Applications of Germanium Compounds
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Germanium compounds have emerged as critically important materials in the fabrication of microelectronics, optics and sensors. Potential new applications in organic transformations and polymer synthesis have also been reported. This article highlights some of the chemistry associated with these applications. It also compares and contrasts the chemistry of germanium with the more widely understood chemistry of silicon. For readers with a deeper interest in the chemistry of germanium, comprehensive reviews provide a detailed description.1,2,3,4,5

Metallic Germanium and Metallization Chemistry
Germanium is a semiconductor. In fact, germanium was the first material to be fabricated into practical semiconductor devices, diodes. As a consequence, a significant body of literature relating to the electrical properties of germanium has developed. The mobility of holes in germanium is greater than that of silicon and of any other common semiconductor. The hole and electron mobilities are closer in germanium than other semiconductors, particularly at low temperatures. This has made germanium an attractive candidate for high performance CMOS technology. In high speed digital communications associated with broadband and cell-phones, SiGe films are used to fabricate heterojunction bipolar transistors (HBTs). In other high speed applications SiGe films are deposited as molecular films which act as templates for the epitaxial deposition of silicon. The resulting lattice mismatch creates a strained silicon layer which exhibits enhanced electron mobility, providing improved device performance. SiGe technology has the potential to replace GaAs in many applications. Other electronic applications of metallic germanium and its alloys include quantum dots, amorphous films for solar energy and LEDs.6,7

Germane, GeH₄, in combination with silane, SiH₄, is the most widely used germanium precursor for chemical vapor deposition (CVD) of SiGe films. Other precursors include methylgermane, n-butylgermane, t-butylgermane and diethylgermane.8

A broader range of germanium compounds have been used to synthesize germanium nanowires including diphenylgermane9,10 and germanium tetraiodide11,i. Amorphous a-GeCO:H films have been deposited from tetramethylgermane by PECVD.12

Bulk germanium metal, fabricated from wafers, is currently of interest in the fabrication of monolithic fiber-optic receivers, since germanium photodiodes perform well at 1.3-1.5 micron wavelengths. Germanium metal is also of utility in infrared detectors, which comprise the metal’s largest current use.

Inorganic Germanium Chemistry
Bond energies of Ge-X bonds are generally considered to be about 10% less than corresponding Si-X bonds. This is reflected in the somewhat lower thermal stability of germanium compounds. The electronegativities of germanium and silicon are 2.01 and 1.90, respectively, on the Pauling scale; their configuration energies are 11.80 eV and 11.33 eV, respectively. While silicon is apparently more electropositive than germanium, reactivity indicates that polarization parameters may be more equivalent. Valence states of +2 are readily accessible for germanium and GeCl₂, GeBr₂ and GeI₂ are isolable compounds. In contrast, silicon dihalides are known as reactive intermediates by studies of emission bands or trapping experiments. The chemistry of both elements proceeds primarily in the +4 state, although hyper-coordinate states, particularly for fluorocompounds, are known.

Both silicon and germanium metal react with halogens and hydrogen halides to give analogous products. Halides of both elements react rapidly with water to give oxides and hydroxides. Germanium oxides can be converted back to the halides by reaction with the appropriate acid. In the case of silicon, only hydrofluoric acid reacts with the oxides to form fluorosilanes.

Germanium compounds have higher optical densities than silicon compounds. This leads to the second major application of germanium compounds: the controlled combustion of germanium tetrachloride with silicon tetrachloride in a hydrogen-oxygen flame in chemical vapor axial deposition (CVAD) for the formation of ingots from which step-index fiber optics are drawn.14,15 Tetaethoxy-germane is a liquid metal-organic precursor with a high vapor pressure that is well-suited for CVD of germanium oxide in optical16 and dielectric17 applications. Sol-gel processing has also been employed as a method of preparing mixed germanium oxides. Again, tetraethoxygermane is the most widely used metal-organic precursor, but other germanium alkoxides containing methoxy and isoproxy groups are used.18

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Organic Chemistry

In contrast to silicon, sterically hindered organogermanium compounds in the +2 state are readily isolated. Examples include dicyclopentadienylgermanium, di[bis(trimethylsilyl)methyl]germanium and bis[bis(trimethylsilyl)amino]germanium.

The bis[bis(trimethylsilyl)amino]germanium forms poly(germanium enolates) upon reaction with $\alpha,\beta$-unsaturated ketones.$^{19}$

Di[bis(trimethylsilyl)amino]germanium also reversibly binds H$_2$ and CO$_2$ in 3-coordinate complexes.

Germanium dihalides, GeI$_2$ and GeCl$_2$ and its readily prepared complexes GeCl$_2$-etherate and GeCl$_2$-dioxanate react with alkyl and aryl halides$^{20}$ to yield alkyl and aryl germanium trihalides.

Most germanium proceeds in the +4 state and is comparable to silicon. The following enumeration is extremely incomplete.

Grignards and alkali metal organics will displace halides bound to germanium and silicon to give the organo-substituted compound.

Germanium forms Ge-Ge bonds readily through Grignard chemistry in addition to alkali metal coupling, which is the most accessible route for Si-Si bond formation. While Si-Si bonds can be readily cleaved by Na-K in ether, Ge-Ge are cleaved only under more rigorous conditions such as the use of higher boiling solvents like tetrahydrofuran. In both cases multiple metal-metal bonds give photoreactive compounds.

