Reaction of Sulfur with Ga−C Bonds: Synthesis and Characterization of $[PyRGaS]_3$ Formed from $Ga(S_2R)_3$ (R = Et, Me)

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Received November 14, 1995[⊗]

The reactions of $Ga(CH_2CH_3)_3$ with variable amounts of elemental sulfur, S_8, in toluene or benzene at different temperatures result in the insertion of sulfur into the Ga−C bonds to form the compounds $Ga[(S{-}S)CH_2CH_3]_3$ (**I**) and $Ga[(S{-}S{-}S)CH_2CH_3]_3$ (**II**). Compound **I** was isolated from the reaction at low temperature while at room temperature; compound **II** was the major product. Compound **II** exhibited the maximum extent of sulfur insertion even when the reactions were carried out with more than 9.0 equiv of sulfur. The reactions of $Ga(CH_3)_3$ with various amounts of sulfur in toluene or benzene only result in the formation of compound **III**, $Ga[(S{-}S)CH_3]_3$. In pyridine at −30 °C, deinsertion of the sulfur atoms from Ga−S−S−C bonds was observed for the first time from compounds **I** and **III** resulting in formation of the six-membered Ga−S ring compounds **IV**, $[PyEtGaS]_3$, and **V**, $[PyMeGaS]_3$, respectively. Compounds **IV** and **V** were characterized by ^1H NMR, ^{13}C NMR, elemental analyses, thermogravimetric analysis, and single-crystal X-ray diffraction. Compound **IV** crystallized in the monoclinic space group $P2_1/n$, with $a = 9.288(2)$ Å, $b = 14.966(2)$ Å, $c = 19.588(3)$ Å, $\beta = 90.690(10)°$, and $Z = 4$. Compound **V** crystallized in the monoclinic space group $P2_1/c$, with $a = 10.385(1)$ Å, $b = 15.300(2)$ Å, $c = 15.949(2)$ Å, $\beta = 107.01(1)°$, $Z = 4$, unit cell volume = 2423.5(5) Å^3, $R = 0.030$, and $R_w = 0.026$. The sulfur insertion reaction pathway was investigated by time-dependent and variable-temperature ^1H NMR spectroscopy.

Introduction

Compounds containing bonds between sulfur and other main group elements exhibit a rich and interesting structural chemistry due to the wide variety of bonding modes available. In addition, these molecules can be used in the synthesis of metal sulfide materials.[1−9] Much of the interest in this area is derived from the observations that molecular metal−sulfur clusters often adopt structures which are similar to the structures of known crystalline solid-state materials. The adamantane-core structure framework of Zn−S and Cd−S clusters and its relationship to sphalerite phase ZnS and CdS is a classical example.[1,5,10]

Although not as comprehensively studied as the **II−VI** compound semiconductors, group 13 chalcogenides have attracted increasing interest, in particular ME and M_2E_3 (M = Ga, In; E = S, Se) because of their potential applications in switching devices,[11] photovoltaics,[12] and nonlinear optics.[13] In addition, gallium sulfide has been shown to passivate GaAs.[14] Many synthetic approaches to prepare compounds containing bonds between the group 13 and 16 elements have been investigated.[1,2,15−21] In some cases, these molecular complexes have been converted into the new phases of solid-state materials, in which the connection between the structure of the solid-state material and the molecular precursor was demonstrated.[22−27]

Insertion of S into M−C bonds is one method to prepare metal−sulfur clusters and recently resulted in the formation of an unusual wurtzite-core zinc thiolate cluster, $Zn_{10}(SEt)_{10}Et_{10}$,[26] and a sphalerite-like neutral molecular zinc thiolate cluster, $Zn_{10}S_4(SEt)_{10}{\cdot}4(3,5\text{-lutidine})$.[27] It has been demonstrated that

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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0020-1669/96/1335-2611$12.00/0

these species can be converted to wurtzite and sphalerite phase ZnS, respectively, under the appropriate conditions, demonstrating that their molecular structure may influence their crystallization behavior. There have been relatively few studies that have dealt with the reactions between the group 13 alkyls and elemental chalcogens.[1,2,15,16,20,21] Barron and co-workers have studied the reaction of Ga^tBu_3 with elemental sulfur and obtained a mixture of $[^tBu_2Ga(\mu\text{-}SS^tBu)]_2$, $[^tBu_2Ga(\mu\text{-}S^tBu)(\mu\text{-}SS^tBu)\text{-}Ga^tBu_2]$, and a trace amount of $[^tBu_2Ga(\mu\text{-}S^tBu)]_2$.[15] On thermolysis in the presence of sulfur, these compounds gave the cubane species $[^tBuGaS]_4$, which on dissolution in pyridine formed $[^tBuPyGaS]_3$.[16]

In this paper, the reactions of $Ga(CH_2CH_3)_3$ and $Ga(CH_3)_3$ with elemental sulfur are described. We report the synthesis and characterization of the sulfur-inserted compounds $Ga[(S-S)CH_2CH_3]_3$ (**I**), $Ga[(S-S-S)CH_2CH_3]_3$ (**II**), and $Ga[(S-S)CH_3]_3$ (**III**) and the trimeric ring compounds **IV**, $[PyEtGaS]_3$, and **V**, $[PyMeGaS]_3$, which were formed from the sulfur deinsertion of **I** and **III** in pyridine, respectively. These compounds were characterized by ^1H NMR, ^{13}C NMR, elemental analyses, GC-MS, IR, and thermogravimetric analysis, and compounds **IV** and **V** were also characterized by single-crystal X-ray diffraction. The reaction pathway for the sulfur insertion was also investigated.

