 (m), 677 (m), 610 (vw), 562 (w), 538 (w), 513 (m), 459 (vw); cryoscopic molecular weight, formula weight $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$, 778.9; molality (obsd mol wt) 0.0990 (549), 0.0687 (491), 0.0540 (452); hydrolysis, 0.0900 g (0.116 mmol) hydrolyzed in 6 M HCl for 48 h at 100 °C gave 0.697 mmol of $SiMe_4$, calcd 0.696. ($SiMe_4$ from hydrolysis was purified by fractionation through two −78 °C traps and isolated at −196 °C, and the quantity was determined by *PVT* measurements on the vacuum line.)

Collection of X-ray Diffraction Data and Solution of Structure for $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$. Single crystals of the air-sensitive compound were isolated by sublimation at 65 °C from an attempted reaction between $Ga(CH_2SiMe_3)_3$ and LiH in $Me_2NC_2H_4NMe_2$ and were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I.

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(1) (a) State University of New York at Buffalo. (b) University of Alabama.

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Table I. Crystal Data for $[Ga(CH_2SiMe_3)_3]_2 \cdot Me_2NC_2H_4NMe_2$

compd	$Ga_2Si_6N_2C_{30}H_{82}$
mol wt	778.90
space group	$P2_1/n$
cell constants	
a, Å	9.911 (4)
b, Å	16.427 (6)
c, Å	14.770 (6)
β, deg	90.43 (4)
cell vol, Å^3	2404.6
molecules/unit cell (Z)	2
ρ(calcd), g cm^{-3}	1.08
ρ(calcd), cm^{-1}	13.46
radiation	Mo Kα
max cryst dimens, mm	0.30 × 0.20 × 0.15
scan width, deg	$0.8 + 0.2 \tan \theta$
std reflctns	0.40, 004
decay of stds	<3%
reflctns measd	2519
2θ range	2-40
obsd reflctns	1598
no. of parameters varied	181
GOF	2.99
R	0.075
R_w	0.075

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. This method has been previously described.[6] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects.

Calculations were carried out with the SHELX system of computer programs.[7] Neutral-atom scattering factors for Ga were taken from Cromer and Waber.[8] Scattering factors stored within the SHELX program were used for the other atoms. The scattering factor for Ga was corrected for both the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[9] The position of the Ga atom was located by using the MULTAN80 system of programs.[10] Difference Fourier maps phased by this atom readily revealed the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0090$. Further refinement with anisotropic thermal parameters led to $R = 0.080$. At this point a difference Fourier map was computed and the hydrogen atoms were located. Further refinement led to final values of $R = 0.075$ and $R_w = 0.075$.

A final difference Fourier showed no feature greater than 0.6 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters of atoms other than hydrogen are given in Table II. Positional parameters for all atoms (Table IV-S) and anisotropic thermal parameters (Table V-S) are deposited as supplementary material.

Results and Discussion

The complex $Ga(CH_2SiMe_3)_3 \cdot Me_2NC_2H_4NMe_2 \cdot Ga(CH_2SiMe_3)_3$ has been isolated from a reaction mixture containing $Ga(CH_2SiMe_3)_3$ and a large excess of $Me_2NC_2H_4NMe_2$ (TMED). It is of interest that the product has both basic nitrogen atoms complexed with Lewis acids, even though the preparative reaction used an excess of TMED. Cryoscopic molecular weight measurements in benzene solution and the relatively low sublimation temperature (45–65 °C) for such a large and heavy molecule suggest that the complex partially dissociates both in solution and in the vapor phase. The observed molecular weight is significantly lower than the formula weight of the compound for all solutions studied. Furthermore, the observed molecular weight is concentration dependent, decreasing with concentration. In contrast, the related complexes of the methyl metal derivatives[4] $Me_3M \cdot Me_2NC_2H_4NMe_2 \cdot MMe_3$ (M = Al, Ga, In), prepared from a reaction mixture having 1 mol of TMED and 2 mol of MMe_3, do not exhibit any solution properties suggestive of significant dissociation. It is also noteworthy that the melting point of $[Ga(CH_2SiMe_3)_3]_2 \cdot$TMED (89–91 °C) is lower than that of $(GaMe_3)_2 \cdot$TMED[4] (102–103 °C), which is as expected if there is partial dissociation of the former complex upon heating. The occurrence of dissociative equilibria during the isolation of the complex can also be used to account for the formation of $[Ga(CH_2SiMe_3)_3]_2 \cdot$TMED rather than $Ga(CH_2SiMe_3)_3 \cdot$TMED, especially from a reaction mixture using excess TMED. If $Ga(CH_2SiMe_3)_3 \cdot$TMED is the initial product, a dissociative reaction