Organogermanium and organosilicon compounds can both be prepared by the copper catalyzed direct reaction of alkyl and aryl halides with the metal.

Silicon undergoes migration from carbon to oxygen in the Brook rearrangement of $\alpha$-silyl ketones. Germanium does not appear to undergo a similar migration.

Doubly bonded silicon-silicon and germanium-germanium compounds have been demonstrated, but are not representative of large classes of chemistry for the elements.

Perfluorinated methyl and ethyl germanes are isolable and stable. Simple trifluoromethyl(methyl)silanes have only recently been prepared. Other perfluorinated methyl and ethyl silanes are thermally unstable, decomposing above 80°.

Repeating silicon-oxygen bonds tend to form extended linear polymers in preference to cyclic structures. Repeating germanium-oxygen bonds tend to form cyclic structures in preference to extended linear polymers.

In contrast to silicon hydrides, germanium hydrides readily undergo metallation. For example, the reaction of triphenylgermane with butyl lithium followed by carbonation yields triphenylgermanecarboxylic acid.

Like organosilanes, organogermanes can be fluorodemetallated. Additionally, organogermanes can be demetallated with bromine.
Germanium hydrides and silicon hydrides react with olefins in hydrogermylation and hydrosilylation reactions. Both are catalyzed by platinum compounds, but catalysis is not a requirement for hydrogermylation. Trichlorogermane is particularly reactive and reaction products are associated with both hydrogermylation and dichlorogermene insertion.21

**Germanium in Organic Synthesis**

For a variety of reasons applications of organogermanes in organic synthesis are limited, while applications of organosilanes in organic synthesis are well-developed. Until recently organogermanes have had relatively poor availability compared to organosilanes. Also, the germanium oxygen bond is somewhat more susceptible to hydrolysis compared to the silicon oxygen bond. Beyond these facts, the largest determinant for differences in applications is the higher cost of germanium compounds. Consequently, only unique applications of organoger- manium compounds are likely to be of importance. Potential applications include trimethylgermylacetonitrile as a carbanion source, trimethylbromogermane and trimethylchlorogermane employed in the preparation of masked dienolates in a variety of regioselective syntheses, trichlorogermane for ether cleavage, and germanium diiodide and cesium trichlorogermetanate for conversion of alkyl halides to alkylgermyltrihalides.

The palladium catalyzed cross-coupling reactions of germanium compounds have been investigated.22,23,24 Tri-n-butylgermane is an effective reducing agent. It reduces benzylic chlorides 70x faster than silyl hydrides and reduces acyl chlorides to aldehydes in the presence of Pd(0).

**Polymers and Polymerization**

The most commercially important application of germanium compounds are as catalysts in polymerization of polyester. Non-yellowing polyester fibers and clear polyester beverage bottles are produced by germanium dioxide and hydroxygermatrane catalyzed condensation of dimethyl terephthalate and selected diols. Copolymers have been prepared from organogermanes with polymerizeable functionality, including allyl, vinyl27 and methacrylate28 groups.
REFERENCES:

5. V. I. Davydov, Germanium, Gordon & Breach, 1966
18. see specific references in the germanium compound section following this article
20. F. Riedmiller et al, Organometallics, 1999, 18, 4317
Stable Homonuclear Double and Triple Bonded Germanium Species and Their Reactions

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“Although germanium is only slightly larger than silicon, it is too large for any \( \pi \)-overlap and no multiple bonded germanium compounds are known.”1

There was widespread agreement with this opinion until relatively recently,2 but in the last quarter of the 20\(^{th}\) century and the beginning decade of the 21\(^{st}\) the synthesis of numerous stable compounds that contain multiple bonds to germanium and other heavier main group elements has not only vitiated this statement, but has also changed our perception of bonding itself. Germanium compounds have played a key role in effecting this change. This is because group 14 element compounds have occupied a central position in the study of multiple bonding among heavier main group elements and germanium is the central element in group 14. In many respects its multiple bonded derivatives represent a transition point in the geometrical, bonding and reactivity changes that occur with increasing atomic number. In this article we provide a brief summary of two classes of multiple bonded germanium compounds. These are the germanium congeners of the double bonded olefins (digermenes) or the triple bonded alkynes (digermynes).

The first multiple bonded germanium species to be isolated had their origin in the work of Lappert and his group in the 1970s. The original objective of their work was the preparation of stable heavier group 14 element carbene analogues of formula: \( \text{ER}_2 \) (\( E = \text{Si, Ge, Sn, or Pb} \); \( R = \text{amido or alkyl group} \)). The key element of the synthetic approach was simply to use large ligands such as the amido or alkyl groups \(-\text{N(SiMe}_3\text{)}_2\) or \(-\text{CH(SiMe}_3\text{)}_2\) to achieve stability by preventing association via ligand bridging or \(E-E\) bond formation. A very simple salt elimination route sufficed to isolate the first red tin and purple lead dialkyl species: \( \text{ER}_2 \) via reaction of the lithium salt of the ligand with the metal dihalide,3 but the corresponding yellow germanium dialkyl \( \text{Ge}\{\text{CH(SiMe}_3\text{)}_2\}_2 \) was most conveniently obtained via the reaction of \( \text{Ge}\{\text{N(SiMe}_3\text{)}_2\}_2 \) with two equivalents of \( \text{LiCH(SiMe}_3\text{)}_2 \).4,5 Like its tin counterpart: \( \text{Ge}\{\text{CH(SiMe}_3\text{)}_2\}_2 \) existed as carbene-like monomers in solution5 and could behave as a Lewis base donor toward transition metals.5 However, it was later shown to have a Ge-Ge double bonded dimeric structure7 of formula \( (\text{Dis})_2\text{GeGe(Dis)}_2 \), \( \text{Dis} = \text{CH(SiMe}_3\text{)}_2 \) (like its tin counterpart \((\text{Dis})_2\text{SnSn(Dis)}_2 \)) in the solid state.4,5,7

