Published in final edited form as:

Eur J Inorg Chem. 2009 December 1; 2009(36): 5550–5560. doi:10.1002/ejic.200900556.

Synthesis and Characterization of Germanium Coordination Compounds for Production of Germanium Nanomaterials

Timothy J. Boyle^{*}, Louis J. Tribby^a, Leigh Anna M. Ottley, and Sang M. Han^a

Sandia National Laboratories, Advanced Materials Laboratory, 1001 University Boulevard SE, Albuquerque, New Mexico, 87106

Abstract

A series of novel germanium(II) precursors was synthesized to initiate an investigation between the precursors' structures and the morphologies of the resulting nanoparticles. The precursors were synthesized from the reaction of $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ or $[\text{Ge}(\text{OBu}^t)_2]_2$ and the appropriate ligand: $\text{N,N}'$ -dibenzylethylenediamine (H_2 -DBED), *tert*-butanol (H-OBu^t), 2,6-di-methyl phenol (H-DMP), 2,6-di-phenyl phenol (H-DPP), *tert*-butyldimethylsilanol (H-DMBS), triphenylsilanol (H-TPS), triphenylsilanethiol (H-TPST), and benzenethiol (H-PS). The products were identified as: $[\text{Ge}(\mu_c\text{-DBED})]_2$ (**1**, μ_c = bridging chelating), $[\text{Ge}(\mu\text{-DMP})(\text{DMP})]_2$ (**2**), $\text{Ge}(\text{DPP})_2$ (**3**), $[\text{Ge}(\mu\text{-OBu}^t)(\text{DMBS})]_2$ (**4**), $[\text{Ge}(\mu\text{-DMBS})(\text{DMBS})]_2$ (**5**), $\text{Ge}(\text{TPS})_3(\text{H})$ (**6**), $[\text{Ge}(\mu\text{-TPST})(\text{TPST})]_2$ (**7**), and $\text{Ge}(\text{PS})_4$ (**8**). The $\text{Ge}(\text{II})$ metal centers were found to adopt a pyramidal geometry for **1**, **2**, **4**, **5**, **7**, a bent arrangement for **3**, and a tetrahedral coordination for the $\text{Ge}(\text{IV})$ species **6** and **8**. Using a simple solution precipitation methodology, $\text{Ge}(0)$ nanomaterials were isolated as dots and wires for the majority of precursors. Compound **7** led to the isolation of amorphous Ge_xS_y . The nanomaterials isolated were characterized by TEM, EDS, and powder XRD. A correlation between the precursor's arrangement and final observed nanomorphology was proffered as part of the 'precursor structure affect' phenomenon.

Keywords

Germanium; alkoxides; thiols; amides; nanomaterials; crystal structure

Introduction

Germanium has come to the forefront of a possible replacement material for silicon in such applications as transistors,^[1–3] nonvolatile memories,^[4–6] photovoltaic devices,^[7–9] long-wavelength photodetectors,^[10] and biological detection systems.^[11, 12] This fundamental materials change is being explored since it is expected that Ge based electronics will display: (i) enhanced electrical properties, owing to higher electron and hole mobility than noted for Si,^[13] (ii) smaller bandgap behavior^[6] (even though bulk Ge is an indirect bandgap material),^[14] and (iii) a more pronounced quantum confinement in comparison to Si due to the larger Bohr exciton radius of Ge.^[15–19] Unfortunately, further development of

^{*} Author to whom correspondences should be sent: Ph. (505)272-7625, Fx (505)272-7336, tjboyle@Sandia.gov.

^aDepartment of Nuclear and Chemical Engineering, 1 University of New Mexico, Albuquerque, NM 87131-0001

Supplementary Information

Powder XRD patterns for **2**, **3**, **4**, and **6** and CIF Check results for the crystal structures of **1** – **8** are available in the supporting information. CCDC 705319 - 705326 contain the supplementary crystallographic data for **1** – **8**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (44) 01223-336033; or deposit@ccdc.cam.ac.uk.

these devices has been hindered by the lack of a simple, rapid, high purity route to Ge nanomaterials.^[20, 21]

Recently, we reported on the synthesis of Ge(0) nano-dots and -wires from the decomposition of select Ge(II) precursors (e.g., amide versus alkoxide)^[21] that avoided the use of high temperatures, high pressures, seed catalysts, and retention of competing salt by-products reported for other literature preparatory routes.^[22–36] For our method, Ge(II) precursors were selected since the reduction potential of Ge(II) to Ge(0) is +0.247 V in comparison to the +0.124 V reported for Ge(IV) to Ge(0).^[37] Of particular note for this route was the fact that the ligand set of the precursor appeared to influence the final observed Ge(0) morphology.^[21] This phenomenon was referred to as the ‘precursor structure affect’ (PSA) and has been investigated and confirmed for a number of other systems.^[38–40]

In order to further probe the PSA for this system, a larger family of varied Ge(II) precursors was necessary. However, a search of the literature^[41, 42] revealed that only a handful of acceptable structurally characterized Ge(II) precursors (i.e., amides, alcohols) for the production of Ge(0) nanomaterials were available.^[21, 43–71] Since both the steric bulk of the pendant chains of the alkoxide^[72] and the bond dissociation energies [Ge-N (55 kcal/mol),^[73] Ge-O (157),^[73] Ge-S (128)^[74]] of a the Ge(II) precursors were shown to play a role in the PSA, the synthesis and characterization of series of Ge(II) coordination compounds bound by a variety of ligands was warranted.

These compounds were generated through either the well-established transamination^[66–71] reaction (equation 1), where $\text{Ge}(\text{NR}_2)_2$ ($\text{R} = \text{SiMe}_3$)^[59, 60, 75] was substituted with a series of amines, alcohols, thiols (collectively referred to as H-L) or the often used alcoholysis exchange (equation 2) involving $[\text{Ge}(\text{O}^t\text{Bu})_2]_2$ ^[47, 76]. The H-L modifiers investigated in this work included N,N'-dibenzylethylenediamine (H₂-DBED), *tert*-butanol (H-OBu^t), 2,6-dimethyl phenol (H-DMP), 2,6-di-phenyl phenol (H-DPP), *tert*-butyldimethylsilanol (H-DMBS), triphenylsilanol (H-TPS), triphenylsilanethiol (H-TPST), and benzenethiol (H-PS). The products were identified as: $[\text{Ge}(\mu\text{-DBED})]_2$ (**1**, $\mu\text{-c}$ = bridging chelating), $[\text{Ge}(\mu\text{-DMP})(\text{DMP})]_2$ (**2**), $\text{Ge}(\text{DPP})_2$ (**3**), $[\text{Ge}(\mu\text{-OBu}^t)(\text{DMBS})]_2$, (**4**), $[\text{Ge}(\mu\text{-DMBS})(\text{DMBS})]_2$ (**5**), $\text{Ge}(\text{TPS})_3(\text{H})$ (**6**), $[\text{Ge}(\mu\text{-TPST})(\text{TPST})]_2$ (**7**), and $\text{Ge}(\text{PS})_4$ (**8**). Once isolated, these compounds were used for the generation of Ge-based nanomaterials following established solution precipitation protocols.^[21] The characterization of these precursors, the nanomaterials produced and the preliminary PSA correlation are discussed.

H-L	Cmpd	Formula
H ₂ -DBED = N,N'-dibenzylethylenediamine	1	$[\text{Ge}(\mu\text{-DBED})]_2$
H-DMP = 2,6-di-methyl phenol	2	$[\text{Ge}(\mu\text{-DMP})(\text{DMP})]_2$
H-DPP = 2,6-di-phenyl phenol	3	$\text{Ge}(\text{DPP})_2$
H-DMBS = <i>tert</i> -butyldimethylsilanol	5	$[\text{Ge}(\mu\text{-DMBS})(\text{DMBS})]_2$
H-TPS = triphenylsilanol	6	$\text{Ge}(\text{TPS})_3(\text{H})$
H-TPST = triphenylsilanethiol	7	$[\text{Ge}(\mu\text{-TPST})(\text{TPST})]_2$
H-PS = benzenethiol	8	$\text{Ge}(\text{PS})_4$

