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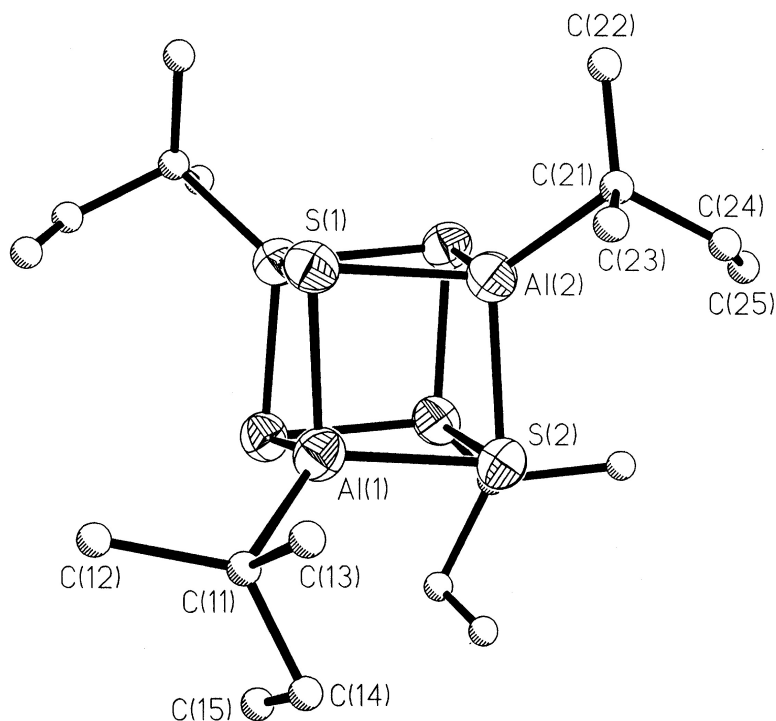Rice University

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tert-Amyl Compounds of Aluminum and Gallium: Halides, Hydroxides, and Chalcogenides

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The reaction of $AlCl_3$ with 3 equiv of the *tert*-amyl Grignard reagent $(Me_2EtC)MgCl$ yields the monomeric trialkyl compound $Al(CMe_2Et)_3$ (**1**). Reaction of compound **1** with MeCN and [PPN]Cl yields the Lewis acid−base complexes $Al(CMe_2Et)_3(MeCN)$ (**2**) and [PPN][AlCl-$(CMe_2Et)_3$] (**3**), respectively. The hydrolysis of $Al(CMe_2Et)_3$ in hexane results in the formation of the trimeric hydroxide $[(Me_2EtC)_2Al(\mu\text{-}OH)]_3$ (**4**), which is converted to the dimer $[(Me_2EtC)_2Al(\mu\text{-}OH)]_2$ (**5**) upon heating. The reaction of $Al(CMe_2Et)_3$ with H_2S at room temperature yields the cubane compound $[(Me_2EtC)Al(\mu_3\text{-}S)]_4$ (**6**). If the reaction is carried out at 0 °C, then the hexamer $[(Me_2EtC)Al(\mu_3\text{-}S)]_6$ (**7**) may be isolated along with compound **6**. The selenide analog of **6**, $[(Me_2EtC)Al(\mu_3\text{-}Se)]_4$ (**8**), is prepared directly from the reaction of compound **1** with H_2Se, while the telluride analog, $[(Me_2EtC)Al(\mu_3\text{-}Te)]_4$ (**9**), is prepared by the direct reaction of compound **1** with tellurium metal. The gallium cubane compounds $[(Me_2EtC)Ga(\mu_3\text{-}E)]_4$, (E = S (**10**), Se (**11**), Te (**12**)) have been prepared from the reaction of $Ga(CMe_2Et)_3$ with the appropriate element. The *tert*-amyl compounds are compared to their *tert*-butyl analogs, and the isolation of compound **7** is used as a precedent to prepare $[(^tBu)Al(\mu_3\text{-}S)]_6$ (**13**). A structural analysis is made of the M_4E_4 cubane cores (M = Al, Ga, In; E = S, Se, Te), and a new topological method is proposed to predict the intracage bond angles in group 13 cage compounds, $[(R)M(\mu_3\text{-}X)]_n$. The molecular structures of compounds **3**, **6**, **8**, and **10**−**12** have been determined by X-ray crystallography, and a discussion of the crystallographic problems associated with the *tert*-amyl group is presented.

Introduction

We have recently reported the synthesis of the *tert*-amyl-substituted gallium sulfide cubane compound $[(Me_2EtC)Ga(\mu_3\text{-}S)]_4$ as a precursor for the chemical vapor deposition (CVD) growth of gallium sulfide.[2] The steric bulk of the *tert*-amyl group precludes the topological rearrangement observed for the *tert*-butyl analog.[3] The increased stability of the *tert*-amyl compound over the *tert*-butyl derivative for gallium has prompted us to investigate the *tert*-amyl chemistry of aluminum as a companion to our work on the *tert*-butyl alumoxanes,[4−6] and to prepare the remaining members of the homologous series $[(Me_2EtC)Ga(\mu_3\text{-}E)]_4$ (E = S, Se, Te). The results of this study are presented herein.

Results and Discussion

***tert*-Amyl Compounds of Aluminum.** The parent aluminum trialkyl compound $Al(CMe_2Et)_3$ (**1**) was prepared from the reaction of $AlCl_3$ with 3 equiv of the Grignard reagent (eq 1). Compound **1**, a clear, waxy

$$AlCl_3 + 3(Me_2EtC)MgCl \rightarrow Al(CMe_2Et)_3 + 3MgCl_2$$
$$\mathbf{1}$$
$$(1)$$
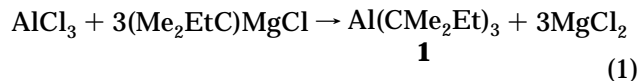
solid which smokes in air, has been characterized by mass spectrometry and ^1H, ^{13}C, and ^{27}Al NMR spectroscopy (see Experimental Section), all of which are consistent with a monomeric compound with a three-coordinate aluminum center.[7] X-ray analysis of crystals of $Al(CMe_2Et)_3$ did not allow for full solution of the solid-state structure; however, partial analysis confirms the planar monomeric structure in the solid state.[8]

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* Authors to whom correspondence should be addressed.
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(1) (a) Rice University. (b) University of North Texas.
(2) Power, M. B.; Barron, A. R.; Hnyk, D.; Robertson, H. E.; Rankin, D. W. H. *Adv. Mater Opt. Electron.* **1995,** *5,* 177.
(3) Power, M. B.; Ziller, J. W.; Barron, A. R. *Organometallics* **1992,** *11,* 2783.
(4) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993,** *115,* 4971.
(5) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994,** *13,* 2957.
(6) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995,** *117,* 6465.

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(7) For examples of monomeric aluminum trialkyl compounds, see: (a) Eisch, J. J.; Biedermann, J. M. *J. Organomet. Chem.* **1971,** *30,* 167. (b) Kroll, W. R.; Hudson, B. E., Jr. *J. Organomet. Chem.* **1971,** *28,* 205. (c) Moriarty, R. M.; Chin, A. *J. Chem. Soc., Chem. Commun.* **1972,** 1300. (d) Haaland, A.; Weidlein, J. *J. Organomet. Chem.* **1972,** *40,* 29. (e) Owens, M. R. *J. Organomet. Chem.* **1973,** *55,* 237. (f) Starowieyski, K. B.; Bandlow, C.; Haage, K. *J. Organomet. Chem.* **1976,** *117,* 215. (g) Jerius, J. J.; Hahn, J. M.; Rahman, A. F. M.; Mols, O.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1986,** *5,* 1812.
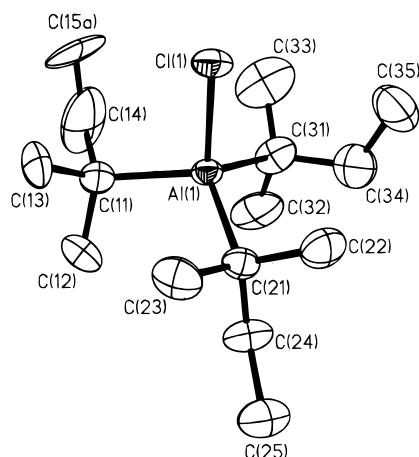
Figure 1. Structure of the [AlCl(CMe$_2$Et)$_3$]$^-$ anion of **3**. Thermal ellipsoids are drawn at the 30% level, and the hydrogen atoms are omitted for clarity.

No complex is observed between Al(CMe$_2$Et)$_3$ and Et$_2$O; however, Lewis acid-base adducts are isolable with acetonitrile[9] and chloride anion,[10] i.e., Al(CMe$_2$Et)$_3$(MeCN) (**2**) and [PPN][AlCl(CMe$_2$Et)$_3$] (**3**) ([PPN]$^+$ = bis(triphenylphosphine)nitrogen(1+); see Experimental Section). The structure of compound **3** has been determined by X-ray crystallography, and the structure of the anion is shown in Figure 1; selected bond lengths and angles are given in Table 1 along with those for the *tert*-butyl analog.[6] The structure of [PPN][AlCl(CMe$_2$Et)$_3$] exists as a discrete anion and cation. The Al–Cl and Al–C bond lengths are identical within experimental error for the two anions, while the interligand angles are clearly similar, suggesting that the steric consequences at aluminum of the ethyl group in *tert*-amyl are negligible as compared to the *tert*-butyl group.[11]

Unlike the majority of aluminum trialkyls,[12] Al(CMe$_2$Et)$_3$ reacts only slowly with water even at room temperature (22 °C). However, hydrolysis over several hours at room temperature leads to the formation of the trimeric hydroxide [(Me$_2$EtC)$_2$Al(μ-OH)]$_3$ (**4**), which is converted to the dimeric form, [(Me$_2$EtC)$_2$Al(μ-OH)]$_2$ (**5**), and other unidentified products upon heating (60 °C, 14 h). While we have previously reported that the conversion of the thermodynamic trimer to the entropically favored dimer is common for dimethylaluminum alkoxide compounds (eq 2),[13] the analogous transformation for [(^{t}Bu)$_2$Al(μ-OH)]$_3$ is accompanied by almost

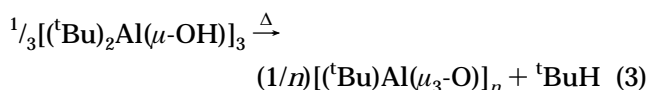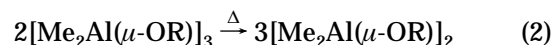(8) Crystal data for Al(CMe$_2$Et)$_3$: hexagonal, $P6_3mc$, a = 8.748(1) Å, c = 14.072(3) Å, V = 932.62(3) Å^3, Z = 4, λ(Mo-Kα) = 0.710 73 Å (graphite monochromator), T = 214 K.

