Organogallium Compounds Containing the Neophyl Substituent. Crystal and Molecular Structure of *trans*-$[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$

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A series of organogallium compounds which contain the neophyl substituent including $Ga(CH_2CMe_2Ph)_3$, $Ga(CH_2CMe_2Ph)_2Cl$, $Ga(CH_2CMe_2Ph)Cl_2$, and $(PhMe_2CCH_2)_2GaN(H)(Pr)$ have been prepared in high yield by reactions typical of organogallium chemistry. The characterization data include elemental analyses, melting points, NMR and IR spectroscopic studies, and cryoscopic molecular weight studies. All data are consistent with the conclusions that $Ga(CH_2CMe_2Ph)_3$ is monomeric in benzene solution whereas $Ga(CH_2CMe_2Ph)_2Cl$, $Ga(CH_2CMe_2Ph)Cl_2$, and $(PhMe_2CCH_2)_2GaN(H)(Pr)$ are dimeric. The gallium amide $[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with $a = 10.739$ (2) Å, $b = 10.844$ (2) Å, $c = 11.125$ (2) Å, $\alpha = 69.14$ (1)°, $\beta = 62.96$ (1)°, $\gamma = 76.74$ (1)°, $V = 1074.7$ (3) Å^3, and $Z = 1$. Diffraction data (Mo Kα, $2\theta = 5$–$50°$) were collected on a Siemens R3m/V automated four-circle diffractometer, and the structure was refined to $R = 3.57\%$ and $wR = 3.46\%$ for all 3803 unique reflections ($R = 2.52\%$, $wR = 2.62\%$ for those 3111 data with $|F_o| > 6\sigma(|F_o|)$). The molecule lies on a crystallographic inversion center and thus has a strictly planar Ga_2N_2 core. Distances of interest include Ga–CH_2CMe_2Ph = 1.992 (2) and 1.994 (3) Å and Ga–N(bridging) = 2.013 (2) and 2.029 (2) Å.

Introduction

The utilization of gallium in electronic materials including semiconductors and superconductors has led to a renewed interest in its chemistry. Even though a variety of organogallium compounds are known, relatively little is known about compounds which incorporate bulky organic substituents. Bulky substituents can lead to compounds with enhanced thermal stability as well as to compounds with unexpected structures. Consequently, our prior research involved investigations of the chemistry of gallium compounds with CH_2SiMe_3,[1] CH_2CMe_3,[2] 2,4,6-$Me_3C_6H_2$,[3,4] and C_5Me_5[5,6] substituents, but only the mesityl derivative $Ga(C_6Me_3H_2)Cl_2$ displayed unusual chemistry. The compound $Ga(C_6Me_3H_2)Cl_2$ was characterized as a unique one-dimensional polymer[4] in which planar $Ga(C_6Me_3H_2)Cl$ units with distorted tetrahedral geometry were linked by bridging chloride ligands. The traditional structure of an organogallium dichloride is a chloride-bridged dimer.

In this paper the synthesis and characterization of organogallium compounds which incorporate the bulky neophyl ligand including $Ga(CH_2CMe_2Ph)_3$, $Ga(CH_2CMe_2Ph)_2Cl$, $Ga(CH_2CMe_2Ph)Cl_2$, and $(PhMe_2CCH_2)_2GaN(H)(Pr)$ are described.

Experimental Section

All compounds described in this investigation were very sensitive to oxygen and moisture and were manipulated by standard vacuum line techniques or under a purified argon atmosphere. All solvents were purified before use. Gallium(III) chloride was purified by sublimation under dynamic high vacuum at 80–85 °C immediately prior to use. Neophyl chloride was purchased from Aldrich Chemical Co. and was distilled prior to use. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, or by E+R Microanalytical Laboratories, Corona, NY. Infrared spectra of Nujol mulls or of the neat compound between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were recorded at 300 or 90 MHz by using either a Varian Gemini 300 or Varian EM-390 spectrometer, respectively. All samples for NMR spectra were contained in sealed NMR tubes. Chemical shifts are reported in δ (ppm) and are referenced to tetramethylsilane (TMS) as $\delta = 0.00$ ppm and benzene as $\delta = 7.15$ ppm. Melting points were observed in a Mel-Temp by using sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.[7]

Synthesis of $Ga(CH_2CMe_2Ph)_3$. In a typical experiment the Grignard reagent, $(PhMe_2CCH_2)MgCl$, was prepared from magnesium turnings (6.217 g, 255.8 mmol) and freshly distilled neophyl chloride (41.193 g, 244.22 mmol) in 100 mL of diethyl ether. The magnesium turnings were activated with iodine without stirring prior to addition of the neophyl chloride/ether solution. The reaction mixture was stirred under reflux for 18 h. A flask charged with 10.0 g (56.9 mmol) of $GaCl_3$ dissolved in 250 mL of dry diethyl ether was fitted with a condenser, mechanical stirrer, and a pressure-equalizing addition funnel. Under a cover of argon the Grignard reagent solution was transferred to the addition funnel and was added to the $GaCl_3$ solution over a period of 30 min. After the addition was complete, the reaction mixture was stirred under reflux for 18 h. The Et_2O was then removed by vacuum distillation at room temperature. The crude product was extracted from the $MgCl_2$ by four to five washings with 150 mL of pentane to provide a yellowish "wet" solid which was purified by vacuum distillation in a short-path still at 120–210 °C. The first fraction which distilled at 120–150 °C was identified as bineophyl $PhMe_2CCH_2CH_2CMe_2Ph$ by its ^1H NMR spectrum[8,9] and melting point.[8,9] The second fraction which distilled at 160–210 °C was identified as pure $Ga(CH_2CMe_2Ph)_3$ and was obtained as a colorless solid (19.8 g, 42.2 mmol, 74.1% yield based on $GaCl_3$). More than one distillation was frequently required for complete removal of the bineophyl. The product isolated by distillation can be further purified, if needed, by recrystallization from pentane at −20 °C.

