Synthesis of Gallium Chalcogenide Cubanes and Their Use as CVD Precursors for Ga_2E_3 $(E = S, Se)$

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Summary: The gallium-*chalcogen heterocubanes* $[Cp*Ga(\mu_3-E)]_4$, $E = S(1)$ and $Se^{O}(2)$, and $[Cp^{\dagger}Ga(\mu_3-E)]_4$ *Se)]4 (3) have been synthesized by dehalosilylation reactions between* $E(SiMe_3)_2$ *(E = S, Se) and RGaCl₂, R*) *Cp* (C5Me5) and Cp† (C5Me4Et), and are characterized by elemental analyses, NMR spectroscopy, and mass spectrometry. The use of compounds 1 and 2 as singlesource MOCVD precursors for the low-temperature growth of Ga2E3 films at 290*-*310* °*C is described. The as-deposited films were amorphous; however, upon thermal annealing (500* °*C) the films crystallized to the thermodynamic cubic phases, while the corresponding tellurium analog decomposed in the solid state at 220* °*C forming a gallium-rich product.*

Introduction

Compounds containing group 13 and group 16 elements are potential precursors for the corresponding 13-16 materials (III-VI materials) by metal organic chemical vapor decomposition (MOCVD).2 Recently, thin films of materials, such as In_xS_y or Ga_xS_y , have been reported³ to be suitable for the fabrication of optoelectronic devices,⁴ as well as for passivation layers on GaAs and InP,⁵ and dielectric layers in GaAs-based MISFET devices.6

While the preparation of cyclic compounds of the type $[R_2M(\mu-ER')]_n$ (M = Al, Ga, In; E = S, Se, Te; *n* = 2, 3, 4) are well-known and have been described in numerous papers,7 it is only recently that examples of cubane cage compounds, $[(R)M(\mu_3-E)]_4$, have been reported.⁸ Cubanes can be synthesized either by reaction of MR_3 (M $=$ Al, Ga, In) with elemental S, Se, or Te^{9,10} or by reaction of tetrameric monovalent group 13 compounds, $[(R)M]_4$ [M = Al, R = Cp^{*}; M = In, R = C(Me₃Si)₃] with the elemental chalcogens.¹¹ Unfortunately, both reaction types are limited to a few group 13 starting compounds.

One attractive feature of cubanes as single-source precursors for CVD reactions are their clean decomposition pathways.¹² Unlike compounds of the type $[R_2M-$ (*µ*-ER′)]*n*, cubanes do not possess strong E-C bonds which are potentially a source for carbon contamination of the resulting thin film material. In addition, we have shown recently the possibility of controlling the solidstate material's crystal structure by using a predesigned molecular motif.3b Our research has focused on developing simple synthetic pathways to group 13-16 cubanes and studying their decomposition reactions. Our particular interest is to find cubanes with a lower decomposition temperature than those of [(t Bu)Ga(*µ*3- S)]₄, which decompose at $350 - 400$ °C, enabling gallium sulfide films to be deposited on a wider variety of thermally sensitive substrates.¹³

Results and Discussion

The reaction of Cp^*GaCl_2 and $Cp^{\dagger}GaCl_2$ with $E(SiMe₃)₂$ (E = S, Se), in toluene, leads to the new gallium chalcogen cubanes [Cp*Ga(*µ*3-S)]4 (**1**), [Cp*Ga-

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⁽⁸⁾ For recent review articles, see: (a) Barron, A. R. *Chem. Soc. Rev*. **1993**, 93. (b) Barron, A. R. *Comm. Inorg. Chem*. **1993**, *14*, 123.

⁽⁹⁾ Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055.

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⁽¹²⁾ Cleaver, W. M.; Späth, M.; Hoyk, D.; McMurdo, G.; Power, M.
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⁽¹³⁾ Our initial efforts in this area have involved the photoassisted MOCVD of GaS thin films; see: Pernot P.; Barron, A. R. *Chem. Vap. Deposition* **1995**, *1*, 75.

Figure 1. Molecular structure of $[Cp*Ga(u_3-Se)]_4$ (2). Thermal ellipsoids are shown at the 45% level, and hydrogen atoms are omitted for clarity.