Experimental Section

General Procedures and Instrumentation. All manipulations were carried out under an atmosphere of dry nitrogen.[28] Solvents were distilled over sodium benzophenone ketyl and stored over predried 4 Å molecular sieves. Triethylgallium and trimethylgallium were used as purchased from Strem. Combustion elemental analyses were performed by Ms. R. Ju in the Department of Chemistry, University of New Mexico. ^1H and $^{13}C\{^1H\}$ NMR spectra (in C_6D_6, C_7D_8, or C_5D_5N) were recorded on a Bruker AC-250 NMR spectrometer by using the protio impurity of the deuterated solvent as reference for ^1H NMR spectroscopy and the ^{13}C resonances of the solvent as reference for $^{13}C\{^1H\}$ NMR spectroscopy. Single-crystal X-ray diffraction data were collected on a Siemens R3m/V diffractometer at the Department of Chemistry, University of New Mexico. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA-7 instrument. GC-MS spectra were recorded using a Finnigan MAT Series 450 instrument. An electron beam energy of 65 eV was used for EI mass spectroscopy of the liquid samples and 35 eV energy was used for the solid samples. Infrared data were recorded on a Perkin-Elmer Model 1620 FTIR spectrophotometer.

Syntheses. A typical experimental procedure is given for each compound, followed by the relevant characterization data.

(a) Compound I, $Ga[(S-S)CH_2CH_3]_3$. To a clear solution of $Ga(CH_2CH_3)_3$ (1.57 g, 0.01 mol) in 40 mL of toluene was added 0.96 g of S_8 (0.03 mol of S). The sulfur subsequently dissolved to form a clear yellow solution after stirring for 20 min at room temperature. Then the reaction flask was cooled to −78 °C, and the mixture was stirred for 7 days. A white suspension was formed. The white suspension was centrifuged, and the white precipitate was collected, washed with pentane, and pumped dry to give 1.50 g of white powder. The final yield of **I** was 86.0% based on S_8. ^1H NMR (in C_6D_6): $\delta = 2.35$ ppm (q, CH_2 of $Ga-S-S-CH_2CH_3$), $\delta = 1.08$ ppm (t, CH_3 of $Ga-S-S-CH_2CH_3$). $^{13}C\{^1H\}$ NMR (in C_6D_6): $\delta = 32.80$ ppm (s, CH_2 of $Ga-S-S-CH_2CH_3$), $\delta = 14.50$ ppm (s, CH_3 of $Ga-S-S-CH_2CH_3$). Anal. Calcd for $C_6H_{15}S_6Ga$: C, 20.63; H, 4.30; N, 0. Found: C, 20.86; H, 3.98; N, 0. IR data (in Nujol, cm^{-1}): 2860 (s), 1468 (s), 1370 (s), 1191 (w), 1001 (w), 934 (w), 726 (w), 691 (w), 649 (m), 541 (m). MS (EI): *m/z* 348.7 (M^+), 154 ($Et-S-S-S-Et$), 122 ($Et-S-S-Et$), 90 ($Et-S-Et$).

(b) Compound II, $Ga[(S-S-S)CH_2CH_3]_3$. The stoichiometric amount of sulfur (2.88 g, 0.09 mol of S) was added to a solution of $Ga(CH_2CH_3)_3$ (1.57 g, 0.01 mol) in 90 mL of benzene over 20 min. After 2 h of stirring, a white precipitate was formed, and after 5 days of stirring at room temperature, the reaction mixture was centrifuged and the white precipitate was collected, washed with pentane, and pumped dry to give 3.60 g of white powder. The final yield was 81.0%. Spectroscopic analysis revealed the presence of a small amount (∼4.5%) of compound **I** in this sample. ^1H NMR (in C_6D_6): $\delta = 2.52$ ppm (q, CH_2 of $Ga-S-S-S-CH_2CH_3$), $\delta = 2.36$ ppm (q, CH_2 of $Ga-S-S-CH_2CH_3$) (the ratio of the two quartets is 99.96:4.69), $\delta = 1.09$ ppm (m, CH_3 of $Ga-S-S-S-CH_2CH_3$ and $Ga-S-S-CH_2CH_3$). $^{13}C\{^1H\}$ NMR (in C_6D_6): $\delta = 38.2$ ppm (s, CH_2 of $Ga-S-S-S-CH_2CH_3$), $\delta = 14.80$ ppm (s, CH_3 of $Ga-S-S-S-CH_2CH_3$). Anal. Calcd for $C_6H_{15}S_9Ga$: C, 16.19; H, 3.37; N, 0. Found: C, 16.85; H, 3.41; N, 0. IR data (in Nujol, cm^{-1}): 2860 (s), 1460 (s), 1377 (s), 1193 (w), 1003 (m), 961 (w), 932 (w), 694 (w), 655 (m), 570 (w), 544 (m). MS (EI): *m/z* 349 ($M^+ - 3S$), 256 (S_8), 186 ($Et-S-S-S-S-Et$), 154 ($Et-S-S-S-Et$), 122 ($Et-S-S-Et$), 90 ($Et-S-Et$).

