

Applications of Germanium Compounds

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Gelest Inc.

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 broad-band 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 diphenylgermane^{9,10} and germanium tetraiodide¹¹. 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.

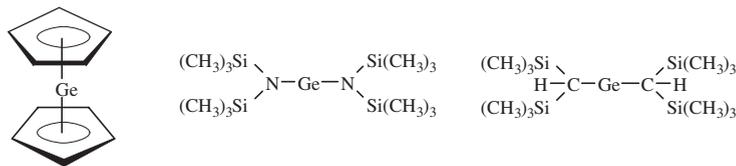
Both silicon and germanium metal react with halogens and hydrogen halides to give analogous products. Halides of both elements react rapidly with water to give oxides and hydroxides. Germanium oxides can be converted back to the halides by reaction with the appropriate acid. In the case of silicon, only 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} Tetraethoxy-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 isopropoxy groups are used.¹⁸

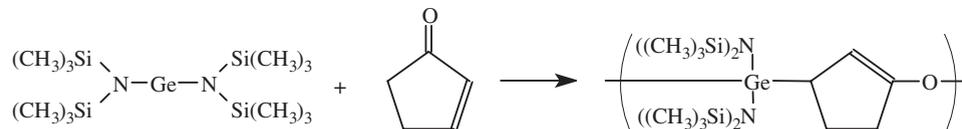
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Organic Chemistry

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.

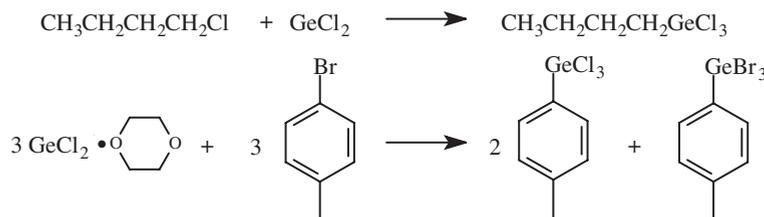


The bis[bis(trimethylsilyl)amino]germanium forms poly(germanium enolates) upon reaction with α,β -unsaturated ketones.¹⁹



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 halides²⁰ 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 α -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.

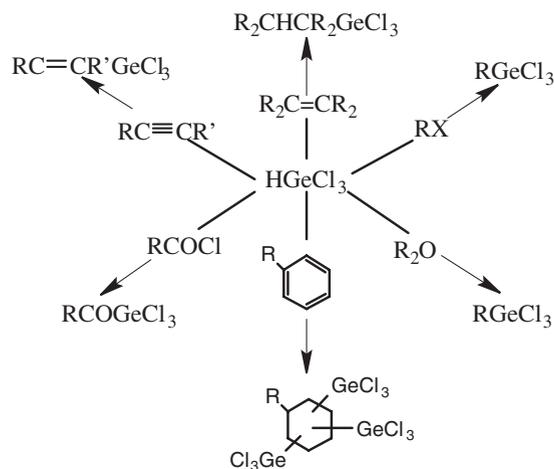
Perfluorinated methyl and ethyl germanes are isolable and stable. Simple trifluoromethyl(methyl)silanes have only recently been prepared. Other perfluorinated methyl and ethyl silanes are thermally unstable, decomposing above 80° .

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 fluorodemetalated. Additionally, organogermanes can be demetalated with bromine.

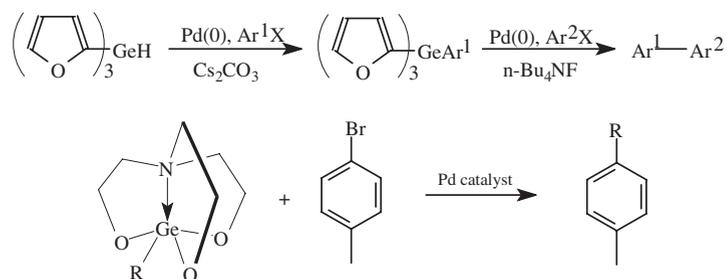
Germanium hydrides and silicon hydrides react with olefins in hydrogermylation and hydrosilylation reactions. Both are catalyzed by platinum compounds, but catalysis is not a requirement for hydrogermylation. Trichlorogermene is particularly reactive and reaction products are associated with both hydrogermylation and dichlorogermene insertion.²¹



