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 ^1H 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.

Acknowledgment. This work was supported in part by the Office of Naval Research and by a generous grant from Eastman Kodak Co. We thank the National Science Foundation for providing funds for the Siemens R3m/V diffractometer through a grant from the Chemical Instrumentation Program (89-13733).

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.

---

[18] Beachley, O. T., Jr.; Bueno, C.; Churchill, M. R.; Hallock, R. B.; Simmons, R. G. *Inorg. Chem.* 1981, *20*, 2423.

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

Michael B. Power,[1a] Joseph W. Ziller,[1b] Andrew N. Tyler,[1a] and Andrew R. Barron*,[1a]

Departments of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and University of California, Irvine, California 92717

Received October 2, 1991

The interaction of $Ga(^tBu)_3$ with S_8 leads to the formation of a mixture of $[(^tBu)_2Ga(\mu\text{-}SS^tBu)]_2$ (**1**) and $[(^tBu)_2Ga(\mu\text{-}S^tBu)(\mu\text{-}SS^tBu)Ga(^tBu)_2]$ (**2**) in a ca. 1:3 molar ratio and trace quantities of $[(^tBu)_2Ga(\mu\text{-}S^tBu)]_2$ (**3**), which may be prepared directly from ^tBuSH and $Ga(^tBu)_3$. 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 $[(^tBu)GaS]_4$ (**4**) and a range of di-*tert*-butyl polysulfides, $^tBuS(S)_nS^tBu$ (n = 1-4). Compound **4** may also be prepared by the thermolysis of $[(^tBu)_2Ga(\mu\text{-}SH)]_2$ (**5**). Repeated sublimation of **4**, at atmospheric pressure, results in its structural rearrangement to the octamer $[(^tBu)GaS]_8$ (**6**). The reaction of $Ga(^tBu)_3$ with Se_8 results in the direct formation of the cubane $[(^tBu)GaSe]_4$ (**7**). In contrast, the use of metallic Se yields $[(^tBu)_2Ga(\mu\text{-}Se^tBu)]_2$ (**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 $Ga(^tBu)_3$ at ambient temperatures to yield $[(^tBu)_2Ga(\mu\text{-}Te^tBu)]_2$ (**9**). Thermolysis of **9** in refluxing toluene in the presence of excess Te metal allows for the isolation of the cubane compound $[(^tBu)GaTe]_4$ (**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 ^1H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopy. In addition, the structure of **7** has been confirmed by X-ray crystallography. The compound $[(^tBu)GaSe]_4$ (**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]

---

* To whom all correspondence should be addressed.

[1] (a) Harvard University. (b) University of California.

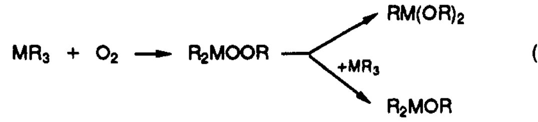
0276-7333/92/2311-1055$03.00/0

to yield, after hydrolysis, low yields of alkanethiols. Further studies showed that, in contrast to the reactions with oxygen, elemental sulfur inserts into only one of the possible three aluminum–carbon bonds to afford good yields of dialkylaluminum thiolates (eq 1).[3] Reactions

$$AlR_3 + E \xrightarrow[E\,=\,S,\,Se]{} R_2Al(ER) \qquad (1)$$

under more forcing conditions lead to the formation of RSR and RSSR;[4] however, the aluminum-containing products were not isolated. Similar results have been reported for the interaction of aluminum alkyls with powdered selenium metal[4,5] (cf. eq 1).

Since the reaction of group 13 alkyls with dioxygen, to give alkoxide products, has been shown to occur via unstable alkylperoxide intermediates (e.g., eq 2),[6] and the propensity for catenation is increased with the heavier group 16 elements, an interesting question may be posed: *is it possible that alkyl dichalcogenides are formed as transient intermediates in the reaction between group 13 alkyls and elemental chalcogens*? Given our recent isolation of the thermally robust alkylperoxides of gallium[7] and indium,[8] from the oxidation of the tri-*tert*-butyl compounds (eq 3), this suggests that the use of sterically



$$M(^tBu)_3 + O_2 \rightarrow \tfrac{1}{2}[(^tBu)_2M(\mu\text{-}OO^tBu)]_2 \qquad (3)$$

hindered alkyl substituents, such as *tert*-butyl, should indeed allow for the isolation of the chalcogenide analogues (i.e., eq 4). In addition, the presence of multiple allotropic

$$M(^tBu)_3 + E\ (\text{excess}) \rightarrow \tfrac{1}{2}[(^tBu)_2M(\mu\text{-}EE^tBu)]_2 \qquad (4)$$

forms of the chalcogenides raises a further question: *does the identity of the products from the reaction of group 13 alkyls with the elemental chalcogens depend on the allotropic form of the chalcogen employed*?

In order to address these questions, and to further understand the reaction chemistry of group 13 alkyls with the group 16 elements, we have investigated the reaction of $Ga(^tBu)_3$ with elemental sulfur, selenium, and tellurium. The results of these studies are presented herein.

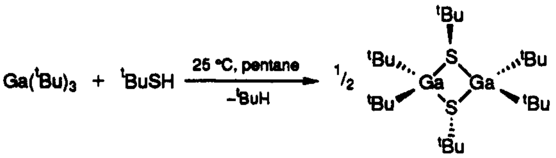
Results and Discussion

Sulfur. The interaction of $Ga(^tBu)_3$[9] with *cyclo*-octasulfur (S_8) at ambient temperatures results in the formation of a mixture of two colorless crystalline compounds (eq 5). Compound 2, the major product, may be readily

$$Ga(^tBu)_3 + S_8\ (\text{excess}) \xrightarrow[\text{pentane}]{25\ °C} 1\ (25\%) + 2\ (75\%) \qquad (5)$$

separated from 1 by fractional crystallization; compound 1, however, could only be obtained in the presence of 2, indicating that the latter is most likely formed as a result of the decomposition of 1 (see below).

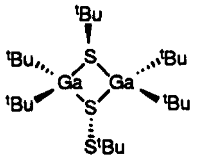
Trace quantities (≤5%) of a third product may be detected from the ^1H NMR spectrum of the reaction mixture, and its identity has been determined as the thiolate complex $[(^tBu)_2Ga(\mu\text{-}S^tBu)]_2$ (**3**), by comparison with an authentic sample synthesized in quantitative yield directly from the appropriate thiol and $Ga(^tBu)_3$ (eq 6). Compound 3 is spectroscopically distinct from either 1 or 2 (see Experimental Section).



(6)

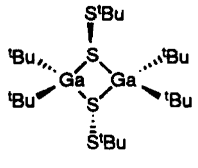
3

The ^1H NMR spectrum of 2 shows the presence of four chemically equivalent *tert*-butyl groups (δ 1.44), which from the ^{13}C NMR spectrum may be assigned as being bound to gallium due to the upfield shift of the quaternary carbon resonance (δ 23.05) as compared to those found for *tert*-butyl groups bound to sulfur (δ 40–50). In addition to the resonance due to the gallium-bound *tert*-butyl groups, the ^1H NMR spectrum of 2 indicates the presence of two sulfur-bound ^tBu groups (δ 1.35 and 1.19). While the latter resonances are close to the single sulfur–^tBu resonance present in 1, the former shifts are similar to that found for 3, i.e., that of a thiolate. The elemental compositon $C_{24}H_{54}Ga_2S_3$ of 2 was established by elemental analysis (see Experimental Section), while the medium-resolution mass spectral fragmentation pattern revealed peaks at *m/z* 521 and 489 corresponding to $M^+ - {}^tBu$ and $M^+ - S^tBu$, respectively. Thus, the analytical and spectroscopic characterization of 2 is consistent with a dimeric structure containing both thiolate and alkyl disulfido bridges, i.e. $(^tBu)_2Ga(\mu\text{-}S^tBu)(\mu\text{-}SS^tBu)Ga(^tBu)_2$ (I).



I

On the basis of a comparison of the ^1H and ^{13}C NMR data of 1 and 2 and by analogy with the alkyl peroxide complex $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$,[7] we propose that 1 is the bis(disulfide)-bridged dimer $[(^tBu)_2Ga(\mu\text{-}SS^tBu)]_2$ (II). Supporting evidence for this is present in the mass spectrum of a mixture of 1 and 2, which, in addition to those peaks assigned to 2, also contains a signal at *m/z* 553 consistent with $2M^+ - {}^tBu$.



II

Alkyl disulfido moieties are known to act as monodentate (η^1; III),[10] bidentate (η^2; IV), and bridging[11] (μ_2; V)[12]

---

[2] (a) Jenkner, H.; Kali-Chemie, A.-G. German Patent 1031306, 1958; *Chem. Abstr.* **1960**, *54*, 17269. (b) Leech, R. E.; Knap, J. E. U.S. Patent 2998455, 1960, Union Carbide Corp.; *Chem. Abstr.* **1962**, *56*, 2333.