Results and Discussion

The utility of Ge(II) amide $[\text{Ge}(\text{NR}_2)_2]$ and alkoxide $[\text{Ge}(\text{OR})_2]$ derivatives for the production of Ge(0) nanomaterials has been previously demonstrated.^[21] In an effort to garner additional morphological control over the Ge(0) nanomaterials by exploiting the PSA phenomenon, a series of well-characterized $\text{Ge}(\text{NR}_2)_2$ and $\text{Ge}(\text{OR})_2$ precursors was necessary. A search of the crystallographically characterized species^[41, 42] constrained to $\text{Ge}(\text{NR}_2)_2$ yielded a complex family of compounds^[50, 52–58] that typically employ chelating amide groups as well as a series of simple $\text{Ge}(\text{N}(\text{SiR}_3)_2)_2$ ^[59–62, 75] species. Further searches for $\text{Ge}(\text{OR})_2$ structures (when calixarenes and hydroxyl ligated species were removed due to inherent problems associated with these compounds for materials production) yielded two structure types: (i) monomeric $\text{Ge}(\text{OR})_2$ where $\text{OR} = \text{OC}(\text{Bu}^t)_3$,^[49] $\text{O}(\text{CH}_2)_2\text{NMe}_2$,^[63] (2,6-di-*R*)phenoxy [where *R* = *tert*-butyl (DBP),^[21] *tert*-butyl-Me-4^[51], 2,6-*iso*-propylphenyl,^[43] phenyl (DPP)^[45]], (2,3,5,6-tetra-phenyl)phenoxy^[45], $\text{Ge}(\text{DPP})_2(\text{NMe}_2)_2$ ^[77] and (ii) dinuclear $[(\text{OR})\text{Ge}(\mu\text{-OR})]_2$ where $\text{OR} = \text{mesityloxo (OMes)}$ ^[45] and 2,6-di-*iso*-propyl phenoxide (DIP)^[45]. Additionally, for Ge(II) siloxides, the heteroligated $[(\text{TPS})\text{Ge}(\mu\text{-OBu}^t)]_2$ ^[47] and $\text{Ge}(\text{TPS})_2\{(\text{TMS})\text{N}=\text{P}(\text{PH})_2)_2(\text{CH}_2)\}$ ^[64] have been disseminated as well as the Ge(IV) *bis*-OSiR₃ complex (porph)Ge(TPS)₂ (porph = 5,10,15,20-tetrakis(2-tri-*iso*-propylsilyl)ethynyl) porphyrinato-N,N',N'',N''')^[78]. We were also interested in the utility of thiolate derivatives as precursors for Ge(0) or single-source precursor for GeS_x. Only a handful of Ge(II) thiolates have been crystallographically reported, including $[\text{Ge}(\mu\text{-SBU}^t)_2(\text{SBU}^t)]_2$,^[79] the hydrido $\text{Ge}(\text{SPh}_3)_3(\text{H})$,^[45] and the salts $[\text{Ge}(\text{SPh}_3)][\text{N}(\text{Et})_4]$ ^[65] or $\{[\text{SCH}_2\text{CH}_2\text{S}]^-\text{Ge}(\mu\text{-SCH}_2\text{CH}_2\text{S})_2\}\{\text{P}(\text{Ph}_4)\}$ ^[65].

Obviously, the systematic variation and the proper ligand composition to investigate the PSA of Ge(0) nanomaterials were not available from this set of compounds.^[21, 38–40, 43–65] Therefore, the syntheses of Ge(II) precursors with ligands selected for both electronic and steric considerations were initiated. Once isolated and characterized, an initial study on the conversion of these precursors to Ge(0) nanomaterials via a solution precipitation route was undertaken.^[21]

Synthesis

The ligands of interest (H-L, eq 1) were individually reacted with $\text{Ge}(\text{NR}_2)_2$ ^[59, 60, 75] in toluene (eq 1); except for **4** which was isolated from the modification of $[\text{Ge}(\text{OBu}^t)_2]_2$ ^[47, 76] (eq 2). After stirring for 10 min, each reaction mixture was set aside and the volatile component was allowed to slowly evaporate. Over an extended period of time under an argon atmosphere, light yellow or colorless X-ray quality crystals were isolated. FTIR data of the dried crystals indicated that the reactive proton for each ligand had been removed. In particular, the H-N stretch for the diamine at $\sim 3300\text{ cm}^{-1}$ for compound **1**, the H-O stretch of the alcohols at $3200 - 3500\text{ cm}^{-1}$ for **2**, **3** and for the silanols of **4 – 6**, as well as the H-S stretch for the thiols at $\sim 2500\text{ cm}^{-1}$ for **7** and **8** were no longer present. For **6**, a new peak at 2130 cm^{-1} was tentatively assigned as a Ge-H stretching band.^[80–83] For **5**, a peak at 2131 cm^{-1} was observed which was tentatively assigned to a Ge-H interaction, possibly from the protons of the $\text{Si}(\text{CH}_3)_3$ group.

Crystal Structures

In order to assist in the characterization of **1 – 8**, single crystal X-ray structures of each were obtained and shown in Figures 1 – 8, respectively. The structure plot of compound **1** (Figure 1) shows the structure of the Ge(II) diamine derivative. For **1**, each pyramidal Ge metal center is fully coordinated by three N atoms - two from the chelating DBED and one from the N of the other DBED. The ethane linkage of each DBED was found to be twisted 24.3° out of the plane with respect to the core, which is in good agreement with the 22.0° twist of

the monomeric $[\text{CH}_2\text{N}(\text{tBu})]^\text{c}_2\text{Ge}$ ($^\text{c}$ = cyclic).^[54] The remainder of comparable metrical data are also in agreement between **1** [Ge-N(1) = 1.86 Å; N-Ge-N = 84.6°] and $[\text{CH}_2\text{N}(\text{tBu})]^\text{c}_2\text{Ge}$ [Ge-N = 1.83 Å; N-Ge-N = 87.9°]^[54]. The Ge_2N_2 core of **1** [Ge-(μ-N) = av 2.01 Å, (μ-N)-Ge-(μ-N) = 80.0°] compares favorably to $[\text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-Pr}^\text{i}_2)_2(\mu\text{-NH}_2)\text{Ge}]_2$ ^[41] [Ge-(μ-N) 2.02 Å; (μ-N)-Ge-(μ-N) angle of 81.5°].

The use of arylalcohols in eq 1, led to the isolation of **2** (Figure 2) and **3** (Figure 3). For the smaller DMP ligand, the dinuclear compound **2** was isolated with a single bridging and terminal DMP ligand bound to each pyramidal coordinated Ge metal center. The terminal DMP ligands adopt a *trans* arrangement (above and below the Ge_2O_2 plane), similar to what was reported for the OMe^s^[45] and DIP^[45] derivatives. As is often noted for metal alkoxides,^[66–71] the Ge-O terminal distances (av 1.82 Å) are shorter than the Ge-(μ-O) bridging bond lengths (av 1.98 Å). The internal Ge_2O_2 core has angles of (μ-O)-Ge-(μ-O) (av 72.5°) and Ge-(μ-O)-Ge (av 107.4°). These data are in agreement with the literature $\text{Ge}(\text{OR})_2$ distances and angles^[45, 84]: Ge-O (av 1.82 Å), Ge-(μ-O) (av 1.98 Å), and (μ-O)-Ge-(μ-O) (av 72.2°) Ge-(μ-O)-Ge (av 107.5 Å). For the more sterically hindering DPP ligand, monomeric **3** was isolated in a bent arrangement as previously reported by Rothwell and co-workers;^[45] however, for this crystal solution, **3** was solved in the higher-ordered orthorhombic space group. The Ge-O bond length of 1.81 Å and O-Ge-O angle of 90.2° are in good agreement with previously reported Ge-O bond lengths of av 1.82 Å and O-Ge-O angles of av 91.6°.^[45]

It was of interest to determine what effect siloxides ligands would have on the final structure of Ge(II) species. The first attempt to generate a homoleptic precursor following an alcoholysis exchange (eq 2) yielded the heteroleptic structure of **4** (Figure 4). For this compound only the terminal OBu^t groups were substituted by DMBS ligands, leaving the original dinuclear pyramidal arrangement around the Ge metal centers intact. The two bridging OBu^t groups had a (μ-O)-Ge-(μ-O) angle of av 74.5° with Ge-(μ-O) distance of av 1.96 Å, and terminal Ge-O distance of av 1.80 Å, similar to the metrical data of $[\text{Ge}(\mu\text{-OBu}^\text{t})(\text{TPS})]_2$ ^[47]: (μ-O)-Ge-(μ-O) av 74.8°; Ge- O_{TPS} av 1.81 Å; Ge-(μ- OBu^t) av 1.96 Å.

