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# Silylated gallium and indium chalcogenide ring systems as potential precursors to ME (E=O, S) materials

**Research Article** 

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Abstract: The reaction of R<sub>3</sub>M (M=Ga, In) with HESiR'<sub>3</sub> (E=0, S; R'<sub>3</sub>=Ph<sub>3</sub>, 'Pr<sub>3</sub>, Et<sub>3</sub>, 'BuMe<sub>2</sub>) leads to the formation of (Me<sub>2</sub>GaOSiPh<sub>3</sub>)<sub>2</sub> (1); (Me<sub>2</sub>GaOSi<sup>B</sup>BuMe<sub>2</sub>)<sub>2</sub> (2); (Me<sub>2</sub>GaOSi<sup>E</sup>t<sub>3</sub>)<sub>2</sub> (3); (Me<sub>2</sub>InOSi<sup>P</sup>h<sub>3</sub>)<sub>2</sub> (4); (Me<sub>2</sub>InOSi<sup>B</sup>BuMe<sub>2</sub>)<sub>2</sub> (5); (Me<sub>2</sub>InOSi<sup>E</sup>t<sub>3</sub>)<sub>2</sub> (6); (Me<sub>2</sub>GaSSiPh<sub>3</sub>)<sub>2</sub> (7); (Et<sub>2</sub>GaSSiPh<sub>3</sub>)<sub>2</sub> (8); (Me<sub>2</sub>GaSSi<sup>P</sup>r<sub>3</sub>)<sub>2</sub> (9); (Et<sub>2</sub>GaSSi<sup>P</sup>r<sub>3</sub>)<sub>2</sub> (10); (Me<sub>2</sub>InSSi<sup>P</sup>h<sub>3</sub>)<sub>3</sub> (11); (Me<sub>2</sub>InSSi<sup>P</sup>r<sub>3</sub>)<sub>n</sub> (12), in high yields at room temperature. The compounds have been characterized by multinuclear NMR and in most cases by X-ray crystallography. The molecular structures of (1), (4), (7) and (8) have been determined. Compounds (3), (6) and (10) are liquids at room temperature. In the solid state, (1), (4), (7) and (9) are dimers with central core of the dimer being composed of a M<sub>2</sub>E<sub>2</sub> four-membered ring. VT-NMR studies of (7) show facile redistribution between four- and six-membered rings in solution. The thermal decomposition of (1)-(12) was examined by TGA and range from 200 to 350°C. Bulk pyrolysis of (1) and (2) led to the formation of Ga<sub>2</sub>O<sub>3</sub>; (4) and (5) In metal; (7)-(10) GaS and (11)-(12) INS powders, respectively.

Keywords: Group 13-16 precursors • Single source precursors • X-ray crystallography • TGA © Versita Sp. z o.o.

## 1. Introduction

Chemical investigations of compounds that contain a combination of group 13-16 elements have recently undergone resurgence due in part to their potential as precursors to III-VI materials. The synthesis of compounds that may be used as precursors for the formation of such materials by chemical vapor deposition (CVD) attracts a great deal of time and effort. The preparation of III-VI semiconductor films has been successful due to the use of 'single-source precursors' (SSPs). SSPs contain all the desired elements in a single molecule. These compounds have attracted much research interest due to the fact that this approach has the potential to control the film stoichiometry, to simplify the precursor delivery, and to gain better film homogeneity. SSPs are promising candidates for the production of thin films and nanoparticles with photovoltaic applications [1]. Vittal et al.

presented a review focused on recent developments of the chemistry of metal thio and selenocarboxylates, in order to remark the potential use of some of these compounds as SSPs for making metal sulfide and selenide bulk materials, thin films, and nanoparticles [2]. Despite the numerous advantages offered by SSPs, better synthetic and reproducible methods have to be investigated for controlled morphologies and stoichiometries before their exploitation in photovoltaic devices is possible.

Research in recent years has been focused on producing precursors that are safe to handle, yet are volatile enough and reactive enough to decompose at low temperature [3]. Compounds that have direct M-E bonds can be prepared in several ways. The chemistry of new precursors is based on the fact that group 13 metal alkyls and halides act as strong Lewis acids, and hence readily complex to electron rich chalcogen-containing ligands.

A number of early reports described the synthesis and the chemical and physical properties of these compounds. These reports provide details on several methods for the synthesis of such compounds and some studies on the chemical reactivity but little information on their structures, behavior in solution, or deposition. In 1995, Oliver *et al.* started a systematic study about the solid-state structures and the aggregation states of these derivatives in solution [4].

A number of group 13 oxide and chalcogenide complexes have been developed as reliable sources for the deposition of group 13 oxides and chalcogenide films. The list includes metal alkoxide complexes [5], alkyl metal  $\beta$ -diketonates [6], alkyl metal chalcogenates [7–9], monothiocarbamates [10], monothiocarboxylates [11], dialkyldithio- and dialkyldiselenocarbamates [12,13] and dialkyldiselenophosphinatocomplexes [14]. The combination of In(Se<sub>2</sub>CNMe<sup>n</sup>Hex)<sub>3</sub> and Cu(Se<sub>2</sub>CNMe<sup>n</sup>Hex)<sub>2</sub> has led to the production of ternary semiconducting materials such as CuINSe<sub>2</sub>[12,13].

Reports on compounds based on silicon-containing ligands are very scarce. It was in 1971 that Charov et al. [15] first reported the use of silicon-containing ligands to prepare group 13-16 organometallic complexes. More recent reports include the use of these silicon-containing ligands as precursors to group 13-15 materials. Numerous reports from Wells et al. clearly demonstrate the advantages in the use of silylated compounds as precursor materials [16-18]. Deposition of GaAs, GaP, and GaSb at low temperatures were possible with the use of these precursors. Some silylamido and silylphosphanyl complexes of gallium have been reported recently [19,20]. Recent efforts in this area have led to the isolation and structural characterization of numerous trimethylsilyl chalcogenolates metal (Cu [21], Ag [22], Zn [23], Fe [24]) complexes that present unique chemical properties. These compounds have been shown to be valuable in the formation of structurally characterized nanoclusters and nanoparticles. It has been recently been shown that the chemistry of silylated metal compounds can be exploited on a modified mesoporous surface to form binary ME (M=Cd, Zn; E=S,Se,Te) and ternary Cd<sub>v</sub>Zn<sub>1v</sub>E (E=S,Se) nanomaterials within the host framework [25,26].