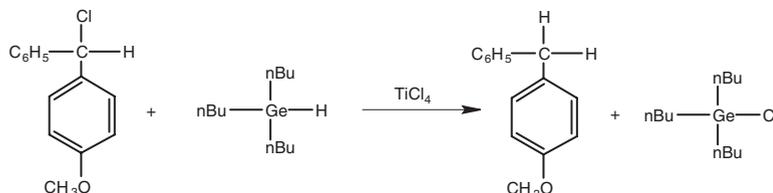
Germanium in Organic Synthesis

For a variety of reasons applications of organogermenes in organic synthesis are limited, while applications of organosilanes in organic synthesis are well-developed. Until recently organogermenes 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 organogermanium compounds are likely to be of importance. Potential applications include trimethylgermylacetonitrile as a carbanion source, trimethylbromogermene and trimethylchlorogermene employed in the preparation of masked dienolates in a variety of regioselective syntheses, trichlorogermene for ether cleavage, and germanium diiodide and cesium trichlorogermanate for conversion of alkyl halides to alkylgermyltrialkyls.

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 organogermenes with polymerizable functionality, including allyl, vinyl²⁷ and methacrylate²⁸ groups.

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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 π -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 20th century and the beginning decade of the 21st 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: ER_2 ($E = Si, Ge, Sn, \text{ or } Pb$; $R = \text{amido or alkyl group}$). The key element of the synthetic approach was simply to use large ligands such as the amido or alkyl groups $-N(SiMe_3)_2$ or $-CH(SiMe_3)_2$ 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: ER_2 via reaction of the lithium salt of the ligand with the metal dihalide,³ but the corresponding yellow germanium dialkyl $:Ge\{CH(SiMe_3)_2\}_2$ was most conveniently obtained via the reaction of $:Ge\{N(SiMe_3)_2\}_2$ with two equivalents of $LiCH(SiMe_3)_2$.^{4,5} Like its tin counterpart: $Ge\{CH(SiMe_3)_2\}_2$ existed as carbene-like monomers in solution⁵ and could behave as a Lewis base donor toward transition metals.⁶ However, it was later shown to have a Ge-Ge double bonded dimeric structure⁷ of formula $(Dis)_2Ge=Ge(Dis)_2$, $Dis = CH(SiMe_3)_2$ ⁸ (like its tin counterpart $(Dis)_2Sn=Sn(Dis)_2$) in the solid state.^{4,5,7}



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 $C_2E=EC_2$ ($E = Ge \text{ or } Sn$) 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 exist^{12,13,14,15,16,17} but the scope of this review is confined to stable species with double or triple bonds between two germanium atoms.

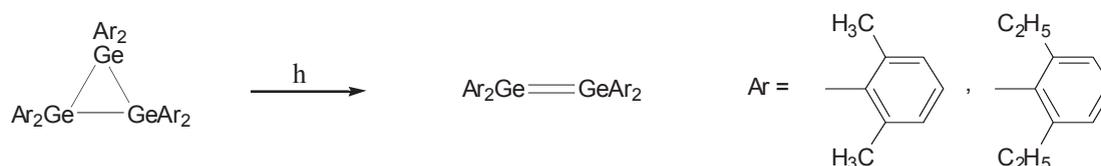
DIGERMENES

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 $(\text{Ar}_2\text{Ge})_3$ (Ar = 2,6-dimethylphenyl or 2,6-diethylphenyl) afforded $\text{Ar}_2\text{Ge}=\text{GeAr}_2$ as shown in Scheme 2.¹⁸



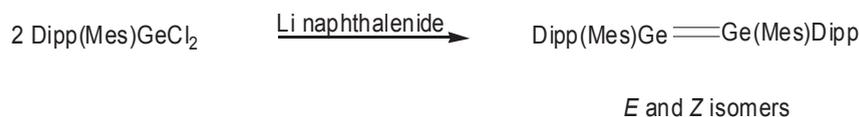
Scheme 2: Photochemical route to digermenes

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)digermene¹⁹ (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. $\text{Mes}_2\text{Si}=\text{SiMes}_2$, Mes = -C₆H₂-2,4,6-Me₃: displacement = 0.22 Å)²¹ but a smaller one than distannenes such as $(\text{Dis})_2\text{Sn}=\text{Sn}(\text{Dis})_2$ (displacement = 0.61 Å)⁷.

Reductive Elimination Synthetic Routes

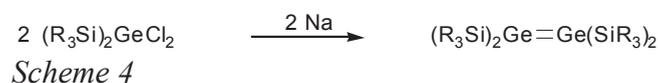
Reductive elimination reactions are a well established method for synthesis of multiple bonded germanium species. These are usually effected by dehalogenation or salt elimination reactions.

Masamune and co-workers used lithium naphthalenide as a reducing agent for dichloro(2,6-diisopropylphenyl)mesitylgermane (Dipp(Mes)GeCl₂), Dipp = C₆H₃-2,6-ⁱPr₂. 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.