\[
\text{Ge}\{\text{N(SiMe}_3\text{)}_2\}_2 + 2 \text{LiDis} \quad \rightarrow \quad 2 \text{LiN(SiMe}_3\text{)}_2 + \text{Ge(Dis)}_2 \quad \quad \text{Scheme 1}
\]

The most surprising aspect of the tin and germanium structures was that they were not planar like ethylene but had a trans-pyramidalized structure with local \( C_{2h} \) symmetry at the \( C_2E=EC_2 \) (\( E = \text{Ge or Sn} \)) cores. Moreover the GeGe and SnSn bond lengths were only slightly shortened compared to single bonds. Synthetic and structural results like these initiated a revolution not only in main group chemistry but have also led to new insights in chemical bonding.9,10,11 Numerous classes of multiple bonded germanium compounds now exist12,13,14,15,16,17 but the scope of this review is confined to stable species with double or triple bonds between two germanium atoms.
DIGERMENES

Syntheses of Digermenes

Whereas the first digermene was synthesized by Lappert via a salt elimination route, several different synthetic approaches have since been developed. These include photochemical conversions, various elimination reactions as well as insertion routes which are summarized in the following sections.

Photochemical Conversions

A photochemical conversion led to the first structural characterization of a stable digermene in the solid state in 1984 by the group of Masamune. Photolysis of \((\text{Ar}_2\text{Ge})_3\) (\(\text{Ar} = 2,6\)-dimethylphenyl or 2,6-diethylphenyl) afforded of \(\text{Ar}_2\text{Ge} = \text{GeAr}_2\) as shown in Scheme 2.\(^{18}\)

![Scheme 2: Photochemical route to digermenes](image)

The Ge-Ge bond length was found to be 2.213(2) Å which is considerably shorter than the single bond distance of 2.44 Å and the coordination of the Ge atoms displayed pyramidal distortion in which the germanium was displaced by 0.15 Å from the plane formed by the two ipso-carbons and the other germanium. Similar structural data were found for tetrakis(2,4,6-triisopropylphenyl)digermene \(^{19}\) (GeGe = 2.213(1) Å) whereas the tetrakis(mesityl)digermene, \(^{20}\) which was synthesized by the same route in 2007, shows a slightly longer Ge-Ge distance of 2.2856(8) Å. These structures had a greater pyramidal distortion (pyramidal displacement = 0.42 Å) than the corresponding disilenes with the same ligands (e.g. Mes\(_2\)Si=SiMes\(_2\), Mes = -C\(_6\)H\(_2\)-2,4,6-Me\(_3\); displacement = 0.22 Å) \(^{21}\) but a smaller one than distannenes such (Dis\(_2\))Sn=Sn(Dis\(_2\)) (displacement = 0.61 Å) \(^{7}\).

Reductive Elimination Synthetic Routes

Reductive elimination reactions are a well established method for synthesis of multiple bonded germanium species. These are usually effected by dehalogenation or salt elimination reactions.

Masamune and co-workers used lithium naphthalenide as a reducing agent for dichloro(2,6-disisopropylphenyl)mesitylgermane (Dipp(Mes)GeCl\(_2\)), Dipp = C\(_6\)H\(_3\)-2,6-iPr\(_2\). Under elimination of lithium chloride the product was formed as two isomers with the Z isomer being more stable than the E isomer but only the Z variant crystallized upon concentration of a solution of the reaction mixture.\(^{22}\) The GeGe bond length is 2.301(1) Å. It was shown by kinetic studies that isomerization proceeds in a straightforward way via rotation around the GeGe bond axis and not through a thermal dissociation-recombination mechanism.

![Scheme 3](image)

\[
2 \text{Dipp(Mes)GeCl}_2 + \text{Li naphthalenide} \rightarrow \text{Dipp(Mes)GeGe(Mes)Dipp}
\]

\(E\) and \(Z\) isomers
Reduction of dichlorobis(diisopropylmethylsilyl)germane with a sodium dispersion afforded the tetrakis(trialkylsilyl)digermene. As shown by the group of Kira\textsuperscript{23} the trialkyl substituents enforce a nearly planar geometry around the GeGe bond and no twisting is observed. The distance between the two germanium atoms is 2.268(1) and 2.266(1) Å, respectively, and is thus shorter than in Dis\textsubscript{2}GeGeDis\textsubscript{2} (2.3458(7) Å)\textsuperscript{7} or Dipp(Mes)GeGe(Mes)Dipp (2.3011(9) Å)\textsuperscript{22}.

\begin{equation}
2 \text{(R}_3\text{Si)}_2\text{GeCl}_2 \xrightarrow{2 \text{Na}} \text{(R}_3\text{Si)}_2\text{Ge\equivGe(SiR}_3\text{)_2}}
\end{equation}