$Ga(CH_2CMe_2Ph)_3$: mp 37.9–39.2 °C; ^1H NMR (C_6D_6, δ) 7.08 (m, 15 H, C_6H_5); 1.23 (s, 18 H, CMe_2), 0.81 (s, 6 H, CH_2); IR (Nujol mull, cm^{-1}) 3110 (sh, m), 3085 (s), 3059 (s), 3035 (s), 3021 (s), 1960 (sh, w), 1941 (w), 1885 (w), 1869 (w), 1800 (w), 1742 (w), 1668 (w), 1598 (s), 1579 (m), 1535 (w), 1490 (vs), 1405 (m), 1305 (w), 1273 (m), 1181 (s), 1155 (m), 1098 (m), 1070 (s), 1065 (sh, m), 1028 (vs),

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998 (w), 961 (w), 925 (w), 901 (m), 858 (w), 838 (w), 761 (vs), 725 (sh, s), 698 (vs), 660 (sh, m), 620 (m), 612 (m), 551 (s), 505 (w), 457 (w), 401 (w), 269 (w). Anal. Calcd: C, 76.77; H, 8.38. Found: C, 76.76; H, 8.56. Cryoscopic molecular weight, benzene solution, formula weight 469.36 (observed molality, observed MW, association): 0.0846, 500.1, 1.07; 0.0536, 516.6, 1.10; 0.0372, 548.1, 1.17. Solubility: soluble in THF, Et_2O, benzene, and pentane. Trineophylgallium(III) formed a stable 1:1 adduct with NMe_3, formed a weak 1:1 adduct with THF that slowly dissociated under dynamic vacuum, but did not form a stable adduct with Et_2O.

Synthesis of $(PhMe_2CCH_2)_2GaCl$. In a typical experiment, $Ga(CH_2CMe_2Ph)_3$ (2.854 g, 6.081 mmol) and $GaCl_3$ (0.5353 g, 3.040 mmol) were weighed into vials in the drybox. Both compounds were dissolved in pentane and then were pipetted into a 100-mL side arm flask. Each vial was rinsed five to seven times with fresh aliquots of pentane to ensure the quantitative transfer of reagents. After the mixture was stirred at room temperature for 24 h, the slightly cloudy solution was filtered through a medium glass frit. The product was then recrystallized from pentane at −10 °C to yield pure $(PhMe_2CCH_2)_2GaCl$ as a colorless solid (3.135 g, 8.436 mmol, 92.5% yield).

$(PhMe_2CCH_2)_2GaCl$: mp 86.4–87.8 °C; ^1H NMR (C_6D_6, δ) 7.15 (m, 10 H, C_6H_5), 1.35 (s, 4 H, CH_2), 1.28 (s, 12 H, CMe_2); IR (Nujol mull, cm^{-1}) 3082 (s), 3055 (s), 3019 (vs), 2722 (s), 1965 (m), 1954 (m), 1898 (m), 1880 (m), 1867 (m), 1809 (m), 1799 (m), 1755 (m), 1740 (m), 1595 (s), 1576 (m), 1490 (vs), 1398 (sh, m), 1272 (s), 1189 (m), 1181 (s), 1153 (m), 1141 (m), 1115 (m), 1101 (m), 1070 (s), 1065 (sh, m), 1025 (s), 1001 (m), 995 (m), 948 (m), 932 (m), 928 (m), 910 (m), 901 (m), 855 (m), 835 (sh, w), 768 (sh, s), 761 (s), 733 (s), 719 (s), 695 (vs), 652 (m), 612 (w), 555 (m), 512 (w), 435 (w), 420 (w), 402 (w), 315 (vs), 280 (w), 258 (m), 242 (sh, m). Anal. Calcd: C, 64.64; H, 7.05. Found: C, 64.35; H, 7.05. Cryoscopic molecular weight, benzene solution, formula weight 371.60 (obeserved molality, observed MW, association): 0.0775, 773.2, 2.08; 0.0504, 769.4, 2.07; 0.0402, 769.1, 2.07. Solubility: soluble in THF, Et_2O, benzene, and pentane. Dineophylgallium(III) chloride formed a stable 1:1 adduct with NMe_3 but did not form a stable adduct with Et_2O or THF.