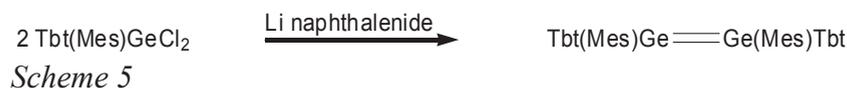


Scheme 3

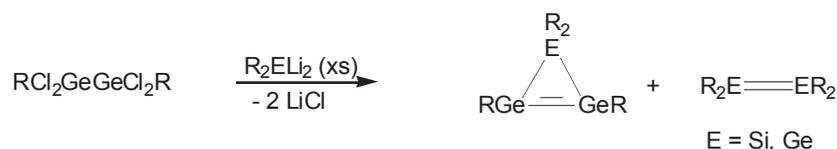
Reduction of dichlorobis(diisopropylmethylsilyl)germane with a sodium dispersion afforded the tetrakis(trialkylsilyl)digermene. As shown by the group of Kira²³ the trialkyl substituents enforce a nearly planar geometry around the GeGe bond and no twisting is observed. The distance between the two germanium atoms is 2.268(1) and 2.266(1) Å, respectively, and is thus shorter than in $\text{Dis}_2\text{GeGeDis}_2$ (2.3458(7) Å)⁷ or $\text{Dipp}(\text{Mes})\text{GeGe}(\text{Mes})\text{Dipp}$ (2.3011(9) Å)²².



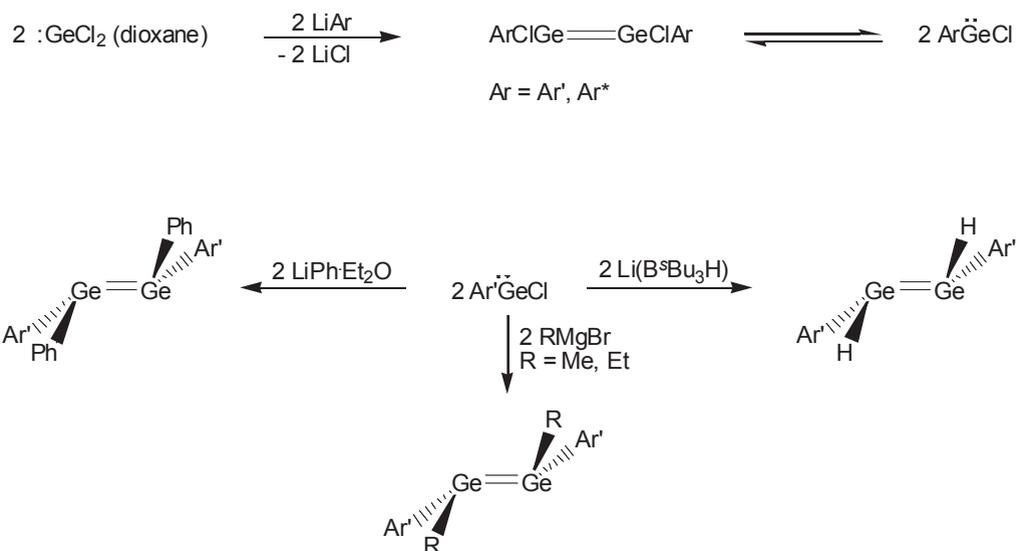
The use of lithium naphthalenide as reducing agent for $\text{Tbt}(\text{Mes})\text{GeCl}_2$ (Tbt = C_6H_2 -2,4,6- $[\text{CH}(\text{SiMe}_3)_2]_3$) by Tokitoh and coworkers afforded MesTbtGeGeMesTbt . The GeGe bond length (2.416(3) Å) in this compound is considerably longer than GeGe double bond lengths of other reported digermenes with carbon substituents and is very close to a normal GeGe single bond of $\text{GeGe} = 2.44$ 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.²⁴



Reaction of a tetrachloro digermene with 1,1-dilithiosilane R_2SiLi_2 ($\text{R} = \text{SiMe}^i\text{Bu}_2$) afforded a heavier group 14 element cyclopropene along with a linear digermene via salt elimination.^{25,26} The GeGe double bond in the three membered ring is a relatively short one (2.2429(5) Å).

