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Formation and Structures of Germanium(II) Aryloxo/Oxo Clusters

Rebecca A. Green,[†] Curtis Moore,[‡] Arnold L. Rheingold,[‡] and Charles S. Weinert*,[†]

[†]*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, and* [‡]*Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093-0303*

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The reaction of $Ge[N(SiMe_3)_2]_2$ with a phenol lacking a substituent in one ortho position results in the formation of polynuclear clusters having terminal aryloxide ligands and bridging O atoms. Structures of this type have not been observed for germanium(II) aryloxides before, and the source of the bridging O atoms in these clusters was determined to be the phenol reactant.

Recent interest in germanium(II) compounds has arisen because of their utility as molecular precursors for germanium-based nanomaterials, which are expected to overcome some of the shortcomings of current silicon-based materials because of the higher electron and hole mobility and smaller band gap in germanium.[1−3] The nature of the ligands attached to the Ge^{II} center in the precursor has an impact on the morphology of the resulting nanomaterials. For example, the germanium(II) amide $Ge[N(SiMe_3)_2]_2$ has been used for the preparation of Ge nanocrystals,[4] but the aryloxide species $Ge(OC_6H_3Bu^t_2\text{-}2,6)_2$ generates Ge nanowires.[5] There is a high probability that variation of the aryloxide ligands in germanium(II) aryloxide precursors will also have an effect on the nature of the resulting Ge nanomaterials, but complexes of this type are still relatively uncommon, and therefore the establishment of a library of these materials is an important endeavor.

The germanium(II) aryloxides that have been prepared and structurally characterized typically adopt one of two possible structural motifs.[5−16] These species can be monomeric or dimeric, where the latter structure includes two terminal and two bridging aryloxide ligands, leading to a Ge_2O_2 rhombus in the center of the molecule. The preference for one structure over the other appears to be related to the steric attributes of the aryloxide ligands because the complexes $[Ge(OAr)_2]_2$ (ArO = $OC_6H_2Me_3$-2,4,6 or $OC_6H_3\text{-}Pr^i_2$-2,6) are dimeric[8] while the complexes $Ge(OAr)_2$ (ArO = $OC_6H_3Ph_2$-2,6,[8] $OC_6H_3Bu^t_2$-2,6,[5] or $OC_6H_2Bu^t_2$-2,6-Me-4[6]) are monomeric. In order to probe the steric threshold for formation of the dimeric structure, we treated the germanium(II) amide $Ge[N(SiMe_3)_2]_2$ with 2 equiv of either $HOC_6H_3Bu^t$-2-Me-6 or $HOC_6H_3Bu^t$-2-Me-4. The former reaction yielded the monomeric complex $Ge(OC_6H_3Bu^t\text{-}2\text{-}Me\text{-}6)_2$ (**1**); however, the latter reaction furnished two Ge^{II} clusters containing terminal aryloxide ligands and bridging O atoms that have unprecedented structures.

$$Ge[N(SiMe_3)_2]_2 + 2\ HOC_6H_3Bu^t\text{-}2\text{-}Me\text{-}6 \xrightarrow[\substack{12\ \text{h},\ 25\ ^\circ\text{C} \\ -2HN(SiMe_3)_2}]{C_6H_6} \underset{\mathbf{1},\ 72\%}{Ge(OC_6H_3Bu^t\text{-}2\text{-}Me\text{-}6)_2} \qquad (1)$$

The structure of **1**, prepared from $Ge[N(SiMe_3)_2]_2$ and 2 equiv of $HOC_6H_3Bu^t$-2-Me-6 (eq 1) in 72% yield, is shown in the Supporting Information. Compound **1** crystallizes with two independent molecules in the unit cell, and the average Ge−O distance is 1.809(2) Å, which is similar to those in other monomeric germanium(II) aryloxides. The average O−Ge−O bond angle of 90.83(9)° is very close to the

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*To whom correspondence should be addressed. E-mail: weinert@chem.okstate.edu.