[3] Zakharkin, L. I.; Gavrilenko, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 1391.

[4] Zakharkin, L. I.; Gavrilenko, V. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1960**, 1294.

[5] Kozikowski, A. P.; Ames, A. *J. Org. Chem.* **1978**, *43*, 2735.

[6] See for example: (a) Odom, J. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 1, Chapter 4. (b) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 1, Chapter 6. (c) Davis, A. G. In *Organic Peroxides*; Swern, D., Ed.; Wiley: London, 1971; Vol. 2, Chapter 4.

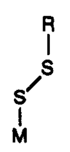
[7] Power, M. B.; Cleaver, W. M.; Apblett, A. W.; Barron, A. R.; Ziller, J. W. *Polyhedron*, in press.

[8] Cleaver, W. M.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 8966.

[9] Kovar, R. A.; Derr, H.; Brandau, D.; Callaway, J. O. *Inorg. Chem.* **1975**, *14*, 2809.

[10] Bhattacharya, S. N.; Senoff, C. V.; Walker, F. S. *Inorg. Chim. Acta* **1980**, *44*, L273.

ligands to transition metals.



III

IV

V

Since the existence of dimers involving bridging ligands is a common feature in group 13 chemistry, it would be logical to expect the alkyl disulfido groups in 1 and 2 to ligate in a manner analogous to that observed for the alkylperoxo ligand in $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$.[7] Unfortunately, we have been unable to confirm this proposal by X-ray crystallographic data.

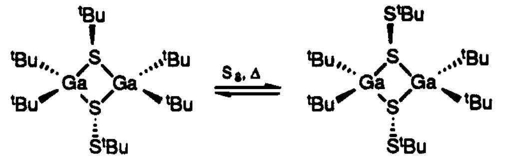
The observation that compound 1 is the first detectable product in the reaction of Ga(^{t}Bu)$_3$ with S_8 poses the following question concerning the mechanism of sulfur atom insertion: does the reaction proceed via the concerted insertion of two sulfur atoms to give the disulfide directly (eq 7) or a stepwise insertion of a single sulfur atom, giving the thiolate, which reacts further to give the disulfide (eq 8)? If the latter (eq 8) is the preferred pathway, then

$$\text{Ga–R} \xrightarrow{\text{“}S_2\text{”}} \text{Ga–S–S–R} \qquad (7)$$

$$\text{Ga–R} \xrightarrow{\text{“S”}} \text{Ga–S–R} \xrightarrow{\text{“S”}} \text{Ga–S–S–R} \qquad (8)$$

it is reasonable to expect that the thiolate 3 should react with excess sulfur to yield 1 and 2. However, under reaction conditions analogous to those employed for the formation 1 and 2 directly from Ga(^{t}Bu)$_3$, i.e., pentane and room temperature, no reaction is observed, even over an extended time. Compound 3 does, however, react with sulfur when refluxed in benzene overnight or placed in a sonic bath for 2 h, to give initially 1 and subsequently 2. It should be noted that, unlike the room-temperature reaction of Ga(^{t}Bu)$_3$ with S_8, these reaction conditions do not lead to 1 and 2 as the only products (see below).

In the absence of a large excess of sulfur, compound 1 slowly decomposes at room temperature to give 2 and elemental sulfur. Conversely, heating a solution of 2 in the presence of S_8 results in the re-formation of 1 (eq 9).



(9)

Given the above, we propose that the bis(disulfide) compound 1 is formed as a direct product of the reaction of Ga(^{t}Bu)$_3$ with S_8. This kinetic product is thermally unstable and decomposes to yield the mixed disulfide–thiolate 2 as the thermodynamic product. The presence of trace quantities of 3 in this reaction mixture may be due to the thermal decomposition of 2 or, alternatively, the formation of 3 directly from Ga(^{t}Bu)$_3$ via a competing minor reaction pathway.

The abstraction of an S_2 unit from an S_8 ring, and its "insertion" into a group 13 metal–carbon bond to give a disulfide, does have similarities to the reaction of an aluminum alkyl with diorganosiloxanes (eq 10).

$$2AlMe_3 + {}^2\!/_x(R_2SiO)_x \rightarrow [Me_2Al(\mu\text{-}OSiR_2Me)]_2 \qquad (10)$$

We have shown[13] that $AlMe_3$ forms a highly fluxional 1:1 Lewis acid–base adduct with the cyclic trisiloxane $(R_2SiO)_3$. This molecular adduct decomposes slowly at room temperature to give the aluminum siloxide and a variety of cyclic and linear siloxanes, all of which consist of multiple $(R_2SiO)_2$ units, i.e., the remaining section from $(R_2SiO)_3$ upon abstraction of "R_2SiO" into the aluminum–methyl bond (eq 11). Thus, by analogy it is reasonable

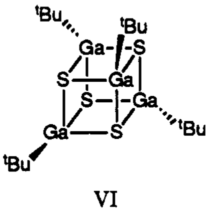
$$(R_2SiO)_3{\cdot}AlMe_3 \rightarrow {}^1\!/_2[Me_2Al(\mu\text{-}ORe_2Me)]_2 + [R_2SiOR_2SiO]_n \qquad (11)$$

to suggest that in a heterogeneous reaction Ga(^{t}Bu)$_3$ abstracts "S_2" from S_8, and the highly reactive cyclohexasulfur, S_6, that results acts as a further source of "S_2".

As noted above, the high-temperature thermolysis of 3 in the presence of excess sulfur yields in addition to 1 and 2 a compound, 4, whose yield increases with increased reaction time, until it is the only gallium-containing product. The same product is also obtained directly from Ga(^{t}Bu)$_3$. In addition, a series of bis(*tert*-butyl polysulfides) are formed as coproducts (eq 12), the identities of which were confirmed from their ^{1}H NMR spectral shifts, which have previously been reported.[14]

$$Ga(^tBu)_3 + S_8\ (\text{excess}) \rightarrow 4 + {}^tBuS(S)_nS^tBu \qquad (12)$$
$$n = 1\text{–}4$$

The composition of 4 was determined by elemental analysis to be (^{t}Bu)GaS, while the mass spectrum exhibits a peak at m/z 636 due to $[(^tBu)GaS]_4$. A fragment peak at m/z 579 corresponds to loss of ^{t}Bu, and this is followed by peaks corresponding to the sequential loss of 2-methylpropene, butane, and ^{t}Bu, respectively. No significant fragmentation of the $(GaS)_4$ unit is observed. The ^{1}H and ^{13}C NMR spectra of 4 (see Experimental Section) are consistent with a single gallium-coordinated *tert*-butyl environment. Thus, the analytical and spectroscopic data for 4 are consistent with a highly symmetrical tetrameric structure, such as Ga_4S_4 cube (VI). This structural assignment has been previously confirmed by X-ray crystallography.[15] Compound 4 may also be prepared by the low-temperature thermolysis (>45 °C) of a pentane solution of the hydrosulfido compound $[(^tBu)_2Ga(\mu\text{-}SH)]_2$ (5; eq 13), whose synthesis and structure we have previously reported.[15]



VI

$$2[(^tBu)_2Ga(\mu\text{-}SH)]_2 \rightarrow [(^tBu)GaS]_4 + 4\,^tBuH \qquad (13)$$
$$\quad\ \ \mathbf{5} \qquad\qquad\qquad\qquad \mathbf{4}$$

Thermogravimetric analysis data indicate that compound 4 sublimes completely above 225 °C, at atmospheric pressure, making it suitable as a single-source precursor for gallium sulfide.[16] Repeated sublimation of 4 at at-

---

[11] Hoots, J. E.; Rauchfuss, T. B. *Inorg. Chem.* **1983**, *22*, 2806.

[12] Eremenko, I. L.; Pasynskii, A. A.; Kilinnikov, V. T.; Struchkov, Y. T.; Aleksandrov, G. G. *Inorg. Chim. Acta* **1981**, *52*, 107.

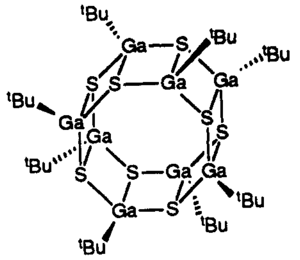
[13] Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137.

[14] Grant, D.; Van Wauzer, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 3012.

[15] (a) Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1315. (b) Power, M. B.; Ziller, J. W.; Barron, A. R. *Abstracts of Papers*, North East Regional Meeting of the American Chemical Society, Amherst, MA. June 1991; American Chemical Society: Washington, DC, 1991.