(c) Compound III, $Ga[(S-S)CH_3]_3$. The stoichiometric amount of sulfur (1.92 g, 0.06 mol) was added to a clear solution of $Ga(CH_3)_3$ (1.15 g, 0.01 mol) in 70.0 mL of toluene. After 2 h of stirring at room temperature, no reaction was found and still some sulfur powder did not dissolve. After 30 min of stirring at 90 °C, all the sulfur dissolved to form a yellow clear solution. Further stirring for 3 h at 90 °C resulted in the formation of a white precipitate. After 8 h of stirring at 90 °C, the reaction mixture was centrifuged and the white precipitate was collected, washed with pentane, and pumped dry to give 2.30 g of white powder. The yield was 75.0%. ^1H NMR (in C_6D_6): $\delta = 2.10$ ppm (s, CH_3 of $Ga-S-S-CH_3$). ^{13}C NMR (in C_6D_6): $\delta = 21.38$ ppm (s, CH_3 of $Ga-S-S-CH_3$). Anal. Calcd for $C_3H_9S_6Ga$: C, 11.74; H, 2.93; N, 0. Found: C, 12.35; H, 2.93; N, 0.

(d) Compound IV, $[PyEtGaS]_3$. Compound **I**, $Ga[(S-S)CH_2CH_3]_3$ (0.5 g, 1.43 mmol), was dissolved in 2.0 mL of pyridine to form a clear solution. The vial containing this solution was put into another larger vial in which there was 2.0 mL of pentane. The large vial was sealed under nitrogen in a drybox and put into a freezer at −30 °C. White, platelike crystals (0.09 g, 0.14 mmol) were obtained after 1 day. The yield was 30.0%. ^1H NMR (in C_5D_5N): $\delta = 0.73$ ppm (q, CH_2 of $-S-Ga-CH_2CH_3$), $\delta = 1.15$ ppm (t, CH_3 of $-S-Ga-CH_2CH_3$), $\delta = 7.08$ ppm (br, 2*H* of pyridine) $\delta = 7.45$ ppm (br, 1*H* of pyridine), $\delta = 8.61$ ppm (br, 2*H* of pyridine). $^{13}C\{^1H\}$ NMR (in C_5D_5N): $\delta = 9.99$ ppm (s, CH_2 of $-S-Ga-CH_2CH_3$), $\delta = 10.87$ ppm (s, CH_3 of $-S-Ga-CH_2CH_3$), $\delta = 123.06$ ppm (t, 2*C* of pyridine), $\delta = 134.75$ ppm (t, 1*C* of pyridine), $\delta = 148.96$ ppm (t, 2*C* of pyridine). Elemental analysis Calcd for $[C_7H_{10}NSGa]_3$: C, 40.0; H, 4.76; N, 6.67. Found: C, 39.74; H, 4.35; N, 6.67.

(e) Compound V, $[PyMeGaS]_3$. Compound **III**, $Ga[(S-S)CH_3]_3$ (0.3 g, 0.98 mmol), was dissolved in 1.5 mL of pyridine, forming a light yellow solution, and pentane vapor was allowed to diffuse in at −30 °C. Clear crystals were obtained after 1 day (0.10 g, 0.17 mmol), a yield of 52.1%. ^1H NMR (in C_5D_5N): $\delta = 0.27$ ppm (s, CH_3 of $-S-Ga-CH_3$). ^{13}C NMR (in C_5D_5N): $\delta = 1.65$ ppm (s, CH_3 of $-S-Ga-CH_3$). Anal. Calcd for $[C_6H_8NSGa]_3$: C, 36.79; H, 4.09; N, 7.15. Found: C, 36.62; H, 3.94; N, 7.03.

X-ray Crystallographic Studies. The clear crystals of $[PyEtGaS]_3$ and $[PyMeGaS]_3$ were grown by dissolving compounds **I** and **III** in pyridine and placing the solutions in a pentane atmosphere at −30 °C for 1 day. Suitable crystals were selected and mounted in thin-walled nitrogen-flushed capillary tubes that were sealed under nitrogen in the drybox.

Crystal data and experimental details for the X-ray diffraction studies of $[PyEtGaS]_3$ and $[PyMeGaS]_3$ are presented in Table 1. The crystallographic data were obtained at 293 K with a 2θ range of 2.0−50° with an ω scan. The solution and refinement results were obtained with Siemens SHELXTL PLUS (PC Version) by direct methods, and the non-hydrogen atoms were located through subsequent least-squares full-matrix cycles and difference Fourier calculations.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL Plus (4.2) program libraries. (G. Sheldrick, Siemens XRD, Madison, WI).