Synthesis of $(PhMe_2CCH_2)GaCl_2$. Neophylgallium(III) dichloride, $(CH_2CMe_2Ph)GaCl_2$, was prepared by a stoichiometric redistribution reaction in the same manner as previously described for $(PhMe_2CCH_2)_2GaCl$. In a typical experiment $Ga(CH_2CMe_2Ph)_3$ (3.042 g, 6.480 mmol) and $GaCl_3$ (2.282 g, 12.96 mmol) were reacted in pentane to yield $Ga(CH_2CMe_2Ph)Cl_2$ (4.849 g, 17.71 mmol, 91.1%). The compound was purified by recrystallization from pentane at −30 °C.

$Ga(CH_2CMe_2Ph)Cl_2$: mp 69.5–70.8 °C; ^1H NMR (C_6D_6, δ) 7.14 (m, 5 H, C_6H_5), 1.52 (s, 2 H, CH_2), 1.23 (s, 6 H, CMe_2); IR (Nujol mull, cm^{-1}) 3110 (w), 3090 (m), 3059 (vs), 3025 (vs), 2342 (vw), 2319 (w), 1965 (m), 1948 (m), 1890 (m), 1871 (m), 1820 (w), 1800 (m), 1778 (w), 1746 (m), 1680 (w), 1598 (s), 1579 (m), 1539 (m), 1509 (m), 1490 (vs), 1402 (sh, m), 1395 (s), 1309 (m), 1288 (sh, m), 1272 (s), 1240 (sh, m), 1205 (sh, m), 1190 (s), 1155 (m), 1131 (m), 1112 (m), 1102 (m), 1075 (m), 1062 (s), 1028 (s), 1005 (m), 995 (m), 980 (m), 960 (m), 945 (m), 931 (m), 905 (m), 862 (m), 835 (m), 767 (vs), 729 (vs), 705 (sh, s), 694 (vs), 639 (s), 554 (s), 509 (m), 440 (m), 415 (m), 380 (vs), 350 (s), 260 (vs), 230 (vs). Anal. Calcd: C, 43.86; 4, 4.79. Found: C, 43.92; H, 4.96. Cryoscopic molecular weight, benzene solution, formula weight 273.83 (observed molality, observed MW, association): 0.0831, 588.5, 2.15; 0.0574, 569.7, 2.08; 0.0428, 573.2, 2.09. Solubility: soluble in THF, Et_2O, benzene, and pentane. Neophylgallium(III) dichloride formed a stable 1:1 adduct with NMe_3 and THF but did not form a stable adduct with Et_2O.

Synthesis of $(PhMe_2CCH_2)_2GaN(H)(Pr)$. In a typical experiment, $Ga(CH_2CMe_2Ph)_3$ (2.16 g, 4.60 mmol) and propylamine (0.314 g, 5.31 mmol) were heated at 140–150 °C for 3 days in a sealed tube. After heating, the volatile products from the elimination reaction, $C_6H_5CMe_3$ and excess NH_2Pr, were removed by vacuum distillation. The organogallium amide $(PhMe_2CCH_2)_2GaN(H)Pr$ was isolated by washing the product out of the reaction tube with pentane through a medium glass frit and was recrystallized at −30 °C to yield 1.514 g, 3.840 mmol, 83.4% yield based on $Ga(CH_2CMe_2Ph)_3$. Crystallographic quality crystals were obtained by slow cooling of a saturated pentane solution to −30 °C.

$(PhMe_2CCH_2)_2GaN(H)(Pr)$: mp 129.3–131.0 °C; ^1H NMR (C_6D_6, δ) 7.37 (d, 4 H, *o*-Ar, $^3J_{CCH}$ = 7.50 Hz), 7.21 (t, 4 H, *m*-Ar, $^3J_{CCH}$ = 7.50 Hz), 7.06 (t, 2 H, *p*-Ar, $^3J_{CCH}$ = 7.20 Hz), 2.11 (q, 2 H, CH_2, $^3J_{CCH}$ = 7.90 Hz), 1.38 (s, 12 H, CMe_2(neophyl)), 0.92 (s, 4 H, CH_2(neophyl)), 0.87 (m, 2 H, NCH_2), 0.66 (t, 3 H, CH_3, $^3J_{CCH}$ = 7.05 Hz), 0.02 (t, 1 H, NH, $^3J_{CNH}$ = 7.65 Hz); IR (Nujol mull, cm^{-1}) 3298 (s), 3082 (s), 3050 (s), 3019 (vs), 2720 (s), 1955 (m), 1940 (m), 1595 (s), 1578 (m), 1531 (m), 1490 (vs), 1439 (sh, vs), 1361 (vs), 1356 (s), 1301 (m), 1276 (m), 1245 (m), 1230 (m), 1225 (m), 1181 (s), 1154 (m), 1130 (m), 1098 (w), 1085 (m), 1071 (m), 1061 (sh, m), 1052 (vs), 1045 (sh, s), 1025 (s), 1010 (s), 999 (m), 989 (sh, m), 979 (m), 955 (m), 926 (w), 900 (m), 889 (m), 862 (s), 845 (s), 829 (sh, m), 760 (vs), 748 (m), 715 (vs), 695 (vs), 686 (s), 620 (m), 599 (m), 568 (s), 550 (m), 505 (w), 499 (m), 459 (s), 439 (sh, w), 409 (sh, w), 399 (m), 268 (vw), 236 (m). Anal. Calcd: C, 70.07; H, 8.69. Found: C, 70.24; H, 8.75. Cryoscopic molecular weight, benzene solution, formula weight 394.25 (observed molality, observed MW, association): 0.0833, 709, 1.80; 0.0663, 713, 1.81; 0.0508, 723, 1.83. Solubility: soluble in benzene and pentane.