Attempts to generate homoleptic siloxides were realized following the transamination methodology (eq 1). Using two equivalents of H-DMBS or H-TPS led to the fully substituted species **5** (Figure 5) and **6** (Figure 6), respectively. Interestingly, the DMBS derivative **5** adopted a dinuclear arrangement where the terminal DMBS ligands of the pyramidal Ge were found in a *cis* conformation. This unusual arrangement for Ge(II) species forces a small out-of-plane twist (4.22°) of the Ge_2O_2 core. The terminal Ge-O distances of $(\text{TPS})_2\text{Ge}\{[(\text{TMS})\text{N}=\text{P}(\text{PH})_2]_2(\text{CH}_2)_2\}$ ^[64], (porph)Ge(TPS)₂, and $[(\text{TPS})\text{Ge}(\mu\text{-OBu}^\text{t})]_2$ ^[47] av 1.80,^[78] 1.86,^[64] and 1.81^[47] Å, respectively are significantly longer in comparison to those noted for **5** (av 1.78 Å). This variation is most likely a reflection of the dinuclear, homoleptic nature of **5** in comparison to the other compounds. Further comparisons were made only to the dinuclear heteroleptic $[(\text{TPS})\text{Ge}(\mu\text{-OBu}^\text{t})]_2$ ^[47]. The internal core distances and angles of **5** [Ge-(μ-O) av 1.98 Å, with O-Ge-(μ-O) angles av 96.0° and (μ-O)-Ge-(μ-O) av 78.0°] appear to be roughly in agreement with $[(\text{TPS})\text{Ge}(\mu\text{-OBu}^\text{t})]_2$ ^[47] [Ge-(μ-O) av 1.96 Å, with O-Ge-(μ-O) angles av 96.3° and (μ-O)-Ge-(μ-O) av 74.7°]. In contrast to what was noted in the FTIR, there were no $\text{CH}_2\text{---H---Ge}$ interactions observed in the solid-state structure of **5**.

For **6**, a monomer was isolated with three TPS groups, which suggests that either one of the TPS ligands is protonated or a hydride formed. The FTIR spectrum (*vide infra*) and ¹H NMR (*vide supra*) data indicated that the latter interpretation was the most appropriate. Further analysis of the electron density map of **6** revealed the presence of a proton located as part of the tetrahedral geometry around the Ge metal center (Figure 6). While the formation

of the unusual compound **6** is not fully understood, a potential mechanism would include the initial formation of the homoleptic $\text{Ge}(\text{TPS})_2$ species, followed by additional coordination of free H-TPS, subsequent β -hydrogen transfer, and conversion to the Ge(IV) hydride species **6**. This is consistent with previously disseminated mechanisms of Ge-H formation for other siloxide systems.^[45, 80, 85] The Ge-H bond distance was resolved at 1.26 Å, which is shorter than the recently published $[\text{Ge}(\text{H})(\mu\text{-O}_3\text{SiR})]_4$, $\text{R} = \text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)$, where the av Ge-H bond length was 1.39 Å.^[80] The short Ge-H bond length is attributed to the decreased electron donation capability of the attached TPS ligands; this is further evidenced in the Ge-H increased ^1H NMR shift downfield. The remainder of the metrical data (Ge-O av 1.73 Å, O-Ge-O angles av 107.5°, H-Ge-O angles of av 111.3°) are in agreement with $[\text{Ge}(\text{H})(\mu\text{-O}_3\text{SiR})]_4$ (Ge-O av 1.74 Å, for O-Ge-O av 108.8°, H-Ge-O av 109.9°).^[80]

Attempts to expand the ligand set to include thiolates were undertaken following eq 1, which yielded **7** (see Figure 7). Compound **7** was found to be dinuclear with two bridging and two terminal *cis* TPST ligands, arranged in a pyramidal geometry around the Ge cations. While four Ge(IV)-S-Si species are available in the literature,^[86–89] **7** is the first report of a Ge(II)-S-Si complex, which complicates metrical comparisons. The TPST species has a Ge_2S_4 core that is significantly distorted from planarity (56.2°) with angles of av 78.4° ($\mu\text{-S}$)-Ge-($\mu\text{-S}$) and av 93.0° (S)-Ge-($\mu\text{-S}$) and distances of av 2.32 Å for Ge-S and av 2.47 Å Ge-($\mu\text{-S}$). These distances and angles do not compare favorably with the only appropriate model $[\text{Ge}(\mu\text{-SBu}^t)(\text{SBu}^t)]_2$:^[79] 27.6° twist of the Ge_2S_4 , angles of av 85.5° ($\mu\text{-S}$)-Ge-($\mu\text{-S}$), 92.1° (S)-Ge-($\mu\text{-S}$), and distances of 2.43 Å for Ge-S. The metrical variations must be due to changes in the steric bulk and electron donation of the SSiR_3 group of **7** to the SR group of $[\text{Ge}(\mu\text{-SBu}^t)(\text{SBu}^t)]_2$.^[79]

The use of the thiol H-PS in eq 1 produced **8** (Figure 8), a monomeric species that has four PS ligands arranged in a distorted tetrahedral geometry around the Ge metal center. Since both the IR and ^1H NMR data indicate the removal of the protons from the PS ligands and the metrical aspects of **8** were comparable to the Ge(IV) thiol species,^[65, 90–93] **8** is considered to be in the +4 oxidation state instead of coordination of two H-PS ligands. In particular, the av Ge-S distance of **8** was found to be 2.21 Å which favorably compares to the Ge(IV)-S literature distances (av. 2.24 Å; range 2.19 – 2.412 Å)^[65, 94] and not with Ge(II)-S terminal distances (av. 2.32 Å; range 2.26 – 2.37 Å)^[65, 79].

Elemental analyses of samples **1** – **8** revealed that the dried bulk crystalline materials are in agreement with the single crystal structures obtained for **1** – **8**. For **6**, it was necessary to subtract the lattice toluene molecule from the elemental composition to obtain an acceptable analysis.

Solution Behavior

Since these compounds are dissolved prior to nanocrystal processing, it is of interest to understand the solution behavior of these compounds. Therefore, crystalline materials of **1** – **8** were individually dissolved in either *tol-d*₈ or CDCl_3 , flame-sealed in an NMR tube, and variable temperature ^1H NMR spectra (VT-NMR range –20 to +45 °C) obtained for each sample. No significant changes were noted in the NMR spectra over this temperature range for all of the samples, unless specifically discussed below.

For **1**, two sets of resonances were expected for the ethylene and methylene protons based on the asymmetry generated by the $\mu\text{-c}$ -DBED ligand. Upon dissolution in *tol-d*₈, singlets at δ 4.00 and δ 2.92 tentatively assigned to the ethylene and methylene moieties, respectively were observed. This indicates a monomer exists in solution; however, the ^{13}C NMR data revealed two sets of resonances that substantiates that the solid-state structure of **1** is maintained in solution. The dinuclear **2** in *tol-d*₈ also displayed a broad singlet for the 2,6-

methyl groups of the aryloxide at δ 2.25 but in contrast to **1**, the ^{13}C spectrum revealed only one set of resonances, suggesting **2** favored a monomer in solution. However, VT-NMR studies on $[\text{Ge}(\mu\text{-DIP})(\text{DIP})]_2$ indicate that this compound maintains its nuclearity upon dissolution, with rapid exchange of the bridging and terminal ligands.^[45] Unfortunately, the lowered solubility of **2** favors precipitation at reduced temperatures, which prevents similar studies and therefore definite statements concerning its nuclearity in solution, cannot be made. In CDCl_3 , **3** revealed a complex multiplet ranging from δ 7.56 - 7.04 assigned to the numerous phenyl protons associated with the DPP ligand. Since it appears that a monomer may be structurally favored for **2** in solution, it would also follow that the more sterically demanding DPP ligand of **3** would also favor a monomeric species in solution.

The mixed alkoxide/siloxide species **4**, in CDCl_3 , presented an NMR spectra with singlets at δ 1.41, 0.90, and 0.06 ppm, assigned to the $\text{OC}(\text{CH}_3)_3$, $\text{OSi}(\text{CH}_3)_2(\text{C}(\text{CH}_3)_3)$, and $\text{OSi}(\text{CH}_3)_2(\text{C}(\text{CH}_3)_3)$ moieties, respectively. Two complete set of ^{13}C NMR resonances and a single ^{29}Si NMR resonance at δ 15.5 ppm were found for **4**. Combined it is not possible to determine the nuclearity of **4**; however, since the previously reported $[\text{Ge}(\mu\text{-OBu}^t)(\text{TPS})]_2$ derivative^[47] was reported to be dinuclear in solution, it is reasonable to think **4** maintains the same central core in solution, with the sterically less demanding DMBS in place of the TPS. For compound **5** dissolved in CDCl_3 , the ^1H (δ 1.81 and 1.01 ppm), ^{13}C , and ^{29}Si peak (δ 15.5 ppm) revealed only one set of DMBS *tert*-butyl and methyl group resonances. This indicates that **5** is a monomer in solution.