[16] Details of the chemical vapor deposition of GaS and Ga_2S_3 thin films using 4 as a single-source precursor are reported elsewhere: Power, M. B.; MacInnes, A. N.; Barron, A. R. *Chem. Mater.*, in press.

mospheric pressure results in its conversion from a tetramer to the octamer [(^{t}Bu)GaS]$_8$ (**6**). The ^{1}H NMR spectrum of **6** shows the presence of a single *tert*-butyl environment and is distinct from that of **4**. The mass spectrum of **6** (see Experimental Section) is consistent with the octamer. Although we have been unable to obtain crystallographic structural data for **6**, we propose, on the basis of the chemistry of tin oxides,[17] that **6** adopts a drum structure (VII), consisting of two fused eight-membered Ga$_4$S$_4$ cycles.



VII

The interaction of Ga(^{t}Bu)$_3$ with an excess of plastic sulfur, S$_\infty$ in a sonic bath does not result in the formation of any detectable quantities of **1**–**4**, but instead a high yield of ^{t}BuSS^{t}Bu is obtained along with an insoluble white solid, Ga$_2$S$_3$ (eq 14). It is clear that in the present case ^{t}BuSS^{t}Bu

$$2\mathrm{Ga}({}^t\mathrm{Bu})_3 + 9\mathrm{S}_\infty \rightarrow 3{}^t\mathrm{BuSS}{}^t\mathrm{Bu} + \mathrm{Ga_2S_3} \qquad (14)$$

must be a primary reaction product and is not due to the decomposition of either a thiolate or alkyl disulfido complex, since under the reaction conditions employed decomposition of such species would have led to the formation of the inert cube, **4**, and a series of higher di-*tert*-butyl polysulfides (see above), neither of which were detected.

Selenium. In contrast to the results observed for S$_8$, the reaction of Ga(^{t}Bu)$_3$ with the analogous selenium allotrope Se$_8$ does not yield a stable alkyl diselenide but results in the direct formation of Ga$_4$Se$_4$ cubane. Thus, the reaction of Ga(^{t}Bu)$_3$ with red selenium (Se$_8$, α-cubic form), in pentane at room temperature, affords in essentially quantitative yield (based on ^{77}Se NMR) ^{t}BuSeSe^{t}Bu (δ 490 ppm) and the colorless solid **7** with an elemental composition corresponding to (^{t}Bu)GaSe (eq 15).

$$\mathrm{Ga}({}^t\mathrm{Bu})_3 + \mathrm{Se}_8 \xrightarrow{\mathrm{Se}_8} \underset{\mathbf{7}}{({}^t\mathrm{Bu})\mathrm{GaSe}} + {}^t\mathrm{BuSeSe}{}^t\mathrm{Bu} \qquad (15)$$

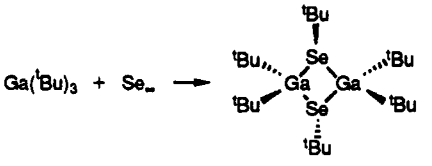
The medium-resolution EI mass spectrum of **7** exhibits a peak at *m/z* 823 due to [^{t}BuGaSe]$_4$. A fragment peak at *m/z* 766 corresponds to loss of ^{t}Bu, and this is followed by peaks at *m/z* 710, 654, and 598 corresponding to the sequential loss of three 2-methylpropene molecules. As with **4**, the ^{1}H and ^{13}C NMR spectra of **7** are consistent with a single gallium-coordinated *tert*-butyl environment, while the ^{77}Se NMR spectrum exhibits a singlet with an unusually low frequency chemical shift (δ −226.73) indicative of a selenide.[18] The spectroscopic and analytical data for **7** are consistent, therefore, with a cubane structure analogous to that of **4**. As with its sulfur analogue, **4**, the cubic structure of **7** has been confirmed by X-ray crystallography (see below). Compound **7** may also be prepared in near-quantitative yield from the reaction of Ga(^{t}Bu)$_3$ with H$_2$Se in pentane at ambient temperatures, presumably via a hydroselenolate intermediate:[19]

$$4\mathrm{Ga}({}^t\mathrm{Bu})_3 + 4\mathrm{H_2Se} \xrightarrow[\text{pentane}]{0\ ^\circ\mathrm{C}} [({}^t\mathrm{Bu})\mathrm{GaSe}]_4 + 8{}^t\mathrm{BuH} \qquad (16)$$

It should be noted that the alkylgallium selenide [(Et)GaSe]$_x$, formed on the thermal decomposition of the triethylsilaneselenolate (eq 17), was proposed to have a highly polymeric structure on the basis of its high thermal stability (mp 360–410 °C dec) and low solubility in noncoordinating solvents.[20]

$$[(\mathrm{Et})_2\mathrm{Ga}(\mu\text{-}\mathrm{SeSiEt_3})]_2 \xrightarrow{\Delta} [(\mathrm{Et})\mathrm{GaSe}]_n + \mathrm{GaEt_3} + \mathrm{Se(SiEt_3)_2} \qquad (17)$$

Treatment of Ga(^{t}Bu)$_3$ with metallic gray selenium (Se$_\infty$) in pentane results in the formation of the selenolate compound [(^{t}Bu)$_2$Ga(μ-Se^{t}Bu)]$_2$ (**8**) as the only gallium-containing product (eq 18).



(18)

8

The dimeric nature of **8** was established by CI mass spectroscopy, which revealed a peak at *m/z* 583 due to 2M$^+$ − ^{t}Bu followed by a fragment ion at *m/z* 503 corresponding to 2M$^+$ − Se^{t}Bu. The ^{1}H, ^{13}C, and ^{77}Se NMR spectra of **8** indicate the presence of equivalent Ga–^{t}Bu groups and a single Se–^{t}Bu environment consistent with an anti conformation of the *tert*-butyl selenide groups.

Compound **8** is readily converted to **7** by heating the former in refluxing benzene in the presence of an excess of metallic selenium:

$$2[({}^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{Se}{}^t\mathrm{Bu})]_2 + 8\mathrm{Se}_\infty \rightarrow [({}^t\mathrm{Bu})\mathrm{GaSe}]_4 + 2{}^t\mathrm{BuSeSe}{}^t\mathrm{Bu} \qquad (19)$$

Compound **7** is also the sole gallium-containing product from the reaction of either red or black selenium with the thiolate **3** (eq 20). However, it is compound **4** that results from the interaction of **8** with S$_8$ (eq 21). Whereas in the

$$2[({}^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{S}{}^t\mathrm{Bu})]_2 \xrightarrow{\text{Se (excess)}} [({}^t\mathrm{Bu})\mathrm{GaSe}]_4 + 4{}^t\mathrm{BuSSe}{}^t\mathrm{Bu} \qquad (20)$$

$$2[({}^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{Se}{}^t\mathrm{Bu})]_2 \xrightarrow{\mathrm{S}_8} [({}^t\mathrm{Bu})\mathrm{GaS}]_4 + {}^t\mathrm{BuSe(S)}_n{}^t\mathrm{Bu} \qquad (21)$$

first two of these reactions (eqs 19 and 20) only a single coproduct is observed by ^{77}Se NMR spectroscopy (^{t}BuSeSe^{t}Bu, δ 490, and ^{t}BuSSe^{t}Bu, δ 511, respectively), the reaction of **8** with excess sulfur (eq 21) leads to a myriad of unidentified organo–sulfur–selenium coproducts. The ^{77}Se NMR spectrum of the reaction mixture shows several peaks within the range of 650–800 ppm consistent with polysulfido selenides, ^{t}BuSe(S)$_n{}^t$Bu.[21]

Tellurium. Unlike either sulfur or selenium, tellurium exists as a single allotropic form, that of a silvery white semimetallic trigonal structure isomorphous with gray selenium. Thus, as may be expected, the reaction of Ga(^{t}Bu)$_3$ with tellurium metal at room temperature proceeds

---

(17) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190.

(18) Granger, P.; Gautheron, B.; Tainturier, G.; Pouly, S. *Org. Magn. Reson.* **1984**, *22*, 701.

(19) (a) Rauchfuss, T. B. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1987; Vol. 1. (b) Bottomley, F.; Day, R. W. *Organometallics* **1991**, *10*, 2560.

(20) Vyazankin, N. S.; Bochkarev, M. N.; Charov, A. I. *J. Organomet. Chem.* **1971**, *27*, 175.