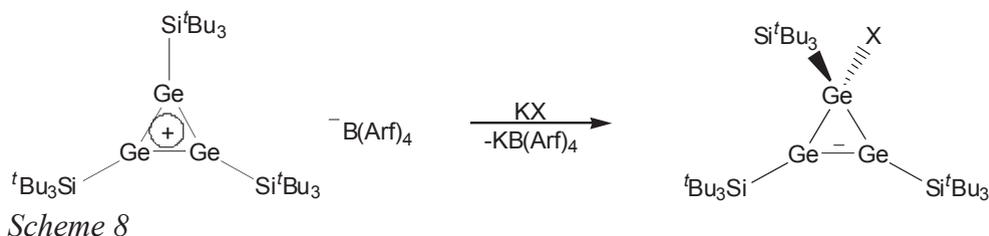


The use of terphenyl groups ($\text{Ar}' = \text{C}_6\text{H}_3$ -2,6(C_6H_3 -2,6- $^i\text{Pr}_2$)₂ or $\text{Ar}^* = \text{C}_6\text{H}_3$ -2,4,6(C_6H_3 -2,6- $^i\text{Pr}_3$)₂) as sterically encumbering ligands enabled halogeno substituted digermenes to be isolated. These species, which are in equilibrium with the corresponding monomeric germynes, allow further digermenes to be readily synthesized by replacement of the chlorines.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.²⁷ Corresponding dihydridigermenes can be easily obtained via reaction of the chloro derivatives with $\text{LiB}(s\text{-Bu}_3)\text{H}$.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.



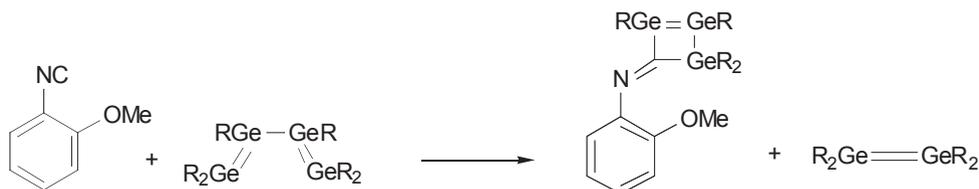
Scheme 7

Reaction of the cationic tricyclic species $(\text{GeSi}^t\text{Bu}_3)_3^+$ (with a $\text{B}(\text{Ar}_F)_4^-$ 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 sp^3 germanium atom and accordingly with the σ^* -aromaticity concept.²⁹



Scheme 8

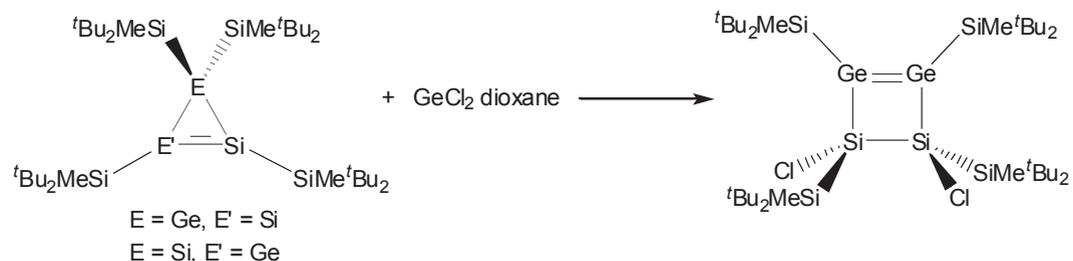
Weidenbruch and co-workers showed that tetragermanium 1,3-butadiene could lead to digermene when it is reacted with 2-methoxyphenyl isocyanate.³⁰ During the reaction an initial germylene cleavage occurs. The four membered ring is planar but it is not clear if the neighboring GeGe and CN double bonds are conjugated. The digermene also formed in this reaction $\text{Tripp}_2\text{GeGeTripp}_2$ ($\text{Tripp} = \text{C}_6\text{H}_2\text{-2,4,6-}^i\text{Pr}_3$) 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.



Scheme 9

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 GeCl_2 dioxane to afford an insertion reaction and a four membered ring product as shown by.³³