Scheme 1. Mass Spectral Fragmentation Pattern for $[Cp*Ga(\mu_3 \cdot E)]_4$, $E = S(1)$ and Se (2), and $[Cp \dagger Ga(\mu_3 \text{-} Se)]_4$ (3)

 $(\mu_3$ -Se)]₄ (2), and [Cp[†]Ga(μ_3 -Se)]₄ (3). These compounds are isolated as white (**1**) or light yellow (**2** and **3**) solids and are characterized by ${}^{1}H$ and ${}^{13}C$ NMR, mass spectroscopy, and elemental analyses; see Experimental Section. Molecular ions peaks (M^+) were observed for all the compounds along with the fragmentation pattern shown in Scheme 1. All the compounds are air and moisture sensitive and discolor (purple) upon exposure to air.

Crystals of compound **2** suitable for X-ray diffraction studies were obtained by slow evaporation of a toluene solution. The molecular structure of **2** is shown in Figure 1; selected bond lengths and angles are given in Table 1. The cubane core shows an unusual axial distortion, with the Ga-Se-Ga angles varying from 78.88(2) to 81.58(2)°, and the Se-Ga-Se angles range from 97.10(3) to 100.70(3)°. As a consequence, two of the Ga-Se bond lengths $[Se(1)-Ga(1)]$ and $Se(2) Ga(2)$] are slightly shorter than the others.¹⁴ However, the bond lengths and angles are comparable to those found in [(t Bu)Ga(*µ*3-Se)]4 ¹⁵ and [(Me2EtC)Ga(*µ*3-Se)]4, 10 and the bond lengths compare well to the distances found in Ga₂Se₃ (2.340 Å).¹⁶ The Cp^{*} rings are σ -bonded to each Ga center.¹⁷ The average $Ga-C$ bond length in **2** is 2.004(8) Å, which is comparable to normal $Ga-C$ distances.¹⁸ In contrast, the Cp^* rings in the aluminum analog are η^5 -bonded,^{11a} and its frame is much more ideally cubic. It appears that the larger gallium atoms prevent a regular cubane formation,¹⁰ thereby causing

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Cp*Ga(\mu_3\text{-}Se)]_4$ **(2)**^{*a*}

$Se(1)-Ga(1)$	2.4454(8)	$Se(1)-Ga(2)$	2.4992(8)
$Se(1)-Ga(2a)$	2.4811(8)	$Se(2)-Ga(1)$	2.4755(8)
$Se(2)-Ga(2)$	2.4424(8)	$Se(2) - Ga(1a)$	2.4802(8)
$Ga(1)-C(1)$	1.997(6)	$Ga(2) - C(11)$	2.0126(6)
$Ga(1) - Se(1) - Ga(2)$	78.88(2)	$Ga(1)-Se(1)-Ga(2a)$	79.89(2)
$Ga(2)-Se(1)-Ga(2a)$	81.58(2)	$Ga(1) - Se(2) - Ga(2)$	79.40(3)
$Ga(2)-Se(2)-Ga(1a)$	79.97(2)	$Ga(1)-Se(2)-Ga(1a)$	81.19(3)
$Se(1)-Ga(1)-Se(2)$	100.70(3)	$Se(1)-Ga(1)-Se(2a)$	99.33(3)
$Se(2)-Ga(1)-Se(2a)$	97.48(3)	$C(1) - Ga(1) - Se(1)$	121.7(2)
$C(1) - Ga(1) - Se(2)$	118.4(2)	$Se(1)-Ga(2)-Se(2)$	100.12(3)
$Se(1)-Ga(2)-Se(1a)$	97.10(3)	$Se(2)-Ga(2)-Se(1a)$	99.38(3)
$C(11) - Ga(2) - Se(1)$	117.1(2)	$C(11) - Ga(2) - Se(2)$	115.8(2)
$C(11) - Ga(2) - Se(1a)$	123.2(2)		

a Symmetry code = x , $-y$, $-z - 1$.

Table 2. CVD Experimental Conditions and Film Analysis

compd	precursor	substrate	film composn,
	temp, $^{\circ}C$	temp, °C	Ga: E
$[Cp^*Ga(\mu_3-S)]_4$	185	310	41(1):59(1)
$[Cp^*Ga(\mu_3-Se)]_4$	205	290	41(1):59(1)

the Cp^{*} rings slippage from η^5 to σ . The same frame distortion was observed for [Cp*Ga(*µ*3-Te)]4, ¹⁹ in which the Cp* rings are also *σ*-bonded.