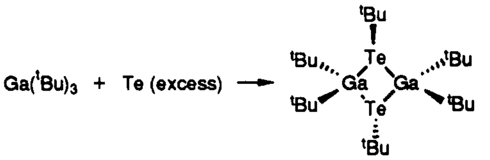
(21) (a) Laitinen, R. S.; Pakkanen, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1381. (b) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1987**, *26*, 2598. (c) Laitinen, R. S.; Pekonen, P.; Hiltunen, Y.; Pakkanen, T. A. *Acta Chem. Scand.* **1989**, *43*, 436.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in [(^{t}Bu)GaE]$_4$ (E = S (4), Se (7))[a]

		[(^{t}Bu)GaSe]$_4$			
[(^{t}Bu)GaS]$_4$[b]		molecule 1		molecule 2	
Ga(1)-S(1)	2.359 (3)	Ga(1)-Se(1)	2.481 (6)	Ga(2)-Se(2)	2.479 (5)
		Ga(1)-Se(1A)	2.481 (5)	Ga(2)-Se(2A)	2.472 (6)
				Ga(2)-Se(2B)	2.477 (6)
Ga(1)-C(1)	1.978 (6)	Ga(1)-C(1)	2.24 (4)	Ga(2)-C(3)	1.89 (4)
S(1)-Ga-S(1A)	97.3 (1)	Se(1)-Ga(1)-Se(1A)	99.3 (1)	Se(2)-Ga(2)-Se(2A)	99.2 (2)
		Se(1A)-Ga(1)-Se(1B)	99.3 (2)	Se(2)-Ga(2)-Se(2B)	99.1 (2)
				Se(2a)-Ga(2)-Se(2B)	98.8 (2)
Ga(1)-S(1)-Ga(1A)	82.1 (1)	Ga(1)-Se(1)-Ga(1A)	79.9 (2)	Ga(2)-Se(2)-Ga(2A)	80.1 (2)
				Ga(2)-Se(2)-Ga(2A)	80.2 (2)
				Ga(2A)-Se(2)-Ga(2B)	80.4 (2)

[a] Crystallographic equivalent bond lengths and bond angles not listed. [b] Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1315.

in a manner analogous to that of gray selenium, resulting in the formation of the telluride dimer [(^{t}Bu)$_2$Ga(μ-Te^{t}Bu)]$_2$ (**9**; eq 22), which has been fully characterized by elemental analysis and ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy (see Experimental Section).



(22)

9

The first example of an organogallium compound containing a Ga–Te bond, recently reported by Beachley and co-workers,[22] was prepared by the reaction of Ga(CH$_2$^{t}Bu)$_2$Cl with the appropriate lithium telluride (eq 23).

$$2Ga(CH_2{}^tBu)_2Cl + 2LiTePh \xrightarrow{Et_2O} [(^tBuCH_2)_2Ga(\mu\text{-}TePh)]_2 + 2LiCl \quad (23)$$

An X-ray structural determination of [(^{t}BuCH$_2$)$_2$Ga(μ-TePh)]$_2$ indicated it to be dimeric with the organotelluride groups in an anti conformation. The analytical and spectroscopic data for **9** (see Experimental Section) is consistent with a similar structure.

One point worth noting is an apparent disparity in the ^{125}Te NMR shifts for the structurally similar μ-TeR groups. The chemical shift observed for [(^{t}BuCH$_2$)$_2$Ga(μ-TePh)]$_2$ (δ 345.4 ppm) is significantly downfield as compared to that of **9** (δ −398 ppm). Although large, and given the lack of expected structural changes, this difference is entirely consistent with shielding of the Te, in the former, due to the ring current of the pendant phenyl group.

The reaction of either Ga(^{t}Bu)$_3$ or **9** with an excess of elemental tellurium in refluxing toluene proceeds in a manner analogous to that of its selenium counterpart, yielding, in addition to a stoichiometric quantity of the organo ditelluride, the gallium–tellurium cubane **10** (eq 24).

$$4Ga(^tBu)_3 + Te\ (excess) \xrightarrow[toluene]{\Delta} \underset{\mathbf{10}}{[(^tBu)GaTe]_4} + 4{}^tBuTeTe{}^tBu \quad (24)$$

Compound **10** is spectroscopically similar to its sulfur and selenium analogues **4** and **7**, respectively (see Experimental Section). However, unlike **4** and **7**, which both sublime readily at atmospheric pressure, the thermogravimetric analysis of **10** indicates that it sublimes with decomposition at ca. 270 °C to give a nonvolatile residue.

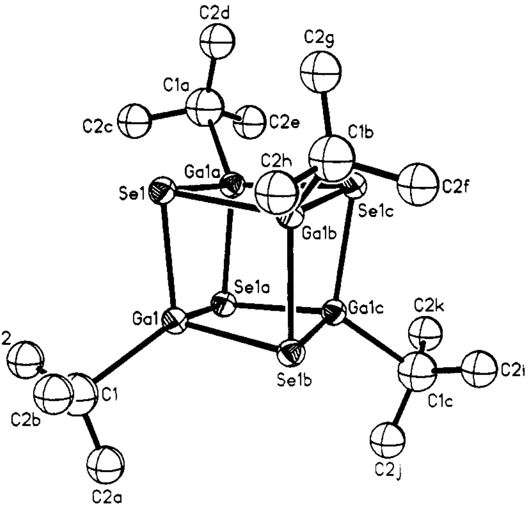


Figure 1. Molecular structure of one of the two independent molecules of [(^{t}Bu)GaSe]$_4$ (**7**). Thermal ellipsoids (anisotropic for gallium and selenium, isotropic for carbon) are drawn at the 40% level, and hydrogen atoms are omitted for clarity.

Under vacuum, however, sublimation occurs with limited decomposition.

X-ray Crystallographic Studies. The molecular structure of **7** is shown in Figure 1. Selected bond lengths and angles are given in Table I along with the corresponding values for **4**. The structure of **7**, as with its sulfur analogue, consists of a distorted-cubane core of four gallium atoms and four μ_3-selenido groups. The pseudotetrahedral coordination sphere at each gallium is completed by a terminally bonded *tert*-butyl group.

Two independent molecules of [(^{t}Bu)GaSe]$_4$ are present in the asymmetric unit. One molecule has point symmetry 23 and is located about the origin (0, 0, 0). The second molecule has point symmetry 4 and is centered at ($-^1/_4$, $-^1/_2$, 0). As can be seen from Table I, the two independent molecules are essentially identical within experimental error.

Due to the paucity of structurally characterized Ga–Se compounds, it is difficult to make realistic comparisons; however, the values observed for the Ga–Se bond distances in **7** are ca. 0.11–0.16 Å longer than those found in Ga$_2$Se$_3$ (2.34 Å).[23] A similar difference (ca. 0.11 Å) is present between **4** and Ga$_2$S$_3$. These differences are undoubtedly due to the strain inherent in the cubane structure, since the Ga–S bond distances in the unstrained adamantane-like Ga$_4$I$_4$(SMe)$_4$S$_2$ (2.204 (8) Å)[24] and [Ga$_4$S$_{10}$]$^{8-}$ (2.289 (2)

---

(22) Banks, M. A.; Beachley, O. T., Jr.; Gysling, H. J.; Luss, H. R. *Organometallics* **1990**, *9*, 1979.

(23) Hahn, V.-H.; Klingler, W. *Z. Anorg. Allg. Chem.* **1949**, *259*, 135.

(24) Boardman, A.; Jeffs, S. E.; Small, R. W. H.; Worrall, I. J. *Inorg. Chim. Acta* **1984**, *83*, L39.

Å)[25] are close to those present in Ga_2S_3. Power et al. have recently reported[26] the X-ray structural characterization of the three-coordinate gallium–selenolate $Ga[Se(2,4,6\text{-}{}^tBuC_6H_2)]_3$, in which the Ga–Se distances (2.322 (1)–2.326 (1) Å) are comparable to those in Ga_2Se_3, i.e. shorter than those in **7**.

The angles E–Ga–E (E = S, 97.3 (1)°; E = Se, 98.8 (2)–99.3 (1)°) are larger than Ga–E–Ga (E = S, 82.1 (1)°; E = Se, 79.9 (2)–80.4 (2)°), such that each face of the Ga_4E_4 polyhedron is a rhomb. The increased atomic radius of selenium over that of sulfur does not force any significant distortion of the cubane but results in a uniformly enlarged core structure.

More than 50 homonuclear cubane clusters of the general class $[(L)ME]_4$ are known;[27] however, while cubane structures have been reported for aluminum imides,[28] phosphides,[29] and indium hydroxides,[30] compounds **4** and **7** are the first group 13–chalcogenide cubanes to be structurally characterized, previous examples being adamantane-like structures.

Possible Pathway to the Formation of $[({}^tBu)GaE]_4$. Whereas the dimeric nature of **5** is perfectly poised for the facile elimination of ${}^tBuH$ and the "spontaneous self assembly" of **4**, it is unclear at first inspection as to the possible pathway for the formation of the $[({}^tBu)GaE]_4$ cubanes from $Ga({}^tBu)_3$ and the elemental chalcogenides. Given that the reactions will be most probably heterogeneous, kinetics measurements will be difficult; however, it is possible to postulate a crude reaction pathway based on the results detailed above and the following observations.