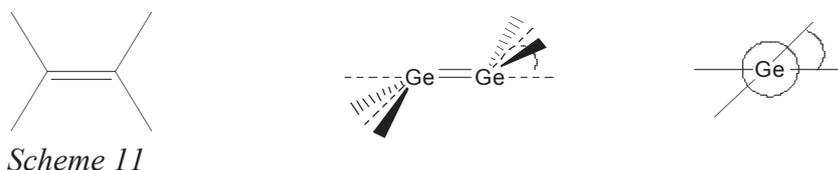


Scheme 10

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

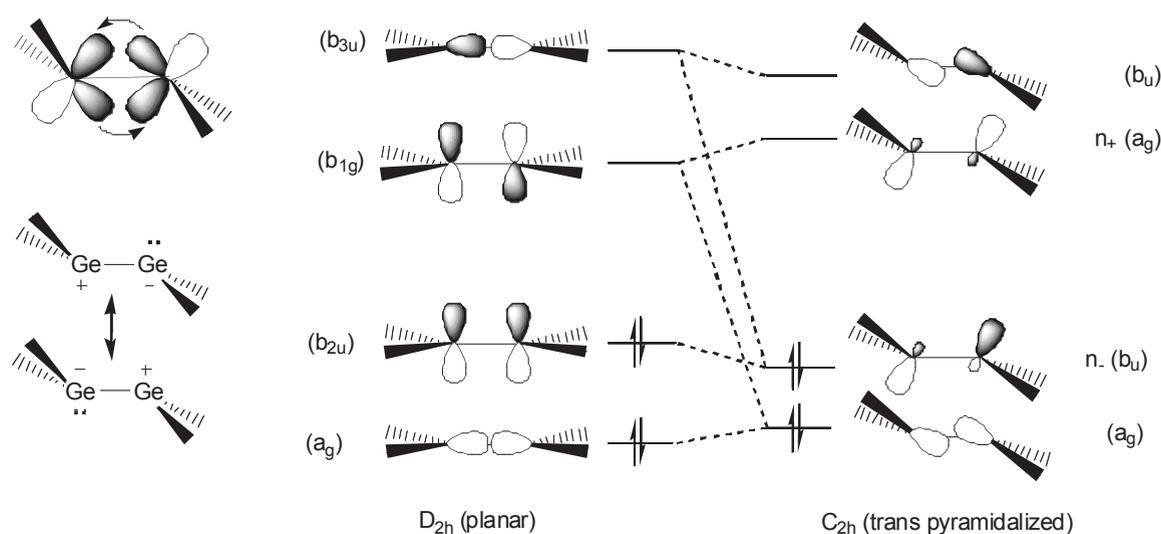


Scheme 11

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 β and τ illustrated above in Scheme 11. Instead of β 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.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) effect²⁵⁻²⁷ 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).^{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 π -orbital) which can have a drastic effect on molecular shape.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.^{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