$$2Ga(CH_2SiMe_3)_3 \cdot \text{TMED} \rightleftarrows [Ga(CH_2SiMe_3)_3]_2 \cdot \text{TMED} + \text{TMED}$$

would lead to the formation of $Ga(CH_2SiMe_3)_3$ and TMED. Since free TMED is the most volatile component, TMED would be removed by vacuum distillation during isolation and/or sublimation to leave $[Ga(CH_2SiMe_3)_3]_2 \cdot$TMED, as observed.

Table II. Final Fractional Coordinates for $[Ga(CH_2SiMe_3)_3]_2 \cdot Me_2NC_2H_4NMe_2$

atom	x/a	y/b	z/c	U(eav), Å^2
Ga(1)	0.6070 (1)	0.14989 (9)	0.37292 (8)	0.050
C(1)	0.779 (1)	0.0860 (7)	0.3706 (8)	0.051
Si(1)	0.9458 (3)	0.1380 (2)	0.3639 (2)	0.061
C(2)	0.975 (2)	0.2084 (9)	0.460 (1)	0.098
C(3)	1.085 (1)	0.062 (1)	0.370 (1)	0.098
C(4)	0.967 (2)	0.196 (1)	0.2577 (9)	0.101
C(5)	0.625 (1)	0.2699 (8)	0.3896 (8)	0.061
Si(2)	0.5173 (5)	0.3474 (3)	0.3369 (3)	0.084
C(6)	0.564 (2)	0.4505 (8)	0.376 (1)	0.106
C(7)	0.335 (2)	0.332 (1)	0.359 (2)	0.230
C(8)	0.534 (3)	0.341 (1)	0.215 (1)	0.259
C(9)	0.460 (1)	0.1130 (8)	0.2916 (3)	0.063
Si(3)	0.4915 (4)	0.0711 (3)	0.1777 (2)	0.068
C(10)	0.533 (2)	−0.0397 (9)	0.185 (1)	0.095
C(11)	0.632 (1)	0.1234 (9)	0.1203 (9)	0.084
C(12)	0.339 (1)	0.079 (1)	0.104 (1)	0.118
N(1)	0.523 (1)	0.1167 (6)	0.5085 (6)	0.058
C(13)	0.457 (2)	0.0339 (8)	0.5148 (9)	0.089
C(14)	0.634 (1)	0.1269 (9)	0.5787 (8)	0.083
C(15)	0.411 (1)	0.176 (1)	0.5277 (9)	0.091

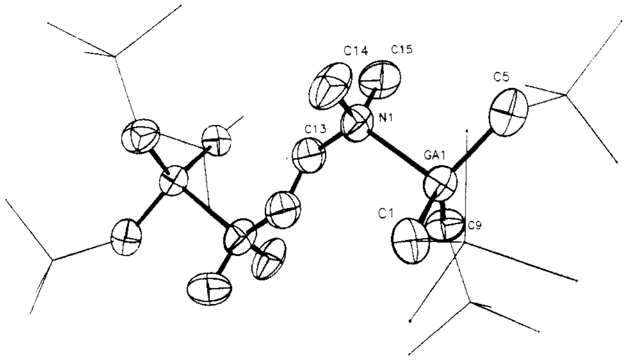

Figure 1. Labeling of atoms in $Ga(CH_2SiMe_3)_3 \cdot Me_2NC_2H_4NMe_2 \cdot Ga(CH_2SiMe_3)_3$. (Trimethylsilyl groups shown as point atoms for clarity; ORTEP-II diagram showing 30% probability contours of the thermal vibration ellipsoids of non-hydrogen atoms.)