Scheme 4

The use of lithium naphthalenide as reducing agent for Tbt(Mes)GeCl\textsubscript{2} (Tbt = C\textsubscript{6}H\textsubscript{2}-2,4,6-[CH(SiMe\textsubscript{3})\textsubscript{3}]) by Tokitoh and coworkers afforded MesTbtGeGeMesTbt. The GeGe bond length (2.416(3) Å) in this compound is considerably longer than GeGe double bond lengths of other reported digermenes with carbon substituents and is very close to a normal GeGe single bond of GeGe = 2.44 Å in elemental germanium. Elongation of the GeGe double bond is consistent with the very large size of the substituents. Considerable geometrical distortion, which also involves twisting of the geometry around the GeGe axis, was also observed\textsuperscript{24}.

\begin{equation}
2 \text{Tbt(Mes)GeCl}_2 \xrightarrow{\text{Li naphthalenide}} \text{Tbt(Mes)Ge\equivGe(Mes)Tbt}
\end{equation}

Scheme 5

Reaction of a tetrachloro digermane with 1,1-dilithiosilane R\textsubscript{2}SiLi\textsubscript{2} (R = SiMe\textsuperscript{t}Bu\textsubscript{2}) afforded a heavier group 14 element cyclopropene along with a linear digermene via salt elimination\textsuperscript{25,26}. The GeGe double bond in the three membered ring is a relatively short one (2.2429(5) Å).

\begin{equation}
\text{RCl}_2\text{GeGeCl}_2\text{R} \xrightarrow{\text{R}_2\text{ELi}_2 (xs)} \text{-2 LiCl} \xrightarrow{R_2\text{E}\equiv\text{ER}_2}
\end{equation}

Scheme 6

The use of terphenyl groups (Ar\textsuperscript{t} = C\textsubscript{6}H\textsubscript{2}-2,6(C\textsubscript{6}H\textsubscript{3}-2,6-\textsuperscript{t}Pr\textsubscript{2})\textsubscript{2} or Ar\textsuperscript{*} = C\textsubscript{6}H\textsubscript{2}-2,4,6(C\textsubscript{6}H\textsubscript{3}-2,6-\textsuperscript{t}Pr\textsubscript{3})\textsubscript{2}) as sterically encumbering ligands enabled halogeno substituted digermenes to be isolated. These species, which are in equilibrium with the corresponding monomeric germylenes, allow further digermenes to be readily synthesized by replacement of the chlorines\textsuperscript{27}. The chlorines can be substituted by methyl, ethyl or phenyl groups in a salt elimination reaction with the corresponding lithium reagents. In contrast the analogous terphenyl tin (II) chlorides display trans-bridged structures with no tin-tin bond.\textsuperscript{27} Corresponding dihydrodigermenes can be easily obtained via reaction of the chloro derivatives with LiB(s-Bu\textsubscript{3})H.\textsuperscript{28} The product has crystallographic 2/m symmetry in which the C-Ge-Ge-C array is incorporated in the mirror plane with a Ge-Ge distance of 2.3724(9) Å. The GeGe bond length is longer than average (see below in Table 1) probably as a result of steric effects.
Reaction of the cationic tricyclic species \((\text{GeSi}^\text{Bu}_3)_3^+\) (with a \(\text{B(Ar}_F)_4^-\) counter anion; \(\text{Ar}_F = -\text{C}_6\text{F}_5\)) with potassium halide afforded the halogen-substituted cyclotrigermene.\(^{29}\) The GeGe double bond (2.2743(8) Å) and the GeGe single bonds (2.4191(9) and 2.4200(9) Å) are relatively short. These effects are explained by introduction of an electronegative group at the endocyclic \(\text{sp}^3\) germanium atom and accordingly with the \(\sigma^*\)-aromaticity concept.\(^{29}\)

Weidenbruch and co-workers showed that tetragermanium 1,3-butadiene could lead to digermene when it is reacted with 2-methoxyphenyl isocyanate.\(^{30}\) During the reaction an initial germylene cleavage occurs. The four membered ring is planar but it is not clear if the neighboring GeGe and CN double bonds are conjugated. The digermene also formed in this reaction \(\text{Tripp}_2\text{GeGeTripp}_2\) (\(\text{Tripp} = \text{C}_6\text{H}_2-2,4,6^-'\text{Pr}_3\)) had been obtained previously.\(^{19,31,32}\) The GeGe bond lengths in this molecule were reported to be 2.2894(6) and 2.2635(15) Å, respectively.
Synthesis via Insertion Reactions

Another interesting approach for the synthesis of ring species containing GeGe double bonds was described by Sekiguchi’s group. Reaction of a three membered ring with GeCl₂ dioxane to afford an insertion reaction and a four membered ring product as shown by.\textsuperscript{33}

![Scheme 10](image)

PROPERTIES

Digermenes are usually colored diamagnetic compounds with the $n_+ \rightarrow n_-$ or $n \rightarrow p$ electronic transitions as the chromophore. Digermenes can dissociate to germylene monomers in solution when the substituents are sufficiently large. Whereas disilenes are usually dimeric in solid state as well as in solution. About half of the digermenes dissociate into monomers in solution whereas almost all distannenes are dissociated when dissolved. They can act as electrophilic compounds.

Structural aspects and bonding

![Scheme 11](image)

In contrast to olefins which usually have planar structures, digermenes typically display considerable distortion from this ideal. These distortions can be defined with use of a number of different parameters that include not only the length of the double bond between germanium atoms, but also the angular parameters $\beta$ and $\tau$ illustrated above in Scheme 11. Instead of $\beta$ also the geometrical displacement of the germanium atom above the plane of the connected atoms can be used to describe the molecular geometry accurately.