Compound	Ref.	GeGe [Å]	trans-bending [°]	twisting [°]	color	λ_{\max} [nm]
(Dis) ₂ Ge=Ge(Dis) ₂	37	2.3458(7)	32	0	bright yellow	not reported
(Et ₂ C ₆ H ₃) ₂ Ge=Ge(C ₆ H ₃ Et ₂)	18	2.212(3)	15	11	yellow	263, 412
Ar ^r HGe=GeHAr ^r	83	2.3025(3)	45	not reported	orange	434
Mes ₂ Ge=GeMes ₂	38	2.2855(7)	33.4	2.9	yellow	not reported
MesDippGe=GeMesDipp	22	2.3011(9)	36	not reported	yellow	280, 412
Tripp ₂ Ge=GeTripp ₂	19	2.213(1)	12.3	13.7	pale yellow	not reported
Ar ^r HGe=GeHAr ^r	28	2.3724(9)	20.5	not reported	orange	not reported
(N(R')C ₂ H ₄ N(R'))Si(R) ₂ Ge ₂ R' = ^t Bu	39	2.4541(15)	41.3, 42.3	not reported	dark red	475
(N(R')C ₂ H ₄ N(R'))Si(R) ₂ Ge ₂ R' = ^t Bu, ^t Pr	40	2.4602(8), 2.4528(9)	„much larger than in any other“	63	violet	557
Ar [*] MeGe=GeMeAr [*]	27	2.316(2)	39.7	not reported	yellow-green	not reported
Ar [*] EtGe=GeEtAr [*]	27	2.347(2), 2.271(6)	37.9	not reported	yellow	not reported
Ar [*] PhGe=GePhAr [*]	27	2.318(3)	33.7	not reported	orange	not reported
Ar [*] ClGe=GeClAr [*]	27	2.363(2)	36.8	not reported	orange	not reported
BbtBrGe=GeBrBbt	41	2.5088(8)	44.6	64.2	orange	449
(^t BuMe ₃ C ₆ H) ₂ Ge=Ge(C ₆ H ^t BuMe ₃) ₂	42	2.2521(8)	0	20.4	orange-yellow	not reported
(Me ^t PrSi) ₂ Ge=Ge(SiMe ^t Pr) ₂	43	2.267(2), 2.270(2)	5.9, 7.1	0, 0	yellow	361, 413
(^t Pr ₃ Si) ₂ Ge=Ge(Si ^t Pr) ₂	43	2.2957(2)	16.4	0	pale yellow	472, 432, 367, 332, 277
Ar ^r ClGe=GeClAr ^r	79	2.4626(4)	38.8	not reported	orange	not reported
(TrippGe) ₂ (Tripp ₂ Ge) ₂ Se	30	2.2975(5)	33.4, 35.1	not reported	yellow	399
(TrippGe) ₂ (Tripp ₂ Ge) ₂ S	44	2.2841(5)	29.9, 35.7	not reported	yellow	400
(^t Bu ₂ Ar) ₂ Ge=Ge(Ar ^t Bu) ₂	45	2.3644(4)	37.2, 42.6	not reported	red	425
(Tripp)Ge=Ge(Tripp)- (Tripp)Ge=Ge(Tripp)	46	2.3568(7), 2.3439(5)	not reported	not reported	greenish black, dark blue hexane solution	405, 560
MesTbtGe=GeTbtMes	24	2.416(3)	not reported	16.5, 34.6	orange, hexane solution: r.t. blue low temp. orange yellow	hexane solution: r.t. 575 (germylene); low temp. 439 (digermene)
GeGe double bonds in three-membered cycles						
(^t Bu ₃ SiGe) ₂ Ge(Cl)Si ^t Bu ₃	47	2.2723(9)	trans-bent, not reported	not reported	dark red	not reported
(^t Bu ₃ SiGe) ₂ Ge(Br)Si ^t Bu ₃	47	2.2742(9)	cis-bent, 45.1, 10.2	not reported	dark red	not reported
(^t Bu ₃ SiGe) ₂ Ge(I)Si ^t Bu ₃	47	2.2720(6)	cis-bent, 43.3, 8.0	not reported	dark red	not reported
(^t Bu ₃ SiGe) ₂ Ge(Si ^t Bu ₃)Si(SiMe ₃)	48	2.264(2)	cis-bent: 12.5, 4.4*	not reported	red	not reported
(^t Bu ₃ SiGe) ₂ Ge(Si ^t Bu ₃) ₂	48	2.2638(11)	0	0	dark red	not reported
(^t Bu ₂ MeSiGe) ₂ Si(Si ^t Bu ₂ Me) ₂	25, 26	2.2429(5)	51.0	not reported	dark red	470, 403, 311, 236
(^t Bu ₂ MeSiGe) ₂ Ge(Si ^t Bu ₂ Me) ₂	25, 26	2.2429(5)	60.5	not reported	dark red	457, 407, 324, 234
(^t Bu ₃ SiGe) ₂ Ge(Si ^t Bu ₃) ₂	49	2.241(4)	not reported	not reported	dark red	not reported
((^t Bu ₃ Ge)Ge) ₂ Ge(Ge ^t Bu ₃) ₂	49	2.240(3)	not reported	not reported	dark red	not reported
GeGe double bonds in four-membered cycles						
((Si ^t Bu ₂ Me)Ge) ₂ (Si(Cl)Si ^t Bu ₂ Me) ₂	33	2.291(6)	not reported	not reported	bright orange	not reported
(Ar ^r Ge) ₂ (CPh) ₂	50	2.4710(8)	not reported	not reported	dark red	375

* 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

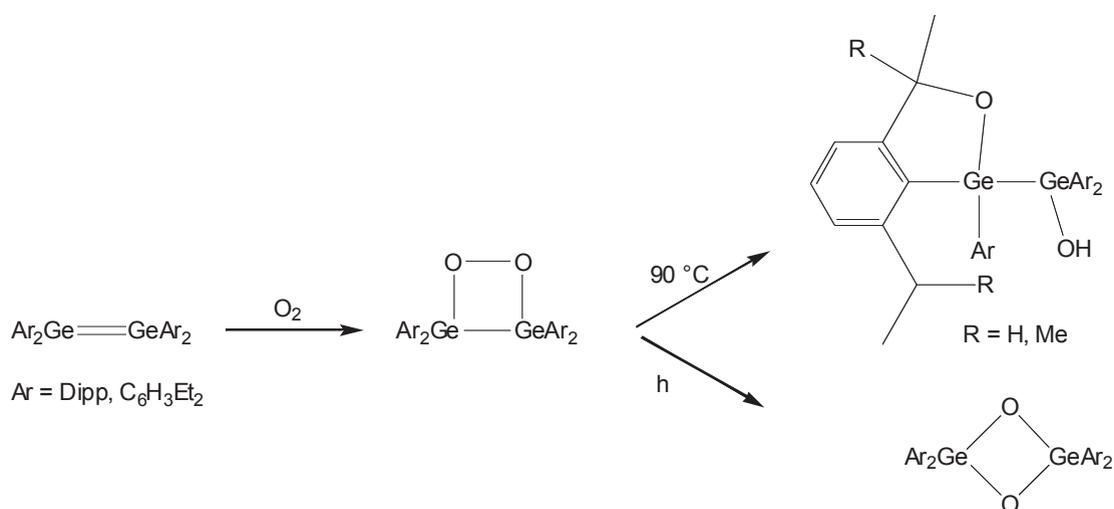
Digermenes display a wide variety of reactions. The range of such reactions is quite diverse but most of them can be classified as additions, coordination reactions or reductions. Products that ensue from the reactions of dissociated digermenes (i.e. germynes) are not considered in this section.