Compound **6** displayed a sharp singlet at δ 6.49 ppm which is farther upfield in comparison to the reported ^1H shift of $[\text{Ge}(\text{H})(\mu\text{-O}_3\text{SiR})]_4$ at δ 5.83 ppm^[80]; however, this data combined with the other analytical data and crystal structure solution, leads to the assignment of **6** as the hydride. Examination of **7**, in CDCl_3 , lead to the identification of multiplets in the expected range of δ 7.39 – 7.22. Attempts to distinguish between mononuclear and dinuclear species was undertaken using VT-NMR; however, the lack of dynamic behavior noted for **7** indicates that a single species is most likely present in solution. While the ^{13}C NMR data was complex and did not add any significant structural information, the ^{29}Si singlet at δ -13.5 ppm argues for the presence of a monomer in solution. Mononuclear **8** was found to have multiplets in the range of δ 7.36 - 7.20 with no indication of a hydride resonance. Table 1 lists the observed NMR solution behavior for these precursors.

Thermal Gravimetric Analysis

In order to gain insight into the decomposition temperature differences for these precursors and their suitability for nanomaterials production, TGA data were collected for each compound: **compound** (temp, % wt loss/calc'd %wt loss): **1** (180 °C, 76 %/ 76 %), **2** (200 °C, 82 %/ 77 %), **3** (200 – 300 °C, 87 %/ 87 %), **4** (130 °C, 85 %/ 74 %), **5** (110 °C, 88 %/ 78 %), **6** (200 – 280 °C, 60 %/ 61 %), **7** (260 °C, 81 %/ 89 %), and **8** (230 °C, 83 %/ 86 %). In general, the data for **1 – 8** (see Figure 9) indicated that the initiation of the organic decomposition occurred at temperatures that were acceptable for the preparatory routes of interest. It should also be noted that for **7**, a lower than expected weight loss was observed which may be explained by the cleavage of the Si-S linkage [i.e., loss of $\text{Si}(\text{C}_6\text{H}_5)$, 79 % weight loss], forming a Ge-S complex, which gradually loses sulfur as the temperature, exceeds 400 °C. The metrical listing of the decomposition temperature of these compounds is included in Table 1.

Nanomaterials

With a set of acceptable precursors that were amenable to our processing routes, the production of Ge(0) nanomaterials was undertaken. The use of a simple solution route

employing the non-coordinating octadecene as the main solvent was selected for the ease of interpretation of any possible PSA phenomenon. The Ge precursors (**1** – **8**) isolated for this study varied in both structural and electronic configuration, which made these a reasonable set of compounds to begin our study. Compound **4** was removed from consideration, since a heteroleptic ligand set would lead to confusion in what ultimately determined the final nanomaterial properties. Since both **6** and **8** were Ge(IV) species, they were not investigated in the initial study. Compounds **1** – **3** and **5** – **7** were thought to be acceptable precursors and used for Ge(0) nanomaterials production. For each reaction, dried crystalline powders of the respective precursors were used to minimize any contamination of the final nanomaterials generated.

The PXRD pattern of the products isolated from the reaction of **1** – **3**, and **5** were collected and found to be consistent with Ge(0) with a preferred crystalline cubic structure (PDF # 04-0545), see Figure 10. Since the materials are nanopowders, the resulting patterns were broad and due to this fact, it is not possible to rule out the potential inclusion of amorphous Ge nanomaterials in the resulting powders.^[35, 36] Transmission electron microscopy analyses were obtained on these materials and their images are shown in Figure 11a–e for **1**, **2**, **3**, and **5**, respectively. The results obtained in this work are consistent with the previously disseminated efforts for production of Ge(0).^[10, 11, 21] For **1**, the nanoparticles isolated appear to be 5 nm in diameter and agglomerated (Figure 11a). In contrast compounds **2**, **3**, and **5** formed nanowires with a diameter (d) and aspect ratio (AR) for compound (d (nm)/AR): **2** (14/20, Figure 11b); **3** (7/13, Figure 11c); **5** (5 – 17 up to 50, Figure 11d). EDS analyses confirmed that Ge was formed in each sample. Additional powder XRD and EDS patterns concerning these compounds can be found in the supplementary information.

With the successful production of Ge(0) nanomaterials it was of interest to compare these results with the previous Ge(II) precursors^[10, 11, 21] to elucidate any PSA influences. Under identical conditions, Ge(N(SiMe₃)₂)₂ was found to produce 5 nm Ge(0) nanodots, whereas Ge(DBP)₂ (DBP = 2,6-dibutylphenol) formed Ge(0) nanowires av 20 nm in diameter (AR = 20).^[21] It is of note that Ge(N(SiMe₃)₂)₂ has been reported to form ~60 nm wires from a chemical vapor route when a SiC_xN_y shell is employed.^[19] Compound **1** allowed for a direct comparison to the previous amide results. High resolution TEM revealed that the resulting nanomaterials from **1** were a conglomerate of nanoparticles that were similar in shape and size of those generated by Ge(N(SiMe₃)₂)₂.^[21] Therefore, the diamine did not drastically alter the morphological properties of the resultant nanomaterials.^[59, 60, 75]

For the alkoxy ligated compounds (**2** and **3**), the decomposition results were also found to be in-line with the previous Ge(DBP)₂ complex.^[21] The smaller wire diameters and lengths noted for **3** suggests that the sterically demanding DPP ligand slows the nucleation and growth of the wires as compared to the DMP ligand of **2** or the DBP ligand of Ge(DBP)₂.^[21] This slower nucleation and growth could reasonably be attributed to the two-step decomposition pathway of the DPP ligands noted in the TGA (Figure 9).

For **5**, a significant difference in decomposition temperature was noted for the homoleptic siloxide precursors. For **5**, the Ge(II) precursor's low decomposition temperature and lack of steric bulk would suggest that a dot morphology should prevail. However, significant amounts of nanowires were noted in the various TEM images which indicates that the lower thermal decomposition temperatures noted in the TGA (Figure 9) does *not* play a significant role in the final morphological properties of these compounds in this system. The nanowires' lengths were under a micron but were much longer than those formed from **2** and **3**. Again, the differing factor was the DMBS ligand, which suggests that siloxides favor longer growth times based on slower decomposition, forming nanowires.

Due to the success of high AR nanowires formed by the siloxide of **5**, coupled with the presence of the hydride, compound **6** became of interest to determine if this Ge(IV) precursor could be converted in our system and how this effected the final morphologies observed. The Ge(IV) siloxane precursor **6**, was expected to result in a wire-like material due to the similar decomposition temperature and bulky alkoxy ligands of Ge(DBP)₂. The PXRD pattern indicated that Ge(0) had indeed been produced and TEM analyses revealed nanowires with widths that ranged from 5 – 25 nm with the larger diameter wires having an AR of up to 50 (Figure 11e) had been formed. These AR are significantly longer than the nanowire lengths of **2** and **3**, and indicate that there may be a significant advantage using siloxide precursors for nanowire production.

The thiol derivative **7** was also processed to determine how these thiol precursors would behave in our system. Based on the TGA data, the silanethiolate **7** was expected to follow a similar decomposition route as the previous compounds and yield either a Ge(0) or a Ge-S nanomaterial. After processing, a broad PXRD pattern of the materials generated from **7** indicated that an amorphous material had been formed. TEM analysis revealed no distinguishable morphology (Figure 11f) but EDS analysis indicated that both Ge and S were present in the nanomaterials; therefore, the material is thought to be an amorphous Ge_xS_y material. A higher processing temperature is obviously required to complete the decomposition/crystallization of **7**.^[95] These results also indicate that **7** was not suitable for Ge(0) nanomaterial syntheses.

Summary and Conclusions

This study increased the number of structurally characterized Ge(II) precursors synthesized from either a transamination or alcoholysis metathesis reaction, including diamide (**1**), alkoxide (**2**, **3**), siloxide (**4**, **5**), silanethiolate (**7**), as well as Ge(IV) hydride-siloxide (**6**), and thiolate (**8**) derivatives. Upon thermal decomposition of these compounds, it was found that nanodots were observed for **1**, while the majority (**2**, **3**, **5**, and **6**) of compounds formed nanowires (alkoxides: AR = 20; siloxides: AR = 50). The variation between the alkoxide and siloxide nanowire AR is of interest and further work to understand the factors behind this phenomenon are underway. The results from this study in general indicate the PSA plays a role in the resulting nanoparticle morphology;^[21] however, it is also obvious from these results that additional parameters and experimental approaches are required to garner the desired control to generate tailored Ge(0) nanomaterials. Studies are currently underway to determine how further system adjustments (i.e., temperature, reaction time, concentration, sterics, electronics, etc) influence the decomposition of the prescribed precursors and subsequent evolution of crystalline Ge based nanomaterials.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glove box techniques. All solvents were stored under argon and used as received (Aldrich) in SureSeal™ bottles, including hexanes (hex), toluene (tol), toluene-*d*₈ (tol-*d*₈), acetone-*d*₆, and chloroform-*d* (CDCl₃). The following chemicals were used as received (Aldrich): GeCl₂•dioxane, LiN(SiMe₃)₂, H₂-DBED, H-OBu^t, H-DMP, H-DPP, H-DMBS, H-TPS, H-TPST, H-PS, oleylamine, and octadecene. Ge[N(SiMe₃)₂]₂^[59, 60, 75] and [Ge(OBu^t)₂]₂^[47, 76] were synthesized according to literature reports.