Collection of X-ray Diffraction Data for $[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$. The crystal selected for the structural study had well-defined faces and approximate dimensions of 0.35 mm × 0.30 mm × 0.30 mm. Due to its extreme air sensitivity it was sealed into a thin-walled capillary under strictly anaerobic conditions. The capillary was then mounted and aligned on a Siemens R3m/V four-circle single-crystal diffractometer. Details of data collection appear in Table I.

The crystal belongs to the triclinic system, possible space groups being the centrosymmetric $P\bar{1}$ and the noncentrosymmetric $P1$. (The former was shown later to be the correct choice). An entire sphere of data (two equivalent forms) was collected for 2θ = 5–50° (Mo Kα radiation). This was done to increase the quality of the crystal structure through the merging of the two forms of data. A total of 6274 reflections were collected and merged to 3803 unique data (R_{int} = 1.8%). The resulting data were corrected for Lorentz and polarization effects. Absorption problems were corrected for by the use of a semiempirical ψ-scan technique.

Solution and Refinement of the Structure of $[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$. The resulting data set was fed into a VAX3100 workstation which was operating with the Siemens SHELXTL PLUS program system.[10] Data reduction, structural solution, and data refinement were performed under this system.

The resulting solution was in the centrosymmetric space group $P\bar{1}$ (C_i^1; No. 2). The structure was solved by the use of direct methods followed by full-matrix least-squares refinement. Positional and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms were refined as well as positional parameters for the unique N-bonded hydrogen atom of the μ-NHPr ligand. All remaining hydrogen atoms were input in calculated positions with d(C–H) = 0.96 Å.[11] Following refinement, the largest features remaining on the electron density difference map were a maximum peak height of 0.30 $e^-/Å^3$ and a minimum of −0.22 $e^-/Å^3$. This corresponded to a structural model which converged with reliability factors of R = 3.57% and R_w = 3.16% for all 3803 unique data. (R = 2.52% and R_w = 2.62% for those 3111 data with $|F_o| > 6\sigma(|F_o|)$.) The structure was also corrected for secondary extinction by refining the parameter χ in the expression $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$; the refined value was χ = 0.0004 (2).

Final atomic coordinates are collected in Table II.

Lewis Acid–Base Studies. The tendency of $Ga(CH_2CMe_2Ph)_3$, $(PhMe_2CCH_2)_2GaCl$, and $(PhMe_2CCH_2)_2GaCl_2$ to form Lewis acid–base adducts with NMe_3, Et_2O, and THF was investigated. In a typical experiment a weighed amount of excess Lewis base was vacuum distilled onto a weighed amount of the Lewis acid. After the resulting sample was warmed to room temperature and stirred for 1–2 h, the excess base was removed

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Table I. Experimental Data for the X-ray Diffraction Study of *trans*-[$(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$

	Crystal Data
empirical formula	$C_{46}H_{68}Ga_2N_2$
color	white
crystal size	0.35 × 0.30 × 0.30 mm
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	$a = 10.739\ (2)$ Å $b = 10.844\ (2)$ Å $c = 11.125\ (2)$ Å $\alpha = 69.140\ (10)°$ $\beta = 62.960\ (10)°$ $\gamma = 76.740\ (10)°$
volume	1074.7 (3) $Å^3$
Z	1
formula weight	788.5
density (calcd)	1.218 Mg/m^3
absorption coefficient	1.279 mm^{-1}
$F(000)$	420
	Data Collection
diffractometer used	Siemens R3m/V
radiation	Mo Kα (λ = 0.71073 Å)
temperature	298 K
monochromator	highly oriented graphite crystal
2θ range	5.0–50.0°
scan type	$2\theta-\theta$
scan speed	constant; 1.00°/min in ω
scan range (ω)	0.70° plus Kα separation
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-13 \le l \le 13$
reflections collected	7606
independent reflections	3803 (R_{int} = 1.93%)
observed reflections	3803 ($F > 0.3\sigma(F)$)
observed reflections	3111 ($F > 6.0\sigma(F)$)
absorption correction	semiempirical
min/max transmission	0.8180/0.9835
	Solution and Refinement
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
extinction correction	$\chi = 0.0004\ (2)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0005F^2$
number of parameters refined	264
final R indices (0.25σ data)	R = 3.57%, R_w = 3.46%
final R indices (6.00σ data)	R = 2.52%, R_w = 2.62%
R indices (all data)	R = 3.57%, R_w = 3.46%
goodness-of-fit	0.97
largest and mean Δ/σ	0.002, 0.000
data to parameter ratio	14.4/1
largest difference peak	0.30 e $Å^{-3}$
largest difference hole	−0.22 e $Å^{-3}$

by vacuum distillation. Mass measurements were used to determine the quantity of base which reacted. The mole ratio of Lewis acid to base which reacted, the melting point, and the ^1H NMR spectrum of the resulting adducts are described below. The Lewis acids $Ga(CH_2CMe_2Ph)_3$, $(PhMe_2CCH_2)_2GaCl$, and $(PhMe_2CCH_2)GaCl_2$ did not form stable adducts with Et_2O or $(PhMe_2CCH_2)_2GaCl$ with THF.