In our group, there is a keen interest on siloxides and silanechalcogenolato derivatives of the group 13 metals, as molecular precursors for III-VI materials. The rationale for employing silicon-based ligands is multiple. First, the E-H (E=O, S) hydrogen in silyl derivatives reacts rapidly at room temperature with trialkyl metal derivatives. Arnold *et al.* demonstrated that silyl thiol, silyl selenol and silyl tellurol are 100 times more acidic than their alkyl counterparts [27]. The increased acidity of silyl derivatives facilitates the alkane elimination reaction to form the corresponding metal-chalcogen organometallic derivatives. Second, the identity of R in (HXSiR'<sub>3</sub>) may be readily varied to alter the physical properties of the precursors. Third, the decomposition (elimination-condensation chemistry) of silanethiolato precursors occurs with lower activation barriers (*e.g.* dehalosilylation, dehydrosilylation) during their conversion to semiconducting group III-VI materials. All these factors strongly motivate us into the research of these precursors.

Here, we report on the synthesis, characterization and thermal decomposition of  $(R_2MESiR'_3)_n$  complexes.

## 2. Experimental procedure

#### 2.1. General procedures

All the reactions were undertaken under dry, oxygen-free argon using a vacuum line and standard inert-atmosphere techniques [28]. All of the glassware used in the synthetic work was oven dried at 140°C. Hexane, pentane, THF, diethyl ether, C<sub>6</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>8</sub>, C<sub>6</sub>D<sub>6</sub> and C<sub>7</sub>D<sub>8</sub> were dried with Na/benzophenone under nitrogen, and distilled prior to use. CH<sub>2</sub>Cl<sub>2</sub> and CD<sub>2</sub>Cl<sub>2</sub> were dried with CaH<sub>2</sub> under nitrogen, and distilled prior to use. Trimethylgallium, triethylgallium and trimethylindium were purchased from Strem and used without purification. HSSiPh,, HSSi/Pr, were purchased from Aldrich and used without purification. <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si, NMR spectra were recorded on either a Varian Inova 400 MHz or a Bruker 300 MHz at ambient temperature. Variable temperature NMR (VT-NMR) experiments were calibrated with methanol. VT-NMR was performed with a computer-controlled variable temperature accessory. Solvent peaks were used to set <sup>1</sup>H and <sup>13</sup>C chemical shifts, and external TMS was used to set <sup>29</sup>Si shifts. Mass spectral data were collected by Georgia Institute of Technology. Elemental analysis was performed by Schwarzkopf Microanalytical Lab. Melting points are uncorrected.

### 2.2. X-ray structure determination

The crystals were mounted in a Cryoloop<sup>TM</sup> with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex<sup>TM</sup> attachment of the Bruker APEX CCD diffractometer. Diffraction data were collected on a Siemens SMART CCD area detector diffractometer (graphite monochromator, Mo-K $\alpha$ ,  $\lambda$ =0,7107 Å,  $\omega$ -scans, T=173 K) using the SMART software [29]. Data reduction and final unit cell refinements were carried out with SAINT+ [30]. The program SADABS [31] was used to perform combined area detector scaling an empirical absorption correction based on equivalent reflections. The structures were solved using direct methods and difference Fourier techniques, and were refined against  $F^2$  data using the SHELXTL [32,33]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added inidealized positions with fixed isotropic temperature factors.

#### 2.3. Thermal analysis

Thermogravimetric analyses were performed on a TA Instruments 2950 HR TGA. Argon carrier gas at a flow rate of 40 cc min<sup>-1</sup> was used unless otherwise indicated. Samples of thephenyl derivatives were quickly loaded into a platinum pan under argon flow and heated at 10°C min<sup>-1</sup> from 30 to 1000°C. In the case of the more volatile and reactive samples, compounds (2), (5), (8), (9) and (12) were loaded into aluminum pans in a nitrogenfilled MBraun dry box. An aluminum lid with a pinhole was crimped to the pan in the dry box and the whole assembly containing the sample was placed in a sample vial. The vial containing the pan assembly was quickly taken to the TGA where the pan assembly was removed from the vial and placed on the TGA pan under an argon flow at 10°C min<sup>-1</sup> from 30 to 500°C. The TGA balance was previously tared with an empty aluminum pan and lid assembly. Melting points were measured in sealed tubes with an electrothermal melting point apparatus. X-ray powder diffraction studies were carried out by a Scintag XDS 2000 diffractometer using monochromated CuKa radiation, excited at 43 kV and 38 mA. The samples were mounted flat and scanned from 6 to 64° in a step size of 0.02° with a count rate of 1.2 seconds. Pyrolysis experiments were performed by placing the sample in an evacuated flame sealed ampoule and heating the ampoule to 400°C for 1 h in a muffle furnace. Gallium oxide powders were placed in a quartz crucible annealed at 1000°C for 1 h in a muffle furnace.

(Me<sub>2</sub>GaOSiPh<sub>3</sub>)<sub>2</sub> (1) Trimethylgallium, 1.0 mL (10 mmol), in 10 mL benzene was dropwise added to triphenylsilanol, 2.7458 g (9.9 mmol), in 35 mL benzene in a 100 mL Schlenk flask. After stirring for several hours, the benzene was removed under vacuum until the volume was around 10 mL. Approximately 7 mL of hexane were added until seed crystals formed. The mixture was put into the refrigerator for 12 hours at a temperature of 0°C, in order to complete crystallization. The crystals were filtered under argon and washed with cold hexane. A white solid, 2.84 g, 77%, mp 165°C, was isolated. Several milligrams of solid were dissolved in benzene and allowed to vapor diffuse with hexane over several days to grow a crystal suitable for X-ray analysis. <sup>1</sup>H NMR ( $C_6D_6$ ,  $\delta$ , ppm): 7.74 (m, 6H, Ph), 7.13(m, 9H, Ph), -0.21(s, 6H, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}: (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 135.81, 135.16, 130.15, 127.85, -1.76; <sup>29</sup>Si{<sup>1</sup>H}: (C<sub>6</sub>D<sub>6</sub>, δ, ppm): -8.04; IR (cm<sup>-1</sup>, KBr pellet) 3069(s),

3030(m), 2965(s), 2916(w), 1965(w), 1894(w),1824(w), 1590(m), 1491(m), 1427(s), 1206(m), 1117(s), 1000(w), 843(s), 746(s), 700(s), 597(m), 547(s), 509(s). Anal. Calcd for  $C_{40}H_{42}Si_2O_2Ga_2$ : C: 64.03%;H: 5.64%. Found: C: 64.12%;H: 5.64%.