Addition Reactions

Addition of Lewis acids or multiple bonded species such as O₂, isonitriles, azides, butadiene, N₂O 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.

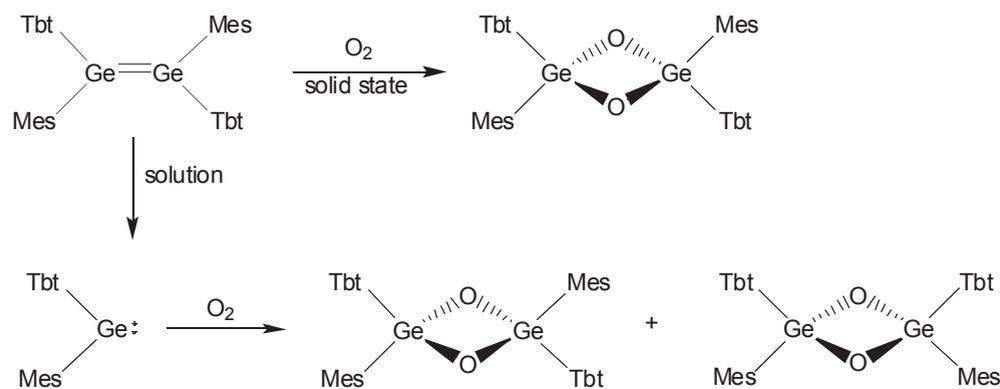
Oxygen

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



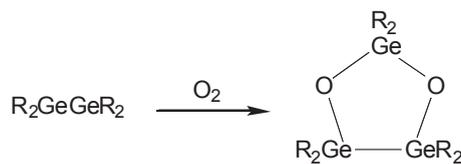
Scheme 13

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.



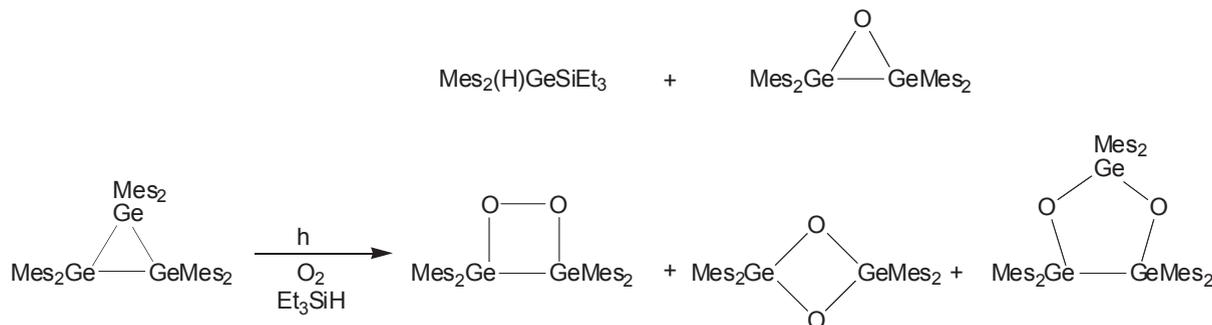
Scheme 14

Exposure of digermene stabilized by 1,4-di-*tert*-butylbenzene ligands afforded a trigerma-1,3-dioxolane product as shown by Weidenbruch's group.⁵⁵



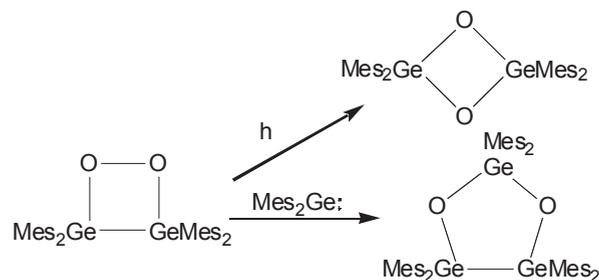
Scheme 15

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 O₂ to tetramesityldigermene resulted in the formation of a 3,4-digermadioxetane with subsequent insertion of a germylene into the O-O single bond.⁵⁶