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Table 1. Crystallographic Data for Compounds **IV**, $[PyEtGaS]_3$, and **V**, $[PyMeGaS]_3$

	IV	**V**
empirical formula	$C_{21}H_{30}Ga_3N_3S_3$	$C_{18}H_{24}Ga_3N_3S_3$
a, Å	9.288(2)	10.385(1)
b, Å	14.966(2)	15.300(2)
c, Å	19.588(3)	15.949(2)
β, deg	90.690(10)	107.01(1)
V, Å^3	2722.5(8)	2423.5(5)
Z	4	4
fw	629.8	587.7
space group	$P2_1/n$	$P2_1/c$
T, K	293	293
λ(Mo, Kα), Å	0.710 73	0.710 73
d(calcd), Mg/m^3	1.537	1.611
abs coeff, mm^{-1}	3.190	3.578
R^a	0.0560	0.0302
$R_w^{\,b}$	0.0474	0.0256

[a] $R = \sum\Delta F/\sum F_o$. [b] $R_w = \sum w^{1/2}\Delta F/\sum w^{1/2}F_o$.

Results and Discussion

Synthesis and Characterization of Gallium−Sulfur Compounds. The reaction of $Ga(CH_2CH_3)_3$ with 3 equiv of sulfur in the form of S_8 at −78 °C for 1 week resulted in the formation of compound **I**, $Ga[(S-S)CH_2CH_3]_3$, as a white solid in ∼86% yield based on S_8. A ^1H NMR spectrum of the filtrate of the reaction mixture after the isolation of compound **I** showed peaks consistent with unreacted $Ga(CH_2CH_3)_3$. The ^1H NMR spectrum of **I** in benzene-d_6 showed one quartet at 2.35 ppm and one triplet at 1.08 ppm, consistent with the literature values for $-CH_2$ and $-CH_3$ resonances of $-S-S-CH_2CH_3$, respectively.[29,30] The relative positions of the CH_2 quartet and the CH_3 triplet showed that sulfur insertion into the Ga−C bonds of $Ga(CH_2CH_3)_3$ had taken place. The elemental analysis data were consistent with the empirical formula $Ga[(S-S)CH_2CH_3]_3$, and the molecular ion peak at *m*/*z* 349 was observed in mass spectrum. The analytical and spectroscopic characterization is consistent with a disulfur-inserted compound, $Ga[(S-S)CH_2CH_3]_3$ (**I**). The reactions of $Ga(CH_3)_3$ with 3.0, 6.0, 9.0, and 12.0 equiv of sulfur at 90 °C all formed a white powder which showed one singlet peak at 2.10 ppm in the ^1H NMR spectrum in benzene-d_6. The elemental analysis data were consistent with the empirical formula $Ga[(S-S)CH_3]_3$.

Unlike the reaction of Ga^tBu_3 with S_8, which showed sulfur insertion into only one Ga−C bond forming a mixture of $[(^tBu)_2Ga(\mu\text{-}SS^tBu)]_2$ and $[(^tBu)_2Ga(\mu\text{-}S^tBu)(\mu\text{-}SS^tBu)Ga(^tBu)_2]$ in an approximately 1:3 molar ratio and a trace quantities of $[(^tBu)_2Ga(\mu\text{-}S^tBu)]_2$,[15] in the present work, sulfur inserted into all three Ga−C bonds of $Ga(CH_2CH_3)_3$ and $Ga(CH_3)_3$, which may be due to the smaller size of ethyl and methyl groups.

In an attempt to improve the yield of **I** based on $Ga(CH_2CH_3)_3$, the stoichiometric reaction of $Ga(CH_2CH_3)_3$ with 6 equiv of sulfur was carried out at low temperature for the same period of time but gave a mixture of **I** and **II**, $Ga[(S-S-S)CH_2CH_3]_3$. Compound **II**, $Ga[(S-S-S)CH_2CH_3]_3$, was also obtained as the major product (95.5% of the isolated white solid) of the reaction between 9.0 equiv of elemental sulfur and $Ga(CH_2CH_3)_3$ at both room temperature and 55 °C. The ^1H NMR spectroscopy of the white precipitate isolated from this reaction mixture gave one quartet at 2.52 ppm, which corresponds to the literature value for CH_2 resonances of $-S-S-S-CH_2CH_3$,[29,30] as well as the peaks corresponding to the presence of 4.5% of compound **I**. Elemental analyses of the white precipitate were consistent with the empirical formula $Ga[(S-S-S)CH_2CH_3]_3$.