General Synthesis

Due to the similarity of the following reactions a general preparation is presented with specific details presented for each reaction below. In a glovebox, the appropriate ligand was dissolved in a minimum amount of toluene and added via pipette to a stirring mixture of $\text{Ge}(\text{NR}_2)_2$ dissolved in toluene. After stirring for 10 min, the resulting reaction mixture was set aside and the volatile portion was allowed to slowly evaporate until light yellow or colorless X-ray quality crystals were isolated.

[Ge(μ_c -DBED)]₂ (1)—Used H_2 -DBED (0.198 g, 0.824 mmol), $\text{Ge}(\text{NR}_2)_2$ (0.324 g, 0.824 mmol), in tol (~5 mL). Yield: 55.0% (0.258 g). FTIR (KBr pellet, cm^{-1}): 3064(s), 3025(m), 2912(m), 2885(m), 2850(w), 2821(m), 2793(m), 2770(w), 1599(s), 1491(m), 1450(w), 1356(m), 1304(m), 1211(m), 1153(w), 1065(w), 1010(m), 872(w), 745(w), 701(w), 635(w). ^1H NMR (250.0 MHz, $\text{tol}-d_8$): δ 7.13–7.23 (10H, m, $(\text{C}_6\text{H}_5)\text{CH}_2\text{N}(\text{CH}_2)_2\text{NCH}_2(\text{C}_6\text{H}_5)$), 4.00 (2H, s, $(\text{C}_6\text{H}_5)\text{CH}_2\text{N}(\text{CH}_2)_2\text{NCH}_2(\text{C}_6\text{H}_5)$), 2.92 (4H, s, $(\text{C}_6\text{H}_5)\text{CH}_2\text{N}(\text{CH}_2)_2\text{NCH}_2(\text{C}_6\text{H}_5)$). ^{13}C NMR (62.86 MHz, CDCl_3): δ 141.5, 129.0, 128.5, 128.4, 128.3, 127.1, 126.8 ($(\text{C}_6\text{H}_5)\text{CH}_2\text{N}(\text{CH}_2)_2\text{NCH}_2(\text{C}_6\text{H}_5)$), 54.4, 54.1, 52.4, 49.4, $(\text{C}_6\text{H}_5)\text{CH}_2\text{N}(\text{CH}_2)_2\text{NCH}_2(\text{C}_6\text{H}_5)$. Elemental Analysis for $\text{C}_{32}\text{H}_{36}\text{Ge}_2\text{N}_4$ (621.83): calcd. C 61.81, H 5.84, N 9.01; found C 62.14, H 5.72, N 9.16.

[Ge(μ -DMP)(DMP)]₂ (2)—Used H-DMP (0.191 g, 1.56 mmol), $\text{Ge}(\text{NR}_2)_2$ (0.308 g, 0.782 mmol), in tol (~5 mL). Yield: 90.8% (0.224 g). FTIR (KBr pellet, cm^{-1}): 3038(m), 3019(m), 2978(m), 2951(m), 2914(m), 2856(m), 1590(m), 1468(w), 1262(w), 1195(w), 1168(w), 1091(w), 840(w), 830(w), 773(w), 761(w), 741(w), 693(w), 680(w), 611(m), 584(w), 535(m), 525(m), 437(w). ^1H NMR (250.0 MHz, $\text{tol}-d_8$): δ 7.00 (2H, d, $\text{OC}_6\text{H}_3(\text{CH}_3)_2$, $J_{\text{H-H}} = 3.75$ Hz), 6.73 (1H, m, $\text{OC}_6\text{H}_3(\text{CH}_3)_2$), 2.25 (6H, s, $\text{OC}_6\text{H}_3(\text{CH}_3)_2$). ^{13}C NMR (62.86 MHz, CDCl_3): δ 152.2, 129.8, 129.0, 123.7 ($\text{OC}_6\text{H}_3(\text{CH}_3)_2$), 17.4 ($\text{OC}_6\text{H}_3(\text{CH}_3)_2$). Elemental Analysis for $\text{C}_{32}\text{H}_{36}\text{Ge}_2\text{O}_4$ (629.79): calcd. C 61.03, H 5.76; found C 60.57, H 5.96.

Ge(DPP)₂ (3)—Used H-DPP (0.623 g, 2.53 mmol), $\text{Ge}(\text{NR}_2)_2$ (0.498 g, 1.27 mmol), in tol (~5 mL). Yield: 80.6% (0.575 g). FTIR (KBr pellet, cm^{-1}): 3080(s), 3060(m), 3051(m), 3034(s), 1595(m), 1493(m), 1455(w), 1439(m), 1408(w), 1276(m), 1241(m), 1216(w), 1085(m), 1071(m), 1028(m), 842(w), 761(w) 746(w), 701(w), 637(w), 625(m), 609(w), 586(m). ^1H NMR (250.0 MHz, CDCl_3): δ 7.56 (4H, d, $\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2$, $J_{\text{H-H}} = 3.75$ Hz), 7.45 (4H, m, $\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2$), 7.36 (2H, m, $\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2$), 7.28 (2H, d, $\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2$, $J_{\text{H-H}} = 3.75$ Hz), and 7.04 (1H, m, $\text{OC}_6\text{H}_3(\text{C}_6\text{H}_5)_2$). Elemental Analysis for $\text{C}_{36}\text{H}_{26}\text{GeO}_2$ (563.16): calcd. C, 76.78, H 4.65; found C 77.36, H 4.92.

[Ge(μ -OBu^t)(DMBS)]₂ (4)—Used $[\text{Ge}(\text{OBu}^t)_2]_2$ ^[47, 76] (0.440 g, 1.00 mmol), H-DMBS (0.266 g, 2.01 mmol), in hexanes (~5 mL). Yield: 86.2% (0.480 g). FTIR (KBr pellet, cm^{-1}): 2958(w), 2931(w), 2894(m), 2857(m), 1467(m), 1388(m), 1365(m), 1251(w), 1177(m), 952(w), 891(w), 833(w), 775(w), 727(m), 673(s), 603(w). ^1H NMR (250.0 MHz, CDCl_3): δ 1.41 (9H, s, $\text{OC}(\text{CH}_3)_3$), 0.90 (9H, s, $\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), 0.06 (6H, s, $\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$). Elemental analysis for $\text{C}_{20}\text{H}_{48}\text{Ge}_2\text{O}_4\text{Si}_2$ (553.94): calcd. C 43.36, H 8.73; found C 43.08, H 8.71.

[Ge(μ -DMBS)(DMBS)]₂ (5)—Crystals were obtained by reduction of solvent and subsequent refrigeration (-30°C) over 24 h. Used H-DMBS (0.232 g, 1.75 mmol), $\text{Ge}(\text{NR}_2)_2$ (0.345 g, 0.877 mmol), in tol (~5 mL). Yield: 97.0% (0.285 g). FTIR (KBr pellet, cm^{-1}): 2954(w), 2933(w), 2890(w), 2859(w), 2131(m), 1468(m), 1408(s), 1391(s), 1361(s), 1255(w), 956(w), 836(w), 805(w), 779(w), 725(w), 679(m), 593(m), 541(s). ^1H NMR (250.0 MHz, CDCl_3): δ 1.81 (9H, s, $\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), 1.01 (6H, s,

$\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$. ^{29}Si NMR (49.66 MHz, $\text{tol}-d_8$): δ 15.5 ($\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$). ^{13}C NMR (62.86 MHz, $\text{tol}-d_8$): δ 25.9 ($\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), 18.5 ($\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), -2.50 ($\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$). Elemental analysis for $\text{C}_{24}\text{H}_{60}\text{Ge}_2\text{O}_4\text{Si}_4$ (670.26): calcd. C 43.01, H 9.02; found C 42.81, H 8.64.

Ge(TPS)₃(H) (6)—Used H-TPS (1.98 g, 7.16 mmol), $\text{Ge}(\text{NR}_2)_2$ (0.939 g, 2.39 mmol), in tol (~20 mL). Yield: 93.1% (2.00 g). FTIR (KBr, cm^{-1}): 3067(m), 3050(m), 3022(w), 3012(w), 2998(w), 2130(m), 1588(w), 1425(s), 1115(s), 971(s), 721(s), 696(s), 591(m), 510(s). ^1H NMR (250.0 MHz, CDCl_3): δ 7.37 (2H, d, $\text{OSi}(\text{C}_6\text{H}_5)_3$, $J_{\text{H-H}} = 3.75$ Hz), 7.13 (2H, m, $\text{OSi}(\text{C}_6\text{H}_5)_3$), 6.49 (1H, s, H-Ge). Elemental Analysis for $\text{C}_{54}\text{H}_{46}\text{GeO}_3\text{Si}_3$ (899.79): calcd. C 72.08, H 5.15; found C 72.18, H 5.51.