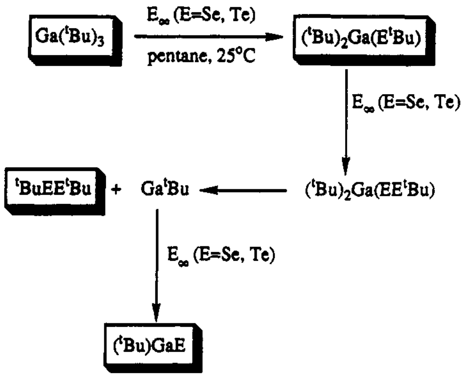
(i) Under the reaction conditions employed for the formation of $[({}^tBu)GaS]_4$, the disulfide ${}^tBuSS{}^tBu$ does not react with elemental sulfur to give polysulfides ${}^tBuS(S)_nS{}^tBu$ (n = 1–3 etc.). In a similar manner, dialkyl ditellurides have been shown to eliminate tellurium metal on thermolysis (eq 25),[31] but under the conditions we employed for the synthesis of $[({}^tBu)GaTe]_4$ (110 °C, 3 days) the reverse reaction does not occur. Thus, the di-*tert* polychalcogenides must be formed as a direct reaction product and not via subsequent reactions with excess elemental chalcogen.

$$RTeTeR \rightarrow RTeR + Te(metal) \qquad (25)$$

(ii) We find no evidence for the insertion of chalcogen into a second gallium–carbon bond (i.e., eq 26). This would suggest that the insertion of a chalcogen atom occurs into the preformed gallium–chalcogen bond (eq 27).

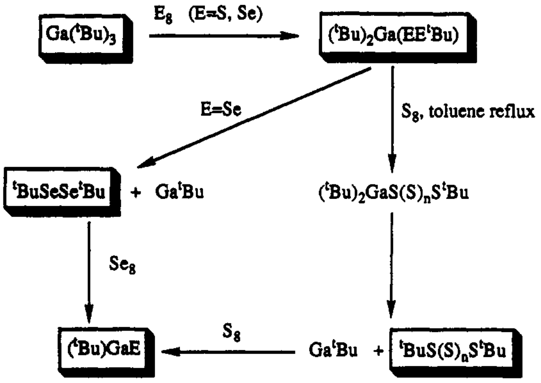
$$({}^tBu)_2Ga(E{}^tBu) + E \rightarrow ({}^tBu)Ga(E{}^tBu)_2 \qquad (26)$$

Scheme I[a]



[a] Isolated species are highlighted.

Scheme II[a]



[a] Isolated species are highlighted.

Supporting evidence for this is the conversion of **3** to **1** and **2** (see above).

$$({}^tBu)_2Ga(E{}^tBu) + E \rightarrow ({}^tBu)_2Ga(EE{}^tBu) \qquad (27)$$

(iii) No ligand exchange is observed between the dimeric thiolate, selenolate, or tellurolate, i.e.

$$[({}^tBu)_2Ga(\mu\text{-}S{}^tBu)]_2 + [({}^tBu)_2Ga(\mu\text{-}Se{}^tBu)]_2 \xrightarrow[C_6H_6]{\Delta,\ 80\ °C} \text{no reaction} \qquad (28)$$

$$[({}^tBu)_2Ga(\mu\text{-}Se{}^tBu)]_2 + [({}^tBu)_2Ga(\mu\text{-}Te{}^tBu)]_2 \xrightarrow[C_6H_6]{\Delta,\ 80\ °C} \text{no reaction} \qquad (29)$$

This would suggest that the dimer, not a transient monomer, is the reactive species for chalcogen insertion.

(iv) Once formed, the Ga_4E_4 cubanes are essentially inert, since no reaction is observed with another chalcogen (eq 30) or other cubanes (eq 31). Thus, the reaction of **3** with selenium metal, yielding **7** (eq 20), cannot proceed via initial formation of the sulfur cube **4**.

$$[({}^tBu)GaS]_4 + Se \rightarrow \text{no reaction} \qquad (30)$$

$$[({}^tBu)GaS]_4 + [({}^tBu)GaSe]_4 \rightarrow \text{no reaction} \qquad (31)$$

On the basis of all the foregoing we propose the following schemes for the reaction of $Ga({}^tBu)_3$ with elemental chalcogens.

Metallic Selenium and Tellurium (Scheme I). The initial reaction results in the insertion of a single Se(Te) atom into one of the Ga–C bonds to yield the isolable selenolate (tellurolate). At elevated temperature this product reacts further with the chalcogen to give an unstable transient alkyl diselenide (telluride), which decomposes to the di-*tert*-butyl diselenide (telluride) and a reactive organogallium fragment, which reacts further to

---

[25] Krebs, B.; Voelker, D.; Stiller, K. *Inorg. Chim. Acta* **1982**, *65*, L101.

[26] Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683.

[27] See for example: (a) Toan, T.; Teo, B. K.; Ferguson, J. A.; Meyer, T. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 408. (b) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455. (c) Bottomley, F.; Grein, F. *Inorg. Chem.* **1982**, *21*, 4170. (d) Nelson, L. L.; Lo, F. Y.-K.; Rae, A. D.; Dahl, L. F. *J. Organomet. Chem.* **1982**, *225*, 309. (e) Williams, P. D.; Curtis, M. D. *Inorg. Chem.* **1986**, *25*, 4562. (f) Bandy, J. A.; Davis, C. E.; Green, J. C.; Green, M. L. H.; Prout, K.; Rodgers, D. P. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1395. (g) Baird, P.; Bandy, J. A.; Green, M. L. H.; Hamnett, A.; Marseglia, E.; Obertelli, D. S.; Prout, K.; Qin, J. *J. Chem. Soc., Dalton Trans.* **1991**, 2378. (h) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc.*, Dalton *Trans.* **1991**, 2471.

[28] Del Piero, G.; Cesari, M.; Dozzi, G.; Mazzei, A. *J. Organomet. Chem.* **1977**, *129*, 281.

[29] Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1409.

[30] Arif, A. M.; Barron, A. R. *Polyhedron* **1988**, *7*, 2091.

[31] (a) McQueen, A. E. D.; Parker, M. B.; Mullin, J. B.; Cole-Hamilton, D. J. *Chemtronics* **1989**, *4*, 264. (b) Mullin, J. B.; McQueen, A. E. D.; Cole-Hamilton, D. J. U.K. Patent 8913799.6, 1990.

give the resulting selenide (telluride). It is highly unlikely that this gallium fragment will be as written, i.e. Ga^{t}Bu; however, the formation of such a species on the chalcogen metal surface cannot be discounted.

***cyclo*-Octasulfur and *cyclo*-Octaselenium (Scheme II).** Unlike the case for the metallic elements, the reaction of S_8 (Se_8) results in the insertion of two sulfur (selenium) atoms. In the case of selenium the resulting alkyl diselenide is unstable and undergoes further reaction as shown in Scheme I. The alkyl disulfide compound is stable, undoubtedly due to the high stability of polysulfur species, and only reacts with excess sulfur under forcing conditions, to give unstable alkyl polysulfides whose decomposition yields the dialkyl polysulfide.

It should be noted that in proposing these reaction pathways we do not imply any mechanistic details; however, they do account for all the observed reaction products. Further studies will be required to further elucidate the intimate details of these cubanes' "spontaneous self-assembly".

Conclusion

The products from the reaction of Ga(^{t}Bu)$_3$ with elemental sulfur, selenium, and tellurium have been determined and found to be highly dependent on the allotropic form of the chalcogen. For the metallic elements, insertion of a single chalcogen atom into one of the Ga–C bonds results, while two atoms are inserted with *cyclo*-octasulfur and *cyclo*-octaselenium. In the case of sulfur, the alkyl disulfide compounds, analogous to the products obtained from the reaction of Ga(^{t}Bu)$_3$ with O_2, are stable and allow for the isolation of the first examples for any of the group 13 elements. The reaction of Ga(^{t}Bu)$_3$ with any of the chalcogens under forcing conditions allows for the isolation of the gallium–chalcogenide cubanes, a product not observed in the reactions with oxygen.[32]

Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. Thermogravimetric and differential thermal analyses were measured on a Seiko 200 TG/DTA instrument. Mass spectra were recorded using a JEOL AX-505H mass spectrometer and associated data system. An electron beam energy of 70 eV was used for EI mass spectra. Isobutane was used as a reagent gas for CI mass spectra. All spectra were recorded at 1500 mass resolution. Reported m/z values are for the predominant ion within the isotope pattern for each signal. The most intense signals within the isotope patterns for the Te-containing compounds appeared two (2) mass units lower than expected on the basis of theoretical calculations. To identify the source of this discrepancy, elemental tellurium was examined by high-resolution fast atom bombardment mass spectroscopy. The tellurium isotope distribution from these measurements is compared with the expected distribution in Table II. Minor isotopes (<1% natural abundance) are omitted. These measurements show that the ^{128}Te isotope is the most abundant in the sample used. This variation is sufficient to explain the anomalous observation in our mass spectra of the tellurium-containing compounds. IR spectra (4000–600 cm^{-1}) were recorded on a Nicolet 5ZDX FTIR spectrometer as Nujol mulls on KBr plates. ^{1}H and ^{13}C NMR spectra (in C_6D_6 unless otherwise stated) were recorded on a Bruker AM-500 spectrometer, and chemical shifts are reported in parts per million relative to external $SiMe_4$ in $CDCl_3$. ^{77}Se and ^{125}Te NMR spectra were recorded on a Bruker WM-300 spectrometer (δ in parts per million relative to external SeO_2 in D_2O (^{77}Se) and external $Te(OH)_6$ in D_2O (^{125}Te) at 25 °C). Ga(^{t}Bu)$_3$, α-Se, and H_2Se were prepared according to published procedures.[33] All manipulations were carried out under an atmosphere of dry nitrogen. Solvents were distilled and degassed before use.