$(PhMe_2CCH_2)_3Ga{\cdot}NMe_3$: mole ratio $Ga(CH_2CMe_2Ph)_3/NMe_3$ = 0.99; mp 119–134 °C dec; ^1H NMR (C_6H_6, δ) 1.61 (s, 9 H, NMe_3), 1.38 (s, 18 H, CMe_2), 0.73 (s, 6 H, CH_2).

$(PhMe_2CCH_2)_2ClGa{\cdot}NMe_3$: mole ratio $(PhMe_2CCH_2)_2GaCl/NMe_3$ = 1.01; mp 76.5–80.1 °C; ^1H NMR (C_6H_6, δ) 1.60 (s, 12 H, CMe_2), 1.52 (s, 9 H, NMe_3), 0.86 (s, 4 H, CH_2).

$(PhMe_2CCH_2)Cl_2Ga{\cdot}NMe_3$: mole ratio $(PhMe_2CCH_2)GaCl_2/NMe_3$ = 0.92; mp 46.4–48.4 °C; ^1H NMR (C_6H_6, δ) 1.67 (s, 15 H, CMe_2 and NMe_3), 1.57 (s, 2 H, CH_2).

Table II. Final Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å × 10^3) for *trans*-[$(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$

	x	y	z	$U(eq)^a$
Ga(1)	3757 (1)	4258 (1)	5639 (1)	30 (1)
N(1)	5819 (2)	4025 (2)	4368 (2)	32 (1)
H(1)	5794 (23)	4060 (21)	3633 (23)	33 (6)
C(20)	3404 (2)	2824 (2)	7450 (2)	43 (1)
C(21)	2207 (3)	2956 (2)	8868 (2)	45 (1)
C(22)	2117 (3)	1598 (2)	9989 (2)	47 (1)
C(23)	3115 (3)	1106 (3)	10522 (3)	84 (2)
C(24)	3076 (4)	−123 (4)	11489 (4)	99 (2)
C(25)	2049 (4)	−907 (3)	11932 (3)	86 (2)
C(26)	1034 (4)	−451 (3)	11444 (3)	80 (2)
C(27)	1068 (3)	792 (3)	10480 (3)	63 (1)
C(28)	2478 (4)	3991 (3)	9329 (3)	76 (2)
C(29)	819 (3)	3416 (3)	8687 (3)	66 (1)
C(30)	2733 (2)	4745 (2)	4402 (2)	41 (1)
C(31)	2441 (2)	3672 (2)	3966 (2)	46 (1)
C(32)	3808 (3)	2933 (2)	3200 (2)	46 (1)
C(33)	4793 (3)	3586 (3)	1917 (3)	61 (1)
C(34)	6015 (4)	2928 (4)	1196 (3)	84 (2)
C(35)	6291 (4)	1608 (4)	1733 (5)	94 (2)
C(36)	5347 (5)	951 (4)	3006 (5)	101 (3)
C(37)	4123 (4)	1602 (3)	3717 (4)	75 (2)
C(38)	1439 (3)	2722 (3)	5289 (3)	64 (1)
C(39)	1681 (3)	4317 (3)	2986 (3)	70 (2)
C(41)	6649 (2)	2774 (2)	4756 (2)	41 (1)
C(42)	8130 (3)	2664 (2)	3672 (3)	50 (1)
C(43)	8934 (3)	1364 (3)	4087 (3)	72 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$(PhMe_2CCH_2)_3Ga{\cdot}THF$: mole ratio $Ga(CH_2CMe_2Ph)_3/THF$ = 0.96; mp 98.7–102.6 °C; ^1H NMR (C_6H_6, δ) 3.40 (m, 4 H, THF), 1.27 (s, 22 H, CMe_2 and THF), 0.80 (s, 6 H, CH_2). $(PhMe_2CCH_2)_3Ga{\cdot}THF$ was observed to dissociate very slowly at room temperature.

$(PhMe_2CCH_2)Cl_2Ga{\cdot}THF$: mole ratio $(PhMe_2CCH_2)GaCl_2/THF$ = 1.05; mp 48.5–49.8 °C; ^1H NMR (C_6H_6, δ) 3.34 (m, 4 H, THF), 1.49 (s, 6 H, CMe_2), 1.38 (s, 2 H, CH_2), 0.99 (m, 4 H, THF).

Results and Discussion

A series of organogallium compounds that incorporate the neophyl ligand including $Ga(CH_2CMe_2Ph)_3$, $Ga(CH_2CMe_2Ph)_2Cl$, $Ga(CH_2CMe_2Ph)Cl_2$, and $(PhMe_2CCH_2)_2GaN(H)(Pr)$ have been prepared by reactions typical of group 13 chemistry. The homoleptic derivative $Ga(CH_2CMe_2Ph)_3$ was prepared by Grignard reaction in diethyl ether solution. The ether was readily removed as no apparent adduct formed. However, the isolation of pure samples of $Ga(CH_2CMe_2Ph)_3$ was hindered by contamination with bineophyl, $PhMe_2CCH_2CH_2CMe_2Ph$. Fractional distillation and recrystallization served to provide an analytically pure, colorless crystalline solid at room temperature. The halide derivatives were prepared from $Ga(CH_2CMe_2Ph)_3$ and $GaCl_3$ by using stoichiometric ligand redistribution reactions. Neophylgallium amide, $(PhMe_2CCH_2)_2GaN(H)(Pr)$, was prepared by an elimination reaction between $Ga(CH_2CMe_2Ph)_3$ and H_2NPr at 140–150 °C.