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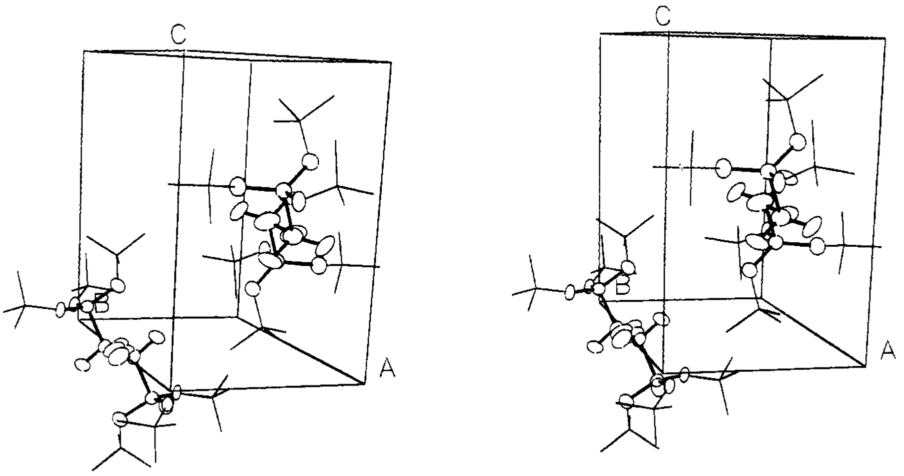

Figure 2. Stereoscopic view of unit cell of $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$.

Table III. Bond Lengths (Å) and Bond Angles (deg) for $[Ga(CH_2SiMe_3)_3]_2{\cdot}Me_2NC_2H_4NMe_2$

Bond Lengths			
Ga(1)-C(1)	2.00 (1)	Ga(1)-C(5)	1.99 (1)
Ga(1)-C(9)	1.98 (1)	Ga(1)-N(1)	2.241 (9)
Si(1)-C(1)	1.87 (1)	Si(1)-C(2)	1.86 (1)
Si(1)-C(3)	1.86 (1)	Si(1)-C(4)	1.85 (1)
Si(2)-C(5)	1.83 (1)	Si(2)-C(6)	1.85 (1)
Si(2)-C(7)	1.85 (2)	Si(2)-C(8)	1.81 (2)
Si(3)-C(9)	1.85 (1)	Si(3)-C(10)	1.87 (2)
Si(3)-C(11)	1.85 (1)	Si(3)-C(12)	1.86 (1)
C(13)-C(13)	1.47 (3)	C(13)-N(1)	1.51 (2)
C(14)-N(1)	1.52 (2)	C(15)-N(1)	1.50 (2)
Bond Angles			
C(1)-Ga(1)-C(5)	116.6 (4)	C(1)-Ga(1)-C(9)	116.9 (5)
C(5)-Ga(1)-C(9)	116.2 (5)	C(1)-Ga(1)-N(1)	102.1 (4)
C(5)-Ga(1)-N(1)	99.3 (4)	C(9)-Ga(1)-N(1)	101.0 (4)
C(1)-Si(1)-C(2)	112.1 (6)	C(1)-Si(1)-C(3)	110.2 (6)
C(2)-Si(1)-C(3)	105.9 (7)	C(1)-Si(1)-C(4)	112.9 (6)
C(2)-Si(1)-C(4)	108.0 (7)	C(3)-Si(1)-C(4)	107.3 (7)
C(5)-Si(2)-C(6)	111.1 (7)	C(5)-Si(2)-C(7)	113.4 (8)
C(6)-Si(2)-C(7)	108.1 (9)	C(5)-Si(2)-C(8)	109.2 (8)
C(6)-Si(2)-C(8)	109.8 (9)	C(7)-Si(2)-C(8)	105 (1)
C(9)-Si(3)-C(10)	110.3 (6)	C(9)-Si(3)-C(11)	112.2 (6)
C(10)-Si(3)-C(11)	108.3 (7)	C(9)-Si(3)-C(12)	111.2 (7)
C(10)-Si(3)-C(12)	106.4 (8)	C(11)-Si(3)-C(12)	108.2 (7)
Ga(1)-C(1)-Si(1)	121.1 (8)	Ga(1)-C(5)-Si(2)	125.9 (6)
Ga(1)-C(9)-Si(3)	122.5 (8)	Ga(1)-N(1)-C(13)	115.9 (7)
Ga(1)-N(1)-C(14)	108.2 (7)	C(13)-N(1)-C(14)	112 (1)
Ga(1)-N(1)-C(15)	106.8 (7)	C(13)-N(1)-C(15)	105 (1)
C(14)-N(1)-C(15)	109 (1)		