[Ge(μ -TPST)(TPST)]₂ (7)—Colorless crystals were obtained by reduction of solvent and subsequent refrigeration (-30°C) over 24 h. Used H-TPST (0.931 g, 1.59 mmol), $\text{Ge}(\text{NR}_2)_2$ (0.313 g, 0.796 mmol), in tol (~5 mL). Yield: 75.2% (0.392 g). FTIR (KBr pellet, cm^{-1}): 3357(w), 3072(m), 3048(m), 3024(w), 3013(w), 2998(w), 2958(m), 2896(w), 2855(w), 1429(s), 1116(s), 736(m), 702(s), 534(s), 514(s), 503(s), 486(m). ^1H NMR (250.0 MHz, CDCl_3): δ 7.39 (6H d, $\text{SSi}(\text{C}_6\text{H}_5)_3$, $J_{\text{H-H}} = 3.75$ Hz), 7.31 (6H, m, $\text{SSi}(\text{C}_6\text{H}_5)_3$), 7.22 (3H, m, $\text{SSi}(\text{C}_6\text{H}_5)_3$). ^{29}Si NMR (49.66 MHz, CDCl_3): δ -13.50 ($\text{SSi}(\text{C}_6\text{H}_5)_3$). Elemental analysis for $\text{C}_{72}\text{H}_{60}\text{Ge}_2\text{S}_4\text{Si}_4$ (1310.98): calcd. C 65.96, H 4.61; found C 65.33, H 4.57.

Ge(PS)₄ (8)—After mixing, the solution produced a deep red oil with a light red solution. The light red solution was decanted off and allowed to dry in the glovebox atmosphere to produce X-ray quality crystals. Used H-PS (0.445 g, 5.12 mmol), $\text{Ge}(\text{NR}_2)_2$ (0.503 g, 1.28 mmol), in tol (~10 mL). Yield: 62.3% (0.407 g). FTIR (KBr, cm^{-1}): 3072(w), 3053(w), 2961(m), 2924(m), 2853(w), 1577(m), 1474(m), 1466(m), 1437(m), 1095(s), 1079(s), 1022(s), 737(s), 688(s). ^1H NMR (250.0 MHz, CDCl_3): δ 7.36-7.20 (5H, m, SC_6H_5). Elemental Analysis for $\text{C}_{24}\text{H}_{20}\text{GeS}_4$ (509.23): calcd. C 56.61, H 3.96; found C 56.69, H 3.64.

Precursor Characterization

Fourier Transform Infrared (FTIR) spectroscopic data were obtained on a Bruker Vector 22 Instrument using KBr pressed pellets with bulk material, under an atmosphere of flowing nitrogen. Elemental analyses were performed on a Perkin-Elmer 2400 CHN-S/O Elemental Analyzer. Reported nuclear magnetic resonance (NMR) spectroscopic data were collected on a 250 MHz Bruker instrument using crystalline material dissolved in $\text{tol}-d_8$ or CDCl_3 . The ^1H and ^{13}C NMR data were referenced against the residual protonated solvent, and 5% TMS in acetone- d_6 for ^{29}Si NMR. Thermogravimetric analyses (TGA) were collected by a TA Instruments SDT Q600 on crystalline materials from room temperature to 700°C at a $10^\circ\text{C}/\text{min}$ heating rate, under a flowing atmosphere of nitrogen.

General Single Crystal X-ray Structure Information

Crystals were mounted onto a glass fiber from a pool of FluorolubeTM and immediately placed in a cold N_2 vapor stream, on a Bruker AXS diffractometer equipped with a SMART 1000 CCD detector using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINTPLUS Version 6.01 software and corrected for absorption using the SADABS program within the SAINT software package.

Structures were solved by direct methods that yielded the heavy atoms, along with a number of the lighter atoms or by using the PATTERSON method, which yielded the heavy atoms. Subsequent Fourier syntheses yielded the remaining light-atom positions. The hydrogen

atoms were fixed in positions of ideal geometry and refined using SHELXS software. The final refinement of each compound included anisotropic thermal parameters for all non-hydrogen atoms. All final CIF files were checked at <http://www.iucr.org/>. Data collection parameters for **1** – **8** are given in Table 2. It is of note that crystal structures of $M(OR)_x$ often contain disorder within the atoms of the pendant hydrocarbon chain, causing higher final correlations than is typically observed for other metalorganic structure solutions.^[66–71] The structures of **2** and **8** were solved with well-behaved thermal ellipsoids in the non-centrosymmetric orthorhombic space groups $Pca2_1$ and $Pba2$, respectively. For **2**, the arrangement of DMP ligands in a *trans* fashion prohibits a mirror plane from bisecting the bridging DMP ligands in the orthorhombic space group. In the case of **8**, it should be noted that the selenium analog $Ge(SePh)_4$, where $Ph = C_6H_5$, also shares the same non-centrosymmetric orthorhombic spacegroup $Pba2$.^[96] For compound **6**, a toluene molecule was located in the crystal lattice but due to significant disordering it was squeezed out to improve refinement values using the Platon (v 1.11, 2007) program.

Nanoparticle Synthesis

The dried crystalline precursor (1.00 mmol) was dissolved in oleylamine and then rapidly injected into a solution of octadecene (10.0 mmol) preheated to 315 °C. The reaction temperature was maintained at 315 °C for 30 min and allowed to cool to room temperature. An aliquot of the Ge nanomaterial solution was dissolved in $CHCl_3$ and precipitated using MeOH, which was collected by centrifugation. After washing in this manner a minimum of three times, the collected Ge nanomaterials were dispersed in $CHCl_3$ and a drop was placed onto a TEM grid for subsequent analyses. It should be noted that size selective precipitation methods were not utilized for TEM analyses.

Nanoparticle Characterization

Powder X-ray diffraction (XRD) was performed by a PANalytical X'Pert Pro XRD in the 2θ range of 15 – 75° at a scan rate of 0.06 °/sec on drop deposited Ge nanomaterials using a zero background holder. Transmission electron microscopy (TEM) analyses were performed on a JEOL JEM-2010 electron microscope equipped with an Oxford Instruments Energy Dispersive X-ray Spectroscopic (EDS) detector.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was partially funded by the National Science Foundation under Grant NSF CBET-0756776, the Office of Basic Energy Sciences of the Department of Energy, and the National Institutes of Health through the NIH Roadmap for Medical Research Grant #1 R21 EB005365-01-. Information on this RFA (Innovation in Molecular Imaging Probes) can be found at <http://grants.nih.gov/grants/guide/rfa-files/RFA-RM-04-021.html>. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

References

1. An X, Huang R, Zhang X, Wang Y. *Semicond. Sci. Technol.* 2005; 20:1034–1038.
2. Khakifirooz A, Antoniadis DA. *Electron Device Letters.* 2004; 25:80–82.
3. Lauhon LJ, Gudiksen MS, Wang CL, Lieber CM. *Nature.* 2002; 420:57–61. [PubMed: 12422212]
4. Tu CH, Chang TC, Liu PT, Weng CF, Liu HC, Chang LT, Lee SK, Chen WR, Sze SM, Chang CY. *J. Electrochem. Soc.* 2007; 154:H435–H439.