The characterization data for all compounds, which include partial elemental analyses (C, H), melting points, ^1H NMR and IR spectroscopic data, cryoscopic molecular weight studies, and solubility properties, are consistent with the molecular formulas $Ga(CH_2CMe_2Ph)_3$, $[Ga(CH_2CMe_2Ph)_2Cl]_2$, and $[Ga(CH_2CMe_2Ph)Cl_2]_2$. It is noteworthy that all of the compounds have melting points which are higher than those for the corresponding neopentyl derivatives.[2] The structures of all three compounds would be expected to be similar to most other organogallium compounds. The homoleptic derivative Ga-

Table III. Important Interatomic Distances (Å) for *trans*-$[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$

Ga(1)-N(1)	2.029 (2)	Ga(1)-C(20)	1.992 (2)
Ga(1)-N(1A)	2.013 (2)	Ga(1)-C(30)	1.994 (3)
Ga(1)···Ga(1A)	2.938 (1)	N(1)-C(41)	1.483 (3)
N(1)···N(1A)	2.776 (3)	N(1)-H(1)	0.817 (30)

Table IV. Important Interatomic Angles (deg) for *trans*-$[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$

N(1)-Ga(1)-N(1A)	86.7 (1)	C(20)-Ga(1)-C(30)	128.3 (1)
N(1)-Ga(1)-C(20)	107.1 (1)	N(1A)-Ga(1)-C(20)	114.3 (1)
N(1)-Ga(1)-C(30)	105.9 (1)	N(1A)-Ga(1)-C(30)	106.2 (1)
Ga(1)-N(1)-Ga(1A)	93.3 (1)	Ga(1)-N(1)-C(41)	119.3 (1)
Ga(1)-N(1)-H(1)	102.5 (15)	Ga(1A)-N(1)-C(41)	120.3 (2)
Ga(1A)-N(1)-H(1)	113.4 (15)	C(41)-N(1)-H(1)	106.4 (14)

$(CH_2CMe_2Ph)_3$ would be expected to be a trigonal-planar molecule (GaC_3) whereas the chloride derivatives would be expected to have chloride bridges with four-coordinate gallium atoms.

Lewis acid–base studies suggest that the neophylgallium compounds have Lewis acidities which are very similar to those of the corresponding neopentylgallium compounds.[2] If there is a difference, the neophyl derivatives might be slightly stronger Lewis acids. The replacement of a methyl group in the neopentyl group by a phenyl group might serve to reduce steric hindrance slightly and make the neophyl derivatives the stronger Lewis acids. Thus, $Ga(CH_2CMe_2Ph)_3$ formed a 1/1 adduct with NMe_3 and THF, but the THF adduct appeared to dissociate slowly at room temperature. In contrast, trineopentylgallium did not form an adduct with THF and the characterization data for the NMe_3 adduct suggested slight dissociation. The monochloride derivative $Ga(CH_2CMe_2Ph)_2Cl$ appears to be the weakest Lewis acid of the three derivatives studied as it was the only one of the three new gallium compounds which did not form an adduct with THF. However, an adduct was formed with NMe_3. The chloride bridge bonds must compete effectively with the THF for the gallium acid site. The dichloride derivative, $Ga(CH_2CMe_2Ph)Cl_2$, formed 1/1 adducts with both THF and NMe_3.

Trineophylgallium(III) undergoes a facile elimination reaction of 140–150 °C with NH_2Pr to form $(PhMe_2CCH_2)_2GaN(H)(Pr)$ and *tert*-butylbenzene. The gallium–nitrogen product was fully characterized including an X-ray structural study. The unit cell contains one dimeric molecule which lies about a center of symmetry. All molecules are separated by normal van der Waals distances, and there are no anomalously short intermolecular contacts. Distances and angles are provided in Tables III and IV.