(Me,GaOSiMe,'Bu), (2) Trimethylgallium,1.0 mL (10mmol), in 10 mL of benzene was added dropwise via an addition funnel to a solution of dimethyl-tertbutylsilanol, 1.6 mL (10 mmol), in 15 mL of benzene. After stirring for several hours, the benzene was distilled off and thick oil was left behind. After being put under vacuum for several hours, a white solid was left, 1.58 g, 68%, mp 45°C. The solid was further purified by vacuum sublimation from the melt, 47°C per 0.04 mmHg. <sup>1</sup>H NMR (C<sub>a</sub>D<sub>a</sub>, δ, ppm): 0.84(s, 9H, <sup>t</sup>Bu) 0.02(s, 6H, SiCH<sub>3</sub>) -0.01(s, 6H, GaCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}: (C<sub>ε</sub>D<sub>ε</sub>, δ, ppm): 25.76(CCH<sub>3</sub>), 18.31(CCH<sub>3</sub>), -2.15(GaC), -2.47 (SiC); <sup>29</sup>Si{<sup>1</sup>H}: (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 22.95; IR (cm<sup>-1</sup>, KBr pellet) 2957(s), 2860(m), 1471(m), 1420(w), 1260(m), 1200(m), 980(w), 841(s), 780(m), 750(m), 670(m), 600(m), 503(s). Anal. Calcd for C<sub>16</sub>H<sub>42</sub>Si<sub>2</sub>O<sub>2</sub>Ga<sub>2</sub>: C: 41.59%; H: 9.16%. Found: C: 41.37%; H: 8.94%.

(Me,GaOSiEt<sub>3</sub>)<sub>2</sub> (3) Triethylsilanol, 1.6 mL (10 mmol), was dissolved in 20 mL benzene in a 100 mL Schlenk flask. Trimethylgallium, 1.0 mL (10 mmol), in 15 mL benzene was subsequently added dropwise to the silanol solution with stirring. The reaction mixture was allowed to stir several hours to ensure complete reaction. The benzene was then distilled off and the remaining liquid put under vacuum and Kugelrohr distilled. The colorless product was isolated at 85°C per 0.05mmHg, 2.10 g, 91% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 0.89(t, 9H, CH<sub>2</sub>CH<sub>3</sub>) 0.50 (q, 6H, CH<sub>2</sub>) -.06 (s, 6H, GaCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}: (C<sub>e</sub>D<sub>e</sub>, δ, ppm): 6.65 (CH<sub>2</sub>CH<sub>2</sub>), 6.40(CH<sub>2</sub>), -3.01(GaC); <sup>29</sup>Si{<sup>1</sup>H}: (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 22.78; IR (cm<sup>-1</sup>, neat on KBr plates) 2957(s), 2913(m), 2880(s), 1458(w), 1414(w), 1240(m), 1206(m), 1004(m), 970(w), 841(s), 743(s), 590(m), 513(s); MS(EI) M<sup>+</sup> -15 calc. 445.1000244, found 445. 099976. Anal. Calcd for C<sub>16</sub>H<sub>42</sub>Si<sub>2</sub>O<sub>2</sub>Ga<sub>2</sub>: C: 41.59% H: 9.16%. Found: C: 41.58%; H: 9.34%.

 $(Me_2InOSiPh_3)_2$  (4) Trimethylindium, 1.6 g (10 mmol), in 10 mL of benzene was added dropwise to a solution of triphenylsilanol, 2.7458 g (9.9 mmol), in 30 mL of benzene contained in a 100 mL Schlenk flask. After stirring for several hours, the benzene was removed under vacuum until the volume was around 10 mL. Approximately 7 mL of hexane were added until seed crystals formed. The mixture was put into the refrigerator for 12 hours at a temperature of 0°C, in order to complete crystallization. The product precipitated from the reaction mixture and was recrystallized from benzene/hexane. Yield: 75%, 3.2 g. mp: 167°C. Several milligrams of solid were dissolved in benzene and allowed to vapor diffuse with hexane over several days to grow a crystal suitable for X-ray analysis. Anal. Calcd for  $C_{40}H_{42}Si_2O_2In_2$ : C: 57.15%; H: 5.03% Found: C: 57.06%; H: 4.95%. <sup>1</sup>H NMR ( $C_6D_6$ ): 0.0 (s, In–CH<sub>3</sub>), 7.3 (m, 9H), 7.9 (m, 6H). <sup>13</sup>C{<sup>1</sup>H}: NMR ( $C_6D_6$ ,  $\delta$ , ppm): 0.0 (In(**C**H<sub>3</sub>)<sub>2</sub>), 131.7 (aryl), 137.2 (aryl), 138.8 (aryl). <sup>29</sup>Si{<sup>1</sup>H}: NMR ( $C_6D_6$ ,  $\delta$ , ppm): -14.5.

(Me<sub>2</sub>InOSiMe<sub>2</sub><sup>t</sup>Bu)<sub>2</sub> (5) Trimethylindium, 1.6 g (10 mmol), was dissolved in 20 mL benzene in a 100 mL Schlenk flask. Dimethyl-tert-butylsilanol, 1.6 mL (10 mmol), in 10 mL of benzene was added dropwise to the indium solution with stirring. The reaction mixture was allowed to stir for 12 hours to make sure reaction was complete. Benzene was removed under vacuum until the volume was around 10 mL. Approximately 20 mL of pentane were added and the solution was cooled to 0°C. A white solid, 2.6 g, 93%, mp 45°C, was isolated. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 0.13(s, In–CH<sub>3</sub>), 0.21 (s, Si–CH<sub>3</sub>), 1.0 (s, Si–'Bu). <sup>13</sup>C{<sup>1</sup>H}: NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): -2.1 (In(CH<sub>3</sub>)<sub>2</sub>), -1.7 (Si–(CH<sub>3</sub>)<sub>2</sub>), 18.5 (Si–C(CH<sub>3</sub>)<sub>3</sub>), 26.1 (Si–C(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H}: NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 15.5.

(Me<sub>2</sub>InOSiEt<sub>3</sub>)<sub>2</sub> (6) Trimethylindium, 1.6 g (10 mmol), was dissolved in 29 mL benzene in a 100 mL Schlenk flask. Triethylsilanol, 1.6 mL (10 mmol), in 10 mL of benzene was added dropwise to the indium solution with stirring. The reaction mixture was allowed to stir several hours to make sure reaction was complete. Benzene was removed under vacuum. Pentane was added and the solution was cooled to -70°C to isolate the product. The product was washed with pentane several times at -70°C and pumped under vacuum to remove solvent. Isolation and purification were difficult and total exclusion of solvent was not possible. <sup>1</sup>H NMR ( $\delta$ , ppm): 0.85 (t, CH<sub>2</sub>CH<sub>3</sub>), 0.37 (q, CH<sub>2</sub>CH<sub>3</sub>), -0.019 (s, InCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}: 6.985 (CH<sub>2</sub>CH<sub>3</sub>), 6.711 (CH<sub>2</sub>CH<sub>3</sub>), -3.067 (InC); <sup>29</sup>Si{<sup>1</sup>H}: -21.971.