5. Gacem K, El Hdiy A, Troyon M, Berbezier I, Szkutnik PD, Karmous A, Ronda A. *J. Appl. Phys.* 2007; 102:093704–093707.
6. Kanoun M, Busseret C, Poncet A, Souifi A, Baron T, Gautier E. *Solid State Electron.* 2006; 50:1310–1314.
7. Pasquier ADT, Mastrogiovanni DD, Klein LA, Wang T, Garfunkel E. *Appl. Phys. Lett.* 2007; 91:183501–183503.
8. Wang R, Guo ZL, Wang GP. *Sol. Energy Mater. Sol. Cells.* 2006; 90:1052–1057.
9. Deshmukh MP, Nagaraju J. *Sol. Energy Mater. Sol. Cells.* 2005; 89:403–408.
10. Gerung H, Boyle TJ, Zhao Y, Wang L, Jain RK, Han SM. *Appl. Phys. Lett.* 2006; 89:111107–111109.
11. Lambert TN, Andrews NL, Gerung H, Boyle TJ, Oliver JM, Wilson BS, Han SM. *Small.* 2007; 3:691–699. [PubMed: 17299826]
12. Hernandez-Sanchez BA, Boyle TJ, Lambert TN, Daniel-Taylor SD, Oliver JM, Wilson BS, Lidke DS, Andrews NL. *IEEE Transactions on Nanobioscience.* 2006; 5:222–230. [PubMed: 17181020]
13. Sze, SM. *Physics of Semiconductor Devices Vol.* John Wiley & Sons, Inc.; New York: 1981.
14. Rosetti R, Hull R, Gibson JM, Brus LE. *J. Chem. Phys.* 1985; 83:1406–1410.
15. Takagahara T, Takeda K. *Phys. Rev. B.* 1992; 46:15578–15581.
16. Melnikov DV, Chelikowsky JR. *Solid State Commun.* 2003; 127:361–365.
17. Bostedt C, van Buuren T, Willey TM, Franco N, Terminello LJ, Heske C, Moller T. *Appl. Phys. Lett.* 2004; 84:4056–4058.
18. Warner JH, Tilley RD. *Nanotechnology.* 2006; 17:3745–3749.
19. Mathur S, Shen H, Donia N, Rugamer T, Sivakov V, Werner U. *J. Am. Chem. Soc.* 2007; 129:9746–9752. [PubMed: 17629271]
20. Gerion D, Zaitseva N, Saw C, Casula MF, Fakra S, Van Buuren T, Galli G. *Nano Letters.* 2004; 4:597–602.
21. Gerung H, Boyle TJ, Tribby LJ, Bunge SD, Brinker CJ, Han SM. *J. Am. Chem. Soc.* 2006; 128:5244–5250. [PubMed: 16608360]
22. Wu YY, Yang PD. *Chemistry of Materials.* 2000; 12:605.
23. Mathur S, Shen H, Sivakov V, Werner U. *Chem. Mater.* 2004
24. Morales AM, Lieber CM. *Science.* 1998; 279:208–211. [PubMed: 9422689]
25. Hanrath T, Korgel BA. *Journal of the American Chemical Society.* 2002; 124:1424–1429. [PubMed: 11841311]
26. Hanrath T, Korgel BA. *Advanced Materials.* 2003; 15:437–440.
27. Shah PS, Hanrath T, Johnston KP, Korgel BA. *Journal of Physical Chemistry B.* 2004; 108:9574–9587.
28. Hanrath T, Korgel BA. *Journal of the American Chemical Society.* 2004; 126:15466–15472. [PubMed: 15563174]
29. Wagner RS, Ellis WC. *Applied Physics Letters.* 1964; 4:89–90.
30. Zaitseva N, Harper J, Gerion D, Saw C. *Applied Physics Letters.* 2005; 86:053105.
31. Wang DW, Dai HJ. *Angewandte Chemie-International Edition.* 2002; 41:4783–4786.
32. Gerung H, Bunge SD, Boyle TJ, Brinker CJ, Han SM. *Chemical Communications.* 2005:1914–1916. [PubMed: 15795786]
33. Xia YN, Yang PD, Sun YG, Wu YY, Mayers B, Gates B, Yin YD, Kim F, Yan YQ. *Advanced Materials.* 2003; 15:353–389.
34. Heath J, Legoues F. *Chemical Physics Letters.* 1993; 208:263–268.
35. Taylor BR, Kauzlarich SMH, Lee HW, Delgado GR. *Chem. Mater.* 1998; 10:22–24.
36. Xuchu M, Fengyi W, Kauzlarich SM. *J. Solid St. Chem.* 2008; 181:1628–1633.
37. Bard, AJ.; Parsons, R.; Jordan in, *J. Standard Potentials in Aqueous Solutions Vol.* New York: IUPAC; 1985.
38. Boyle TJ, Hernandez-Sanchez BA, Baros CM, Rodriguez MA, Brewer LN. *Chem. Mater.* 2007; 19:2016–2026.

39. Boyle TJ, Bunge SD, Alam TM, Holland GP, Headley TJ, Avilucea G. *Inorg. Chem.* 2005; 44:1309–1318. [PubMed: 15732971]
40. Boyle TJ, Bunge SD, Andrews NL, Matzen LE, Sieg K, Rodriguez MA, Headley TJ. *Chem. Mater.* 2004; 16:3279–3288.
41. Stanciu S.S CH, Stender M, Richards AF, Olmstead MM, Power PP. *Inorg. Chem.* 2005; 44:2774–2780. [PubMed: 15819565]
42. Allen FH. *Acta Cryst.* 2002; B58:380–388.
43. Stanciu C, Richards AF, Stender M, Olmstead MM, Power PP. *Polyhedron.* 2006; 25:477–483.
44. Pineda LW, Jancik V, Starke K, Oswald RB, Roesky HW. *Angew. Chem., Int. Ed.* 2006; 45:2602–2605.
45. Weinert CS, Fenwick AE, Fanwick PE, Rothwell IP. *Dalton Trans.* 2003:532–539.
46. Bazinet P, Yap GPA, Richeson DS. *J. Am. Chem. Soc.* 2001; 123:11162–11167. [PubMed: 11697959]
47. Veith M, Mathur C, Huch V. *J. Chem. Soc., Dalton Trans.* 1997:995–999.
48. Meller A, Ossig G, Maringele W, Noltemeyer M, Stalke D, Herbst-Irmer R, Freitag S, Sheldrick GM. *Z. Naturforsch., B: Chem. Sci.* 1992; 47
49. Fjeldberg T, Hitchcock PB, Lappert MF, Smith SJ, Thorne AJ. *Chem. Commun.* 1985:939–941.
50. Lappert MF, Slade MJ, Atwood JL, Zaworotko MJ. *Chem. Commun.* 1980:621–622.
51. Cetinkaya B, Gumrukcu I, Lappert MF, Atwood JL, Rogers RD, Zaworotko MJ. *J. Am. Chem. Soc.* 1980; 102:2088–2089.
52. Hahn FE, Zabula AV, Pape T, Hepp A. *Eur. J. Inorg. Chem.* 2007:2405–2408.
53. Driess M, Yao S, Brym M, van Wullen C. *Angew. Chem. Int. Ed.* 2006; 45:4349–4352.
54. Herrmann WA, Denk M, Behm J, Scherer W, Klingan F-R, Bock H, Solouki B, Wagner M. *Angew. Chem., Int. Ed.* 1992; 31:1485–1488.
55. Fedushkin IL, Skatova AA, Chudakova VA, Khvoinova NM, Baurin AY, Dechert S, Hummert M, Schumann H. *Organometallics.* 2004; 23:3714–3718.
56. Kuhl O, Lonnecke P, Heinicke J. *Polyhedron.* 2001; 20:2215–2222.
57. Gans-Eichler T, Gudat D, Nattinen K, Nieger M. *Chem. -Eur. J.* 2006; 12:1162–1173. [PubMed: 16250060]
58. Zabula AV, Hahn FE, Pape T, Hepp A. *Organometallics.* 2007; 26:1972–1980.
59. Schnepf A. *Z. Anorg. Allg. Chem.* 2006; 632:935–938.
60. Chorley RW, Hitchcock PB, Lappert MF, Leung W-P, Power PP, Olmstead MM. *Inorg. Chim. Acta.* 1992; 198:203.
61. Veith M, Rammo A. *Z. Anorg. Allg. Chem.* 2001; 627:662–668.
62. Ding YQ, Ma QJ, Roesky HW, Herbst-Irmer R, Uson I, Noltemeyer M, Schmidt HG. *Organometallics.* 2002; 21:5216–5220.
63. Zemlyansky NN, Borisova IV, Kuznetsova MG. *Organometallics.* 2003; 22:1675–1681.
64. Leung W-P, Kan K-W, So C-W, Mak TC. *Appl. Organomet. Chem.* 2007; 21:814–818.
65. Kersting B, Krebs B. *Inorg. Chem.* 1994; 33:3886–3892.
66. Bradley DC. *Chem. Rev.* 1989; 89:1317–1322.
67. Bradley, DC.; Mehrotra, RC.; Gaur, DP. *Metal Alkoxides.* Academic Press; New York: 1978.
68. Caulton KG, Hubert-Pfalzgraf LG. *Chem. Rev.* 1990; 90:969–995.
69. Chandler CD, Roger C, Hampden-Smith MJ. *Chem. Rev.* 1993; 93:1205–1241.
70. Hubert-Pfalzgraf LG. *New. J. Chem.* 1987; 11:663–675.
71. Turova, NY.; Turevskaya, EP.; Kessler, VG.; Yanovskaya, MI. *The Chemistry of Metal Alkoxides.* Kluwer Academic Publishers; Boston: 2002.
72. Boyle TJ, Tribby LJ, Bunge SD. *Eur. J. Inorg. Chem.* 2006:4553–4563.
73. Lappert, P.P, MFP.; Sanger, AR.; Srivastava, RC. *Metal and Metalloid Amides*, Vol. Chichester, U.K.: Halsted Press; 1980.
74. O'Hare PAG, Curtiss LA. *J. Chem. Thermodynamics.* 1995; 27:643–662.
75. Davidson PJ, Harris DH, Lappert MF. *J. Am. Chem. Soc., Dalton Trans.* 1976:2268–2274.