As shown in Figures 1 and 2, the dimeric molecule contains a Ga_2N_2 core which is required by symmetry to be planar. The *n*-propyl groups are arranged trans to each other across the ring. The Ga–N distances are Ga(1)–N(1A) = Ga(1A)–N(1) = 2.013 (2) Å and Ga(1)–N(1) = Ga(1A)–N(1A) = 2.029 (2) Å. These distances are slightly longer than the Ga–N distances observed for some other related gallium–nitrogen compounds (Table V). The two gallium atoms are separated by 2.938 (1) Å whereas the two nitrogen atoms are 2.776 (3) Å apart. The internal ring angles are N(1)–Ga(1)–N(1A) = 86.7 (1)° and Ga(1)–N(1)–Ga(1A) = 93.3 (1)°. The CH_2CMe_2Ph ligands are bonded to gallium at distances of Ga(1)–C(20) = 1.992 (2) Å and Ga(1)–C(30) = 1.994 (3) Å, with an interligand angle of C(20)–Ga(1)–C(30) = 128.3 (1)°. These ligands are displaced out of the Ga_2N_2 plane (as indicated by the Ga(1A)···Ga–C angles) by 61.0° and 67.6°, respectively. The Ga–C distances are slightly longer than the distances observed for the methyl groups bound to the gallium atoms that form the related Ga_2N_2 ring in $[Me_2Ga]_2 14aneN_4[GaMe_3]_2$[15] of 1.933 (7) Å but comparable to the average gallium–carbon distance in $[(Me_3CCH_2)_2GaPPh_2]_2$[16] of 2.003 ± 0.009 Å and in $[(t\text{-}Bu)_2GaP(C_5H_9)(H)]_2$[17] of 2.011 (3) Å. The position of the unique hydrogen atom on nitrogen was refined, yielding an N–H distance of 0.817 (30) Å, and is comparable to the N–H distance in the closely

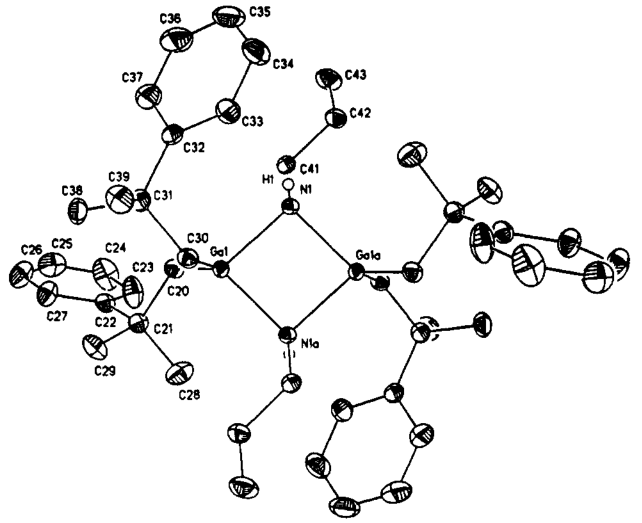

Figure 1. $[(PhMe_2CCH_2)GaN(H)(Pr)]_2$, with all C-bonded hydrogen atoms omitted.

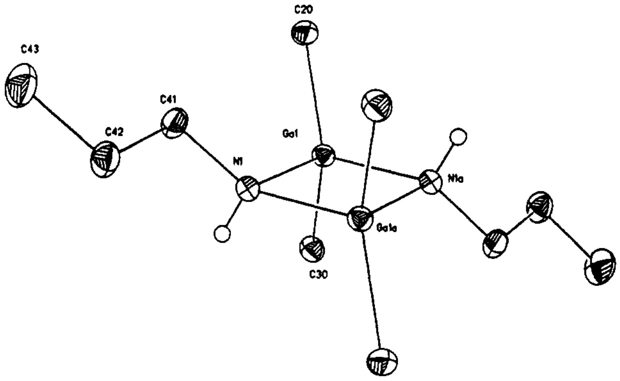

Figure 2. $[Ga(C)_2(\mu\text{-}NHC_3)]_2$ core of the molecule.

Table V. Comparisons of Ga–N and Ga–C Bond Distances in Gallium–Nitrogen Compounds

compound	Ga–N	Ga–C	ref
$[Cl_2GaN(H)(SiMe_3)]_2$	1.974 (4) 1.964 (4)		12
$[Cl_2GaN(Me)(SiMe_3)]_2$	1.985 (5) 1.983 (5) 1.987 (5) 1.989 (5)		12
$[H_2GaN(CH_2)_2]_3$	1.97 (2)		13
$[H_2GaNH_2]_3$	1.96 (2) 1.96 (2) 1.98 (2) 1.96 (1)		14
$[Me_2Ga]_2[14]aneN_4[GaMe_3]_2$	2.014 (6) 2.003 (6)	1.933 (7)	15
$[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$	2.013 (2) 2.029 (2)	1.992 (2) 1.994 (3)	this work

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related compound $[Cl_2GaN(H)(SiMe_3)]_2$[12] of 0.838 (47) Å. The unique hydrogen in $[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$ is displaced from the gallium–nitrogen plane by 64.0° (defined by the angle N(1A)···N(1)–H(1)). The α-carbon atom of the *n*-propyl group is displaced from the Ga_2N_2 plane by 43.7° and is associated with the distance N(1)–C(41) = 1.483 (3) Å. Angles around nitrogen are Ga(1)–N(1)–C(41) = 119.3 (1)°, Ga(1A)–N(1)–C(41) = 120.3 (2)°, Ga(1)–N(1)–H(1) = 102.5 (15)°, Ga(1A)–N(1)–H(1) = 113.4 (15)°, and C(41)–N(1)–H(1) = 106.7 (14)°. Symmetry restraints require that the two amide hydrogens are trans to each other across the ring. All other distances and angles in the structure are normal.