(9) Acetonitrile complexes of aluminum alkyls have been previously reported; see: (a) Jennings, J. R.; Lloyd, J. E.; Wade, K. *J. Chem. Soc.* **1965**, 5083. (b) Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1991**, *10*, 597.

(10) The formation of an anionic Lewis base complex is commonly observed whenever ionic salts react with aluminum alkyls; see: (a) Sneddon, G. J. *Chem. Ind. (London)* **1961**, 1492. (b) Zakharkin, L. I.; Gavrilenko, V. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1962**, 688. (c) Ziegler, K.; Köster, R.; Lehmkuhl, H.; Reinert, K. *Justus Liebigs Ann. Chem.* **1960**, *629*, 33. (d) Ziegler, K.; Lehmkuhl, H.; Linder, E. *Chem. Ber.* **1959**, *92*, 2320.

(11) On the basis of the structural data described herein and the Tolman cone angle (θ) for *tert*-butyl (126°), the cone angle for *tert*-amyl may therefore be estimated to be 135–140°; see: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(12) 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.

(13) Rogers, J. H.; Apblett, A. W.; Cleaver, W. M.; Tyler, A. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 3179.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [PPN][AlCl(CMe$_2$Et)$_3$] (3) and [PPN][AlCl(^{t}Bu)$_3$]^a

|	[AlCl(CMe$_2$Et)$_3$]$^-$	[AlCl(^{t}Bu)$_3$]$^-$
Al(1)–Cl(1)	2.251(2)	2.251(3)
Al(1)–C(11)	2.062(5)	2.014(7)
Al(1)–Cl(21)	2.040(4)	2.003(7)
Al(1)–C(31)	2.044(5)	2.017(6)
Cl(1)–Al(1)–C(11)	104.0(1)	106.5(2)
Cl(1)–Al(1)–C(21)	104.2(1)	101.5(2)
Cl(1)–Al(1)–C(31)	107.7(2)	106.0(2)
C(11)–Al(1)–C(21)	113.4(2)	114.7(3)
C(11)–Al(1)–C(31)	112.9(2)	111.2(3)
C(21)–Al(1)–C(31)	113.6(2)	115.6(3)

^{a} Data for [AlCl(^{t}Bu)$_3$]$^-$ taken from: Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465.
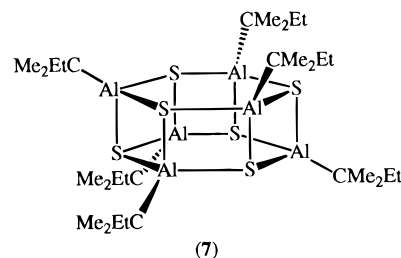

(4)   (5)
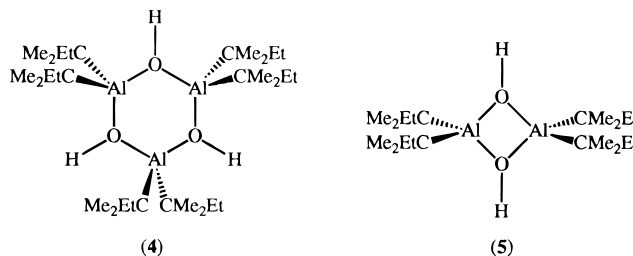
exclusive alumoxane formation (eq 3).[4,6] Therefore we propose that the colorless solids isolated from the thermolysis of **4** are *tert*-amyl alumoxanes although we are unable to isolate individual species.

$$2[Me_2Al(\mu\text{-}OR)]_3 \xrightarrow{\Delta} 3[Me_2Al(\mu\text{-}OR)]_2 \qquad (2)$$

$$^1/_3[(^tBu)_2Al(\mu\text{-}OH)]_3 \xrightarrow{\Delta}$$
$$(1/n)[(^tBu)Al(\mu_3\text{-}O)]_n + {^tBuH} \quad (3)$$

Reaction of Al(CMe$_2$Et)$_3$ with H$_2$S at 25 °C yields the cubane sulfide compound [(Me$_2$EtC)Al(μ_3-S)]$_4$ (**6**) (eq 4), presumably via an unstable hydrosulfido compound, i.e., [(Me$_2$EtC)$_2$Al(μ-SH)]$_2$.[14] Attempts to isolate a hydro-

$$4Al(CMe_2Et)_3 \xrightarrow[-8HCMe_2Et]{+4H_2S} [(Me_2EtC)Al(\mu_3\text{-}S)]_4 \quad (4)$$
$$\mathbf{6}$$
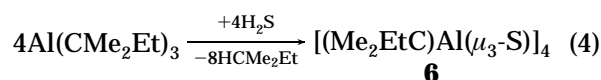
sulfido compound via the low-temperature (0 °C) reaction of Al(CMe$_2$Et)$_3$ with H$_2$S led to the isolation of [(Me$_2$EtC)Al(μ_3-S)]$_6$ (**7**), in addition to compound **6**.

(7)

Compounds **6** and **7** may be separated via fractional crystallization. Compound **7** is the first Al–S hexameric cage to be reported, although we have previously prepared the Ga–S analog,[3] and the hexameric imino-

(14) Reaction of Ga(^{t}Bu)$_3$ with H$_2$S yields the dimeric hydrosulfido compound, [(^{t}Bu)$_2$Ga(μ-SH)]$_2$, which is converted only slowly to the cubane [(^{t}Bu)Ga(μ_3-S)]$_4$ upon heating in refluxing toluene; see: Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1315.

alanes[15] and alumoxane[4] have been structurally characterized. The formation of the hexamer $[(Me_2EtC)Al(\mu_3\text{-}S)]_6$ during the low-temperature reaction of $Al(CMe_2Et)_3$ with H_2S suggests the possible intermediacy of a trimeric hydrosulfido compound, i.e., eq 5.[16]

$$6Al(CMe_2Et)_3 \xrightarrow[-6HCMe_2Et]{+6H_2S}$$

$$2[(Me_2EtC)_2Al(\mu\text{-}SH)]_3 \xrightarrow{-6HCMe_2Et}$$
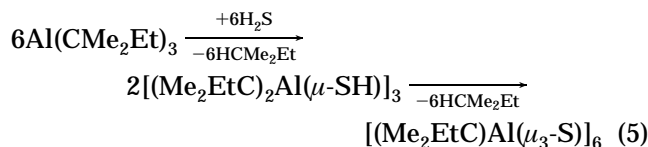
$$[(Me_2EtC)Al(\mu_3\text{-}S)]_6 \quad (5)$$

The selenium cubane compound $[(Me_2EtC)Al(\mu_3\text{-}Se)]_4$ (**8**) is prepared in a manner analogous to that for compound **6** using H_2Se, (c.f. eq 4). The reaction of $Al(CMe_2Et)_3$ with tellurium metal in refluxing toluene yields $[(Me_2EtC)Al(\mu_3\text{-}Te)]_4$ (**9**) directly (eq 6). The

$$Al(CMe_2Et)_3 + Te_\infty \rightarrow$$

$$\underset{\textbf{9}}{[(Me_2EtC)Al(\mu_3\text{-}Te)]_4} + \text{organic side products} \quad (6)$$
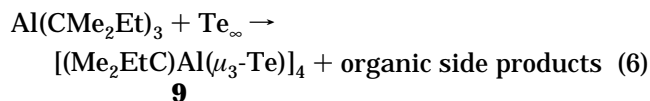
detection of 2-methylbutene, $Me_2C=C(H)Me$, and 2,2-dimethylpentane, $Me_2C(H)Et$, as the organic side products, and the absence of organotellurium side products suggest that compound **9** is formed via the decomposition of the *tert*-amyl telluralate, i.e., **I**. A reaction involving a similar transition state (**II**) has been proposed to account for the formation of $H_2C=CMe_2$ and CH_4 during the MOCVD growth of InS from $[(^tBuS)\text{-}MeIn(\mu\text{-}S^tBu)]_2$.[17]

$$(\textbf{I}) \qquad (\textbf{II})$$
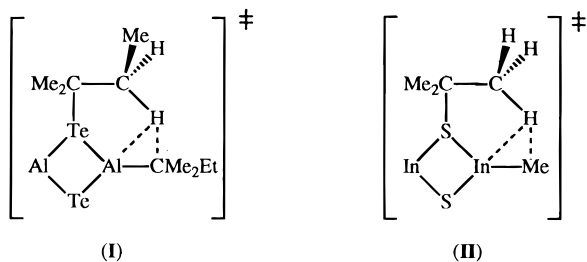
The molecular structures of $[(Me_2EtC)Al(\mu_3\text{-}E)]_4$ (E = S, Se) have been determined by X-ray crystallography and are shown in Figures 2 and 3; selected bond lengths and angles are given in Table 2. X-ray analysis of $[(Me_2EtC)Al(\mu_3\text{-}Te)]_4$ showed it to be isostructural with $[(Me_2EtC)Ga(\mu_3\text{-}Te)]_4$ (see below); however, due to severe disorder of the *tert*-amyl groups no satisfactory solution was obtained.[18] The Al_4E_4 core bond distances in compounds **6** and **8** are comparable to those reported previously for Al−S[19] and Al−Se[20] bonds. The structure of $[(\eta^5\text{-}C_5Me_5)Al(\mu_3\text{-}Se)]_4$, previously reported,[21] shows a significant distortion of the Al_4Se_4 core as compared to compound **8**. The Al−Se−Al angle is larger in $[(\eta^5\text{-}C_5Me_5)Al(\mu_3\text{-}Se)]_4$ than in $[(Me_2EtC)Al(\mu_3\text{-}Se)]_4$, while the Se−Al−Se angles are smaller, resulting in a more
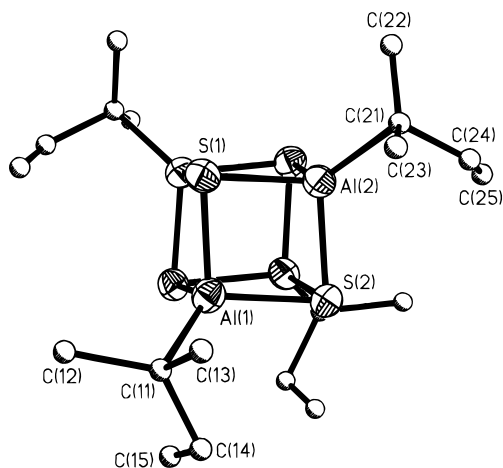