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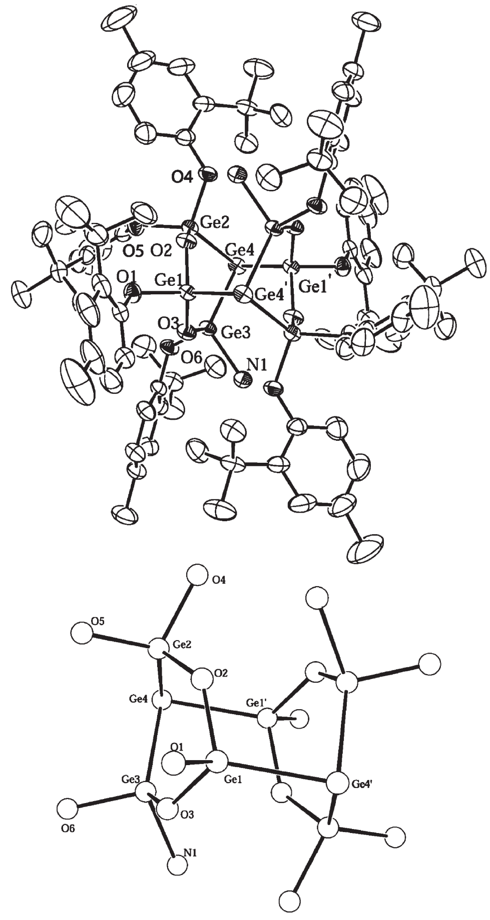
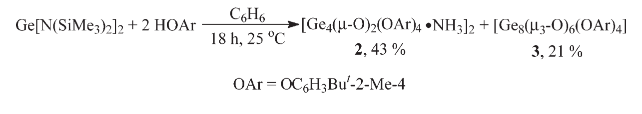


Figure 1. ORTEP diagram (top, thermal ellipsoids are drawn at 50% probability) and molecular structure (bottom) of **2**·2C$_6$H$_6$.

Scheme 1. Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ with 2 equiv of HOC$_6$H$_3$Bu^t-2-Me-4



$$\mathrm{Ge[N(SiMe_3)_2]_2 + 2\ HOAr \xrightarrow[18\ h,\ 25\ ^\circ C]{C_6H_6} \underset{\mathbf{2},\ 43\ \%}{[Ge_4(\mu\text{-}O)_2(OAr)_4 \bullet NH_3]_2} + \underset{\mathbf{3},\ 21\ \%}{[Ge_8(\mu_3\text{-}O)_6(OAr)_4]}}$$

$$\mathrm{OAr = OC_6H_3Bu^{\mathit{t}}\text{-}2\text{-}Me\text{-}4}$$

expected value of 90°. Treatment of Ge[N(SiMe$_3$)$_2$]$_2$ with 2 equiv of HOC$_6$H$_3$Bu^t-2-Me-4 furnished two different germanium aryloxide products, **2** and **3** (Scheme 1), which were selectively crystallized out of solution using benzene or hexane/toluene as the solvent, and both of these compounds have previously unknown structural motifs. The silyl ether Me$_3$SiOC$_6$H$_3$Bu^t-2-Me-4 (**4**) and a second byproduct, which appears to be the amine HN(C$_6$H$_3$Bu^t-2-Me-4)$_2$ (vide infra), were also detected in the product mixture. The dimeric species [Ge$_4$(μ-O)$_2$(OC$_6$H$_3$Bu^t-2-Me-4)$_4$·NH$_3$]$_2$ (**2**) was obtained in 43% yield upon crystallization from a hot benzene solution, and ORTEP and molecular structure diagrams of **2** are shown in Figure 1.

All four Ge atoms in **2** are in the 2+ oxidation state, and **2** contains two Ge$_4$O$_2$ rings related by a center of inversion that are held together by two Ge–Ge single bonds that measure 2.499(1) Å. The two Ge–Ge bonds within the individual Ge$_4$O$_2$ rings measure 2.482(1) and 2.492(1) Å, and all three of these distances are typical for Ge–Ge single bonds.[17] The Ge2–Ge4–Ge3 angle is 83.03(2)°, which is significantly more acute than the ideal angle of 90°, while the Ge2–Ge4–Ge1′ [88.04(3)°] and Ge3–Ge4–Ge1′ [85.28(4)°] angles are closer to the ideal bond angle. The Ge4 atom is attached to three other Ge atoms, while Ge2 and Ge3 are connected to Ge1 via two μ-O atoms. The Ge–μ-O distances in **2** are relatively uniform in length with an average value of 1.783(2) Å, and the Ge–O distances to the terminal aryloxide ligands lie within the typical range, with an average value of 1.801(2) Å. A molecule of ammonia, shown as N1 in Figure 1, is bound to Ge3 with a Ge–N bond distance of 1.998(2) Å, which is indicative of a dative Ge–N interaction. The source of the ammonia is the silylation reaction that converts HOC$_6$H$_3$Bu^t-2-Me-4 to **4**. Silylation reactions of –OH moieties that involve the conversion of –N(SiMe$_3$)$_2$ groups to NH$_3$ have been previously described.[7,12,18] For example, one hydroxyl group of 3,3′-bis(trimethylsilyl)binaphthol is converted to a silyl ether upon reaction with Ge[N(SiMe$_3$)$_2$]$_2$.[7,12] The environment about Ge1 and Ge2 in **2** is approximately tetrahedral, with average bond angles of 108.99(8) and 109.04(9)°, respectively. However, at each Ge atom, the Ge–Ge–O angles [114.83(8) and 116.24(8)°] are significantly more obtuse than the O–Ge–O angles [103.14(8) and 101.84(8)°]. A similar environment is present at Ge3, which has an average bond angle of 108.83(9)°, while Ge4 is present in a distorted pyramidal geometry, with an average Ge–Ge–Ge angle of 85.45(3)°.