(Me,GaSSiPh<sub>3</sub>), (7) Trimethylgallium, 1.0mL (10mmol), in 10mL toluene was dropwise added to a solution of triphenylsilanethiol, 2.928 g (9.9mmol), in 30 mL of toluene contained in a 100 mL Schlenk flask. After stirring for several hours, the toluene was removed under vacuum until the volume was around 15mL. The flask was put in the refrigerator for 12 hours at a temperature of 0°C. The product precipitated from the reaction mixture and was recrystallized from toluene/ hexane. Yield: 95%. Several milligrams of solid were dissolved in toluene and allowed to vapor diffuse with hexane over several days to grow a crystal suitable for X-ray analysis. Anal. Calcd for C<sub>40</sub>H<sub>42</sub>Si<sub>2</sub>S<sub>2</sub>Ga<sub>2</sub>: C: 61.4%; H: 5.41%. Found: C: 60.6%; H: 5.51%. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, δ, ppm): 0.0 (s, Ga-CH<sub>3</sub>, 7.94 (o, 6H), 7.72 (m, 6H), 7.77 (p, 3H). <sup>13</sup>C{<sup>1</sup>H}: NMR (C<sub>e</sub>D<sub>e</sub>, δ, ppm): 1.21 (Ga(CH<sub>3</sub>)<sub>2</sub>), 136.03 (aryl), 135.62 (aryl), 134.7 (aryl), 130.4 (aryl) . <sup>29</sup>Si{<sup>1</sup>H}: NMR (C<sub>6</sub>D<sub>6</sub>, δ, ppm): -2.44.

(Et,GaSSiPh,), (8) Triethylgallium, 1.1 mL (10 mmol) in 10 mL of toluene was dropwise added to a solution of triphenylsilanethiol, 2.928 g (9.9mmol), in 30 mL of toluene contained in a 100 mL Schlenk flask. After stirring for several hours, the toluene was removed under vacuum until the volume was around 15 mL. The flask was put in the refrigerator for 12 hours at a temperature of 0°C. The product precipitated from the reaction mixture and was recrystallized from toluene/ hexane. Yield: 70%. <sup>1</sup>H NMR (C<sub>2</sub>D<sub>0</sub>, δ, ppm): 1.07 (t, CH<sub>2</sub>CH<sub>3</sub>, 6H), 0.654 (quart, CH<sub>2</sub>CH<sub>3</sub>, 4H), J<sub>HH</sub>=6.6Hz; 7.92 (o, 6H), 7.7 (m, 6H), 7.75 (p, 3H). <sup>13</sup>C{<sup>1</sup>H}: NMR (C<sub>e</sub>D<sub>e</sub>, δ, ppm): 11.02 (CH<sub>2</sub>CH<sub>3</sub>), 10.1 (CH<sub>2</sub>CH<sub>3</sub>), 136 (aryl), 135.62 (aryl), 135 (aryl), 130.3 (aryl). <sup>29</sup>Si{<sup>1</sup>H} NMR: (C<sub>6</sub>D<sub>6</sub>, δ, ppm): -2.35.

(Me<sub>2</sub>GaSSi'Pr<sub>3</sub>)<sub>2</sub> (9) Trimethylgallium, 1.0 mL (10 mmol), in 10 mL pentane was dropwise added to a solution of triisopropylsilanethiol, 2.16 mL (9.9 mmol), in 25 mL of pentane contained in a 100 mL Schlenk flask. After stirring for several hours, the pentane was removed under vacuum until the volume was around 15 mL. Product precipitated from solution at -40°C. Yield: 65%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 0.0 (s, GaCH<sub>3</sub>, 6H), 0.97 (d, CH(CH<sub>3</sub>)<sub>2</sub>, 18H), 1.11 (sept., CH(CH<sub>3</sub>)<sub>2</sub>, 3H): <sup>13</sup>C{<sup>1</sup>H}: NMR(C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 1.0 (GaCH<sub>3</sub>), 21.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 14.07 (CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H}: NMR(C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 30.64.

(Et<sub>2</sub>GaSSi'Pr<sub>3</sub>)<sub>2</sub> (10) Triethylgallium, 1.1 mL (10 mmol), in 10 mL of pentane was dropwise added to a solution of triisopropylsilanethiol, 2.16 mL (9.9 mmol), in 25 mL of pentane contained in a 100 mL Schlenk flask. Pentane was removed by distillation. The viscous product was purified by first washing with pentane at -70°C and then by vacuum distillation, oil bath at 70°C; boiling point 75°C (< 10<sup>-3</sup> mmHg). Yield: 70%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 0.8 (unresolved multiplet), 1.0 (d, CH(CH<sub>3</sub>)<sub>2</sub>), 1.3 (m, CH(CH<sub>3</sub>)<sub>2</sub>): <sup>13</sup>C{<sup>1</sup>H}: NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 10.2 (GaCH<sub>2</sub>CH<sub>3</sub>), 11.7 (GaCH<sub>2</sub>CH<sub>3</sub>), 22.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 14.39 (CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR(C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 30.37.

(**Me**<sub>2</sub>**InSSiPh**<sub>3</sub>)<sub>3</sub> (11) Trimethylindium, 1.6 g (10 mmol), in 1 mL benzene was dropwise added to a solution of triphenysilanethiol, 2.928 g (9.9 mmol), in 30 mL of benzene contained in a 100 mL Schlenk flask. After stirring for several hours, the benzene was removed under vacuum until the volume was around 15 mL. The flask was put in the refrigerator for 12 hours at a temperature of 0°C. The product precipitated from the reaction mixture and was recrystallized from benzene/ hexane. Yield: 91%, 3.7g. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 0.0 (s, InCH<sub>3</sub>, 6H), 7.2 (m, 9H), 7.9 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 11.02 (CH<sub>2</sub>CH<sub>3</sub>), 10.1 (CH<sub>2</sub>CH<sub>3</sub>), 136 (aryl), 135.62 (aryl), 135 (aryl), 130.3 (aryl). <sup>29</sup>Si{<sup>1</sup>H} NMR(C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): -2.35.

### 3. Results and discussion

#### 3.1. Gallium and indium siloxides

The silanols (HOSiR'<sub>3</sub>; R'=Ph, Et, R'<sub>3</sub>= Me<sub>2</sub>'Bu,Et) and the silanethiols (HSSiR<sub>3</sub>; R'=Ph, 'Pr) react rapidly at room temperature with trialkylgallium (Me, Et) and trimethyl indium compounds in a 1:1 stoichiometry, liberating the alkane and affording the corresponding siloxides and silanethiolato complexes of gallium and indium, in high yield according to the general reaction scheme of the following equation:

 $R_3M+HESiR'_3 \rightarrow (1/n)(R_2MESiR'_3)_n+RH$ 

M=Ga,In; E=O,S 1: M=Ga; R=Me; R'=Ph; yield: 77%

2: M=Ga; R=Me; R'=Me, Bu; yield: 68%

3: M=Ga; R=Me; R'=Et; yield: 91%

4: M=In; R=Me; R'=Ph; yield: 75%

5: M=In; R=Me; R'<sub>3</sub>=Me<sub>2</sub><sup>t</sup>Bu; yield: 94%

6: M=In; R=Me; R'=Et; yield: not quantified

7: R=Me; M=Ga; R'=Ph; yield: 95%

8: R=Et; M=Ga; R'=Ph; yield: 75%

9: R=Me; M=Ga; R'=<sup>i</sup>Pr; yield: 75%

**10:** R=Et; M=Ga; R'=<sup>i</sup>Pr; yield: 70%

11: R=Me; M=In; R'=Ph; yield: 91%

12: R=Me; M=In; R'=<sup>i</sup>Pr; yield: 78%

Compounds (1), (2), (4), (5), (7), (8), (9), (11) and (12) have been isolated as colorless, transparent crystals that are both air- and moisture-sensitive. They are soluble in hydrocarbon solvents such as benzene, and toluene, and in the donor solvents such as diethyl ether and tetrahydrofuran. Compound (3) is a colorless liquid. The liquid triethylsiloxy gallium compound decomposes in the open atmosphere to an insoluble white solid over several minutes, while compounds (1) and (2) decompose more slowly to white insoluble solids. Compound (6) is a dense white liquid that is difficult to isolate and purify. Compound (9) decomposes over a period of few minutes in the solid state on exposure to air. Compound (10) is a colorless liquid. Physical and spectroscopic properties of (1)-(12) are summarized in Table 1.

The melting point of these complexes shows the role of the organic ligands in the modification of their physical properties. An increase in the alkyl chain attached to the metal lowers the melting point; the silyl substituent potentially adds a unique degree of high volatility and hydrocarbon solubility to the molecule. General <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR parameters for the individual compounds are listed in the experimental section. The <sup>1</sup>H NMR shifts for the methyl gallium groups and the methyl indium groups are in agreement with other related compounds [3,34]. The room temperature <sup>1</sup>H NMR spectra indicate a highly symmetric structure, with only one set of peaks for the siloxy substituents and singlets for the methyl groups bonded to the metal.

Crystals of (1) and (4) were grown from a benzene/ hexane (1:1) solution at 0°C. Parameters from the crystal structure determination of (1) and (4) are presented in Table 2. Compounds (1) and (4) are dimeric in the solid state with planar M2O2 rings. An ORTEP diagram of the molecular unit for (1) is shown in Fig. 1, and the molecular unit for (4) is shown in Fig. 2. Both crystals are triclinic and belong to the space group P-1. As with most other group 13-oxygen four-membered rings;  $[Ga(\mu-OCMe_2Et)(OCMe_2Et)_2]_2$  [2],  $[Me_2In(acac)]_2$  [5],  $[\ln(\mu - OR)(OR)_2]_2$  [4], (<sup>t</sup>Bu<sub>2</sub>InOEt)\_2 [35]; the ring is planar, but not square. The M-O-M bond angle is 97.4(2)° for gallium and 100.62(4)° for indium, while the O-M-O angle is 82.6(2)° for gallium and 79.38(4)° for indium. Important bond lengths and angles are summarized in Table 3.

The Ga(1)–O–Ga bond angle in (1) is smaller than other known Ga<sub>2</sub>O<sub>2</sub> compounds such as  $(H_2GaOtBu)_2$ ,  $([Bu_2Ga(OOBu)]_2$  and  $(Bu_2GaOH)_3$ ; but is larger than the Ga–E–Ga bond angles where oxygen is replaced by sulfur or phosphorous. The gallium siloxide **(1)** has a Ga<sub>2</sub>O<sub>2</sub> ring that is closer to being square than the gallium

Compound	Appearance	mp °C	<sup>29</sup> Si{ <sup>1</sup> H} NMR	<sup>1</sup> H NMR (C <sub>6</sub> D <sub>6</sub> ) δR <sub>2</sub> M
(1) (Me <sub>2</sub> GaOSiPh <sub>3</sub> ) <sub>2</sub>	White solid	165	-8.04	-0.21
(2)(Me <sub>2</sub> GaOSi <sup>t</sup> BuMe <sub>2</sub> ) <sub>2</sub>	White solid waxy	45	22.95	-0.01
(3) (Me <sub>2</sub> GaOSiEt <sub>3</sub> ) <sub>2</sub>	Liquid	-	22.78	-0.1
(4) (Me <sub>2</sub> InOSiPh <sub>3</sub> ) <sub>2</sub>	White solid	168	-14.5	0.0
(5) (Me <sub>2</sub> InOSi <sup>t</sup> BuMe <sub>2</sub> ) <sub>2</sub>	White solid waxy	45	15.5	0.1
(6) (Me <sub>2</sub> InOSiEt <sub>3</sub> ) <sub>2</sub>	Liquid	-	-21.9	-0.02
(7) (Me <sub>2</sub> GaSSiPh <sub>3</sub> ) <sub>2</sub>	Colorless solid	195-196	-2.44	0.0
(8) (Et₂GaSSiPh₃)₂	Colorless solid	156-157	-2.35	0.65 (CH <sub>2</sub> , quart), 1.07 (CH <sub>3</sub> , t), J <sub>HH</sub> =6.61Hz
(9) (Me <sub>2</sub> GaSSi <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	White solid waxy	47-48	30.64	0.153
(10) (Et <sub>2</sub> GaSSi <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	Liquid	-	30.37	0.8(unresolved multiplet)
(11) (Me <sub>2</sub> InSSiPh <sub>3</sub> ) <sub>2</sub>	White solid	158	-2.35	0.0
(12) (Me <sub>2</sub> InSSi <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	White solid waxy	45	29.02	0.18

Table1. Summary of physical and spectroscopic properties of compounds (1)-(12).



Figure 1. ORTEP diagram of (1) with H-atoms omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level. The crystallographic center of symmetry lies at the center of the four-membered Ga<sub>2</sub>O<sub>2</sub> ring.

alkoxides [36], but is not perfectly square as the one encountered for  $[Ar'GaO]_2$ [37]. In contrast to aluminum and gallium, not many examples of the heavier group 13 analogues of these oxides have been isolated. The coordination geometry at the indium center is tetrahedral. The In–O distance [2.1815(11) Å] and the In–O–In angle [100.62(4)°] are similar to those found for other In<sub>2</sub>O<sub>2</sub> cores [38-40], and the In–C bond length [2.1348(19)Å] is in the region previously observed for In–C bonds(2.09-2.25 Å).

The silicon atoms also lie in the plane with the metal and oxygen atoms. This is in contrast to the gallium sulfur-containing analogs (7) [41] and (8) [42] where the triphenylsilyl groups are in *trans* configuration. For indium, the sulfur-containing analogue has a sixmembered  $(InS)_3$  ring in a skew-boat conformation [43]. Since the delocalization of the oxygen lone pair over the metal and silicon atoms would contribute to the planarity, the sulfur lone pair electrons are not as well delocalized. A comparison of bond angles around oxygen and sulfur in other gallium dimeric systems shows that oxygen is usually planar, with the sum of the bond angles near 360°. Sulfur atoms are closer to tetrahedral, with the sum of the bond angles less than  $327^{\circ}$ .