Figure 2. Molecular structure of $[(Me_2EtC)Al(\mu_3\text{-}S)]_4$ (**6**). Thermal ellipsoids are drawn at the 30% level. Only one of the positions for the disorder of the *tert*-amyl groups is shown. Carbon atoms are shown as shaded spheres, and hydrogen atoms are omitted for clarity.
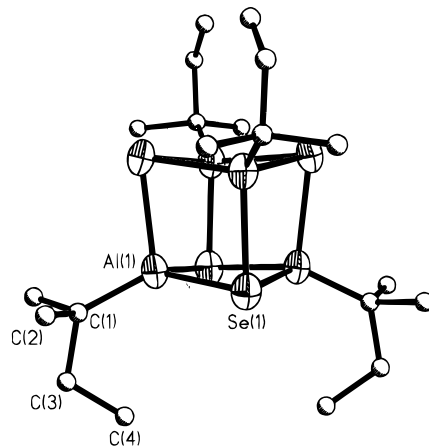

Figure 3. Molecular structure of $[(Me_2EtC)Al(\mu_3\text{-}Se)]_4$ (**8**). Thermal ellipsoids are drawn at the 30% level. Carbon atoms are shown as shaded spheres, and the hydrogen atoms are omitted for clarity.

cubic core in $[(\eta^5\text{-}C_5Me_5)Al(\mu_3\text{-}Se)]_4$ than in $[(Me_2EtC)\text{-}Al(\mu_3\text{-}Se)]_4$. We presume these changes either are a consequence of the strong electron donor effect of the $\eta^5\text{-}C_5Me_5$ ligand or are due to the η^5-coordination of the C_5Me_5 ligand compared to the λ^1-coordination available to the *tert*-amyl group.

In contrast to the other cubane molecules (see below) the *tert*-amyl groups in $[(Me_2EtC)Al(\mu_3\text{-}Se)]_4$ show a well-defined orientation reminiscent of a lobster's claws. The interlocking of these *tert*-amyl pincers results in the adoption of an unusual intermolecular relationship between adjoining molecules, giving a supramolecular

(15) (a) Cesari, M.; Perego, G.; Del Piero, G.; Cucinella, S.; Cernia, E. *J. Organomet. Chem.* **1974**, *78*, 203. (b) Del Piero, G.; Perego, G.; Cucinella, S.; Cesari, M.; Mazzei, A. *J. Organomet. Chem.* **1977**, *136*, 13.

(16) We have previously demonstrated that the formation of $[(^tBu)Al(\mu_3\text{-}O)]_6$ occurs via the dimerization of two trimeric hydroxides, $[(^tBu)_2Al(\mu\text{-}OH)]_3$.[5]

(17) MacInnes, A. N.; Power, M. B.; Hepp, A. F.; Barron, A. R. *J. Organomet. Chem.,* **1993**, *449*, 95.

(18) Crystal data for $[(Me_2EtC)Al(\mu_3\text{-}Te)]_4$: cubic, $P\bar{4}3n$, $a = 18.832(2)$ Å, $V = 6678.6(8)$ Å^3, $Z = 8$, $\lambda(Mo\text{-}K\alpha) = 0.710\,73$ Å (graphite monochromator), $T = 214$ K.

(19) See for example: (a) Brauer, D. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 5462. (b) Haaland, A.; Stokkeland, O.; Weidlein, J. *J. Organomet. Chem.* **1975**, *94*, 353. (c) Shakir, R.; Zaworotko, M. J.; Atwood, J. L. *J. Organomet. Chem.* **1979**, *171*, 9. (d) Boardman, A.; Small, R. W. H.; Worrall, I. J., *Inorg. Chim. Acta* **1986**, *120*, L23. (e) Kumar, R.; de Mel, V. C. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2488. (f) de Mel, V. C. J.; Kumar, R.; Oliver, J. P. *Organometallics* **1990**, *9*, 1303. (g) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2633.

(20) See for example: (a) Atwood, J. E.; Seale, S. K. *J. Organomet. Chem.* **1976**, *42*, 557. (b) Burford, N.; Royan, B. W.; Spence, R. E. v. H.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1990**, 2111. (c) Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H. *J. Crystallogr. Spectrosc. Res.* **1990**, *20*, 53.

(21) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729.
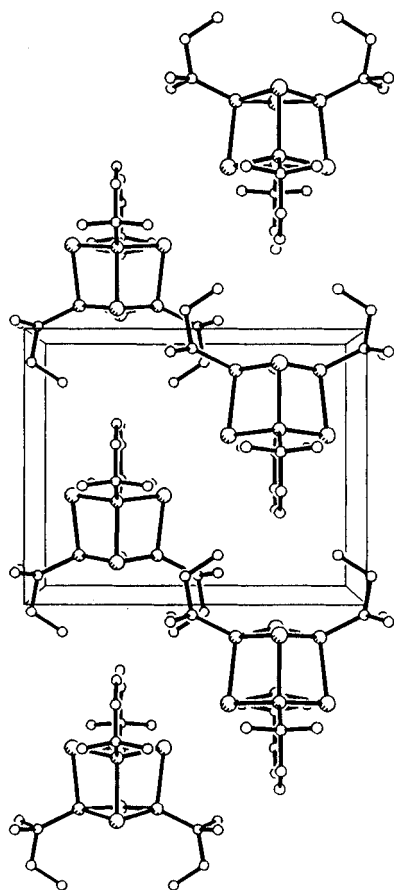
Figure 4. Unit cell of [(Me₂EtC)Al(μ_3-Se)]₄ (**8**) showing the chains formed due to the interlocking of adjacent *tert*-amyl group "lobster claws". Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [(Me₂EtC)Al(μ_3-E)]₄ (E = S (6), Se (8))

[(Me₂EtC)Al(μ_3-S)]₄		[(Me₂EtC)Al(μ_3-Se)]₄	
Al(1)−S(1)	2.316(9)	Al(1)−Se(1)	2.444(6)
Al(1)−S(2)	2.295(8)	Al(1)−Se(1a)	2.444(6)
Al(1)−S(2a)	2.318(4)	Al(1)−Se(1b)	2.481(9)
Al(2)−S(1)	2.319(9)		
Al(2)−S(2)	2.315(8)		
Al(2)−S(1a)	2.317(5)		
Al(1)−C(11)	2.05(3)	Al(1)−C(1)	1.86(3)
Al(2)−C(21)	2.04(2)		
S(1)−Al(1)−S(2)	97.7(3)	Se(1)−Al(1)−Se(1a)	98.7(3)
S(1)−Al(1)−S(2a)	97.5(2)	Se(1)−Al(1)−Se(1b)	99.2(2)
S(2)−Al(1)−S(2a)	97.1(3)		
S(1)−Al(2)−S(2)	97.1(3)		
S(1)−Al(2)−S(1a)	96.7(2)		
S(2)−Al(2)−S(1a)	97.6(3)		
S(1)−Al(1)−C(11)	116.2(8)	Se(1)−Al(1)−C(1)	122.5(5)
S(2)−Al(1)−C(11)	120.5(7)	Se(1a)−Al(1)−C(1)	110(1)
S(1)−Al(2)−C(21)	117.8(8)		
S(2)−Al(2)−C(21)	120.6(7)		
Al(1)−S(1)−Al(2)	81.8(3)	Al(1)−Se(1)−Al(1a)	80.4(3)
Al(1)−S(1)−Al(2a)	82.0(2)	Al(1)−Se(1)−Al(1b)	80.1(3)
Al(2)−S(1)−Al(2a)	82.7(2)		
Al(1)−S(2)−Al(2)	82.4(3)		
Al(1)−S(2)−Al(1a)	82.3(2)		

architecture consisting of parallel chains within the unit cell running along the crystallographic *c* axis (see Figure 4). No such intermolecular interaction exists for [(Me₂EtC)Al(μ_3-S)]₄, possibly as a consequence of the disordered organic substituents (see below).

tert-Amyl Compounds of Gallium. We have previously reported the synthesis of [(Me₂EtC)Ga(μ_3-S)]₄ (**10**)

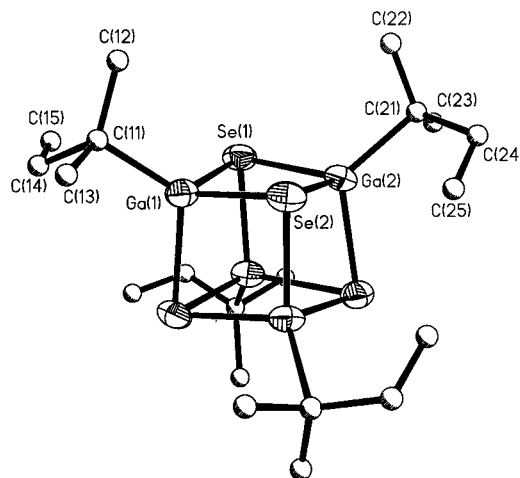**Figure 5.** Molecular structure of [(Me₂EtC)Ga(μ_3-Se)]₄ (**11**). Thermal ellipsoids are drawn at the 30% level. All carbon atoms are shown as shaded spheres, and the hydrogen atoms are omitted for clarity.
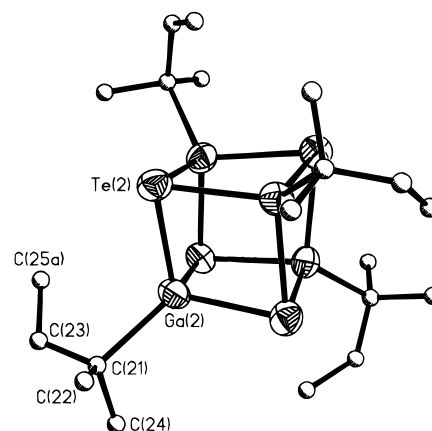
Figure 6. Molecular structure of one of the two independent molecules of [(Me₂EtC)Ga(μ_3-Te)]₄ (**12**). Thermal ellipsoids are drawn at the 30% level. Only one of the positions for the disorder of the CMe₂Et groups is shown. All carbon atoms are shown as shaded spheres, and hydrogen atoms are omitted for clarity.

by solid-state thermolysis of [(Me₂EtC)₂Ga(μ-SH)]₂, isolated from the reaction of Ga(CMe₂Et)₃ with H₂S.[2] However, a one-pot synthesis allows for the isolation of [(Me₂EtC)Ga(μ_3-S)]₄ in comparable yield. The selenide and telluride cubane compounds [(Me₂EtC)Ga(μ_3-Se)]₄ (**11**) and [(Me₂EtC)Ga(μ_3-Te)]₄ (**12**) may be prepared by the reaction of Ga(CMe₂Et)₃ with the appropriate metallic element (see the Experimental Section).