Deposition Studies. Two of the aforementioned cubanes, $[Cp*Ga(u_3-S)]_4$ (1) and $[Cp*Ga(u_3-Se)]_4$ (2), were determined to be suitably volatile for use as CVD precursors for the deposition of gallium chalcogenide thin films. By an appropriate choice of precursor volatilization and substrate temperatures, uniform reflective films were grown on Si(100) and GaAs(100) wafers; see Table 2. Microprobe analysis revealed that the precursors composition $(Ga:E = 1)$ was not conserved in the resulting film; instead the composition was found to be Ga_2E_3 .^{20,21} Oxygen was undetectable in these films $($ $<$ 0.1 atomic $%$), while carbon (including any adsorbed carbon species on the film surface) was present at levels less than 10 atomic %. Scanning electron microscopy (SEM) demonstrated that these films were smooth and featureless down to a 1 *µ*m level. There were, however, a few spherical features on the order of 100 nm evident on the $Ga₂Se₃$ surface. Thinfilm X-ray diffraction (XRD) scans of the as-deposited films indicated them to be essentially amorphous. After annealing films grown on Si for 5 h at 500 °C, broad peaks corresponding to the most intense reflections of the cubic Ga_2E_3 phase were evident in both systems.²²

(21) Core cleavage of $[(^tBu)Ga(\mu₃-S)]_4$ is only observed above 450 °C; see ref 12 and 3b.

(22) JCPDF-ICDD file nos. $43-916$ (Ga₂S₃) and $5-724$ (Ga₂Se₃).

⁽¹⁴⁾ It has been previously reported that the solid-state structures of several transition metal-chalcogenide cubane clusters, e.g., [(X)FeS]₄ⁿ⁻, show distortion due to crystal packing forces; see: Snyder, B. S.; Holm, R. H. *Inorg. Chem.* **1988**, *27*, 2339 and references therein. (15) Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun*. **1991**, 1315.

⁽¹⁶⁾ Hahn, V.-H.; Klingler, W. *Z. Anorg. Allg. Chem.* **1949**, *259*, 135. (17) The observation of a single resonance in the 1H and 13C NMR spectra for the cyclopentadienyl's methyl groups suggests the presence of either ring slippage to η^5 -coordination or ring-wizzing in solution at room temperature.

⁽¹⁸⁾ See: Cleaver, W. M.; Barron, A. R.; McGufey, A. R.; Bott, S. G. *Polyhedron* **1994**, *13*, 2831 and references therein. (19) Schulz, S.; Andruh, M.; Pape, T.; Heinze, T; Roesky, H. W.;

Häming, L.; Kuhn, A.; Herbst-Irmer, R. Organometallics 1994, 13, 4004.

⁽²⁰⁾ Phase diagrams indicate the both GaE and Ga_2E_3 are thermodynamically stable compositions for these systems; see: *Binary Alloy Phase Diagrams*; Massalski, T. B., Ed.; ASM Intl.: Materials Park, OH, 1990; Vol. 2, p 1849.

Their peak broadening translated to crystalline domains of approximately 40 and 55 Å for Ga_2S_3 and Ga_2Se_3 , respectively.23

The formation of gallium-deficient film compositions relative to the cubane precursor's stoichiometry strongly suggests that there is significant core fragmentation occurring during the deposition process. The thermal degradation of the cubane core is apparently more significant during the CVD process than is observed during the mass spectral analysis and, given the stability previously observed for the *tert*-butyl and *tert*-amyl analogs, suggests that core cleavage is related to the presence of the cyclopentadienyl ligand.

In contrast to the sulfur and selenium analogs, $[Cp^*Ga(\mu_3-Te)]_4^{18}$ could not be volatilized intact into the deposition zone of the furnace. Upon heating of this cubane at 220-230 °C for 2 h, decomposition in the solid state occurred, giving a black metallic-looking powder with an approximate composition of $Ga_{0.7}Te_{0.3}$ and a low carbon content (\leq 5 atomic %). It is not surprising that the gallium tellurium cubane decomposes in the solid state because it suffers from low volatility due to its high molecular weight and contains the weakest gallium chalcogen bonds of the series. Even though film formation in a hot wall system was unsuccessful, it may be possible to use $[Cp^*Ga(u_3Te)]_4$ in a CVD process using a higher vacuum or a cold walled/heated substrate geometry.