Compound	(4)	(1)	(9)	(7)
Empirical formula	$\mathrm{C_{40}H_{42}ln_2O_2Si_2}$	$C_{40H_{42}Ga_2O_2Si_2}$	$C_{_{22}}H_{_{54}}Ga_2S_2Si_2$	$C_{40H_{42}Ga_2S_2Si_2}$
Formula weight	840.56	750.36	578.39	782.48
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P1 (No. 2)	P1	P2 <sub>1</sub> /n (No. 14)	P1
Unit cell dimensions a [Å] b [Å] c [Å]	8.8205(6) 9.5990(6) 13.1037(9)	9.591(2) 12.964(3) 8.846(3)	9.1183(5) 9.0036(5) 18.3012(10)	8.9667(6) 13.7580(9) 16.2507(11)
α [deg] β [deg] γ [deg]	69.2940(10) 73.1500(10) 64.4000(10)	105.42(2) 115.87(2) 70.30(2)	90 94.9730(10) 90	102.0000(10) 95.0880(10) 103.0100(10)
Volume (Å <sup>3</sup> )	923.48(11)	922.5(4)	1496.83(14)	1891.2(2)
Z	2	1	2	2
Density (calculated) [g cm⁻³]	1.511	1.351	1.283	1.374
Absorption coefficient [mm <sup>-1</sup> ]	1.346	1.558	2.027	2.027
F(000)	424	388	616	808
Crystal size [mm]	0.04×0.20×0.22	0.33×0.26×0.13	0.05×0.25×0.27	0.35×0.28×0.23
Temperature (K)	100	100	100	100
Radiation MoKα [Å]	0.71073	0.71073	0.71073	0.71073
0 range for data collection [°]	1.7 to 28.3	1.69 to 25.07	2.2 to 28.3	1.29 to 28.31
Tot., Uniq. Data, R (int)	8289, 4278, 0.013	3504, 3287, 0.0292	12942, 3585, 0.022	17058, 8802, 0.015
Observed data [I>2σ(I)]	4122	3504	3204	8115
Data, parameters	4278, 210	3287, 210	3585, 135	3585, 135
Final R <sub>1</sub> , wR <sub>2</sub> [I>2σ(I)]	0.0192, 0.0508	0.1214, 0.1953	0.0222, 0.0581	0.0280, 0.0699
Goodness-of-fit on F <sup>2</sup>	1.06	1.03	1.07	1.062

#### Table2. Crystal data and structure refinement for (1), (4), (9) and (7).

### 3.2. Silanethiolato complexes of Gallium and Indium

Details regarding general synthetic aspects, physical properties and NMR characterization of silanethiolato complexes were presented in the previous section. The room temperature <sup>1</sup>H NMR spectrum of (7) shows a broadened line ( $\delta$ = 0ppm) for the methyl groups attached to gallium, suggesting fluxionality in the molecule. Earlier, Taghiof [44] reported that aluminum thiolates establish equilibria between different aggregates (most commonly dimers and trimers) and conformations (*syn* and *anti*) in hydrocarbon solutions. The dynamic behavior of (7) in solution was investigated.

Although in the solid state, (7) shows the presence of a puckered  $(GaS)_2$  core with *anti* orientation of the bridging ligands, there exists a possibility that (7) may exhibit redistribution or conformation equilibria in solution. In order to explore this possibility, the effects of temperature and concentration on (7) were evaluated.

Variable-temperature and variable-concentration NMR studies were conducted. The chemical shift of the methyl groups on the  $(CH_3)_2$ Ga moiety was found to be temperature-dependent. Results are presented in Fig. 3. At temperatures below 10°C, we observe two chemical shifts that correspond to the dimer-trimer species (the resonance for the dimer and trimer are assigned on the basis of a comparison of chemical shifts reported for  $(Me_2AISSiPh_3)_2$ ) [29]. In order to corroborate that the solution equilibrium presented by (7) corresponds to a redistribution rather than a conformational process, an additional study was carried out in which the concentration of (7) was varied. The experiment was carried at a constant temperature of -20°C. Results are presented in Fig. 4. The data from this study show that

Bond lengths(Å)	C <sub>40</sub> H <sub>42</sub> Ga <sub>2</sub> O <sub>2</sub> Si <sub>2</sub> (1)	$C_{40}H_{42}In_{2}O_{2}Si_{2}$ (4)
M-C(2)	1.929(8)	2.1348(19)
M-C(1)	1.933(8)	2.1373(19)
M-O(1)	1.968(4)	2.1815(11)
M-O	1.978(4)	2.1939(11)
Si-O	1.651(4)	1.6370(11)
О-М	1.968(4)	2.1940(11)
Bond Angles(deg)		
C(2)-M-C(1)	127.1(4)	137.21(9)
C(2)-M-O(1)	110.9(3)	107.53(6)
C(1)-M-O(1)	109.9(3)	107.33(6)
C(2)-M-O	106.4(3)	103.07(6)
C(1)-M-O	110.9(3)	107.06(7)
O(1)-M-O	82.6(2)	79.38(4)
Si-O-M(1)	130.7(2)	128.16(6)
Si-O-M	130.3(2)	129.99(6)
М(1)-О-М	97.4(2)	100.62(4)
Bond lengths(Å)	$C_{40}H_{42}Ga_2S_2Si_2$ (7)	$C_{22}H_{54}Ga_2S_2Si_2(9)$
Ga(1)-C(1)	1.9546(17)	1.9616(15)
Ga(1)-C(2)	1.9597(17)	1.9605(15)
Ga(1)-S(2)	2.4094(4)	2.3974(4)
Ga(1)-S(1)	2.4363(4)	2.4113(4)
S(1)-Si(1)	2.1461(5)	2.1732(5)
S(1)-Ga		2.4113(4)
Bond angles (deg)		
C(1)-Ga(1)-C(2)	125.94(8)	119.40(7)
C(1)-Ga(1)-S(2)	113.77(6)	116.52(5)
S(2)-Ga(1)-S(1)	87.144(14)	87.820(13)
C(3)-Ga(2)-S(2)	113.57(5)	105.80(5)
S(2)-Ga(2)-S(1)	87.592(14)	87.820(13)
Si(1)-S(1)-Ga(2)	119.09(2)	122.509(18)
Si(1)-S(1)-Ga(1)	114.882(19)	115.628917)
Ga(2)-S(1)-Ga(1)	90.163(14)	92.180(13)

 Table 3.
 Selected bond lengths [Å] and angles [deg] for (1) and (4), and for (7) and (9).
 Symmetry transformations used to generate equivalent atoms: -x, -y+1, -z+2.

dimers predominate in diluted solution, whereas trimers predominate in concentrated solutions  $(2(Me_2GaSSiPh_3)_3 \leftrightarrow 3(Me_2GaSSiPh_3)_2)$ .