The cubane compounds have been characterized by ¹H and ¹³C NMR spectroscopy and mass spectrometry (see the Experimental Section). In addition, the molecular structures of all three compounds have been confirmed by X-ray crystallography. The structures of [(Me₂EtC)Ga(μ_3-Se)]₄ and [(Me₂EtC)Ga(μ_3-Te)]₄ are shown in Figures 5 and 6, respectively; selected bond lengths and angles are given in Table 3. The Ga−E bond distances, as well as the E−Ga−E and Ga−E−Ga angles, in compounds **10** and **11** are almost identical with those observed for the *tert*-butyl analogs in both the solid state and the vapor phase,[2,22−24] consistent with the highly stable nature of the Ga₄E₄ cores.

(22) Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [(Me₂EtC)Ga(μ_3-E)]₄ (E = S (10), Se (11), Te (12))

[(Me₂EtC)Ga(μ_3-S)]₄		[(Me₂EtC)Ga(μ_3-Se)]₄		[(Me₂EtC)Ga(μ_3-Te)]₄	
Ga(1)−S(1)	2.357(8)	Ga(1)−Se(1)	2.467(2)	Ga(1)−Te(1)	2.676(3)
Ga(1)−S(2)	2.357(7)	Ga(1)−Se(2)	2.482(2)	Ga(2)−Te(2)	2.685(6)
Ga(2)−S(1)	2.358(7)	Ga(2)−Se(1)	2.476(2)		
Ga(2)−S(2)	2.350(8)	Ga(2)−Se(2)	2.470(3)		
Ga(1)−C(11)	2.12(3)	Ga(1)−C(11)	1.97(3)	Ga(1)−C(11)	2.04(3)
Ga(2)−C(21)	2.15(3)	Ga(2)−C(21)	2.00(1)	Ga(2)−C(21)	2.334(5)
S(1)−Ga(1)−S(2)	97.4(3)	Se(1)−Ga(1)−Se(2)	98.7(1)	Te(1)−Ga(1)−Te(1a)	99.8(1)
S(1)−Ga(1)−S(1a)	96.9(1)	Se(1)−Ga(1)−Se(1a)	98.8(1)	Te(2)−Ga(2)−Te(2a)	99.0(2)
S(2)−Ga(1)−S(1a)	97.2(1)	Se(1)−Ga(2)−Se(2)	98.8(1)		
S(2)−Ga(2)−S(2)	97.6(3)	Se(2)−Ga(2)−Se(2a)	98.3(1)		
S(1)−Ga(2)−S(2a)	97.4(1)				
S(2)−Ga(2)−S(2a)	96.9(1)				
S(1)−Ga(1)−C(11)	118(1)	Se(1)−Ga(1)−C(11)	118.5(7)	Te(1)−Ga(1)−C(11)	118.0(5)
S(2)−Ga(1)−C(11)	116.1(9)	Se(2)−Ga(1)−C(11)	116.9(8)	Te(1)−Ga(1)−C(11)	114.6(2)
S(1)−Ga(2)−C(21)	118.6(9)	Se(1)−Ga(2)−C(21)	117.9(6)		
S(2)−Ga(2)−C(21)	120(1)	Se(2)−Ga(1)−C(21)	118.3(6)		
Ga(1)−S(1)−Ga(2)	81.8(3)	Ga(1)−Se(1)−Ga(2)	80.6(1)	Ga(1)−Te(1)−Ga(1a)	79.2(1)
Ga(1)−S(1)−Ga(2a)	82.0(2)	Ga(1)−Se(1)−Ga(1a)	80.4(1)	Ga(2)−Te(2)−Ga(2a)	79.8(2)
Ga(2)−S(1)−Ga(2a)	82.7(2)	Ga(1)−Se(2)−Ga(2)	80.4(1)		
Ga(1)−S(2)−Ga(2)	82.4(3)	Ga(2)−Se(2)−Ga(2a)	80.9(1)		
Ga(1)−S(2)−Ga(1a)	82.3(2)				
Ga(2)−S(1)−Ga(1a)	82.0(2)				

Further evidence for the stable nature of the Ga₄E₄ core is that the intracubane bond lengths and angles for the two crystallographically independent molecules of [(Me₂EtC)Ga(μ_3-Te)]₄ are all the same within experimental error (see Table 3).[25]

Crystallographic Problems Associated with the *tert*-Amyl Ligand. While the *tert*-amyl group appears to have several "chemical" advantages over the more usual *tert*-butyl group (see below), it has proved highly problematic for X-ray crystallographic structure solution. Every structure, except [(Me₂EtC)Al(μ_3-Se)]₄, exhibits some form of disorder (static or dynamic) or, at the very least, high thermal motion.

The *tert*-amyl groups in [(Me₂EtC)Al(μ_3-S)]₄ show an interesting site occupancy disorder. While the α- and γ-carbon atoms have fixed positions, the β-carbon atoms exhibit rotation about the Al−C vector, resulting in a reversal of the conformation of the ethyl substituent (see Figure 7). The rotation of the *tert*-amyl group about the Al−C bond, and the fixed position of the γ-carbon, suggests that its conformation is defined by the crystal packing of the γ-carbon, i.e., AlC(CH₃)₂CH₂*C*H₃. This form of static disorder, while not common, is sometimes observed for short yet "floppy" ligands. Thus, each of the β-silicon atoms in the C(SiMe₃)₃ group have been observed to be disordered over two sites,[26] as have the β-carbons in the SiMe₂ᵗBu group.[27] The phenomenon has also been observed to occur for the two central atoms in a four-membered chain (the so-called "slinky" effect).[28]
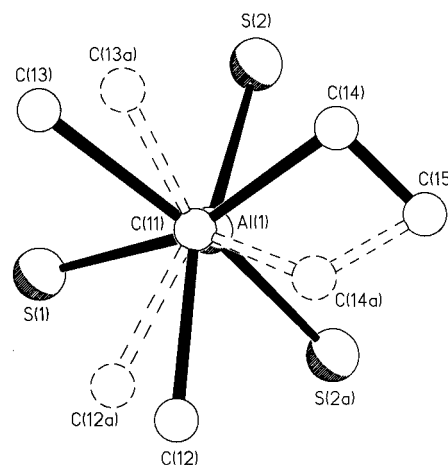

Figure 7. Partial coordination sphere of Al(1) in [(Me₂EtC)Al(μ_3-S)]₄ (**6**) viewed along the C(11)−Al(1) vector, showing the disordered *tert*-amyl ligand. Hydrogens have been omitted for clarity.

The more common form of disorder is a dynamic one, in which the thermal motion of the atoms increases along the "chain". This is manifested crystallographically in three ways. The first, most drastic, is that the electron density of the terminal atoms is so "smeared out" as to be impossible to define. We were unable to locate the *tert*-amyl γ-carbon in [(Me₂EtC)Ga(μ_3-S)]₄, and no significant electron density was found at a suitable distance from the β-carbon atoms. However, the presence of a *tert*-amyl group, rather than *tert*-butyl, was confirmed by the molecular volumes: 779.2 Å³ for [(Me₂EtC)Ga(μ_3-S)]₄ versus 635.6 Å³ for [(ᵗBu)Ga(μ_3-S)]₄.[24] Two possible causes of this effect are disorder of the carbon group and/or large thermal motion resulting in low electron density. A similar problem of the inability to observe the γ-carbon was observed for the room-temperature structure of [(Me₂EtC)Ga(μ_3-Se)]₄.[29] The inability to locate terminal atoms has also been

(23) Cleaver, W. M.; Späth, M.; Hoyk, D.; McMurdo, G.; Power, M. B.; Stuke, M.; Rankin, D. W. H.; Barron, A. R. *Organometallics* **1995**, *14*, 690.

(24) Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1315.

(25) The molecular structure of [(η⁵-C₅Me₅)Ga(μ_3-Te)]₄ shows significant and unexplained distortions of the Ga₄Te₄ core: Ga−Te = 2.650(2)−2.691(1) Å, Te−Ga−Te = 96.59(4)−102.52(3)°, Ga−Te−Ga = 76.92(3)−80.98(4)°. However, the average values (Ga−Te$_{av}$ = 2.67 Å, Te−Ga−Te$_{av}$ = 99.9°, Ga−Te−Ga$_{av}$ = 78.5°) are similar to those found in [(Me₂EtC)Ga(μ_3-Te)]₄; see: Schulz, S.; Andruh, M.; Pape, T.; Heinze, T.; Roesky, H. W.; Häming, L.; Kuhn, A.; Herbst-Irmer, R. *Organometallics* **1994**, *13*, 4004.

(26) Atwood, J. L.; Bott, S. G.; Eaborn, C.; El-Khali, M. N. A.; Smith, J. D. *J. Organomet. Chem.* **1985**, *294*, 23.

(27) See for example: Abboud, K. A.; Eaborn, E. J.; Trivellas, A. *Acta Crystallogr.* **1992**, *C48*, 1695.

(28) Aitken, C. L.; Barron, A. R. *J. Chem. Cryst.* **1996**, *26*, 297.