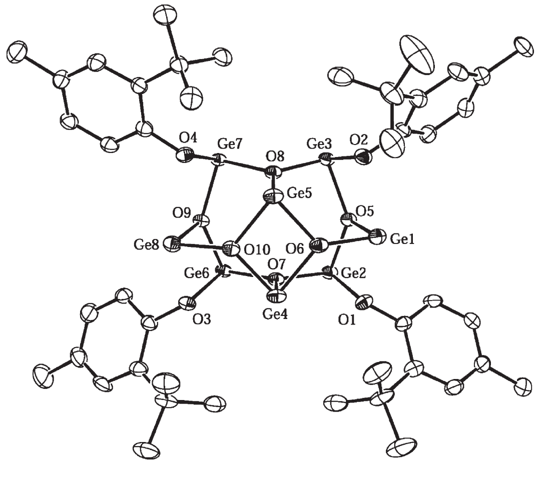


Figure 2. ORTEP diagram of **3**·2C$_6$H$_6$. Thermal ellipsoids are drawn at 50% probability.

The second product isolated in 21% yield from the reaction shown in Scheme 1 was the cluster [Ge$_8$(μ_3-O)$_6$(OC$_6$H$_3$Bu^t-2-Me-4)$_4$] (**3**), via recrystallization from a hexane/toluene solvent mixture at −35 °C. An ORTEP diagram of **3** is shown in Figure 2. Complex **3** contains eight Ge atoms held together by six μ_3-O atoms, and four terminal aryloxide ligands are also present; thus, all eight of the Ge atoms in **3** are in the 2+ oxidation state. A Ge$_4$O$_4$ eight-membered ring containing Ge2, Ge3, Ge6, Ge7, O5, O7, O8, and O9 is present in **3** (Figure 2). The environment about O5, O7, O8, and O9 in **3** can be regarded as a distorted trigonal-planar geometry, with average Ge–O–Ge bond angles of 117.6(1), 120.0(1), 120.0(1), and 118.2(1)°, respectively. The four Ge atoms in the Ge$_4$O$_8$ ring adopt a highly distorted pyramidal geometry, with bond angles of 88.1(1), 89.8(1), 88.4(1), and

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90.4(1)° for Ge2, Ge3, Ge6, and Ge7, respectively. A Ge_2O_2 rhombus, which has been reported for several other germanium(II) aryloxide species,[8,10,11,14] is also present in **3**. The bond angles within the rhombus average 99.6(1) and 80.4(1)° for the Ge–O–Ge and O–Ge–O angles, respectively, which are similar to those found in related germanium(II) aryloxide structures. The Ge_2O_2 rhombus is tethered to the Ge_4O_4 macrocycle by two bridging Ge atoms, having O–Ge–O bond angles of 90.1(1) and 91.3(1)°, which are close to the expected value of 90°.

The bond distances in **3** from the Ge atoms to the O atoms of the terminal aryloxide ligands are long compared to those in monomeric or dimeric germanium(II) aryloxides and vary from 1.891(3) to 1.994(3) Å, with an average value of 1.950(3) Å. The Ge–O distances within the Ge_4O_4 macrocycle also span a wide range, from 1.878(2) to 1.928(3) Å, with an average value of 1.906(2) Å. The Ge–O distances within the Ge_2O_2 rhombus average 1.948(3) Å, while those between the O atoms in the Ge_2O_2 rhombus and Ge1 and Ge8 are short and average 1.882(3) Å. The remaining Ge–O distances, which connect the Ge_2O_2 rhombus to the Ge_4O_4 macrocycle either directly or via the two bridging Ge atoms, average 1.954(3) and 1.930(3) Å, respectively. The Ge–O distances between the Ge and O atoms are therefore longer than those typically found between Ge and μ_2-O atoms, and overall these distances span the wide range between 1.878(3) and 1.994(3) Å.