The strength of the double bond between the two germanium atoms is relatively low. This, and the observed geometry can be interpreted as a double donor-acceptor bond or, alternatively, by the valence bond representation.\textsuperscript{7}
The molecular orbital (MO) treatment of their bonding also affords valuable insights. In this approach the geometrical distortions are explained on the basis of mixing of anti-bonding and bonding levels within the molecule. This mixing is a second order Jahn-Teller (SOJT) effect\textsuperscript{25-27} which arises from a symmetry allowed, intramolecular mixing of an anti-bonding orbital with a bonding orbital (generally the HOMO (highest occupied molecular orbital) in multiple bonded species)\textsuperscript{28,29}. This can lead to very large deformations in molecular geometry because the orbital mixing introduces non-bonding, lone pair character in a HOMO (originally a purely $\pi$-orbital) which can have a drastic effect on molecular shape\textsuperscript{30}. The extent of the mixing is inversely proportional to the energy separation of the orbitals and this is maximized in the heavier elements because the weakened bonding often permits a close approach (<4eV) of the molecular levels. The initial stages of the SOJT distortion and orbital interactions are shown in Scheme 12.

Scheme 12

The GeGe bond lengths in digermenes (Table 1) can be strongly influenced by the spatial and electronic properties of the coordinating ligands. However, a correlation between steric bulk around the germanium and its double bond length is not feasible\textsuperscript{34,35,36}. The nature of the ligands also influences the twisting and bending around the GeGe double bond. It can be seen from Table 1 that the GeGe bond lengths in digermenes vary from ca. 2.21 to 2.50 Å and have an average value of ca. 2.32 Å. Thus the shortest (and presumably the strongest) Ge-Ge double bonds are about 9.4 % shorter than the 2.44 Å single bond length in elemental germanium.
#### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>GeGe [Å]</th>
<th>trans-bending [°]</th>
<th>twisting [°]</th>
<th>color</th>
<th>λ_{max} [nm]</th>
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<tr>
<td>(Disi)2Ge=Ge(Disi)2</td>
<td>37</td>
<td>2.3458(7)</td>
<td>32</td>
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<td>18</td>
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<td>15</td>
<td>11</td>
<td>yellow</td>
<td>263, 412</td>
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<tr>
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<td>63</td>
<td>2.3025(3)</td>
<td>45</td>
<td>not reported</td>
<td>orange</td>
<td>434</td>
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<tr>
<td>Me3Ge=GeMes2</td>
<td>38</td>
<td>2.2855(7)</td>
<td>33.4</td>
<td>2.9</td>
<td>yellow</td>
<td>not reported</td>
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<tr>
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<td>22</td>
<td>2.3011(9)</td>
<td>36</td>
<td>not reported</td>
<td>yellow</td>
<td>280, 412</td>
</tr>
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<td>TrippGe=GeTripp</td>
<td>19</td>
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<td>12.3</td>
<td>13.7</td>
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<td>2.3724(9)</td>
<td>20.5</td>
<td>not reported</td>
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<td>(N(R')C6H3)(N(R')Si(SiGeGe double bonds in four-membered cycles</td>
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<td>not reported</td>
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<tr>
<td>Compound</td>
<td>Ref.</td>
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<td>twisting [°]</td>
<td>color</td>
<td>λ_{max} [nm]</td>
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<td>2.2642(2)</td>
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<td>red</td>
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<tr>
<td>(DiBu3Ge)Ge=Ge(Bu3Ge)2</td>
<td>49</td>
<td>2.2403(3)</td>
<td>not reported</td>
<td>not reported</td>
<td>dark red</td>
<td>not reported</td>
</tr>
</tbody>
</table>

* No energy minimum was found for the trans-bent form. The introduction of electropositive substituents leads to rather small trans bent angles.

see → Ref. 43
REACTIVITY

Digermenes display a wide variety of reactions. The range of such reactions is quite diverse but most of them can be classified as additions, coordination reactions or reductions. Products that ensue from the reactions of dissociated digermenes (i.e. germynes) are not considered in this section.

Addition Reactions

Addition of Lewis acids or multiple bonded species such as O\(_2\), isonitriles, azides, butadiene, N\(_2\)O and diazomethane, to double bonds are well known from the chemistry of olefins and more recently from the chemistry of disilenes. Addition reactions of digermenes have also been extensively studied.

Oxygen

Reactions of digermenes with dioxygen have been investigated by several research groups. Very shortly after their structures had been established, digermenes were shown to react with oxygen by a 1,2-addition process affording 3,4-digermadioxetanes which rearrange to 2,4-digermadioxetanes with irradiation.\(^51\) The GeGe distance (2.441(2) Å) in the 3,4-digermadioxetane is essentially the same as a normal GeGe single bond length (2.44 Å).\(^52\)