The species $Ga(CH_2CH_3)_3$ was also reacted with 12.0 equiv of elemental sulfur at both room temperature and 55 °C to determine whether more than three-sulfur atoms could be inserted. However, compound **II**, $Ga[(S-S-S)CH_2CH_3]_3$, was again the major product with a small amount of compound **I**. Therefore, it appears that compound **II** represents the maximum extent of sulfur insertion. Insertion of three sulfur atoms did not take place with $Ga(CH_3)_3$. This could be due to the lower solubility of the methyl compared to the ethyl products or the electronic effect difference of ethyl and methyl substituents. The Ga−C bond of $Ga-CH_3$ is slightly stronger than that of $Ga-CH_2CH_3$ due to the different electron-releasing abilities of methyl and ethyl substituents.[32]

To investigate the relationship between **I** and **II**, a series of NMR experiments were conducted at different temperatures. The reaction of $Ga(CH_2CH_3)_3$ with 3.0 equiv of sulfur at −78 °C was monitored by ^1H NMR spectroscopy. It was found that, after the addition of elemental sulfur, peaks consistent with the presence of only compound **II**, $Ga[(S-S-S)CH_2CH_3]_3$, were observed first and after 1 week of standing at −78 °C, compound **I**, $Ga[(S-S)CH_2CH_3]_3$, was isolated as the only solid product. The proton NMR spectroscopy of the same reaction at room temperature also showed that **II** formed first as the only product and after 1 week of standing at room temperature, only a small amount of **I** was formed. However, when this reaction mixture was cooled to −30 °C for 2 weeks, compound **I** was isolated as the only product. Compound **I** did not react with sulfur at room temperature even over an extended time. However, on heating to 80 °C, **I** did react with sulfur to form **II**.

We interpret these observations in the following way. The kinetic product of the reaction between sulfur and $Ga(CH_2CH_3)_3$ at low temperature is $Ga[(S-S-S)CH_2CH_3]_3$ (**II**), which rearranges on standing at low temperature to form compound **I**, $Ga[(S-S)CH_2CH_3]_3$, the thermodynamic product, and sulfur. Addition of an excess of sulfur to a toluene solution of **I** results in formation of **II** upon heating, consistent with the presence of an equilibrium between all three species according to eq 1.

$$\underset{\mathbf{II}}{Ga[(S-S-S)CH_2CH_3]_3} \underset{\text{high temperature (80 °C)}}{\overset{\text{low temperature (−30 °C to −78 °C)}}{\rightleftharpoons}} \underset{\mathbf{I}}{Ga[(S-S)CH_2CH_3]_3} + 3S \tag{1}$$

Sulfur insertion into Ga−C bonds does not appear to proceed via stepwise insertion but rather involves insertion of the −S−S−S− unit followed by deinsertion of one sulfur atom to form the −S−S− unit. Experiments to further elucidate the mechanism of sulfur insertion gave results that could not be interpreted unambiguously, but prior coordination of S_8 to $Ga(CH_2CH_3)_3$ is a possible reaction intermediate from the time-dependent proton NMR spectroscopy results monitoring the sulfur insertion reaction of $Ga(CH_2CH_3)_3$.

Reactivity of I−III in Pyridine. The product isolated from the dissolution of **I** in pyridine showed that a reaction occurred. The ^1H NMR spectrum of compound **I**, $Ga[(S-S)CH_2CH_3]_3$, dissolved in C_5D_5N showed a quartet at 0.73 ppm and a triplet at 1.15 ppm corresponding to one type of ethyl group in the

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for the Ring Compound **IV**, [PyEtGaS]$_3$

	x	*y*	*z*	*U*(eq)^a
Ga(1)	919(1)	4360(1)	7107(1)	52(1)
S(1)	2687(3)	5131(2)	7618(2)	64(1)
N(1)	−963(9)	5003(6)	7376(4)	46(3)
C(1)	958(14)	4503(9)	6102(6)	87(6)
C(2)	−143(16)	4003(10)	5711(7)	118(8)
C(3)	−2016(13)	4602(8)	7704(6)	69(5)
C(4)	−3295(13)	5013(10)	7866(7)	84(6)
C(5)	−3465(15)	5866(11)	7695(7)	91(7)
C(6)	−2405(15)	6311(8)	7348(7)	71(6)
C(7)	−1184(13)	5859(7)	7205(6)	60(5)
Ca(2)	2071(2)	5286(1)	8715(1)	64(1)
S(2)	668(4)	4211(2)	9139(2)	81(2)
C(8)	3687	5690	9316	146(9)
C(9)	3264	5825	10016	187(12)
C(9′)	4038	6644	9422	187(12)
N(2)	635(11)	6366(6)	8697(5)	58(4)
C(10)	−615(15)	6371(9)	9035(6)	68(6)
C(11)	−1479(15)	7107(10)	9043(7)	92(7)
C(12)	−1044(16)	7868(9)	8682(8)	92(7)
C(13)	247(16)	7868(7)	8361(7)	82(6)
C(14)	1055(13)	7106(8)	8368(6)	71(5)
Ca(3)	1431(2)	3057(1)	8518(1)	62(1)
S(3)	550(3)	2955(2)	7447(2)	65(1)
C(15)	3415	2627	8544	75(7)
C(16)	3876	2441	9262	140(11)
C(15′)	3483	2488	8841	110(13)
C(16′)	4581	3059	8637	103(12)
N(3)	212(11)	2051(6)	8978(5)	59(4)
C(17)	−894(17)	2221(9)	9375(7)	92(7)
C(18)	−1717(17)	1550(12)	9655(8)	109(8)
C(19)	−1442(20)	740(14)	9522(8)	112(9)
C(20)	−338(20)	507(9)	9108(9)	102(8)
C(21)	448(15)	1197(9)	8823(6)	76(6)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

solution. The relative positions of the C*H*$_2$ quartet and the C*H*$_3$ triplet were consistent with a bonding of the ethyl group to the gallium center. A reaction has clearly taken place presumably as a result of deinsertion of sulfur atoms from the Ga−S−S−C bonds. Evidence for deinsertion of sulfur atoms from Ga−C bonds has not been observed previously. The elimination of a range of diethyl polysulfide species, Et−(S)$_n$−Et ($n = 1-4$) and the formation of S$_4$ species were detected in GC-MS measurements of the filtrate. It has been reported that the species of S$_n$ ($n = 2-7$) are also known allotropes of elemental sulfur.[31]