(29) Room-temperature data for [(Me₂EtC)Ga(μ_3-Se)]₄: monoclinic, C2/c, a = 20.082(2) Å, b = 9.534(1) Å, c = 18.844(2) Å, β = 119.94(1)°, V = 3187.4(7) Å³, Z = 4, D(calcd) = 1.872 g cm⁻³, λ(Mo-Kα) = 0.710 73 Å (graphite monochromator), T = 298 K.
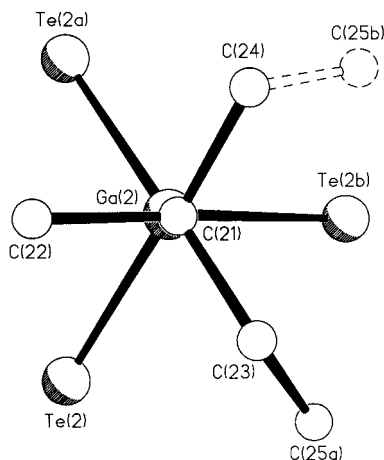
Figure 8. Partial coordination sphere of Ga(2) in [(Me$_2$-EtC)Ga(μ_3-Te)]$_4$ (**12**) viewed along the C(21)−Ga(2) vector, showing the disordered *tert*-amyl ligand. Hydrogens have been omitted for clarity.

reported for similar groups such as the SiMe$_2$^{t}Bu group.[30] The second problem is exemplified in the low-temperature data set of compound **11**, in which the methyl groups were located, albeit with very high thermal parameters. Although there was residual electron density in the room-temperature structure of [(Me$_2$EtC)Ga(μ_3-S)]$_4$, this could not be treated as a rational disorder model. Bond lengths and angles within the group, therefore, substantially deviate from the norm. This problem was also observed for *tert*-amyl compounds of tin.[31]

The third possible crystallographic result of the increased thermal motion is multiple sites for the terminal atoms. Thus, the two independent molecules of [(Me$_2$EtC)Ga(μ_3-Te)]$_4$ show separate crystallographic disorder of the *tert*-amyl groups. Molecule 1 is disordered about a C_3 axis. A similar disorder was observed for the substituents in [(MeEt$_2$C)Ga(μ_3-S)]$_4$.[2] In contrast, molecule 2 exhibits only two sites (out of a possible three) for the γ-carbon not as a consequence of crystallographic symmetry (see Figure 8). This situation is well-represented in the literature.[32]

***tert*-Amyl- versus *tert*-Butylaluminum Compounds.** Given the similarity between *tert*-butyl and *tert*-amyl, one would expect their chemistry to follow similar trends. However, on the basis of the preceding results it would appear that the small steric differences between the two ligands results in some significant differences in stability.

The high thermal stability of [(Me$_2$EtC)$_2$Al(μ-OH)]$_3$ (**4**) with respect to alumoxane formation as compared to its *tert*-butyl analog cannot be due to differences in the acidity of the hydroxide proton versus that observed for the *tert*-butyl analog. It is difficult to estimate the relative acidity of the aluminum hydroxide groups;

however, a crude correlation between the hydroxide acidity and the ^{1}H NMR chemical shift has been previously observed:[33] a downfield hydroxide proton correlates with an acidic hydroxide.[34] The ^{1}H NMR chemical shift of the hydroxide in [(Me$_2$EtC)$_2$Al(μ-OH)]$_3$ (δ 2.06) is clearly similar to that for [(^{t}Bu)$_2$Al(μ-OH)]$_3$ (δ 2.02[4]). In the absence of structural data we suggest that the steric bulk of the *tert*-amyl substituents precludes facile elimination of alkane, and thus significant quantities of the thermodynamically favored dimer, [(Me$_2$EtC)$_2$Al(μ-OH)]$_2$, are attained rather than alumoxanes, as seen in the *tert*-butyl case.[4]

Given the isolation of [(Me$_2$EtC)Al(μ_3-S)]$_6$, we have reinvestigated the reaction of Al(^{t}Bu)$_3$ with H$_2$S. The primary component of the as-synthesized product from the low-temperature reaction of Al(^{t}Bu)$_3$ with H$_2$S is [(^{t}Bu)Al(μ_3-S)]$_4$. However, minor amounts of other species are observed in the ^{1}H NMR spectrum. Upon vacuum sublimation, nearly half of the crude product sublimed, the ^{1}H NMR (δ 1.12) and mass spectra of the sublimed material are consistent with [(^{t}Bu)Al(μ_3-S)]$_4$, while the ^{1}H NMR (δ 1.45) and mass spectra of the unsublimed solid are consistent with a hexameric compound, [(^{t}Bu)Al(μ_3-S)]$_6$ (**13**). The growth of X-ray-

(**13**)
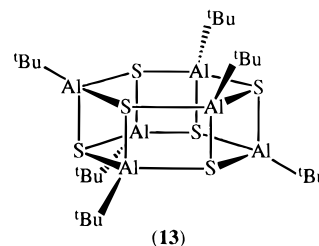
quality crystals of this hexamer was complicated by either polymeric impurities present in the unsublimed solid or a rearrangement and/or decomposition of the hexamer in solution to polymeric species.

Since there is some of the hexamer present in the as-synthesized solid, one may speculate that this compound is forming during the initial reaction of Al(^{t}Bu)$_3$ with H$_2$S. The cooling of the reaction may act to slow its conversion to the more stable cubane. When the sublimed [(^{t}Bu)Al(μ_3-S)]$_4$ was resublimed under vacuum, the remaining solid did not show evidence of hexamer, precluding the thermal topological reorganization of [(^{t}Bu)Al(μ_3-S)]$_4$ to [(^{t}Bu)Al(μ_3-S)]$_6$.[35] The as-synthesized material displayed no evidence for formation of [(^{t}Bu)$_2$Al-(μ-SH)]$_3$, analogous to that postulated for the formation of [(Me$_2$EtC)Al(μ_3-S)]$_6$ or similar to the hydroxide trimer observed for the hydrolysis of Al(^{t}Bu)$_3$.[4]

Topological Approach to the Prediction of Core Geometries of Group 13 Cage Molecules. We have previously observed[2,3] that for the *tert*-butyl cubane molecules [(^{t}Bu)Ga(μ_3-E)]$_4$ (E = S, Se) the increased atomic radius of selenium over that of sulfur results in an enlarged core structure; however, we were previously unable to comment on the factors controlling the shape

(30) Ferguson, G.; Siew, P. Y.; Whally, W. B.; Yeates, C. L. *Cryst. Struct. Commun.* **1982**, *11*, 775.

(31) (a) Puff, H.; Schuh, W.; Sievers, R.; Wals, W.; Zimmer, R. *J. Organomet. Chem.* **1984**, *260*, 271. (b) Puff, H.; Bach, C.; Schuh, W.; Zimmer, R. *J. Organomet. Chem.* **1986**, *312*, 313.

(32) See for example: (a) Heaton, S. B.; Jones, G. B.; Pennington, W. T. *Acta Cryst.* **1993**, *C49*, 1749. (b) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragala, I.; Herbskin, F. H.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7748. (c) Kolb, H. C.; Ley, S. V.; Slavin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2735. (d) Piers, E.; Friesen, R. W.; Kao, P.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1993**, *71*, 1463.

(33) Apblett, A. W.; Warren, A. C.; Barron, A. R. *Chem. Mater.* **1992**, *4*, 167.

(34) For a correlation of ^{1}H NMR chemical shifts for aluminum hydroxides, see: Storre, J.; Klemp, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Fleisher, R.; Stalke, D. *J. Am. Chem. Soc.* **1996**, *118*, 1380.

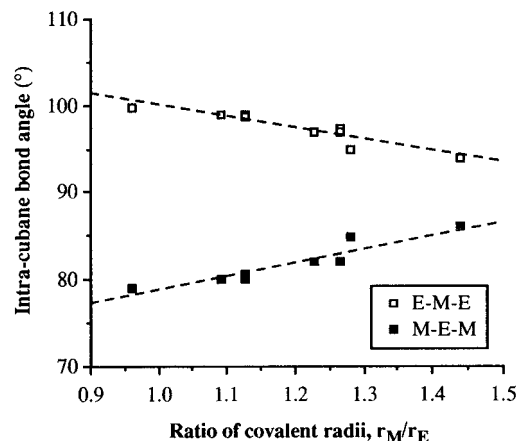(35) Gallium sulfido cages have been demonstrated to undergo a series of topological reorganization reactions.[3]

Figure 9. Plot of the intracubane bond angles $M-E-M$ and $E-M-E$ as a function of the ratio of the covalent radii for M and E, r_M/r_E, for the group 13 chalcogenide cubane molecules $[(R)M(\mu_3\text{-}E)]_4$.
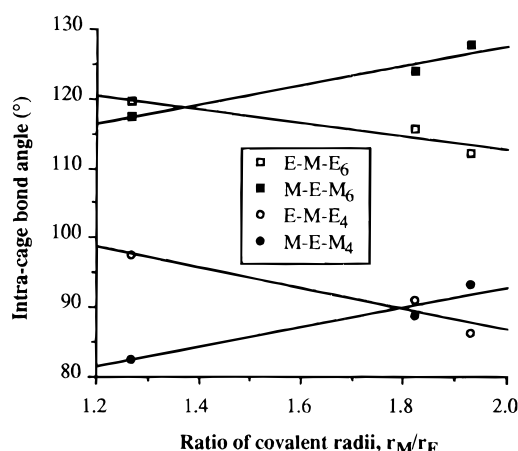
Figure 10. Plot of the intracage bond angles $M-E-M$ and $E-M-E$ as a function of the ratio of the covalent radii for M and E, r_M/r_E, for the group 13 chalcogenide hexameric cage molecules $[(R)M(\mu_3\text{-}E)]_6$.

of the M_4E_4 core, i.e., the magnitude of any rhombohedral distortion from a geometric cube.