In 2003 Tokitoh and coworkers showed that exposure of solid TbtMesGe=GeTbtMes to an oxygen atmosphere in the absence of light led to the formation of trans-1,3,2,4-dioxadigermetanes in two conformational isomers. Formation of the corresponding cis isomer was not observed. Interestingly, when the reaction was conducted with a digermene in solution a mixture of one of the trans isomers and the cis isomer were formed. Most likely this can be explained by a dissociation of the digermene into two germylene fragments in solution which react with dioxygen.\(^24\) The Ge-Ge distances (2.653(2), 2.660(2) and 2.691(4) Å, respectively) are much longer than typical Ge-Ge single bonds (2.457-2.463 Å).\(^53,54\) This is in contrast to the behaviour of the analogous silicon species in which the separation can be even shorter than typical Si-Si single bond lengths. This can be explained by the shorter Si-O bond lengths which impose closer Si...Si approaches.
Exposure of digermene stabilized by 1,4-di-tert-butylbenzene ligands afforded a trigerm-1,3-dioxolane product as shown by Weidenbruch's group.\textsuperscript{55}

The geometry of the five-membered ring is nearly planar. The Ge-Ge bond length of 2.513(1) Å is slightly longer than a typical GeGe single bond. Earlier, Baines and coworkers had shown that the addition of O\textsubscript{2} to tetramesityldigermene resulted in the formation of a 3,4-digermadioxetane with subsequent insertion of a germylene into the O-O single bond.\textsuperscript{56}

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Digermaoxirane was formed as part of the reaction mixture and proved to be relatively stable since it could be stored for several months under ambient conditions without decomposition. Nevertheless, attempts at a direct synthesis from digermene and m-chloroperbenzoic acid failed even though a similar approach had been used for the preparation of disilaoxiranes by West and coworkers. Instead, only 1,3 digermadioxetane, the pentacycle and only in very small amounts the digermaoxirane were obtained.

A tetragermabuta-1,3-diene was reacted with dry air to yield in a tetraoxatetragermabicyclo[4.1.1]-octane skeleton. The folded cyclodigermoxane ring can be seen as a result of a [2+4] addition of O₂ to the terminal germanium atoms, followed by a 1,2-addition of a second O₂ molecule.

Diazomethane

MesDipGe=GeDipMes reacted with diazomethane R'HCN₂ (R' = H, SiMe₃) to give an azodigermirane in a [2+1] cycloaddition. No subsequent loss of nitrogen was observed, however. In contrast Ando and coworkers obtained a digermirane in low yield as shown in Scheme 19. The azodigermirane features a GeGe bond with a distance of 2.4237(4) Å, which is typical for a single bond. A similar ring system was isolated as a product of the reaction of tetramesityldisilene with phenyldiazomethane.
**1,3-Butadiene**

1,3-butadienes are well known reagents in olefin chemistry, particularly in connection with Diels-Alder reactions. The first use of 1,3-butadiene in digermene chemistry in 2000 by Sekiguchi involved an attempt to trap the digermene $\text{tBu}_3\text{Si(Cl)}\text{Ge=Ge(Cl)}\text{Si'tBu}_3$ which decomposes during warming above a temperature of $-8^\circ\text{C}$. Its reaction with isoprene and 2,3-dimethyl-1,3-butadiene, respectively, afforded only a single stereoisomer of the addition product.$^{60}$

![Scheme 20](image)

*Scheme 20*

Stereoselective Diels-Alder reactions are extensively studied.$^{60}$ The addition of 1,3-butadienes to a diastereotopic digermene afforded interesting results. For example it has been found that the cis-bent geometry around the Ge=Ge double bond of halogen substituted cyclotrimerenes has an effect on selectivity in the reaction with dimethyl butadiene. Thus, the dimethylbutadiene attacks the GeGe double bond from the side having the bulkier $\text{tBu}_3\text{Si}$ and only one stereoisomer is formed during the reactions. This is opposite to the selectivity of mesityl substituted cyclotrimerenes.$^{61,62,52}$

![Scheme 21](image)

*Scheme 21*

When $\text{Mes}_3\text{Ge=GeMes}_2$ was reacted with 1,3-butadiene, formation of mesityl(trimesitylgermyl)-germacyclopentene was observed. This was explained on the basis of a 1,2 shift of one mesityl group from one to the second germanium atom followed by trapping with the diene. A trapping reaction using $\text{Et}_3\text{SiH}$ led to the same result.$^7$

![Scheme 22](image)

*Scheme 22*
Reactions with Protic Lewis Acids and Halogen Reagents

Reactions of digermenes with protic reagents can either lead to addition products or eliminations. For example, the reaction of digermenes with alcohols has been investigated by several groups. Masamune and coworker observed the addition of methanol to tetra(diethylphenyl)digermene (Ar₂GeGeAr₂). The same reactivity was found for Mes₂GeGeMes₂ and methanol, carbonic acids and chloroform, respectively. In the case of chloroform the addition involved the C-Cl bond rather than the C-H bond.

The reaction of R₂GeGeR₂ (R = 2,5-tBu₂C₆H₃) with water resulted in a digermanol. This is in contrast to reactions of (Dis)₂GeGe(Dis)₂ with ethanol or Tbt(Mes)GeGe(Mes)Tbt with methanol, respectively, which provided the corresponding alkoxides via an elimination reaction.

Interestingly, the reaction of the hexakis(tripp)tetragerma-1,3-butadiene leads not to a direct addition product but to a cyclic oxatetragermapentane as a result of an initial 1,2 addition of water to one of the GeGe double bonds followed by 1,3-hydride shift and ring formation.