Clear platelike crystals were obtained at −30 °C by vapor phase diffusion of pentane into a pyridine solution of **I**. Elemental analysis of the crystals was consistent with an empirical formula of [PyEtGaS]$_n$. A solid-state single-crystal X-ray structure determination showed that the compound is trimeric forming a six-membered (Ga−S)$_3$ ring. The crystallographic data for compound **IV**, [PyEtGaS]$_3$, are given in Table 1, the fractional coordinates in Table 2, and the relevant bond lengths in Table 3 and angles in Table 4. The molecular structure of [PyEtGaS]$_3$ is given in Figure 1. The methyl analog, **V**, [PyMeGaS]$_3$, was obtained in a similar way. The crystallographic data for **V** are given in Table 1, the fractional coordinates in Table 5, and the relevant bond lengths in Table 6 and angles in Table 7. The molecular structure of **V**, [PyMeGaS]$_3$, is given in Figure 2. In the solid state, the Ga center is tetrahedrally coordinated by two bridging sulfido groups, one pyridine molecule, and one ethyl group. The whole six-membered ring is in a distorted boat conformation. The Ga−S distances (2.232(3)−2.247(3) Å for **IV**, 2.230(2)−2.244(2) Å for **V**) are comparable to those observed for [Py(^{t}Bu)GaS]$_3$ (2.231(3)−2.253(3) Å).[16] Also the Ga−S bond lengths are found to be within the range observed in the adamantane-like Ga$_4$I$_4$(SMe)$_4$S$_2$ (2.204(8) Å)[17] and [Ga$_4$S$_{10}$]$^{8-}$ (2.289(2) Å).[18]

Table 3. Selected Bond Lengths (Å) for Compound **IV**, [PyEtGaS]$_3$

Ga(1)−S(1)	2.233(3)	Ga(1)−C(1)	1.981(12)
S(1)−Ga(2)	2.243(4)	N(1)−C(7)	1.340(14)
Ga(2)−S(2)	2.236(4)	Ga(2)−N(2)	2.097(9)
N(2)−C(10)	1.344(17)	Ga(3)−S(3)	2.247(3)
Ga(3)−C(15’)	2.174(1)	N(3)−C(17)	1.320(18)
Ga(1)−N(1)	2.068(8)	Ga(1)−S(3)	2.234(3)
N(1)−C(3)	1.320(15)	Ga(2)−C(8)	1.991(1)
S(2)−Ga(3)	2.232(3)	N(2)−C(14)	1.340(15)
Ga(3)−C(15)	1.951(1)	Ga(3)−N(3)	2.095(10)
N(3)−C(21)	1.333(17)		

Table 4. Selected Bond Angles (deg) for Compound **IV**, [PyEtGaS]$_3$

S(1)−Ga(1)−N(1)	105.4(2)	N(1)−Ga(1)−C(1)	103.2(5)
N(1)−Ga(1)−S(3)	103.2(3)	Ga(1)−S(1)−Ga(2)	106.7(1)
Ga(1)−N(1)−C(7)	120.5(7)	Ga(1)−C(1)−C(2)	116.1(9)
S(1)−Ga(2)−S(2)	116.0(1)	S(2)−Ga(2)−C(8)	116.0(1)
S(2)−Ga(2)−N(2)	100.8(3)	Ga(2)−S(2)−Ga(3)	99.4(1)
Ga(2)−C(8)−C(9’)	122.7(1)	Ga(2)−N(2)−C(14)	117.2(8)
S(2)−Ga(2)−C(15)	123.1(1)	S(2)−Ga(3)−N(3)	98.3(3)
C(15)−Ga(3)−N(3)	105.5(3)	Ga(1)−S(3)−Ga(3)	99.1(1)
Ga(3)−C(15)−C(16′)	129.7(1)	Ga(3)−N(3)−C(17)	122.9(8)
S(1)−Ga(1)−C(1)	111.6(4)	S(1)−Ga(1)−S(3)	117.8(1)
C(1)−Ga(1)−S(3)	113.7(4)	Ga(1)−N(1)−C(3)	123.1(7)
S(1)−Ga(2)−C(8)	113.5(1)	S(1)−Ga(2)−N(2)	103.4(3)
C(8)−Ga(2)−N(2)	104.5(3)	Ga(2)−C(8)−C(9)	113.0(1)
Ga(2)−N(2)−C(10)	123.3(8)	S(2)−Ga(3)−S(3)	116.5(1)
S(3)−Ga(3)−C(15)	109.6(1)	S(3)−Ga(3)−N(3)	99.2(3)
Ga(3)−C(15)−C(16)	110.3(1)	Ga(3)−N(3)−C(21)	120.0(8)