Table II. Comparison of Measured with Expected Isotope Distribution for Tellurium[a]

	abundance, %			abundance, %	
isotope	measd	expected[b]	isotope	measd	expected[b]
122	1.9	2.6	126	20.9	19.0
124	7.3	4.8	128	33.1	31.7
125	5.7	7.2	130	31.1	33.8

[a] Measured numbers taken on the signal for [Te(glycerol)(H_2O)$_4$(OH)]*. [b] Lederer, C. M.; Shirley, V. S. *Table of Isotopes*, 7th ed.; Wiley: New York, 1978.

[(^{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). To a suspension of S_8 (1.32 g, 4.14 mmol) in pentane (40 mL) at −78 °C was added Ga(^{t}Bu)$_3$ (5.5 g, 2.28 mmol). The resulting yellow suspension was warmed to room temperature, during which time a clear colorless solution formed. The solution was set aside in the freezer (−20 °C) overnight. A small quantity of white precipitate formed, which was shown to be [(^{t}Bu)GaS]$_4$ by ^{1}H NMR spectroscopy. Further reduction of the solvent volume and cooling (−20 °C) resulted in the formation of white crystals, which were shown to be a mixture of [(^{t}Bu)$_2$Ga(μ-S^{t}Bu)(μ-SS^{t}Bu)Ga(^{t}Bu)$_2$] and [(^{t}Bu)$_2$Ga(μ-SS^{t}Bu)]$_2$ by ^{1}H NMR spectroscopy. More of this mixture was obtained from the filtrate; yield ca. 70%. Analytically pure **2** may be isolated by fractional crystallization; however, **1** can only be obtained in the presence of **2**.

[(^{t}Bu)$_2$Ga(μ-SS^{t}Bu)]$_2$ (1). MS (EI): m/z 553 (2M$^+$ − ^{t}Bu). NMR (δ, in C_6D_6): ^{1}H, 1.49 [36 H, s, GaC(CH_3)$_3$], 1.20 [18 H, s, SSC(CH_3)$_3$]; ^{13}C, 47.43 [SS*C*(CH$_3$)$_3$], 31.47 [GaC(*C*H$_3$)$_3$], 29.47 [SSC(*C*H$_3$)$_3$], 23.05 [Ga*C*(CH$_3$)$_3$].

[(^{t}Bu)$_2$Ga(μ-S^{t}Bu)(μ-SS^{t}Bu)Ga(^{t}Bu)$_2$] (2). Mp: 156–158 °C. Anal. Calcd for $C_{24}H_{54}Ga_2S_3$: C, 49.84; H, 9.41; S, 16.63. Found: C, 49.22; H, 9.40; S, 16.72. MS (EI): m/z 521 (M$^+$ − ^{t}Bu), 489 (M$^+$ − S^{t}Bu), 401 (M$^+$ − S$_2$^{t}Bu). IR (Nujol): 1234 (w), 1217 (w), 1166 (s), 1144 (s), 1013 (s), 1007 (s) 933 (m), 810 (s), 722 (m), 577 (m), 533 (s), 522 (s), 425 (w), 391 (s) cm^{-1}. NMR (δ, in C_6D_6): ^{1}H, 1.44 [36 H, s, GaC(CH_3)$_3$], 1.35 [9 H, s, SC(CH_3)$_3$], 1.19 [9 H, s, SSC(CH_3)$_3$]; ^{13}C, 47.43 [SS*C*(CH$_3$)$_3$], 47.24 [S*C*(CH$_3$)$_3$], 35.93 [SC(*C*H$_3$)$_3$], 31.51 [GaC(*C*H$_3$)$_3$], 29.29 [SSC(*C*H$_3$)$_3$], 23.05 [Ga*C*(CH$_3$)$_3$].

[(^{t}Bu)$_2$Ga(μ-S^{t}Bu)]$_2$ (3). A slight excess of ^{t}BuSH (2.0 mL, 1.77 mmol) was added, via syringe, to Ga(^{t}Bu)$_3$ (3.51 g, 1.45 mmol) in pentane (40 mL). After about 5 min a white precipitate formed. After the mixture was stirred for 2 h, all volatiles were removed under vacuum, leaving a white powder: yield ca. 95%, 1.88 g; mp 260–262 °C. Anal. Calcd for $C_{12}H_{27}GaS$: C, 52.77; H, 9.96; S, 11.73. Found: C, 52.95; H, 10.20; S, 10.85. MS (EI): m/z 545 (2M$^+$), 273 (M$^+$), 183 (M$^+$ − S^{t}Bu). IR (Nujol): 1216 (w), 1185 (s), 1146 (s), 1077 (w), 1025 (w), 1007 (m), 937 (m), 809 (s), 722 (w), 577 (m), 532 (m), 427 (m), 392 (s) cm^{-1}. NMR (δ, in C_6D_6): ^{1}H, 1.40 [18 H, s, GaC(CH_3)$_3$], 1.37 [9 H, s, SC(CH_3)$_3$]; ^{13}C, 48.08 [S*C*(CH$_3$)$_3$], 36.17 [SC(*C*H$_3$)$_3$], 31.60 [GaC(*C*H$_3$)$_3$], 28.33 [Ga*C*(CH$_3$)$_3$].

[(^{t}Bu)GaS]$_4$ (4). Method 1. Ga(^{t}Bu)$_3$ (1.2 g, 4.97 mmol) in hexane solution (10 mL) was added to a suspension of S_8 (0.47 g, 1.83 mmol) in hexane (30 mL), and the resulting mixture was refluxed overnight. After the solution was cooled to room temperature, the volume of solvent was reduced under vacuum and the solution set aside in the freezer (−27 °C) overnight. A white powder formed, which was filtered and dried under vacuum, and the filtrate was set aside in the freezer. More crystalline product was obtained from the filtrate: yield 72%, 0.56 g.

Method 2. Excess H_2S gas was bubbled through a cooled (0 °C) pentane (50 mL) solution of Ga(^{t}Bu)$_3$ (5.0 g, 20.74 mmol) for 2 min. The solution was then warmed to room temperature. After the mixture was stirred for ca. 1 h, excess H_2S was removed under vacuum. The solution was then refluxed overnight and the solvent removed to give a white solid. The solid was then heated under

---

(32) Following our initial communication of these results,[15] another group has subsequently verified portions of this work; see: Cowley, A. H.; Jones, R. A.; Harris, P. R.; Atwood, D. A.; Contreras, L.; Burek, C. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1143.

(33) Fehér, F. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1963; Vol. 1, p 415.

nitrogen at 100 °C for 1 h to ensure complete conversion of the $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-SH})]_2$ dimer. After the mixture was cooled to room temperature, the solid was Soxhlet-extracted overnight, using hexane as the solvent. When this solution was cooled, a white solid precipitated, which was filtered and dried under vacuum. The filtrate was set aside in the freezer to yield further product: combined yield 85%, 2.8 g; mp 225 °C (sublimed). Anal. Calcd for $\mathrm{C_4H_9GaS}$: C, 30.23; H, 5.70; S, 20.17. Found: C, 30.49; H, 5.50; S, 20.74. MS (EI): *m/z* 636 ($4\mathrm{M}^+$), 579 ($4\mathrm{M}^+ - {}^t\mathrm{Bu}$), 523 ($4\mathrm{M}^+ - {}^t\mathrm{Bu} - \mathrm{CH_2CMe_2}$), 465 ($4\mathrm{M}^+ - 3{}^t\mathrm{Bu}$), 419 ($4\mathrm{M}^+ - 4{}^t\mathrm{Bu}$). IR (Nujol): 1325 (w), 1308 (w), 1261 (w), 1171 (s), 1008 (m), 941 (w), 807 (m), 723 (w), 529 (w) cm^{-1}. NMR (δ, in $\mathrm{C_6D_6}$): ^{1}H, 1.165 [s, $\mathrm{C(C}H_3)_3$]; ^{13}C, 26.85 [$\mathrm{C(}C\mathrm{H_3)_3}$ and $C\mathrm{(CH_3)_3}$].