76. Veith M, Hans J, Stahl L, May P, Huch V, Sebold A. *Z. Naturforsch., Teil B.* 1991; 16:403–424.
77. Smith GD, Fanwick PE, Rothwell IP. *Inorg. Chem.* 1990; 29:3221–3226.
78. Krivokapic A, Anderson HL, Bourhill G, Ives R, Clark S, McEwan KJ. *Adv. Mater.* 2001; 13:652–656.
79. Veith M, Hobein P, Rosler R. *Z. Naturforsch., B: Chem. Sci.* 1989; 44:1067–1081.
80. Nehete UN, Chandrasekhar V, Roesky HW, Magull J. *Angew. Chem., Int. Ed.* 2005; 44:281–284.
81. Patai, S.; Rappoport in, *Z. The Chemistry of Organic Germanium, Tin and Lead Compounds*, Vol. 1-2. New York: Wiley; 1995-2002.
82. Lappert S.J MFM, Atwood JL, Zaworotko MJ, Carty AJ. *J. Organomet. Chem.* 1981; 212:C4–C6.
83. Lesbre, M.; Mazerolles, P.; Satgé in, *J. The Organic Compounds of Germanium* vol. New York: Wiley-Interscience; 1971. p. 702
84. Weatherby AE Jr, Goeller LR, DiPasquale AG, Rheingold AL, Weinert CS. *Inorg. Chem.* 2007; 46:7579–7586. [PubMed: 17691771]
85. Weinert CS. *Main Group Met. Chem.* 2003; 30
86. Ossig G, Meller A, Bronneke C, Muller O, Schafer M, Herbst-Irmer R. *Organometallics.* 1997; 16:2116–2120.
87. Herzog U, Bohme U, Brendler E, Rheinwald G. *J. Organomet. Chem.* 2001; 630:139–148.
88. Herzog U, Rheinwald G. *Organometallics.* 2001; 20:5369–5374.
89. Herzog U, Borrmann H. *J. Organomet. Chem.* 2003; 675:42–47.
90. Klasens HA, Backer HJ. *Rec. Trav. Chim. Pays-Bas.* 1939; 58:941–947.
91. Pfeiffer J, Noltemeyer M, Meller A. *Z. Anorg. Allg. Chem.* 1989; 572:145–150.
92. Chen D-H, Chiang H-C, Ueng C-H. *Inorg. Chim. Acta.* 1993; 208:99–101.
93. Holmes RR, Day RO, Sau AC, Holmes JM. *Inorg. Chem.* 1986; 25:600–606.
94. Drake JE, Mislanker AG, Yang J. *Inorg. Chem.* 1992; 31:5543–5548.
95. Perakis A, Kotsalas IP, Pavlatou EA, Raptis C. *Phys. Stat. Sol. (b).* 1999; 211:421–427.
96. Gysling HJ, Luss HR. *Organometallics.* 1989; 8:363–368.

Figure 1. Structure plot of **1**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 2. Structure plot of **2**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 3. Structure plot of **3**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 4. Structure plot of **4**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 5. Structure plot of **5**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 6. Structure plot of **6**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 7.
Structure plot of **7**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 8. Structure plot of **8**. Thermal ellipsoid plots are drawn at 30 % level. Carbon atoms drawn as ball and stick and hydrogens omitted for clarity.

Figure 9.
TGA of compounds 1 – 8.

Figure 10.
Powder XRD of Ge(0) nanocrystals from **1** and nanowires from **5** showing the characteristic cubic germanium crystal structure.

Figure 11.
TEM images of Ge-based nanomaterials synthesized from: (a) **1**, (b) **2**, (c) **3**, (d) **5**, (e) **6**, (f) **7**.

Table 1Structural and analytical data for **1 – 8**.

Cmpd	Ligand Type	Solid State Structure	Solution Behavior	Decomp. Temp. (°C)	Nano Morph	AR	EDS	PXRD
1	NR ₂	di	di	180	ND	1	Ge	Ge(0)/Cubic
2	OR	di	mono	200	NW	20	Ge	Ge(0)/Cubic
3	OR	mono	mono	200 – 300	NW	13	Ge	Ge(0)/Cubic
4	OR/OSiR ₃	di	di	130	-----	-----	-----	-----
5	OSiR ₃	di	mono	110	NW	50	Ge	Ge(0)/Cubic
6	OSiR ₃	mono (+4)	mono	200 – 280	NW	50	Ge	Ge(0)/Cubic
7	SSiR ₃	di	mono	260 – 400	Amorph	NA	Ge/S	Amorph
8	SR	mono (+4)	mono	230	-----	-----	-----	-----

----- not used as a precursor;

AR = aspect ratio,

ND = nanodot;

NW = nanowire

Table 2

Data collection parameters for **1 – 8**

Compound	1	2	3	4
chem. form.	C ₃₂ H ₃₆ Ge ₂ N ₄	C ₃₂ H ₃₆ Ge ₂ O ₄	C ₃₆ H ₂₆ GeO ₂	C ₂₀ H ₄₈ Ge ₂ O ₄ Si ₂
form. wt	621.83	629.79	563.16	553.94
temp (K)	144(2)	203(2)	203(2)	173(2)
space group	Monoclinic <i>P2₁/n</i>	Orthorhombic <i>Pca2₁</i>	Orthorhombic <i>Pccn</i>	Monoclinic <i>C2/c</i>
<i>a</i> (Å)	8.7362(8)	17.014(5)	22.0568(19)	23.361(3)
<i>b</i> (Å)	9.1574(8)	10.879(3)	11.0189(9)	14.455(2)
<i>c</i> (Å)	18.7120(16)	16.282(5)	11.6412(10)	16.994(2)
β (deg)	95.9070(10)			90.344(2)
<i>V</i> (Å ³)	1489.0(2)	3013.7(15)	2829.3(4)	5738.5(14)
<i>Z</i>	2	4	4	8
D _{calc'd} (mg/m ³)	1.386	1.388	1.324	1.282
μ, (Mo, Kα) (mm ⁻¹)	2.045	2.028	1.115	2.198
R1 ^a (%) (all data)	6.02 (6.32)	6.15 (7.74)	2.85 (3.36)	3.41 (4.97)
wR2 ^b (%) (all data)	11.47 (11.59)	11.78 (12.37)	7.41 (7.74)	8.25 (9.18)
Compound	5	6	7	8
chem. form.	C ₂₄ H ₆₀ Ge ₂ O ₄ Si ₄	C ₅₄ H ₄₆ GeO ₃ Si ₃	C ₇₂ H ₆₀ Ge ₂ S ₄ Si ₄	C ₂₄ H ₂₀ GeS ₄
form. wt	670.26	899.79	1310.98	509.23
temp (K)	203(2)	203(2)	203(2)	203(2)
space group	Monoclinic <i>P2₁/c</i>	Monoclinic <i>P2₁/n</i>	Monoclinic <i>C2/c</i>	Orthorhombic <i>Pba2</i>
<i>a</i> (Å)	10.948(4)	21.580(3)	31.370(3)	8.595(5)
<i>b</i> (Å)	14.225(5)	9.9527(11)	9.2183(9)	16.852(10)
<i>c</i> (Å)	23.645(8)	24.529(3)	23.357(2)	8.142(5)
β (deg)	90.336(5)	113.988(2)	105.996(2)	
<i>V</i> (Å ³)	3682.0(2)	4813.4(9)	6492.7(11)	1179.3(12)
<i>Z</i>	4	4	4	2
D _{calc'd} (mg/m ³)	1.209	1.242	1.341	1.434
μ, (Mo, Kα) (mm ⁻¹)	1.786	0.753	1.170	1.661
R1 ^a (%) (all data)	7.71 (11.91)	4.80 (7.02)	5.59 (6.80)	4.69 (6.35)
wR2 ^b (%) (all data)	19.49 (21.60)	10.69 (11.54)	11.27 (11.77)	7.10 (7.65)

$$^a \text{R1} = \Sigma ||\text{F}_\text{O}| - |\text{F}_\text{C}|| / \Sigma |\text{F}_\text{O}| \times 100$$

$$^b \text{wR2} = [\Sigma w (\text{F}_\text{O}^2 - \text{F}_\text{C}^2)^2 / \Sigma (w |\text{F}_\text{O}|^2)^2]^{1/2} \times 100$$