The X-ray structural study demonstrates that the crystal consists of isolated molecules of $[Ga(CH_2SiMe_3)_3]_2{\cdot}$TMED, separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. Selected interatomic distances are presented in Table III. Figure 1 shows the scheme used in labeling the atoms, while Figure 2 provides a stereoscopic view of the unit cell. The molecule lies on a crystallographic inversion center. The gallium and nitrogen atoms are in rather distorted tetrahedral environments. The gallium–alkyl distances (Ga–CH_2SiMe_3) are Ga–C(1) = 2.00 (1) Å, Ga–C(5) = 1.99 (1) Å, and Ga–C(9) = 1.98 (1) Å; the average Ga–C(sp^3) distance is 1.99 [1] Å.[11] These distances are shorter than the gallium–alkyl distances[12] in $KGa(CH_2SiMe_3)_3H$ which range from 2.030 (9) to 2.003 (9) Å, the average value being 2.029 [14] Å. The gallium–nitrogen distance in $[Ga(CH_2SiMe_3)_3]_2{\cdot}$TMED is 2.241 (9) Å which is significantly longer than that observed in the urotropine–trimethylgallium adducts,[13] $GaMe_3{\cdot}C_6H_{12}N_4$ and $(GaMe_3)_2{\cdot}C_6H_{12}N_4$, 2.139 (17) and 2.138 (9) Å, respectively. The average Ga–C bond distances in the urotropine complexes are 1.992 [14] and 1.981 [19] Å, respectively. For comparison, an electron diffraction study[14] of $Me_3Ga{\cdot}NMe_3$ reveals a Ga–N distance of 2.20 (3) Å and an average Ga–C distance of 1.998 [4] Å. The angles around gallium in $[Ga(CH_2SiMe_3)_3]_2{\cdot}$TMED in decreasing order are C(1)–Ga–C(9) = 116.9 (5)°, C(1)–Ga–C(5) = 116.6 (4)°, C(5)–Ga–C(9) = 116.2 (5)°, C(1)–Ga–N(1) = 102.1 (4)°, C(9)–Ga–N(1) = 101.0 (4)°, and C(5)–Ga–N(1) = 99.3 (4)°. The Ga–C(α)–Si angles which range from 125.9 (6)° to 121.1 (6)° are substantially greater than the ideal tetrahedral angle of 109.47°. All other parameters of the molecule seem normal.

Acknowledgment. This work was suported in part by the Office of Naval Research (O.T.B.) and the National Science Foundation (Grant CHE-81-11137) (J.L.A.).

Registry No. $Ga(CH_2SiMe_3)_3{\cdot}Me_2NC_2H_4NMe_2{\cdot}Ga(CH_2SiMe_3)_3$, 94324-88-6; $Ga(CH_2SiMe_3)_3$, 72708-53-3.

Supplementary Material Available: Tables IV-S–VI-S showing positional parameters, anisotropic thermal parameters, and observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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(11) Esd's of average values, calculated by the "scatter formula" below, are enclosed in square brackets.

$$[\sigma] = [\sum_{i=1}^{i=N} (\bar{d} - d_i)^2/(N-1)]^{1/2}$$

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