The cryoscopic molecular weight studies of $(PhMe_2CCH_2)_2GaN(H)(Pr)$ identify the presence of dimeric molecules in benzene solution. The ^{1}H NMR spectrum of the compound further suggests the presence of only molecules in the trans conformation in solution as only one set of lines for CH_2 and CMe_2 protons for the neophyl ligand or for the propyl group protons was observed. If the cis isomer had been present, two sets of lines of equal intensity, one for each type of proton, would have been expected. Thus, the molecule in solution is the same as the molecule present in the crystalline solid. There was no change in either the degree of association or the conformation of the molecule upon dissolution in benzene. In comparison, $[Me_2GaN(Me)(Ph)]_2$[18] existed as a mixture of cis (70%) and trans (30%) isomers in benzene solution. The sharp melting point of $[Me_2GaN(Me)(Ph)]_2$ (112–114 °C) and the presence of only one crystalline form were used to suggest only one isomer (probably trans) in the solid state. The related compound $[Me_2InN(Me)(Ph)]_2$[18] existed as a trans isomer in the solid state according to a structural study whereas a mixture of cis and trans isomers was observed in solution. Thus, at least one metal–nitrogen bond in these dimeric species was broken upon dissolution in order to have isomerization.

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Registry No. $Ga(CH_2CMe_2Ph)_3$, 138667-97-7; $[(PhMe_2CCH_2)_2GaCl]_2$, 138667-98-8; $[(PhMe_2CCH_2)GaCl_2]_2$, 138667-99-9; *trans*-$[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$, 138668-00-5; $(PhMe_2CCH_2)MgCl$, 35293-35-7; $GaCl_3$, 13450-90-3; $(PhMe_2CCH_2)_3Ga{\cdot}NMe_3$, 138668-01-6; $(PhMe_2CCH_2)_2ClGa{\cdot}NMe_3$, 138668-02-7; $(PhMe_2CCH_2)Cl_2Ga{\cdot}NMe_3$, 138668-03-8; $(PhMe_2CCH_2)_3Ga{\cdot}THF$, 138668-04-9; $(PhMe_2CCH_2)Cl_2Ga{\cdot}THF$, 138668-05-0; propylamine, 107-10-8.

Supplementary Material Available: Complete lists of distances and angles, anisotropic thermal parameters, and calculated positions of hydrogen atoms for $[(PhMe_2CCH_2)_2GaN(H)(Pr)]_2$ (4 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Interaction of Tris-*tert*-butylgallium with Elemental Sulfur, Selenium, and Tellurium

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The interaction of Ga(^{t}Bu)$_3$ with S_8 leads to the formation of a mixture of [(^{t}Bu)$_2$Ga(μ-SS^{t}Bu)]$_2$ (**1**) and [(^{t}Bu)$_2$Ga(μ-S^{t}Bu)(μ-SS^{t}Bu)Ga(^{t}Bu)$_2$] (**2**) in a ca. 1:3 molar ratio and trace quantities of [(^{t}Bu)$_2$Ga(μ-S^{t}Bu)]$_2$ (**3**), which may be prepared directly from ^{t}BuSH and Ga(^{t}Bu)$_3$. Compound **1** decomposes in the absence of excess S_8 to give **2**, while in the presence of S_8 the thermolysis of compound **1**, **2**, or **3** yields the cubane [(^{t}Bu)GaS]$_4$ (**4**) and a range of di-*tert*-butyl polysulfides, ^{t}BuS(S)$_n$S^{t}Bu (n = 1–4). Compound **4** may also be prepared by the thermolysis of [(^{t}Bu)$_2$Ga(μ-SH)]$_2$ (**5**). Repeated sublimation of **4**, at atmospheric pressure, results in its structural rearrangement to the octamer [(^{t}Bu)GaS]$_8$ (**6**). The reaction of Ga(^{t}Bu)$_3$ with Se_8 results in the direct formation of the cubane [(^{t}Bu)GaSe]$_4$ (**7**). In contrast, the use of metallic Se yields [(^{t}Bu)$_2$Ga(μ-Se^{t}Bu)]$_2$ (**8**) as the only gallium-containing product; however, prolonged thermolysis of **8** in the presence of excess Se metal also results in the formation of **7**. In a similar manner, metallic Te reacts with Ga(^{t}Bu)$_3$ at ambient temperatures to yield [(^{t}Bu)$_2$Ga(μ-Te^{t}Bu)]$_2$ (**9**). Thermolysis of **9** in refluxing toluene in the presence of excess Te metal allows for the isolation of the cubane compound [(^{t}Bu)GaTe]$_4$ (**10**). The reaction pathway to the formation of the cubane clusters, **4**, **7**, and **10** is discussed. Compounds **1**–**10** have been characterized by elemental and thermogravimetric analysis, mass spectrometry, and ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopy. In addition, the structure of **7** has been confirmed by X-ray crystallography. The compound [(^{t}Bu)GaSe]$_4$ (**7**) crystallizes in the cubic space group $P\bar{4}3n$, with a = 17.667 (1) Å, Z = 8, 337 observed data, R = 0.047, and R_w = 0.055.

Introduction

Whereas the often violent reaction of group 13 alkyls with dioxygen has, for obvious reasons, been a subject of both practical concern and academic interest for many years, few studies have dealt with their reactions with the elemental chalcogens, sulfur, selenium, and tellurium.

The direct reaction of sulfur with trialkylaluminum compounds was first reported, in the patent literature,[2]

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