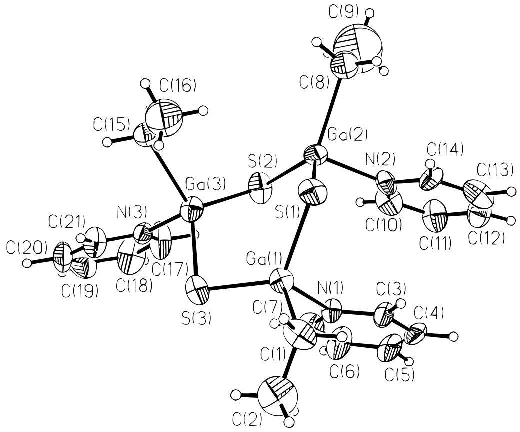

Figure 1. Molecular structure of compound **IV**, [PyEtGaS]$_3$.

The analogous compound [Py(^{t}Bu)GaS]$_3$ was prepared by the thermolysis of [(^{t}Bu)$_2$Ga(μ-SS^{t}Bu)]$_2$ or [(^{t}Bu)$_2$Ga(μ-S^{t}Bu)(μ-SS^{t}Bu)Ga(^{t}Bu)$_2$] in the presence of sulfur in hexane, resulting in formation of the cubane compound [^{t}BuGaS]$_4$.[15] The cubane compound was then dissolved in pyridine, yielding the trimeric ring compound [^{t}BuPyGaS]$_3$.[16] In contrast, the ethyl and methyl analogs reported here were formed by sulfur insertion into all the Ga−C bonds of Ga(CH$_2$CH$_3$)$_3$ and Ga(CH$_3$)$_3$, followed by sulfur deinsertion, presumably initiated by the presence of the donor solvent pyridine.

The sulfur deinsertion reactions of compounds **I** and **II** in pyridine were monitored by variable-temperature ^{1}H NMR spectroscopy from −38 °C to room temperature in an attempt to detect reaction intermediates. After the addition of pyridine to compound **I** or **II**, the peaks consistent with the Ga-bonded ethyls were immediately observed. No evidence for a stepwise deinsertion of S was found. No intermediates were observed

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Compound **V**, $[PyMeGaS]_3$

	x	*y*	*z*	*U*(eq)[a]
Ga(1)	7815(1)	1423(1)	5345(1)	41(1)
Ga(2)	7462(1)	3690(1)	4784(1)	46(1)
Ga(3)	4648(1)	2412(1)	4867(1)	41(1)
S(1)	8296(2)	2423(1)	4462(1)	53(1)
S(2)	5254(2)	3771(1)	4646(1)	56(1)
S(3)	6109(2)	1633(1)	5913(1)	47(1)
N(1)	9464(5)	1470(3)	6484(3)	45(2)
C(1)	9344(6)	1466(4)	7283(4)	58(3)
C(2)	10422(7)	1395(5)	8013(4)	75(3)
C(3)	11685(7)	1305(5)	7908(5)	75(3)
C(4)	11822(7)	1315(5)	7080(5)	73(3)
C(5)	10695(6)	1396(4)	6389(4)	58(3)
C(6)	7983(6)	224(4)	4939(4)	59(3)
N(2)	8441(5)	3794(3)	6132(3)	50(2)
C(7)	7773(7)	3891(4)	6713(5)	67(3)
C(8)	8384(9)	3911(5)	7596(5)	89(4)
C(9)	9762(10)	3846(5)	7890(5)	86(4)
C(10)	10457(8)	3751(5)	7297(5)	78(4)
C(11)	9783(6)	3716(4)	6420(4)	63(3)
C(12)	8137(6)	4728(4)	4302(4)	69(3)
N(3)	4606(4)	1733(3)	3720(3)	44(2)
C(13)	4420(6)	861(4)	3673(4)	50(3)
C(14)	4415(6)	398(4)	2951(4)	57(3)
C(15)	4606(7)	803(5)	2236(4)	65(3)
C(16)	4789(7)	1693(5)	2271(4)	62(3)
C(17)	4804(6)	2125(4)	3024(4)	52(3)
C(18)	2803(5)	2317(4)	4950(4)	59(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Selected Bond Lengths (Å) for Compound **V**, $[PyMeGaS]_3$

Ga(1)−S(1)	2.233(2)	Ga(1)−S(3)	2.237(2)
Ga(1)−N(1)	2.102(4)	Ga(1)−C(6)	1.971(6)
Ga(2)−S(1)	2.244(2)	Ga(2)−S(2)	2.241(2)
Ga(2)−N(2)	2.098(5)	Ga(2)−C(12)	1.981(7)
Ga(3)−S(2)	2.230(2)	Ga(3)−S(3)	2.241(2)
Ga(3)−N(3)	2.093(5)	Ga(3)−C(18)	1.964(6)
N(1)−C(1)	1.317(8)	N(1)−C(5)	1.334(8)
N(2)−C(7)	1.319(10)	N(2)−C(11)	1.339(8)
N(3)−C(13)	1.346(8)	N(3)−C(17)	1.331(9)

in the reaction of **I** or **II** with pyridine by low-temperature ^1H NMR spectroscopy.