Experimental Section

All manipulations were performed using standard Schlenk line and glovebox techniques under dried and deoxidized argon. Solvents were dried over potassium and distilled under argon before use, and all glassware was oven-dried. $GaCl₃$ was purchased from Aldrich and used as received. S(SiMe3)2 and $Se(SiMe₃)₂$ were prepared by the literature methods.²⁴ ¹H and 13C NMR spectra were recorded on a Bruker WM-360 NMR spectrometer. The proton and carbon chemical shifts were referenced to $C_6D_5H(\delta = 7.15$ ppm) and $C_6D_6(\delta = 128.0$ ppm), respectively. Mass spectra were recorded on a Fisons Trio-1 mass spectrometer using electron ionization (70 eV). Elemental analyses were performed at Galbraith Laboratories, and melting points were measured in wax-sealed capillaries and are uncorrected.

 $Cp^*GaCl_2^{25}$ and $Cp^{\dagger}GaCl_2^{26}$ were freshly prepared using the following procedure: $Cp*Sime_3$ or Cp^*Sime_3 was added to an equimolar suspension of $GaCl₃$ in hexane. The mixture was refluxed for 2 h, and all volatiles were removed *in vacuo*. Cp^*GaCl_2 and Cp^*GaCl_2 were obtained as white solids, which rapidly decompose within 2 h.

Synthesis of $[Cp*Ga(\mu_3-S)]_4$ **(1).** S(SiMe₃)₂ (0.54 g, 3.0) mmol) was added *via* syringe to a solution of Cp*GaCl₂ (0.83) g, 3.0 mmol) in toluene (60 mL). The mixture was stirred for 2 h and then was refluxed for 2 h. All volatiles were removed *in vacuo* yielding a white powder.²⁷ Yield: 0.60 g, 85%. Mp: >250 °C. Anal. Found (calcd): C, 49.19 (50.67); H, 7.00 (6.38). EI-MS $(m/z, %)$: 948 $(M^+, 5)$, 813 $(M^+ - Cp^*, 3)$, 678 $(M^+ 2Cp^*$, 7), 543 (M⁺ - 3Cp^{*}, 10), 474 (M⁺/2, 3), 408 (M⁺ - 4Cp^{*}, 2), 135 (Cp*, 100). 1H NMR: *δ* 1.88 (15H, s, C*H*3). 13C NMR: *δ* 11.5 (*C*H3), 119.3 (ring-*C*).

Table 3. Summary of X-ray Diffraction Data for $[Cp^*Ga(\mu_3-Se)]_4$ (2)

$[Cp*Ga(\mu_3-Se)]_4$ (2)
$C_{40}H_{60}Ga_4Se_4$
$0.40 \times 0.40 \times 0.80$
orthorhombic
$C222_1$
13.6242(2)
16.1914(2)
19.6630(1)
4337.56(9)
4
1.739
5.841
Mo Kα ($λ$ = 0.71073 Å)
graphite monochromator
173(2)
$1.95 - 27.96$
9723
4981
4832 ($ F_{\rm o} > 2\sigma F_{\rm o} $)
$W^{-1} = \sigma^2 F_0^2 + (0.0766P)^2 +$
$23.3676P^a$
0.0457, 0.0433
0.1260, 0.1196
0.86

 $P = (F_0^2 + 2F_c^2)/3$.

Synthesis of $[Cp*Ga(\mu_3-Se)]_4$ **(2).** Se(SiMe₃)₂ (0.68 g, 3.0) mmol) was added *via* syringe to a solution of Cp*GaCl₂ (0.83) g, 3.0 mmol) in toluene (60 mL). The mixture was stirred for 2 h and then was refluxed for 2 h. All volatiles were removed *in vacuo* yielding a light yellow powder.²⁷ Yield: 0.68 g, 80%. Mp: >250 °C. Anal. Found (calcd): C, 41.73 (42.30); H, 5.41 (5.33). EI-MS $(m/z, %): 1001 (M⁺ – Cp[*], 1), 866 (M⁺ – 2Cp[*],$ 2), 731 (M^+ – 3Cp^{*}, 4), 596 (M^+ – 4Cp^{*}, 2), 135 (Cp^{*}, 100). 1H NMR: *δ* 1.86 (15H, s, C*H*3). 13C NMR: *δ* 11.7 (*C*H3), 119.1 (ring-*C*).