Thermodynamic and activation energy parameters were calculated from variable-temperature NMR data. The ratio of the concentration of these species at

different temperatures can be obtained by integration of the resonances; from here, the equilibrium constant can be determined. Our results and additional results from a number of related systems are given in Table 4 for comparison. Some interesting generalizations can be drawn from the thermodynamic parameters encountered



Figure 2. ORTEP diagram of (4) with H-atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.



Figure 3. VT<sup>1</sup>H NMR for (Me<sub>2</sub>GaSSiPh<sub>3</sub>)<sub>2</sub>.

for (7). First, the value 1.236 of  $K_{eq}$  at room temperature indicates that concentration of the different aggregates is nearly equivalent. The exchange between them takes place at a rate faster than the NMR timescale, giving rise to a single broad resonance for both aggregates at room temperature. The large positive value for  $\Delta S^{\circ}$  is in agreement with the formation of a greater number of molecules going from trimers to dimers. Second, the

trimer is enthalpically favored and predominates at low temperatures. The origin of the favorable enthalpy is likely due to ring strain found for the dimers but not for the trimers. At room temperature, a balance between the entropy and enthalpy terms leads to a small negative  $\Delta G^{\circ}$  value and an equilibrium constant near unity.

VT-NMR data for (8) shows that ethyl resonances are not temperature-dependent. The increased bulk of

the organic substituents bound to gallium favor dimeric aggregates in solution. These observations are in accordance with Oliver [3] and Beachley [41].

Crystals of (7) were grown from a toluene/hexane (1:1) solution at 0°C. Crystals of (9) were grown from



Figure 4. <sup>1</sup>H NMR for (Me<sub>2</sub>GaSSiPh<sub>3</sub>)<sub>2</sub> as a function of precursor concentration.

pentane at -40°C. The parameters from the crystal structure determination of (7) and (9) are presented in Table 2.

Compound (7) was found to be in the triclinic cell system, and (9) was in the monoclinic cell system. Both compounds have a dimeric structure with a  $Ga_2S_2$  central core. An ORTEP diagram of the molecular unit for (7) is shown in Fig. 5 and the molecular unit for (9) is shown in Fig. 6. Compound (7) and compound (9) differ mainly in the shape of the central ring which is flat in (9) but bent in (7).

The molecular structures for the aluminum and indium analogues of (7) were previously determined. The aluminum and gallium thiolates, show (MS), ring cores, whereas the indium derivative, has a sixmembered (InS)<sub>3</sub> ring in a skew-boat conformation. The bridging groups in these compounds are found in the anti conformation. The sulfur atom is pyramidal. The butterfly conformation of (7) compares with that observed in (Et<sub>2</sub>GaSSiPh<sub>3</sub>)<sub>2</sub> [29], [Me<sub>2</sub>GaS(C<sub>6</sub>F<sub>5</sub>)]<sub>2</sub> [45] and [I2GaS(Pr)]2 [46]. The planar conformation of (9) compares with that observed in ['Bu,Ga(µ-SH)], [47], [Ph<sub>2</sub>GaSEt]<sub>2</sub> [48], and{Ph<sub>2</sub>GaS[Sn(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>]}<sub>2</sub> [49]. The geometry around the gallium atom is normal for this type of compounds and can be best described as distorted tetrahedral. Selected bond lengths and angles are given in Table 3.

#### 3.3. TGA measurements

Thermal stability and thermal decomposition behavior of complexes (1), (2), (4), (5), (11) and (12) were



Figure 5. ORTEP diagram of (7) with H-atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.



Figure 6. ORTEP diagram of (9) with H-atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Compound	K <sub>eq</sub> 25℃	∆ <b>H°kJmol</b> ⁻¹	∆S°Jmol⁻¹	∆ <b>G°kJmol</b> ⁻¹
(Me <sub>2</sub> AISMe) <sub>n</sub>	0.4	23.1	70.0	12.8
(Me <sub>2</sub> AlSeMe) <sub>n</sub>	180.0	11.5	81.5	8.5
(Me <sub>2</sub> AISSiPh <sub>3</sub> ) <sub>n</sub>	31.0	5.8	220	9.4
(Me <sub>2</sub> GaSSiPh <sub>3</sub> ) <sub>2</sub> (7)	1.236	50.9(34)	172(13)	-0.5255
(Me <sub>2</sub> AIS-2-FC <sub>6</sub> H <sub>4</sub> ) <sub>n</sub>	44.5	68.0	260.0	1.5
(Me <sub>2</sub> AIS-2,6-C <sub>6</sub> H <sub>3</sub> ) <sub>n</sub>	0.6	26.5	85.0	2.2

**Table 4.** Thermodynamic parameters for the equilibrium process, 2 trimer  $\leftarrow \rightarrow$  3 dimer, in selected (R<sub>2</sub>MER')<sub>n</sub> systems.

investigated by thermogravimetric analysis (TGA) and pyrolysis experiments under an atmospheric pressure of argon. A detailed study of the thermal behavior of gallium silane thiolates (7)-(10) was previously reported [50]. TGA was used to monitor the loss of sample mass as function of temperature. In order to elucidate the mechanism of precursor fragmentation, an evolved gas analysis using TGA-MS was performed. As pointed out before [46], analyses of the evolved gases was not possible due to condensation of the gases before reaching the detector. Bulk pyrolysis of the compounds yielded residues that were characterized by XRD. Results are summarized in Table 5.

The TGA results for the siloxide derivatives show that in general, complexes that contain  $(-SiPh_3)$ substituents on the group 16 atom decomposed at higher temperatures compared to the  $(-Si'BuMe_2)$ derivatives. The thermal behavior of (3) and (6) could not be evaluated by TGA due to the fast event of mass loss observed for such complexes. The TGA curve of  $(Me_2GaOSiPh_3)_2$  (1) is presented in Fig. 7. The plot shows that the decomposition of (1) occurs as a multistep process. The main event of weight loss occurs within a temperature range of 220-400°C. It may be possible that this mass loss is associated to the loss of SiPh, ligands, nevertheless the percent of mass lost (60%) is lower than the theoretical mass percent in the molecule (69%). A second step of mass loss followed. The rate of mass loss in this step is slower than the one observed. The temperature range for the second event of mass loss goes from 425-650°C. The residual weight at the end of the experiment (20.5%) is slightly lower than the theoretical weight for the formation of GaO (22.8%). Compound (2) decomposes at lower temperature than (1). The weight loss is complete around 200°C. There is only 9% residual weight by the end of the experiment (500°C). The TGA for (2) was carried out under different conditions to try to minimize the loss of sample due to sublimation. The results obtained show no significant differences.