Ring compounds featuring GeGe double bonds also react with methylene dichloride and tetrachloro methane at room temperature. In the case of CCl₄ a 1,2-addition occurs and the resulting cyclodigermane can be isolated using an excess of dichloromethane the product of a ring expansion is obtained. For chloroform only formation of a mixture of products was obtained.
Reactions with Heavier Chalcogens

Heating of tetragerma-1,3-butadiene with excess of selenium in the presence of a small amount of Et₃P as a chalcogen transfer reagent afforded the formation of selenatetragermacyclopentene as yellow crystals.³⁰ The same reactivity is observed in the presence of elemental sulfur. Tetramerma-1,3-butadiene forms with sulfur a thiotoriermacyclopentane.⁴³ Both structures are very similar. The five membered ring products are almost planar. The Ge1Ge2 and Ge3Ge4 bond lengths which have an average value mean 2.46 Å are typical for GeGe single bonds, but the Ge2Ge3 bonds, which are 2.2841(5) and 2.2975(5) Å are typical for a GeGe double bond.

![Scheme 26](image)

Scheme 26

Photolysis of trigermirane in the presence of elemental sulfur gave two reaction products. One is the addition product of the formed digermene and sulfur whereas the second product can be viewed as a result of the head-to-tail dimerized germathione, Mes₂Ge=S, intermediate that is formed by reaction of sulfur and the corresponding germylene.⁶⁴

![Scheme 27](image)

Scheme 27

Reaction of digermene dihydride with PMe₃ results in an isomerization reaction to afford a mixed valent species. In this compound the GeGe distance of 2.5304(7) Å is at the longer end of the GeGe single bond range.²⁸,⁶⁵
Reduction Reactions

Reduction of the dihydridigermene Ar'(H)GeGe(H)Ar' with alkaline metals (Li, Na or K) gave highly reactive salts M₂[Ar'(H)GeGe(H)Ar'] as deep red/black crystals. Depending on the nature of the alkali metal counterions the nature of the structural type formed differed. In the potassium salt the [Ar'(H)GeGe(H)Ar']²⁻ core is trans pyramidal with terminal Ge-H bonds and a long GeGe distance of 2.6468(4) Å. In contrast in the sodium salt the [Ar'(H)GeGe(H)Ar']²⁻ core has bridging hydrogen atoms, the GeGe distance with 2.5904(5) Å is long. On the other hand the structure of the lithium salt resembles that of the potassium salt, but has a much shorter GeGe distance of 2.395(2) Å. Theoretical calculations show that the different isomeric structures are close in energy.

DIGERMYNES

These compounds are analogous to their alkyne carbon counterparts. A stable example was first reported in 2002 via the reduction of a digermene. Only a few examples of stable digermynes are currently known although they have already been shown to have a rich chemistry.

Synthesis of digermynes

The synthesis of dichlorobis(terphenyl)digermanes offered not only the chance for further substitution reactions leading to heteroleptic digermanes but also afforded an easy access route for germanium analogues of alkynes. The synthesis of the first stable digermyne by this route was described in 2002. Reduction of Ar'(Cl)GeGe(Cl)Ar' with potassium furnished Ar'GeGeAr' as orange-red crystals. This digermyne has a planar trans bent core and is centrosymmetric. The GeGe distance with 2.2850(6) Å is considerably shorter than a GeGe single bond indicating considerable multiple-bonding character. The Ge-C(ipso) is 1.996(3) Å and the GeGeC bending angle is 128.67(8)°.
A similar reaction was also reported in 2006 by Tokitoh and co-workers.\textsuperscript{69} Starting with BbtBrGeGeBrBbt, Bbt = C\textsubscript{6}H\textsubscript{2}-2,6-(CH(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}-4-C(SiMe\textsubscript{3})\textsubscript{3}, a reduction with KC\textsubscript{8} led to BbtGeGeBbt. For this compound two nonidentical molecules were found in the unit cell. The GeGe bond lengths [2.2060(7) and 2.2260(7) Å] are shorter than that in Ar'GeGeAr'. The GeGeC bending angles vary from 123.60(13) to 138.66(14)° and are in the same range observed for Ar'GeGeAr' (128.67(8)°).

Although Ar'GeGeAr' and BbtGeGeBbt are both digermynes, they show different reactivities which is apparently caused by the different germanium substituents. In Ar'GeGeAr' the bond order is decreased from idealized triply bonded to approximately two and contains some lone-pair character at the germanium atoms. The lower bond order may be accounted for in terms of a second-order Jahn-Teller effect involving the mixing of a $\sigma^*$ orbital and the in plane $\pi$-orbital upon trans bending of the linear skeleton (Scheme 32).\textsuperscript{70,71,72} The structure can also be written in several resonance forms as shown on the left hand side of Scheme 32. One of these has a diradicaloid character form and this is reflected in the reactivity of Ar'GeGeAr' as discussed below.
Reactivity of Ar'GeGeAr'

Ar'GeGeAr' and BbtGeGeBbt displayed different reactivities. When BbtGeGeBbt was heated in presence of Et₃SiH with its reactive Si-H bond no reaction was observed, whereas, during addition reactions with water or methanol formation of the 1,1-dimethoxydigermane and 1,1-dihydroxydigermane, respectively, was observed. Reaction with 2,3-dimethyl-1,3-butadiene yielded the product of a [4+1] addition.⁷⁰

This is in contrast to the observed reactivity of Ar'GeGeAr' and 2,3-dimethyl-1,3-butadiene. Three molecules of 2,3-dimethyl-1,3-butadiene react with one germylene molecule to form two germacyclopentenes bridged via an olefin.⁷³ This difference in reactivity emphasizes the different nature of the GeGe bond in Ar*GeGeAr* versus BbtGeGeBbt.