Synthesis of $[Cp^{\dagger}Ga(\mu_3 \text{-} Se)]_4$ **(3).** Se(SiMe₃)₂ (0.68 g, 3.0) mmol) was added *via* syringe to a solution of Cp[†]GaCl₂ (0.87) g, 3.0 mmol), which led to a white powder.²⁷ Yield: 0.63 g, 70%. Mp: dec 190 °C. Anal. Found (calcd): C, 45.01 (44.34); H, 6.76 (6.75). EI-MS (*m/z*, %): 894 (M⁺ - 2Cp† , 0.5), 745 (M⁺ - 3Cp† , 3), 596 (M⁺/2, 1), 149 (Cp† , 100). 1H NMR: *δ* 0.85 [3H, t, $J(H-H) = 7.4$ Hz, CH_2CH_3], 1.91 (6H, s, CH_3), 1.96 (6H, s, CH₃), 2.27 [2H, q, $J(H-H) = 7.4$ Hz, CH₂CH₃). ¹³C NMR: *δ* 11.7 (*C*H3), 11.8 (*C*H3), 13.4 (*C*H2CH3), 20.2 (CH2*C*H3), 101.3 (Ga-*C*), 124.6 (R-ring-*C*), 125.3 (*â*-ring-*C*).

Crystallographic Studies. A transparent crystal of **2** was mounted on a fiber and transferred to the goniometer of a Siemens SMART CCD area detector diffractometer. The crystal was cooled to -100 °C during data collection by using a stream of cold nitrogen gas. The space group was determined to be the acentric $C222_1$ from the systematic absences. The structure was solved using the direct methods program SHELXTL.28 The hydrogen atoms were included as rigid groups with rotational freedom at the bonded carbon atom [*B* $\stackrel{\textstyle \cup}{=}$ 1.2 U_{eqv} (C)]. Refinement of non-hydrogen atoms was carried out with anisotropic temperature factors. The structure was refined as a racemic twin. A summary of cell parameters, data collection, and structure solution is given in Table 3.

Deposition Studies. The volatility of the $[Cp^*Ga(u_3-E)]_4$ $(E = S, Se, Te)$ was determined by thermogravimetic analysis (Seiko TG/DTA 900) under argon flow and dynamic vacuum (<200 mTorr) conditions. In general, larger and more uniform weight losses due primarily to sublimation occurred under vacuum. At the point where weight losses were sharpest for [Cp*Ga(*µ*3-S)]4 and [Cp*Ga(*µ*3-Se)]4, their vacuum DTA showed a sharp endothermic event (melting) at 135 and 190 °C, respectively. There are indications of solid-state thermal decomposition at temperatures approximately 60 °C above

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⁽²⁶⁾ Schulz, S. Diplom, University of Göttingen, 1991.

⁽²⁷⁾ Purification of compounds **1**-**3** by recrystallization is preferable to sublimation, since some decomposition was observed even under vacuum sublimation.

⁽²⁸⁾ SHELXTL V. 5.0: Siemens Industrial Automation, Analytical Instrumentation Business Unit, Madison, WI, 1996.

decomposition is evident. Chemical vapor deposition studies with $[Cp^*Ga(\mu_3-S)]_4$ and [Cp*Ga(*µ*3-Se)]4 were accomplished using a horizontal hot wall reactor similar to that described previously.29 Typically 50 mg of the cubane was loaded into a Pyrex reactor tube containing Si(100) and GaAs(100) substrates and then evacuated (*P* < 10^{-2} Torr) for 2 h. Due to the sensitivity of the precursors to air and moisture, care was taken to minimize air exposure when the precursors were loaded into the CVD chamber. A small argon carrier gas flow $(1.5 \text{ cm}^3, \text{ system pressure of } 300$ mTorr) was introduced, and precursors and substrates were heated to appropriate temperatures as listed in Table 2.

The as-deposited films were analyzed using thin-film X-ray diffraction (Siemens *θ*-2*θ*). Compositional analysis was performed using wavelength dispersive spectroscopy (Cameca SX 50 microprobe) relative to calibrated standards. Surface morphology was probed with scanning electron microscopy (SEM-Jeol JSM 5300).

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Supporting Information Available: Tables of atomic coordinates, displacement parameters, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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