Since the cubane cages are electron precise, cluster bonding should not therefore be present and the intracage bonding should be predominantly covalent.[36] Thus, the cage geometry should be easily approximated by the close packing of covalent spheres. If this is true, the geometry of the M_4E_4 core, as determined by the intracage bond angles ($E-M-E$ and $M-E-M$), should be dependent on the ratio of the covalent radii for the group 13 metal and the chalcogenide, i.e., r_M/r_E. Such a relationship is indeed observed (see Figure 9).[37] It is worthwhile noting that using Figure 9 the $N-Al-N$ and $Al-N-Al$ bond angles predicted for an iminoalane cubane, $[RAl(\mu_3\text{-}NR')]_4$ (89.2 and 91.5°, respectively), are in good agreement with the values observed for crystallographically characterized compounds (89.3–90.6 and 89.0–90.4°, respectively).[38]

There have been several methods used to predict structures of cage compounds. We have shown that for compounds of the general formula $[(R)M(X)]_n$, the cage structures may be simply defined as a polyhedron consisting of 6 four-membered faces and $n-4$ six-membered faces. However, the preceding represents a topological approach for the prediction of the geometries of cage compounds. In this regard, our method represents a departure from other approaches and may be likened to Johnson's topological method for the rationalization of structures and the prediction of M—M bond distances in transition-metal carbonyl clusters.[39]

If a topological approach is valid for the cubane molecules, then it should also be suitable for larger cage compounds. In the case of the hexameric cages $[(R)M(\mu_3\text{-}E)]_6$ (E = O, S, NR'; c.f. **7**) two bond angles must be defined for each vertex: i.e., $E-M-E$ within the square M_2E_2 faces, $E-M-E_4$, and $E-M-E$ within the hexagonal M_3E_3 faces, $E-M-E_6$ (see **III**). As is shown in
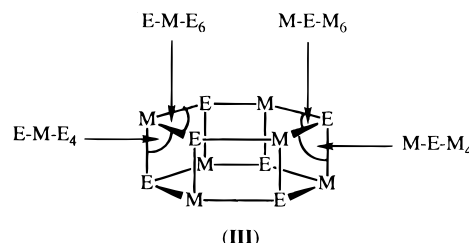
(III)

Figure 10, there is a reasonable correlation between r_M/r_E and the intracage bond angles for the group 13 hexameric cage compounds $[(^tBu)Al(\mu_3\text{-}O)]_6$,[4] $[(^tBu)Ga(\mu_3\text{-}S)]_6$,[3] and $[ClAl(\mu_3\text{-}N^iPr)]_6$.[15] More important than fitting data from known structures, it would be desirable for such a relationship to be predictive. We are continuing our investigations to confirm our predictions.[40]

Experimental Section

Mass spectra were obtained on either a JEOL AX-505 H or Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. FAB mass spectra were obtained using a JEOL SX102A mass spectrometer. Spectra were obtained by bombarding the prepared sample with a beam of 6 keV xenon atoms. Infrared spectra ($4000-400$ cm^{-1}) were obtained using an Perkin-Elmer 1600 Series FT-IR infrared spectrometer. IR samples were prepared as mulls on KBr plates. NMR spectra were obtained on Bruker AM-250 and AM-300 spectrometers using (unless otherwise stated) d_6-benzene solutions. Chemical shifts are reported relative to internal solvent resonances (^1H and ^{13}C) and external $[Al(H_2O)_6]^{3+}$ (^{27}Al). $(Me_2EtC)MgCl$, and H_2Se[41] were prepared according to standard procedures. $AlCl_3$, [PPN]-Cl, H_2S, Se (99.99%, 325 mesh), and Te metal (99.8%, 200 mesh) were obtained from commercial sources and used as received. Elemental analyses were performed using a Perkin-Elmer Magna 400 ICP atomic emission spectrometer. All compounds were digested in nitric acid to enable analysis.

(36) Gas-phase photoelectron spectroscopic measurements of $[(^tBu)Ga(\mu_3\text{-}E)]_4$ (E = S, Se, Te) indicate the Ga–E bonds are predominantly covalent: Subramanian, L.; Lichtenberger, D. L.; Power, M. B.; Barron, A. R. Unpublished results.

(37) $E-M-E = 113.22 - 13.175(r_M/r_E)$, $M-E-M = 63.239 + 15.529(r_M/r_E)$.

(38) (a) Del Piero, G.; Cesari, M.; Dozzi, G.; Mazzei, A. *J. Organomet. Chem.* **1977**, *129*, 281. (b) McDonald, T. R. R.; McDonald, W. S. *Acta Crystallogr.* **1972**, *B28*, 1619. (c) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.*, in press.

(39) See for example: (a) Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1976**, 211. (b) Johnson, B. F. G.; Benfield, R. E. *J. Chem. Soc., Dalton Trans.* **1978**, 1554. (c) Benfield, R. E.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1743.

(40) Values for the oxo–cubane compounds may be calculated from Figure 7: $[RAl(\mu_3\text{-}O)]_4$, O–Al–O = 87.8°, Al–O–Al = 93.2°; $[RGa(\mu_3\text{-}O)]_4$, O–Ga–O = 87.0°, Ga–O–Ga = 94.1°; $[RIn(\mu_3\text{-}O)]_4$, O–In–O = 83.3°, In–In = 98.4°.

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

Caution! Digestion of organoaluminum compounds in acidic solutions should be undertaken with care. Unfortunately, the selenium and tellurium compounds of aluminum gave irreproducible analyses (high Al, low chalcogenide) due to the formation of volatile H_2E (E = S, Se, Te). Analytical results are given as an average of multiple samples.

Al(CMe₂Et)₃ (1). (Me₂EtC)MgCl (1.8 L, 0.95 M solution in Et₂O, 1.7 mol) was added to AlCl₃ (75 g, 0.56 mol) suspended in hexane (500 mL). Upon addition of the Grignard reagent heat was liberated and the AlCl₃ dissolved. Hexane (1 L) was added, and the Et₂O was removed by atmospheric pressure distillation. After most of the Et₂O was removed, additional hexane (500 mL) was added to the reaction flask and the distillation continued until hexane began to distill. The flask was cooled, and the hexane solution was filtered from the white precipitate. The hexane solution was concentrated *in vacuo* to obtain a viscous liquid, which was trap-to-trap-distilled under vacuum at 160 °C to yield 55 g of a clear viscous oil of about 90% purity as determined by ¹H NMR. The crude product was redistilled, separating the first 5 g to distill from the bulk, resulting in analytically pure material. Yield: 50 g, 37%. Mp: ca. 35 °C. MS (EI, %): *m/z* 169 (M⁺ − CMe₂Et, 100%). IR (neat film on KBr, cm⁻¹): 2954 (s), 2903 (s), 2831 (s), 2749 (m), 2718 (m), 2708 (m), 1456 (s), 1374 (s), 1359 (w), 1318 (w), 1174 (w), 1174 (w) 1139 (w), 1041 (m), 1000 (m), 990 (m), 933 (w), 897 (m), 810 (m), 769 (s) 610 (w). ¹H NMR: δ 1.41 [6H, q, *J*(H−H) = 7.4 Hz, C*H₂*CH₃], 1.12 [18H, s, C(C*H₃*)₂], 0.92 [9H, t, *J*(H−H) = 7.4 Hz, CH₂C*H₃*]. ¹³C NMR: δ 37.1 (CH₂*C*H₃), 28.1 [C(*C*H₃)₂], 15.0 (*C*H₂CH₃). ²⁷Al NMR: δ 261 ($w_{1/2}$ = 4700 Hz).

Al(CMe₂Et)₃(MeCN) (2). Al(CMe₂Et)₃ (ca. 1 g) was dissolved in hexanes (25 mL), and an excess of MeCN (4 mL) was quickly added; the resulting solution was stirred for about 15 min. The volatiles were removed under vacuum, the solid material was dissolved in hexanes (10 mL), and this solution was cooled overnight (−24 °C) to yield a colorless crystalline solid. Yield: 0.60 g. Mp: 65−67 °C. Anal. Found (calcd): Al, 9.4 ± 1 (9.5). IR (Nujol mull, cm⁻¹): 1455 (s), 1375 (s), 1320 (m), 1260 (w), 1169 (w), 1133 (w), 1044 (m), 1028 (m), 1002 (m), 990 (m), 938 (m), 891 (m), 809 (m), 771 (s), 602 (m). ¹H NMR: δ 1.78 [6H, q, *J*(H−H) = 7.4 Hz, C*H₂*CH₃], 1.31 [18H, s, C(C*H₃*)₂], 1.14 [9H, t, *J*(H−H) = 7.4 Hz, CH₂C*H₃*], 0.33 [3 H, s, C*H₃*CN]. ¹³C NMR: δ 36.6 [CH₂*C*H₃], 28.7 [C(*C*H₃)₂], 21.2 [*C*(CH₃)₂], 10.0 [*C*H₂CH₃], −1.0 [*C*H₃CN]. ²⁷Al NMR: δ 153 ($w_{1/2}$ = 6300 Hz).

[PPN][AlCl(CMe₂Et)₃] (3). Al(CMe₂Et)₃ (0.5 g, 2.1 mmol) and [PPN]Cl (1.2 g, 2.1 mmol) were combined as solids, and toluene (25 mL) was added, resulting in the formation of a light yellow oil. The suspension was stirred overnight, and volatiles were removed *in vacuo*. The resultant solid was extracted with Et₂O; the extract was filtered, concentrated (ca. 15 mL), and cooled (−24 °C) overnight, yielding large, off-white blocks. Yield: 0.9 g, 53%. Mp: 125−127 °C. Anal. Found (calcd): Al, 3.6 ± 1 (3.3). MS (neg ion FAB, %): *m/z* 275 (M⁺, 100%). IR (Nujol mull, cm⁻¹): 1586 (m), 1573 (w), 1481 (m), 1456 (s), 1436 (s), 1374 (s), 1366 (s), 1336 (s), 1305 (s), 1272 (m), 1182 (m), 1159 (w), 1115 (s). 1069 (w), 1041 (w), 1025 (w), 996 (m), 930 (w), 898 (w), 772 (w), 749 (m), 743 (m), 723 (s), 690 (s). ¹H NMR (CDCl₃): δ 7.7−7.6 (6H, m, *o*-CH), 7.5−7.4 (24H, m, *m*-CH and *p*-CH), 1.47 [6H, q, *J*(H−H) = 7.4 Hz, C*H₂*CH₃], 0.94 [18H, s, C(C*H₃*)₂], 0.79 [3H, t, CH₂C*H₃*]. ¹³C NMR: δ 134.0 (*p*-*C*H), 132.1 [m, *J*(P−C) = 7.5 Hz, *m*-*C*H], 129.6 [m, *J*(P−C) = 12.5 Hz, *o*-*C*H], 127.0 [d, *J*(P−C) = 140 Hz, P−C], 36.2 (CH₂*C*H₃), 28.3 [C(*C*H₃)₂], 21.0 [*C*(CH₃)₂], 8.7 [*C*H₂CH₃]. ²⁷Al NMR: δ 153 ($w_{1/2}$ = 4975 Hz).

[(Me₂EtC)₂Al(μ-OH)]₃ (4). Al(CMe₂Et)₃ (5.0 g, 21 mmol) was dissolved in hexane (100 mL), this solution was cooled to 0 °C, and H₂O (0.4 mL, 22 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 4 h, during which time droplets of unreacted water dissolved. The solution was concentrated (15 mL) and cooled (−24 °C) overnight, yielding a colorless crystalline solid.