Reductions

Digermynes can undergo further one and two step reductions with alkali metals. Experiments with stoichiometric quantities of alkali metal reductant (1:1 ratio of alkali metal : Ar'/Ar*GeCl) (Ar* = C₆H₆-2,6-(C₆H₂-2,4,6-Pr₃)₂) showed that the reduced mono- and dianions were produced in addition to the neutral species, especially if short reaction times were used.⁷⁴,⁷⁵ Planarity of the core trans bent geometry as seen in the precursors are preserved in the monoanionic radical and dianionic diradical compounds. No dimerization like that seen for diarylacetylenes⁷⁶,⁷⁷ was observed, presumably because of steric effects. The GeGe distances (NaAr*GeGeAr*: 2.3089(8) Å, KAr'GeGeAr*: 2.3331(4) Å) are slightly longer than observed in the neutral (2.2850(6) Å) compound but the GeGeC angles (112.60(5)-115.32(12)°) are ca. 15° narrower than in Ar'GeGeAr' (128.67(8)°). These changes are probably caused by an increase of the electronegative character of Ge after addition of one electron to the GeGe unit. As a result, the electronegativity of the ligands relative to the central element is increased so that greater bending is observed. The differences between the Ar' and Ar* derivatives are only minor.⁷⁸
Reaction of Ar'GeCl and Ar*GeCl with an excess of lithium, sodium or potassium afforded the doubly reduced salts. The alkali metal countercations are sandwiched between the flanking aryl rings and the structures are very similar. The GeGe distances are somewhat increased (Li: 2.455(9) Å, Na: 2.394(1) Å, K: 2.3912(6) Å) in comparison to the monoanionic salts at 2.32 Å and the GeGeC angles are narrower than those in the monoanions. This is consistent with the addition of the second electron to the n+ orbital of Scheme 32 in the GeGe unit. Also the [Ar'GeGeAr']2- is isoelectronic to double bonded Ar’SbSbAr80 and the GeGe bond can be considered a double one.

Reactions with Unsaturated Molecules

Several of the reactions of Ar'GeGeAr' are suggestive of diradical character (Scheme 36-38). For instance, very recently it has been shown the addition of two equivalents O2 to a bis terphenyl digermyne yielding the unique species {Ar'Ge(O)2(μ1,1;1,μ2-O2)GeAr'}. In this species the two germanium atoms are connected via an peroxo bridge and μ2-oxo groups.80 The Ge–Ge distance is quite short (2.4127(10) Å), although there is no GeGe bond.

In Scheme 37 reaction with the radical TEMPO (tetramethylpiperidineoxide) cleanly affords :Ge(Ar')(TEMPO). Scheme 38 shows that upon reaction with Me3SiN3 the diradicaloid Ar'Ge(μ-NSiMe3)Ge(Ar') is obtained. In addition the reactions of Ar'GeGeAr' with tin reagents is consistent with its radical character. Several of the reactions in Scheme 39 are consistent with the participation of radicals as exemplified by the activation of the flanking aryl ring of an Ar' group upon reaction with Me3SiCCH or the one electron coupling to give a C-C bonded product upon reaction with PhCN.
The reaction of Ar'GeGeAr' with different isonitriles (Scheme 37) showed different reactivity depending on the nature of the isonitrile. The reaction with 'BuNC afforded a 1:1 adduct in which the isonitrile is coordinated to one of the Ge centers. As a consequence the GeGe distance increased slightly (2.3432(8) Å) and has the nature of a double bond. The addition of a second Lewis base molecule was not observed with 'BuNC as Lewis base but when Ar'GeGeAr' was reacted with two equivalents MesNC yielding a digermylene which is a characterized by a very long GeGe bond (2.6626(8) Å).

Scheme 37

Scheme 38
Addition of Hydrogen

The digermene Ar’GeGeAr' reacts spontaneously with hydrogen under ambient conditions to give, depending on the stoichiometry, differing quantities of germanium hydrides Ar'(H)GeGe(H)Ar', Ar'(H)2GeGe(H)2Ar' and ArGeH3. These compounds represent germanium hydrides with formal oxidation states at the Ge atom of +2, +3 and +4, respectively. This was the first example of a successful addition of hydrogen to a main group molecule at ambient conditions (25 °C and 1 atm).

CONCLUSIONS

Digermenes, of which more than thirty have been isolated and characterized, can be readily synthesized by photochemical reactions, insertion routes and various elimination reactions. In contrast to olefins, however, they do not have planar structures but show in most cases a trans pyramidalized geometry and Ge-Ge bond lengths shorter than a single one. The germanium congeners of triple bonded alkynes, digermynes, have been synthesized via reduction of digermenes. These have a trans-bent structure in contrast to their carbon congeners and Ge-Ge bond lengths similar to the “short” Ge-Ge double bonds.
Both digermenes and digermynes have very rich chemistries which have many differences from unsaturated carbon species. The most notable feature is the very high reactivity that is generally observed. This is exemplified by the fact that both digermenes and digermynes react directly with hydrogen – the first example of a reaction between hydrogen and a main group molecule under ambient conditions.

ABBREVIATIONS

Scheme 41
REFERENCES

8. For a summary of all abbreviations: see appendix.
44. Ramaker, G.; Schafer, A.; Saak, W.; Weidenbruch, M. Organometallics 2003, 22, 1302.