In order to determine the composition of the inorganic products produced by thermolysis of (1) and (2), bulk



Figure 7. TGA curve for (Me<sub>2</sub>GaOSiPh<sub>3</sub>)<sub>2</sub> (1). Heat rate 10°C min<sup>-1</sup> under argon.



Figure 8. TGA curve for (Me<sub>2</sub>GaOSi' BuMe<sub>2</sub>)<sub>2</sub> (2). Heat rate 2°C min<sup>-1</sup> under argon.

pyrolysis of these complexes was carried out, and the resulting powders were characterized by XRD. Typically, the precursor was sealed under vacuum in a Pyrex ampoule which was then placed in a muffle furnace at 400°C for 1 h. After cooling to room temperature, the ampoules were open and the solid metal oxides were washed with benzene and allowed to dry. The color of the powders produced was dark gray for both precursors. The XRD analysis of the powders prepared at 400°C showed the presence of amorphous material since no well-defined peaks are observed in the XRD pattern. Since the peaks were extremely broad, these powders were annealed by heating them up to a 1000°C for 1 h on a quartz crucible. The powders turned colorless and the XRD showed sharp features that correspond to the reference spectrum of monoclinic Ga2O3 (JCDPS #43-1012).

The indium siloxides exhibited a similar thermal behavior to gallium siloxide analogues. The TGA curve

of (Me<sub>2</sub>InOSiPh<sub>3</sub>)<sub>2</sub> (4) shows a uniform mass loss as the temperature is taken up to 1000°C with a heating rate of 10°C/min under argon. There is a major stage of mass loss and it occurs in a narrow temperature range from 250°C to 360°C. The residual mass at the end of this event of mass loss is 41% which correlates to the loss of the SiPh, substituents. The temperature of maximum mass loss is 265°C, which is close to that observed for the gallium analogous compound (270°C); this observation supports that this event may correspond to the loss of the triphenylsilyl groups. The second step of mass loss shows an onset temperature of 595°C. This step may correspond to the loss of alkyl groups attached to the metal. The residual mass at the end of the experiment is lower (27 vs. 31.1%) than the theoretical percentage for the formation of InO, but it is in agreement to the formation of indium metal (27.3%).

The XRD spectrum of the pyrolysis products from precursors (4) and (5) corresponds to indium metal (tetragonal, JCDPS #05-0642). Trace amount of cubic  $In_2O_3$  (JCDPS #65-3170) were also observed. XRD data indicates that the formation of In metal is important and therefore explains the higher than expected weight loss observed by TGA. The deposition of  $In_2O_3$  films from these precursors may be possible using  $O_2$  as a carrier gas, since it was shown that they decompose cleanly at low temperatures.

As it was noticed above, a detailed study on the thermal behavior of complexes (7)-(10), was previously presented [50]. The complexes decompose from 200-350°C to give the hexagonal phase of GaS. The ethyl gallium derivatives were found to undergo an initial loss of ethylene followed by a second unresolved mode of decomposition. In contrast, the methyl gallium derivatives decompose in one uniform stage to give hexagonal gallium sulfide. Isopropylsilyl derivatives were in general more volatile and decomposed at lower temperatures than the triphenylsilyl derivatives.

TGA data for (11) and (12) is in agreement with the data for the gallium analogous. Results are summarized in Table 5. The resulting powders from the bulk pyrolysis of compounds (11) and (12) were characterized by XRD. The diffraction features of the powder resulting from the pyrolysis of (11), correspond to indium metal, multiple phases of  $\ln_x S_y$  and amorphous material. In contrast, the diffraction features of the powder resulting from the pyrolysis of (12) showed sharp peaks that correspond to indium sulfide (InS) (orthorhombic, JCDPS #86-0637). Compound (11) was found not suitable as precursor to indium sulfide, but the alternate compound (12), decomposes cleanly at low temperatures resulting in pure crystalline In and InS.

Compound		TGA resu	ults	Pyrolysis product	
	Decomposition		Residua		al weight
	range and (T <sub>dec</sub> )/°C		Obsvd.	Calcd. (%)	(by XRD)
(1) (Me <sub>2</sub> GaOSiPh <sub>3</sub> ) <sub>2</sub>	250-380(300)		20.5	22.8	Ga2O3
(2) (Me <sub>2</sub> GaOSi <sup>t</sup> BuMe <sub>2</sub> ) <sub>2</sub>	75-220 (142)		9.0	37.1	Ga2O3
(4) (Me <sub>2</sub> InOSiPh <sub>3</sub> ) <sub>2</sub>	230-600(280)	for InO	27.0	31.1	In (tetragonal)
		for In	27.0	27.3	
(5) (Me <sub>2</sub> InOSi <sup>t</sup> BuMe <sub>2</sub> ) <sub>2</sub>	225-400(230)	for InO	35.5	47.4	In (tetragonal)
		for In	35.5	41.5	
(7) (Me₂GaSSiPh₃)₂	140-440(338)		28.9	26.0	GaS (amorphous)
(8) (Et <sub>2</sub> GaSSiPh <sub>3</sub> ) <sub>2</sub>	120-507(348)		26.9	24.3	GaS (hexagonal)
(9) (Me <sub>2</sub> GaSSi <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	113-352(306)		29.7	35.2	GaS (hexagonal)
(10) (Et <sub>2</sub> GaSSi <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	95-256(198)		28.0	32.1	GaS (hexagonal)
(11) (Me₂InSSiPh₃)₃	200-450(352)	for InS	38.0	33.6	In (tetragonal)
		for In	38.0	26.3	InS (multiple phases)
(12) (Me <sub>2</sub> InSSi <sup>i</sup> Pr <sub>3</sub> ) <sub>n</sub>	172-330(305)	for InS	38.5	43.9	In (tetragonal)
		for In	38.5	34.34	InS (orthorhombic)

 Table 5. Summary for thermal decomposition of (1)-(12). Residual mass and composition of solid residue. Decomposition temperatures (T<sub>dec</sub>) are defined as the temperature at which half of the sample's eventual weight loss occurs.

## 4. Conclusions

A series of indium and gallium siloxide complexes and silanethiolato complexes were prepared and characterized by various spectroscopic and physical techniques. These compounds are versatile for tailoring chemical and physical properties at the molecular level. Changing the substituents attached to the metal or to the silicon atom can easily modify the physical properties of these compounds. For (7), VT NMR studies showed that in solution, (7) undergoes rapid reversible interconversion between dimer to trimer. The gallium siloxides, gallium silanethiolates and indium silanethiolates complexes tend to decompose to their core elements at low temperatures.

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# **Supplementary Materials**

Supplementary crystallographic data are available from the CCDC, Union Road, Cambridge CB2 1EZ, UK on request quoting the deposition numbers CCDC 931603 - 931606 (fax: +44 1223 336 033; e-mail: deposit@ccdc. cam.ac.uk).

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