$[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-SH})]_2$ (5). Excess $\mathrm{H_2S}$ gas was bubbled through a pentane (50 mL) solution of $\mathrm{Ga(^tBu)_3}$ (5.0 g, 20.74 mmol) at room temperature. An exothermic reaction took place with the result of refluxing the pentane briefly. $\mathrm{H_2S}$ gas was continually passed through the mixture until the solution cooled. The solvent was then removed under vacuum to yield a white powder. This powder, mainly 4, was washed once with pentane (50 mL). The mixture was filtered and the filtrate reduced in volume and set aside in the freezer overnight. Colorless X-ray-quality crystals of $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-SH})]_2$ were deposited; yield ca. 10%, 0.45 g, 1.0 mmol. If the above reaction is carried out and worked up at lower temperatures (i.e. −78 °C), then higher yields of 5 may be obtained. Mp: 145–147 °C dec; partial conversion to 4 occurs prior to melting. Anal. Calcd for $\mathrm{C_8H_{19}GaS}$: C, 44.27; H, 8.82; S, 14.77. Found: C, 43.41; H, 8.53; S, 14.85. MS (EI): *m/z* 401 ($2\mathrm{M}^+ - \mathrm{SH}$, 100%), 287 ($2\mathrm{M}^+ - \mathrm{SH} - 2{}^t\mathrm{Bu}$, 20%), 183 ($^t\mathrm{Bu_2Ga}$, 90%). IR (Nujol mull): 2552 (ν(SH), br, s), 1261 (w), 1171 (s), 1009 (s), 940 (m), 810 (s), 722 (w), 539 (m), 518 (m), 503 (m) cm^{-1}. NMR (δ, in $\mathrm{CDCl_3}$): ^{1}H, 1.11 [18 H, s, $\mathrm{C(C}H_3)_3$], 0.642 (1 H, s, SH); ^{13}C, 30.56 [$\mathrm{C(}C\mathrm{H_3)_3}$], 26.24 [$C\mathrm{(CH_3)_3}$].

$[(^t\mathrm{Bu})\mathrm{GaS}]_8$ (6). Repeated sublimation of $[(^t\mathrm{Bu})\mathrm{GaS}]_4$ at 225–235 °C and atmospheric pressure under argon yields **6** in ca. 50% yield, based on ^{1}H NMR spectroscopy. MS (EI): *m/z* 1214 ($8\mathrm{M}^+ - {}^t\mathrm{Bu}$, 100%), 1158 ($8\mathrm{M}^+ - {}^t\mathrm{Bu} - \mathrm{H_2C{=}CMe_2}$, 20%), 1102 ($8\mathrm{M}^+ - {}^t\mathrm{Bu} - 2\mathrm{H_2C{=}CMe_2}$, 18%), 1056 ($7\mathrm{M}^+ - {}^t\mathrm{Bu}$, 25%), 999 ($7\mathrm{M}^+ - 2\,{}^t\mathrm{Bu}$, 10%), 941 ($6\mathrm{M}^+$, 15%), 705 ($5\mathrm{M}^+ - 5{}^t\mathrm{Bu}$, 70%). NMR ($\delta$, in $\mathrm{C_6D_6}$): ^{1}H, 1.54 [s, $\mathrm{C(C}H_3)_3$].

$[(^t\mathrm{Bu})\mathrm{GaSe}]_4$ (7). Method 1. $\mathrm{Ga(^tBu)_3}$ (2.0 g, 0.829 mmol) was added, at room temperature, to an excess of red $\mathrm{Se_8}$ (α-cubic form; 1.96 g, 2.48 mmol) in pentane (40 mL). The resulting suspension was stirred overnight and then filtered, leaving 0.3 g of unreacted red Se and a clear yellow solution. ^{77}Se NMR spectroscopy of the crude reaction mixture indicated the presence of ca. 60% $^t\mathrm{Bu_2Se_2}$ (δ 490.21), ca. 5% $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-Se}^t\mathrm{Bu})]_2$ (δ 156.24), and ca. 35% of another species (δ −231.68). The yellow solution was set aside in the freezer (−27 °C) to yield a white precipitate, which was filtered and dried under vacuum. Further product was obtained from the filtrate in a similar fashion: yield ca. 50% (isolated).

Method 2. Excess $\mathrm{H_2Se}$ gas was bubbled through a pentane (50 mL) solution of $\mathrm{Ga(^tBu)_3}$ (5.0 g, 20.74 mmol) at 0 °C. After a few minutes a white precipitate formed. The mixture was warmed to room temperature slowly. After it was stirred at room temperature for about 0.5 h, the solution was filtered and the white precipitate was dried under vacuum. The filtrate was reduced in volume and set aside in the freezer overnight. More crystalline product was obtained from the filtrate: yield ca. 75%; mp ca. 210 °C (sublimed). Anal. Calcd for $\mathrm{C_4H_9GaSe}$: C, 23.34; H, 4.40; Se, 38.36. Found: C, 23.43; H, 4.26; Se, 32.46. MS (EI): *m/z* 823 ($4\mathrm{M}^+$, 40%), 766 ($4\mathrm{M}^+ - {}^t\mathrm{Bu}$, 100%), 710 ($4\mathrm{M}^+ - {}^t\mathrm{Bu} - \mathrm{H_2C{=}CMe_2}$, 20%), 654 ($4\mathrm{M}^+ - {}^t\mathrm{Bu} - 2\mathrm{H_2C{=}CMe_2}$, 10%), 598 ($4\mathrm{M}^+ - {}^t\mathrm{Bu} - 3\mathrm{H_2C{=}CMe_2}$, 10%). IR (Nujol): 1328 (w), 1310 (w), 1160 (s), 1010 (s), 940 (w) 802 (s) 740 (sh), 725 (m), 670 (m) cm^{-1}. NMR (δ, in $\mathrm{C_6D_6}$): ^{1}H, 1.08 (s); ^{13}C, 26.676 [$\mathrm{C(}C\mathrm{H_3)_3}$ and $C\mathrm{(CH_3)_3}$]; ^{77}Se, −226.73 (s), −231.68 (s, in pentane).

$^t\mathrm{BuSeSe}^t\mathrm{Bu}$. NMR ($\delta$, in $\mathrm{CCl_4}$): ^{1}H, 1.63 (s); ^{13}C, 41.27 [$C\mathrm{(CH_3)_3}$], 32.97 [$\mathrm{C(}C\mathrm{H_3)_3}$]; ^{77}Se 490.21 (s, in pentane).

$[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-Se}^t\mathrm{Bu})]_2$ (8). A pentane (40 mL) solution of $\mathrm{Ga(^tBu)_3}$ (4.0 g, 1.65 mmol) was added to a slurry of black Se powder (100 mesh, 1.31 g, 1.65 mmol) at −78 °C, and the resulting black suspension warmed to room temperature. The solution was stirred overnight and then filtered to leave a pale yellow-green solution. The volume of solvent was reduced under vacuum and the solution set aside in the freezer (−27 °C). A small quantity of white powder was obtained, which was shown to be $[(^t\mathrm{Bu})\mathrm{GaSe}]_4$ by ^{1}H NMR spectroscopy. Filtration followed by further removal of the solvent and cooling (−27 °C) yielded crystalline $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-Se}^t\mathrm{Bu})]_2$: yield ca. 64%; mp 235 °C. Anal. Calcd for $\mathrm{C_{12}H_{27}GaSe}$: C, 45.03; H, 8.50; Se, 24.67. Found: C, 45.59; H, 9.03; Se, 21.28. MS (CI): *m/z* 583 ($2\mathrm{M}^+ - {}^t\mathrm{Bu}$, 100%), 503 ($2\mathrm{M}^+ - \mathrm{Se}^t\mathrm{Bu}$, 100%), 321 ($\mathrm{M}^+$, 10%). IR (Nujol): 1190 (sh), 1170 (m), 1145 (s), 1027 (sh), 1010 (m), 940 (w), 920 (w), 900 (w), 835 (w), 810 (s), 755 (w), 725 (w), 590 (w), 545 (sh), 520 (m) cm^{-1}. NMR (δ, in $\mathrm{CCl_4}$): ^{1}H, 1.80 [18 H, s, $\mathrm{SeC(C}H_3)_3$], 1.35 [36 H, s, $\mathrm{GaC(C}H_3)_3$]; ^{13}C, 46.94 [$\mathrm{Se}C\mathrm{(CH_3)_3}$], 37.47 [$\mathrm{SeC(}C\mathrm{H_3)_3}$], 31.54 [$\mathrm{GaC(}C\mathrm{H_3)_3}$], 29.26 [$\mathrm{Ga}C\mathrm{(CH_3)_3}$]; ^{77}Se, 156.24 (s, in pentane).