Yield: 1.0 g, 26%. Mp: >200 °C dec. MS (EI, %): *m/z* 487 (M⁺ − CMe₂Et, 100%), 415 (M⁺ − CMe₂Et − C₅H₁₂, 35%), 345 (M⁺ − CMe₂Et − HCMe₂Et − C₅H₁₀, 75%). IR (solution in C₆D₆, cm⁻¹): 3578 (s), 1463 (s), 1451 (s), 1359 (m), 1277 (w), 1174 (m), 1138 (m), 1044 (s), 1001 (s), 989 (m), 935 (m), 895 (s), 774 (s). ¹H NMR: δ 2.06 (3H, s, O*H*), 1.47 [12H, q, 12H, *J*(H−H) = 7.4 Hz, C*H₂*CH₃], 1.15 [36H, s, C(C*H₃*)₂], 0.94 [18H, t, *J*(H−H) = 7.4 Hz, CH₂C*H₃*]. ¹³C NMR: δ 36.3 (CH₂*C*H₃), 28.3 [C(*C*H₃)₂], 21.4 [*C*(CH₃)₂], 12.2 (*C*H₂CH₃).

[(Me₂EtC)₂Al(μ-OH)]₂ (5). [(Me₂EtC)₂Al(μ-OH)]₃ (2.5 g, 13 mmol) was refluxed in hexane (35 mL) for 14 h. The solution was concentrated (ca. 5 mL) and cooled overnight (−24 °C), yielding a small amount of colorless crystals Yield: 0.4 g, 16%. Mp: >200 °C dec. MS (EI, %): *m/e* 301 (M⁺ − *tert*-amyl, 100%), 231 (M⁺ − CMe₂Et − C₅H₁₀, 60%), 161 [M⁺ − CMe₂Et − 2(C₅H₁₀), 10%]. IR (Nujol mull, cm⁻¹): 3673 (s), 1737 (w), 1455 (s), 1375 (s), 1317 (m), 1272 (w) 1174 (s), 1139 (m), 1045 (m), 1002 (m), 936 (m), 897 (s), 814 (s), 773 (m). ¹H NMR: δ 1.55 (2H, s, O*H*), 1.45 [8H, q, J(H−H) = 7.5 Hz, C*H₂*CH₃], 1.08 [24H, s, C(C*H₃*)₂], 0.89 [12H, t, J(H−H) = 7.5 Hz, CH₂C*H₃*]. ¹³C NMR: δ 36.6 (CH₂*C*H₃), 28.7 [C(*C*H₃)₂], 22.5 [*C*(CH₃)₂], 13.0 (*C*H₂CH₃).

Reaction of Al(CMe₂Et)₃ with H₂S. Method 1. H₂S was bubbled slowly through a toluene (60 mL) solution of Al(CMe₂Et)₃ (5.60 g, 23.3 mmol) at room temperature. The flask began to warm, and the addition of H₂S was continued until the flask cooled to room temperature (ca. 25 min). The solution was stirred at room temperature for 30 min after which time volatiles were removed *in vacuo* and the remaining solid extracted with hexane (40 mL) and filtered. The first crop of crystals consisted predominantly of a compound whose ¹H NMR is consistent with [(Me₂EtC)₂Al(μ-SH)]₂⁴² as well as small amounts of [(Me₂EtC)Al(μ₃-S)]₄ and traces of [(Me₂EtC)-Al(μ₃-S)]₆. Upon recrystallization from hexane at −24 °C pure [(Me₂EtC)Al(μ₃-S)]₄ is obtained.

Method 2. H₂S was bubbled slowly through a toluene solution of Al(CMe₂Et)₃ (4.0 g, 16.7 mmol) at 0 °C for 30 min. The solution was stirred at room temperature for 1 h, after which time volatiles were removed *in vacuo* and the remaining solid extracted with hexane (40 mL) and filtered. The hexane solution was concentrated and cooled to −24 °C, resulting in the formation of colorless crystalline product. This crop consisted primarily of compound **7** with a small amount of compound **6**. Further recrystallization of the first crop of crystals yielded pure **7** along with a small amount of pure **6**. Additional amounts of compound **7** could be obtained by concentrating and cooling the supernatant.

[(Me₂EtC)Al(μ₃-S)]₄ (6). Mp: >200 °C dec. Anal. Found (calcd): Al, 22 ± 1 (20.7). MS (EI, %): *m/e* 520 (M⁺, 100%), 449 (M⁺ − CMe₂Et, 90%). IR (Nujol mull, cm⁻¹): 1455 (s), 1376 (s), 1358 (m), 1323 (m), 1276 (w), 1178 (s), 1145 (m), 1046 (m), 1020 (w), 1004 (m), 990 (m), 938 (w), 898 (m), 769 (s), 621 (m). ¹H NMR: δ 1.49 [8H, q, *J*(H−H) = 7.5 Hz, C*H₂*CH₃], 1.13 [24H, s, 24H, C(C*H₃*)₂], 1.07 [12H, t, *J*(H−H) = 7.5 Hz, CH₂C*H₃*]. ¹³C NMR: δ 35.1 (CH₂*C*H₃), 24.5 [C(*C*H₃)₂], 12.5 (*C*H₂CH₃). ²⁷Al NMR: δ 133 ($w_{1/2}$ = 5560 Hz).

[(Me₂EtC)Al(μ₃-S)]₆ (7). Mp: 251−253 °C. Anal. Found (calcd): Al, 23 ± 1 (20.7). MS (EI, %): *m/e* 709 (M⁺ − CMe₂Et, 60%). IR (Nujol mull, cm⁻¹): 1455 (s), 1376 (s), 1358 (m), 1323 (m), 1276 (w), 1178 (s), 1145 (m), 1046 (m), 1020 (w), 1004 (m), 990 (m), 938 (w), 898 (m), 769 (s), 621 (m). ¹H NMR: δ 1.55 [12 H, q, *J*(H−H) = 7.5 Hz, C*H₂*CH₃], 1.17 [36 H, s, C(C*H₃*)₂], 1.04 [18 H, t, *J*(H−H) = 7.5 Hz, CH₂C*H₃*]. ¹³C NMR: δ 34.4 (CH₂*C*H₃), 25.0 [C(*C*H₃)₂], 11.6 (*C*H₂CH₃).

[(Me₂EtC)Al(μ₃-Se)]₄ (8). H₂Se was bubbled through a toluene solution of Al(CMe₂Et)₃ (3.90 g, 16.2 mmol) at room temperature until H₂Se evolution ceased. Volatiles were removed under vacuum, and the remaining solid was extracted

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(42) ¹H NMR: δ 1.50 [8H, q, *J*(H−H) = 7.4 Hz, C*H₂*CH₃], 1.09 [24H, s, C(C*H₃*)₂], 0.97 [12 H, t, *J*(H−H) = 7.4 Hz, CH₂C*H₃*], 0.84 [2 H, s, S*H*].

Table 4. Summary of X-ray Diffraction Data

	[PPN][AlCl-(CMe₂Et)₃] (**3**)	[(Me₂EtC)Al-(μ_3-S)]₄ (**6**)	[(Me₂EtC)Al-(μ_3-Se)]₄ (**8**)	[(Me₂EtC)Ga-(μ_3-S)]₄ (**10**)	[(Me₂EtC)Ga-(μ_3-Se)]₄ (**11**)	[(Me₂EtC)Ga-(μ_3-Te)]₄ (**12**)
empir formula	$C_{51}H_{63}AlClNP_2$	$C_{20}H_{44}Al_4S_4$	$C_{20}H_{44}Al_4Se_4$	$C_{20}H_{44}Ga_4S_4$	$C_{20}H_{44}Ga_4Se_4$	$C_{20}H_{44}Ga_4Te_4$
cryst size, mm	$0.15 \times 0.42 \times 0.44$	$0.21 \times 0.23 \times 0.24$	$0.25 \times 0.25 \times 0.40$	$0.18 \times 0.21 \times 0.24$	$0.22 \times 0.32 \times 0.38$	$0.14 \times 0.17 \times 0.19$
cryst syst	triclinic	monoclinic	tetragonal	monoclinic	monoclinic	cubic
space group	$P\bar{1}$	$C2/c$	$P4_2/nmc$	$C2/c$	$C2/c$	$P\bar{4}3n$
a, Å	9.1171(7)	19.841(2)	12.504(8)	19.872(1)	19.900(4)	18.894(1)
b, Å	13.940(1)	9.561(2)		9.4996(8)	9.518(2)	
c, Å	19.789(2)	18.774(2)	10.17(2)	19.782(2)	18.703(4)	
α, deg	107.022(7)					
β, deg	97.649(6)	118.722(8)		123.415(6)	118.05(3)	
γ, deg	96.217(7)					
V, Å³	2354.5(4)	3123.2(8)	1591(3)	3117.1(4)	3126(1)	6745(1)
Z	2	4	2	4	4	8
D(calcd), g/cm³	1.149	1.107	1.479	1.474	1.868	2.115
μ, mm⁻¹	0.197	0.409	0.472	3.675	8.076	6.513
radiation	Mo-Kα (λ = 0.710 73 Å), graphite monochromator					
temp, K	298	298	298	298	214	298
2θ range, deg	2.0–50.0	2.0–42.0	4.0–40.0	2.0–44.0	7.0–45.0	2.0–36.0
no. of collected reflns	8278	2111	1480	3786	2115	5067
no. of indep rflns	8278	2055	414	2037	2046	934
no. of obsd rflns	5008 ($|F_o| >$ 6.0$\sigma|F_o|$)	679 ($|F_o| >$ 5.0$\sigma|F_o|$)	331($|F_o| >$ 6.0$\sigma|F_o|$)	899 ($|F_o| >$ 6.0$\sigma(|F_o|)$)	1331 ($|F_o| >$ 5.0$\sigma|F_o|$)	368 ($|F_o| >$ 6.0$\sigma(|F_o|)$)
weighting scheme	$w^{-1} = \sigma^2(|F_o|) +$ 0.04$(|F_o|)^2$	$w^{-1} = \sigma^2(|F_o|) +$ 0.04$(|F_o|)^2$	$w^{-1} = \sigma^2(|F_o|)$	$w^{-1} = \sigma^2(|F_o|) +$ 0.04$(|F_o|)^2$	$w^{-1} = \sigma^2(|F_o|) +$ 0.0037$(|F_o|)^2$	$w^{-1} = \sigma^2(|F_o|) +$ 0.04$(|F_o|)^2$
R	0.0492	0.0868	0.0618	0.0660	0.0565	0.0401
R_w	0.0498	0.0900	0.0618	0.0749	0.0826	0.0456
largest diff peak, e Å⁻³	0.42	0.36	0.57	0.12	0.58	0.77