Analysis of the reaction mixture by gas chromatography/mass spectrometry (GC/MS) lead to the identification of two volatile components. The first was identified as the silyl ether **4**, which exhibited a retention time of 12.1 min and a mass spectrum that contained a molecular ion peak at *m*/*z* 236 as well as a second peak at *m*/*z* 221 corresponding to the loss of a methyl group. The presence of **4** was further confirmed by analysis of an authentic sample of this material[19] that exhibited the same retention time and mass spectrum. These findings indicate that some of the phenol $HOC_6H_3Bu^t$-2-Me-4 is silylated to form **4** via reaction with $HN(SiMe_3)_2$, which is also the source of NH_3 found in the structure of **2**. The second volatile component exhibited a retention time of 17.5 min and a mass spectrum with a molecular ion at *m*/*z* 309. This species is tentatively assigned as the amine $HN(C_6H_3Bu^t\text{-2-}CH_3\text{-4})_2$, which incorporates the remaining portion of the phenol $HOC_6H_3Bu^t$-2-Me-4 left from transfer of oxygen to the clusters **2** and **3**.

Monitoring the reaction of $Ge[N(SiMe_3)_2]_2$ with $HOC_6H_3Bu^t$-2-Me-4 by ^1H NMR spectroscopy indicated that that complete consumption of the phenol and concomitant formation of $HN(SiMe_3)_2$ occurred immediately after mixing of the two reagents. Five resonances at δ 7.15, 7.00, 6.71, 2.11, and 1.50 were also observed, which correspond to an intermediate germanium aryloxide product that we speculate to be the dimeric species $[Ge(OC_6H_3Bu^t\text{-2-Me-4})_2]_2$. These features disappeared from the spectrum after 3.5 h, and several additional resonances had appeared at this time, suggesting that other intermediate species were present. The presence of clusters **2** and **3** was detected in the reaction mixture after a reaction time of 1.5 h, and after 18 h, only resonances for **2**, **3**, and the byproducts **4** and $HN(C_6H_3Bu^t\text{-2-Me-4})_2$ were present.

No further change was observed in the ^1H NMR spectrum of the reaction after 18 h, but exposure of the NMR tube to dioxygen gas resulted in the complete conversion of **2** to **3** within 6 h, suggesting that **2** is an intermediate formed along the pathway that generates the cluster **3**. The interconversion of **2** to **3** must involve migration of the aryloxide ligands and also insertion of oxygen into the Ge–Ge bonds of **2**, and the latter process has been reported for several germanium species that contain Ge–Ge bonds.[20–23] Because the germanium-to-oxygen ratio in **3** is 4:5, the reaction of a 4:5 stoichiometric ratio of $Ge[N(SiMe_3)_2]_2$ to $HOC_6H_3Bu^t$-2-Me-4 was monitored by ^1H NMR spectroscopy, which indicated that the formation of cluster **3** was complete within 8 h. The presence of **2** was also detected during the course of this reaction, but none of this material remained after the reaction had concluded, and therefore all of the bridging O atoms in cluster **3** result from the phenol reagent. The same reaction carried out on a preparative scale provided cluster **3** in 74% yield.

In conclusion, it has been determined that the reaction of $Ge[N(SiMe_3)_2]_2$ with a phenol substrate lacking substitution in one ortho position can lead to the formation of large germanium(II) aryloxide/oxo clusters having bridging O atoms, where the source of the bridging O atoms is the phenol reactant. Phenol substrates that bear substituents in both of the ortho postions yield either a monomeric or dimeric product. The large Ge_8 cluster **3** is of interest from a structural standpoint because a large aggregate containing only divalent Ge atoms has not been previously described. In addition, the preparation of Ge^0 nanomaterials from **3** might also furnish species having unusual morphologies because **3** contains an ensemble of Ge atoms while precursors currently employed for these investigations contain only one or two Ge atoms. The synthesis of other Ge_n cluster complexes from $Ge[N(SiMe_3)_2]_2$ and other sterically unencumbered phenols, as well as investigations into the use of these compounds as molecular precursors for germanium nanomaterials, is currently underway.

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Supporting Information Available: Full experimental and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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