Finally, thermogravimetric analysis of compound **IV** in N_2 gave 38.0% mass loss at 100 °C corresponding to the loss of three pyridine molecules (calculated mass loss = 37.7%) and 14.0% mass loss at 445 °C corresponding to the loss of three ethyl groups (calculated mass loss = 13.8%). Crystalline GaS powder was obtained as shown by powder X-ray diffraction. Similar results were also obtained for compound **V**, $[PyMeGaS]_3$.

Summary and Conclusions

The insertion of elemental sulfur into Ga−C bonds of $Ga(CH_2CH_3)_3$, at different temperatures, produced compound **I**, $Ga[(S-S)CH_2CH_3]_3$, and compound **II**, $Ga[(S-S-S)CH_2CH_3]_3$. The insertion reaction pathway was studied, and an equilibrium between compound **II** and compound **I** was found. Compound **II** was the kinetic product of the low-temperature sulfur insertion reaction and rearranged to compound **I**, the thermodynamic product, upon standing at low temperature. In contrast, for $Ga(CH_3)_3$, only compound **III**, $Ga[(S-S)CH_3]_3$, was observed. For the first time, deinsertion of the sulfur atoms from Ga−S−S−C bonds was observed in the transformation from **I**, $Ga[(S-S)CH_2CH_3]_3$, and **III**, $Ga[(S-S)CH_3]_3$, to the sulfido-bridged ring compounds **IV**, $[PyEtGaS]_3$, and **V**, $[PyMeGaS]_3$, respectively. It appears that compound **II**, $Ga[(S-S-S)CH_2CH_3]_3$, showed the maximum extent of sulfur insertions into M−C bonds of group 13 metal alkyl compounds.

Table 7. Selected Bond Angles (deg) for Compound **V**, $[PyMeGaS]_3$

S(1)−Ga(1)−S(3)	120.51(1)	S(1)−Ga(1)−N(1)	104.21(1)
S(3)−Ga(1)−N(1)	100.8(2)	S(1−Ga(1)−C(6)	111.9(2)
S(3)−Ga(1)−C(6)	115.0(2)	N(1)−Ga(1)−C(6)	100.8(2)
S(1)−Ga(2)−S(2)	118.5(1)	S(1)−Ga(2)−N(2)	101.3(1)
S(2)−Ga(2)−N(2)	105.8(2)	S(1)−Ga(2)−C(12)	113.5(2)
S(2)−Ga(2)−C(12)	112.7(2)	N(2)−Ga(2)−C(12)	102.5(2)
S(2)−Ga(3)−S(3)	116.9(1)	S(2)−Ga(3)−N(3)	105.1(2)
S(3)−Ga(3)−N(3)	102.9(1)	S(2)−Ga(3)−C(18)	113.9(2)
S(3)−Ga(3)−C(18)	111.8(2)	N(3)−Ga(3)−C(18)	104.5(2)
Ga(1)−S(1)−Ga(2)	105.9(1)	Ga(2)−S(2)−Ga(3)	105.1(1)
Ga(1)−S(3)−Ga(3)	102.6(1)	Ga(1)−N(1)−C(1)	123.5(4)
Ga(1)−N(1)−C(5)	117.7(4)	Ga(2)−N(2)−C(7)	122.1(4)
Ga(2)−N(2)−C(11)	119.3(5)	Ga(3)−N(3)−C(13)	120.5(4)
Ga(3)−N(3)−C(17)	122.4(4)		

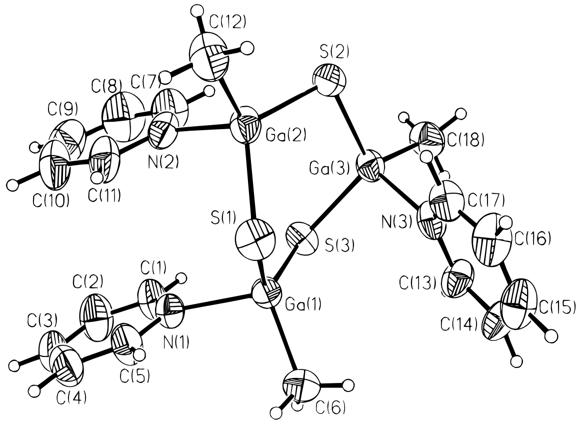

Figure 2. Molecular structure of compound **V**, $[PyMeGaS]_3$.

Acknowledgment. We thank the Office of Naval Research, Departments of Chemistry and Materials Research, for funding this research, the National Science Foundation Chemical Instrumentation Program for the purchase of a low-field NMR spectrometer, and the Dreyfus Foundation and AFOSR for the purchase of an X-ray powder diffractometer.

Supporting Information Available: Tables giving structure determination summaries, bond lengths and angles, anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients for **IV** and **V** (23 pages). Ordering information is given on any current masthead page.

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