with hexane (40 mL) and filtered. The hexane solution was concentrated and cooled to −24 °C, resulting in the formation of colorless crystalline product. Yield: 2.4 g, 86%. Mp: 255–257 °C. Anal. Found (calcd): Al, 15.6 ± 0.1 (15.2). MS (EI, %): m/z 709 (M⁺, 45%), 637 (M⁺ − CMe₂Et, 100%). IR (Nujol mull, cm⁻¹): 1455 (s), 1375 (s), 1358 (s), 1323 (m), 1274 (w), 1169 (w), 1145 (w), 1047 (w), 1019 (w), 1004 (m), 986 (m), 936 (w), 898 (m), 811 (m), 769 (s), 724 (w), 673 (w). ¹H NMR: δ 1.51 [8H, q, J(H−H) = 7.5 Hz, CH_2CH₃], 1.11 [24H, s, C(CH_3)₂], 1.07 [12H, t, J(H−H) = 7.5 Hz, CH₂CH_3]. ¹³C NMR: δ 35.1 (CH₂CH₃), 24.5 [C(CH₃)₂], 12.5 (CH₂CH₃). ²⁷Al NMR: δ 121 ($w_{1/2}$ = 5300 Hz).

[(Me₂EtC)Al(μ_3-Te)]₄ (9). A toluene (40 mL) solution of Al(CMe₂Et)₃ (4.00 g, 16.7 mmol) was refluxed with Te powder (2.1 g 16.6 mmol) for 12 h. Volatiles were removed in vacuo, and the remaining solid was extracted with hexane (40 mL) and filtered. The hexane solution was concentrated and cooled to −24 °C, resulting in the formation of colorless crystalline product. Yield: 2.1 g, 55%. Mp: >275 °C dec. MS: 904 (M⁺, 25%), 834 (M⁺ − C₅H₁₀, 100%). IR (Nujol mull, cm⁻¹): 1455 (s), 1375 (s), 1355 (s), 1321 (m), 1272 (m), 1181 (w), 1161 (m), 1142 (w), 1046 (m), 1018 (m), 1004 (m), 985 (m), 936 (w), 897 (m), 806 (m), 767 (s), 724 (w), 615 (w). ¹H NMR: δ 1.50 [6H, q, J(H−H) = 7.4 Hz, CH_2CH₃], 1.06 [9H, t, J(H−H) = 7.4 Hz, CH₂CH_3], 1.05 [18H, s, C(CH_3)₂]. ¹³C NMR: δ 35.2 [CH₂CH₃], 24.6 [C(CH₃)₂], 15.8 [C(CH₃)₂], 12.0 [CH₂CH₃]. ²⁷Al NMR: δ 75 ($w_{1/2}$ = 6070 Hz).

[(Me₂EtC)Ga(μ_3-S)]₄ (10) was prepared by a modification of our previously published synthesis.² Gaseous H₂S was bubbled rapidly through a solution of Ga(CMe₂Et)₃ (5.0 g, 17.7 mmol) in hexane (150 mL). A white precipitate formed after 15 min, and a heated water bath (ca. 50 °C) was placed under the reaction vessel after 30 min. After 1 h the reaction mixture was cooled and the hexane was removed under vacuum. The product was redissolved in toluene and set aside in the freezer (−29 °C) overnight, to yield transparent colorless crystals. Yield: ca. 75%.

[(Me₂EtC)Ga(μ_3-Se)]₄ (11). Ga(CMe₂Et)₃ (8.1 g, 28.5 mmol) was dissolved with toluene (200 mL) and mixed with excess metallic selenium powder (8.0 g, 0.10 mol). After stirring overnight, the reaction was heated to reflux. The toluene was removed, under vacuum, and the product was separated from the excess Se by a Soxhlet extraction with hexane. The solvent was reduced, and transparent colorless needles grew at room

temperature. Yield: ca. 60%. Mp: 224–230 °C, sublimes. Anal. Found (calcd): Ga, 31 ± 2 (31.7). Se, 32 ± 2 (35.9). MS (EI, %): m/e 879 (M⁺, 30%), 808 (M⁺ − C₅H₁₁, 100%), 738 (M⁺ − 2 C₅H₁₁, 25%), 668 (M⁺ − 3 C₅H₁₁, 15%), 596 (M⁺ − 4 C₅H₁₁, 25%), 589 (M⁺ − 2 C₅H₁₁ − GaSe, 15%), 518 (M⁺ − 2 C₅H₁₁ − Ga₂Se, 15%). IR (Nujol mull, cm⁻¹): 1273 (s), 1164 (s), 1150 (s), 1051 (m), 1007 (m), 989 (w), 907 (w), 768 (s), 523 (w), 464 (m). ¹H NMR: δ 1.05 [3H, t, J(H−H) = 7.4 Hz, CH₂CH_3], 1.09 (6H, s, CH_3), 1.52 [2H, q, J(H−H) = 7.4 Hz, CH_2CH₃]. ¹³C NMR: δ 12.2 (CH₂CH₃), 24.7 (CH₃), 32.85 (Ga-C), 35.29 (CH₂CH₃).

[(Me₂EtC)Ga(μ_3-Te)]₄ (12). A solution of Ga(CMe₂Et)₃ (3.5 g, 12.4 mmol) in toluene (100 mL) was added to a slight excess of metallic tellurium (6.0 g, 47 mmol); this mixture was stirred 3 days at room temperature and then briefly heated to reflux to ensure complete reaction. The solution was filtered and the toluene removed under vacuum. The resulting powder was redissolved in a minimum amount of hexane and set aside in the freezer (−29 °C). Pale yellow blocks grew out of solution. Yield: ca. 60%. Mp: 180 °C, sublimes with decomposition. Anal. Found (calcd): Ga, 25 ± 1 (26.0). Te, 42 ± 2 (47.5). MS (EI, %): m/e 1076 (M⁺, 25%), 1005 (M⁺ − C₅H₁₁, 100%), 933 (M⁺ − 2 C₅H₁₁, 20%), 859 (M⁺ − 3 C₅H₁₁, 55%), 789 (M⁺ − 4 C₅H₁₁, 25%). IR (Nujol mull, cm⁻¹): 1358 (s), 1327 (m), 1260 (s), 1163 (m), 1145 (m), 1058 (w), 913 (w), 799 (s), 765 (w), 458 (w). ¹H NMR: δ 0.85 (6H, s, CH₃), 1.02 [3H, t, J(H−H) = 7.7 Hz, CH₂CH_3], 1.34 [2H, q, J(H−H) = 7.7 Hz, CH_2CH₃]. ¹³C NMR: δ 11.3 (CH₂CH₃), 24.7 (CH₃), 21.2 (Ga−C), 35.3 (CH₂CH₃).

[(ᵗBu)Al(μ_3-S)]₆ (13). Al(ᵗBu)₃ (4.00 g, 20.2 mmol) was combined with degassed pentane (100 mL) in a Schlenk flask. The flask was cooled in an ice bath (0 °C), and H₂S was bubbled through the stirred solution for 45 min. All the volatiles were removed under vacuum, yielding a white solid (2.1 g). This crude product was separated into two fractions by vacuum sublimation (170−190 °C at 10⁻² Torr). The volatile fraction was determined to be [(ᵗBu)Al(μ_3-S)]₄, while the nonvolatile material was collected. Yield: ca. 20%. Mp: >200 °C dec. MS (EI, %): m/z 697 (M⁺, 5%), 638 (M⁺ − ᵗBu, 100%), 582 (M⁺ − 2 ᵗBu, 2%), 524 (M⁺ − 3ᵗBu, 6%). ¹H NMR: 1.45 [s, C(CH_3)₃].

Crystallographic Studies. Crystals of compounds **3**, **6**, **10**, and **12** were sealed in a glass capillary under argon and mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Data collection and cell determinations

were performed in a manner previously described.[4] The locations of the majority of non-hydrogen atoms were obtained by using either SIR (for **3**),[43] SHELXS-86 (for **6** and **10**),[44] or Patterson methods (**12**), while the remaining atomic coordinates were determined through the generation of difference Fourier maps using MolEN.[45] Hydrogen atoms were included with fixed thermal parameters and constrained to "ride" upon the appropriate atoms (d(C−H) = 0.95 Å). A summary of cell parameters, data collection, and structure solution is given in Table 4. Scattering factors were taken from ref 46.

A crystal of compounds **8** was mounted in a glass capillary attached to the goniometer head of a Nicolet R3m/V four-circle diffractometer. Data collection and unit cell and space group determination were all carried out in a manner previously described in detail.[47] The structures were solved using the direct methods program XS,[48] which readily revealed the positions of the Al and Se atoms. Subsequent difference Fourier maps revealed the position of all of the non-hydrogen atoms. Subsequently, full refinement was successful. All the hydrogen atoms were placed in calculated positions (U_{iso} = 0.08; d(C−H) = 0.96 Å) for refinement. Neutral-atom scattering factors were taken from the usual source.[46] Refinement of positional and anisotropic thermal parameters led to convergence (see Table 4).

A crystal of compound **11** was mounted on a glass fiber attached to the goniometer head of a Rigaku four-circle diffractometer. Data collection and unit cell and space group determination were all carried out in a manner similar to that previously described in detail.[47] The structures were solved using the direct methods program XS,[48] which readily revealed the positions of the Ga, Se, and some of the C atoms. Subsequent difference Fourier maps revealed the position of all of the non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in calculated positions (U_{iso} = 1.2U_C; d(C−H) = 0.96 Å) for refinement. Neutral-atom scattering factors were taken from the usual source.[46] Refinement of positional and anisotropic thermal parameters led to convergence (see Table 4).

Supporting Information Available: Full listings of bond lengths and angles, anisotropic thermal parameters, and atomic positional parameters for **3**, **6**, **8**, and **10**−**12** and reproductions of all ^{1}H and ^{13}C NMR spectra for **1**−**9** and **11**−**13** (56 pages). Ordering information is given on any current masthead page.

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