Table III. Summary of X-ray Diffraction Data for $[(^t\mathrm{Bu})\mathrm{GaSe}]_4$ (7)

formula	$\mathrm{C_{16}H_{36}Ga_4Se_4}$
space group	$P\bar{4}3n$
a, Å	17.667 (1)
V, Å^3	5514.6 (7)
Z	8
D(calcd), g cm^{-3}	1.983
cryst size	0.20 × 0.27 × 0.33
temp, K	183
radiation (λ, Å)	Mo Kα (0.71073), graphite monochromator
2θ limits, deg	4.0–45.0
index range	$0 \le h \le 10$, $0 \le k \le 13$, $0 \le l \le 18$
no. of collected rflns	788
no. of unique rflns	538
no. of obsd data	337
R	0.047
R_w	0.055
final residual, e Å^{-3}	1.61

$[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-Te}^t\mathrm{Bu})]_2$ (9). $\mathrm{Ga(^tBu)_3}$ (5.0 g, 20.73 mmol) and a 3-fold excess of tellurium metal (7.9 g, 61.91 mmol) were stirred for 24 h in pentane (100 mL). The next day the orange solution was filtered to leave excess Te metal (6.7 g) behind. The filtrate was reduced in volume and set aside in the freezer overnight. Crystalline material was deposited, which was filtered and dried under vacuum. The volume of the filtrate was reduced further and again set aside in the freezer overnight. More product was obtained: combined yield ca. 60%; mp 213–215 °C. IR (Nujol): 1305 (w), 1163 (m), 1135 (s), 1020 (m), 1006 (s), 935 (w), 806 (s), 768 (w), 722 (w), 588 (w), 530 (w), 490 (w) cm^{-1}. NMR (δ, in $\mathrm{C_6D_6}$): ^{1}H, 1.63 [18 H, s, $\mathrm{TeC(C}H_3)_3$], 1.42 [36 H, s, $\mathrm{GaC(C}H_3)_3$]; ^{13}C, 39.45 [$\mathrm{TeC(}C\mathrm{H_3)_3}$], 32.54 [$\mathrm{Te}C\mathrm{(CH_3)_3}$], 31.30 [$\mathrm{GaC(}C\mathrm{H_3)_3}$], 28.64 [$\mathrm{Ga}C\mathrm{(CH_3)_3}$]; ^{125}Te, −398.

$[(^t\mathrm{Bu})\mathrm{GaTe}]_4$ (10). $\mathrm{Ga(^tBu)_3}$ (5.0 g, 20.74 mmol) and tellurium metal (7.9 g, 61.91 mmol) were refluxed in toluene (100 mL) for 4 days. The cloudy orange mixture was then cooled to room temperature and was filtered to leave unreacted Te metal (3.1 g). The filtered solution upon further cooling (−25 °C) yielded a pale yellow precipitate. This was filtered and dried under vacuum. More product was obtained from the filtrate: isolated yield ca. 50–60%; mp >260 °C dec. Anal. Calcd for $\mathrm{C_4H_9GaTe}$: C, 18.88; H, 3.56; Te, 50.15. Found: C, 19.10; H, 3.32; Te, 45.85. MS (EI): *m/z* 1019 ($4\mathrm{M}^+$, 30%), 964 ($4\mathrm{M}^+ - \mathrm{H_2C{=}CMe_2}$, 100%), 907 ($4\mathrm{M}^+ - \mathrm{H_2C{=}CMe_2} - {}^t\mathrm{Bu}$, 25%), 849 ($4\mathrm{M}^+ - \mathrm{H_2C{=}CMe_2} - 2{}^t\mathrm{Bu}$, 26%), 793 ($3\mathrm{M}^+ - \mathrm{H_2C{=}CMe_2} - {}^t\mathrm{Bu}$, 14%), 595 ($3\mathrm{M}^+ - 2\,\mathrm{H_2C{=}CMe_2} - {}^t\mathrm{Bu}$, 10%). IR (Nujol): 1207 (w), 1176 (sh), 1154 (s), 1097 (w), 1047 (w), 1029 (w), 1003 (s), 977 (w), 941 (w), 898 (w), 800 (m), 752 (m), 722 (w), 695 (m) cm^{-1}. NMR (δ, in $\mathrm{C_6D_6}$): ^{1}H, 0.857 [$\mathrm{C(C}H_3)_3$]; ^{13}C, 26.60 [$\mathrm{C(}C\mathrm{H_3)_3}$ and $C\mathrm{(CH_3)_3}$]; ^{125}Te, −1113.

$^t\mathrm{Bu_2Te_2}$. NMR (δ): ^{1}H, 1.16 [$\mathrm{C(C}H_3)_3$]; ^{125}Te, 489.

X-ray Crystallographic Studies. A crystal data summary is given in Table III; fractional atomic coordinates are listed in Table IV. X-ray data were collected on a Syntex $\mathrm{P2_1}$ diffractometer, which is equipped with a modified LT-1 low-temperature system. Laue symmetry determination, crystal class, unit cell parameters, and the crystal orientation matrix were carried out by previously described methods.[34] Intensity data were collected at 183 K using a θ–2θ scan technique with Mo Kα radiation under

---

[34] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, 16, 265.

Table IV. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$ Å^2) for the Non-Hydrogen Atoms in [(^{t}Bu)GaSe]$_4$ (7)

	x	*y*	*z*	*U*(eq)[a]
Se(1)	−757 (2)	−757 (2)	−757 (2)	325 (8)
Ga(1)	638 (2)	−638 (2)	−638 (2)	315 (9)
Se(2)	−3257 (2)	−4256 (2)	−760 (2)	338 (13)
Ga(2)	−1863 (2)	−4369 (2)	−647 (3)	329 (15)
C(1)	1373 (42)	−1373 (42)	−1373 (42)	794 (559)
C(2)	1169 (29)	−1136 (33)	−2156 (28)	636 (150)
C(3)	−1235 (16)	−3778 (33)	−1283 (16)	316 (80)
C(4)	−1557 (27)	−2966 (26)	−1303 (21)	527 (140)
C(5)	−1263 (43)	−3841 (48)	−2102 (31)	1421 (271)
C(6)	−471 (25)	−3941 (33)	−1081 (32)	1014 (200)

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

the conditions described in Table III.

All data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. The crystal belongs to the cubic system, and axial photographs indicated that the diffraction symmetry was *mmm*. Systematic absences were consistent with either the centrosymmetric $Pm\bar{3}n$ (No. 233) or the noncentrosymmetric $P\bar{4}3n$ (No. 218). E-statistics strongly favored the former space group, but structure solution using this space group was unsuccessful. The correct space group was ultimately determined to be $P\bar{4}3n$ by the successful solution of the structure.

All crystallographic calculations were carried out by using either the UCI-modified version of the UCLA Crystallographic Computing Package[35] or the SHELXTL PLUS program set.[36] The analytical scattering factors for neutral atoms were used throughout the analysis;[37a] the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[24b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma(|F_o|) + 0.0003(|F_o|)^2$.

The structures were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and thermal parameters (isotropic for carbon) led to convergence. A final difference-Fourier synthesis yielded ρ(max) = 1.61 e Å^{-3} at a distance of 1.66 Å from Se(2).

There is a large standard deviation in the Ga–C distances between the two independent molecules, 2.24 (4) versus 1.89 (4) Å, and they are on either side of the expected values.[15] The differences in the Ga(1)–C(1) and Ga(2)–C(3) distances are, however, close to the 3σ criteria. The positions of these carbon atoms as well as the gallium atoms are based on an averaging of positions due to the site symmetries of the molecules. Therefore, it is not unexpected that the bond lengths may be ill-defined.

Acknowledgment. Financial support of this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Funds for the purchase of the Nicolet R3m/V diffractometer system were made available from the NSF under Grant No. CHE-85-14495. The Harvard MS Facility is supported by grants from the NSF and NIH. Dr. A. W. Apblett is gratefully acknowledged for assistance with the ^{77}Se NMR measurements.

Registry No. 1, 138571-98-9; 2, 138571-99-0; 3, 138572-00-6; 4, 135283-83-9; 5, 138663-19-1; 6, 138572-01-7; 7, 138572-02-8; 8, 138605-32-0; 9, 138572-03-9; 10, 135258-40-1; Ga(^{t}Bu)$_3$, 55681-99-7; ^{t}BuSH, 75-66-1; ^{t}Bu$_2$Se$_2$, 34172-61-7; ^{t}Bu$_2$Te$_2$, 79971-74-7.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (3 pages); a listing of calculated and observed structure factors (2 pages). Ordering information is given on any current masthead page.

---

[35] UCLA Crystallographic Computing Package, University of California, Los Angeles, 1981. Strouse, C. Personal communication.

[36] Nicolet Instrument Corp., Madison, WI, 1988.

[37] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; pp 99–101. (b) *Ibid.*, pp 149–150.