Scheme 16

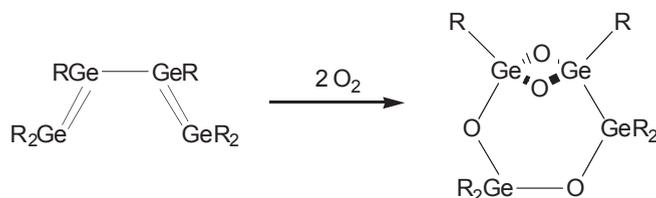
The GeGe single bond (2.504(3) Å) is slightly shorter than that in the five-membered ring reported by Weidenbruch. Formation of the 1,3-digermadioxetane results from rearrangement during irradiation of the 3,4 digermadioxetane as already shown above for Ar₂GeGeAr₂ by Masamune.⁵¹



Scheme 17

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.⁵⁷ Instead, only 1,3 digermadioxetane, the pentacycle and only in very small amounts the digermaoxirane were obtained.⁵⁶

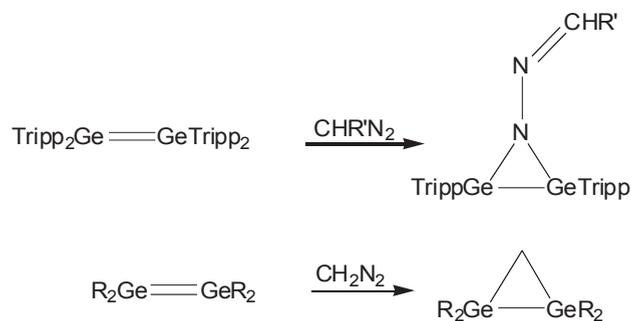
A tetragermabuta-1,3-diene was reacted with dry air to yield in a tetraoxatetragermabicyclo[4.1.1]-octane skeleton. The folded cyclodigermoxane ring can be seen as a result of a [2+4] addition of O₂ to the terminal germanium atoms, followed by a 1,2-addition of a second O₂ molecule.⁴³



Scheme 18

Diazomethane

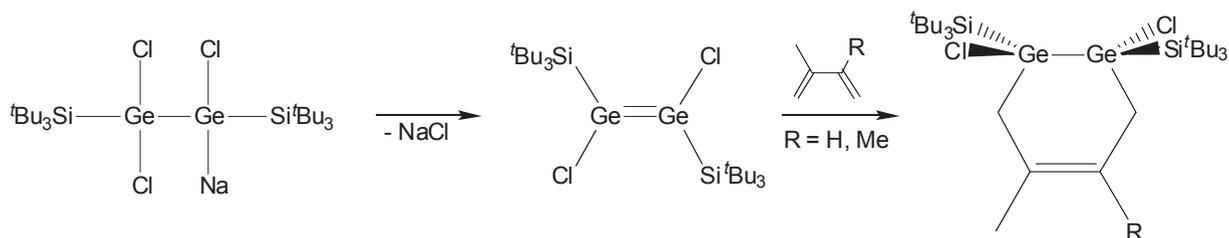
MesDipGe=GeDipMes reacted with diazomethane R'HCN₂ (R' = H, SiMe₃) to give a azodigermirane in a [2+1] cycloaddition. No subsequent loss of nitrogen was observed, however.¹⁹ In contrast Ando and coworkers,⁵⁸ obtained a digermirane in low yield as shown in Scheme 19. The azodigermirane features a GeGe 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.⁵⁹



Scheme 19

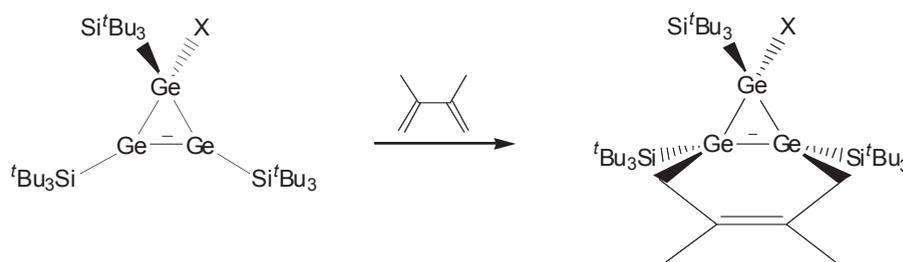
1,3-Butadiene

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 $t\text{Bu}_3\text{Si}(\text{Cl})\text{Ge}=\text{Ge}(\text{Cl})\text{Si}^t\text{Bu}_3$ which decomposes during warming above a temperature of $-8\text{ }^\circ\text{C}$. Its reaction with isoprene and 2,3-dimethyl-1,3-butadiene, respectively, afforded only a single stereoisomer of the addition product.⁶⁰



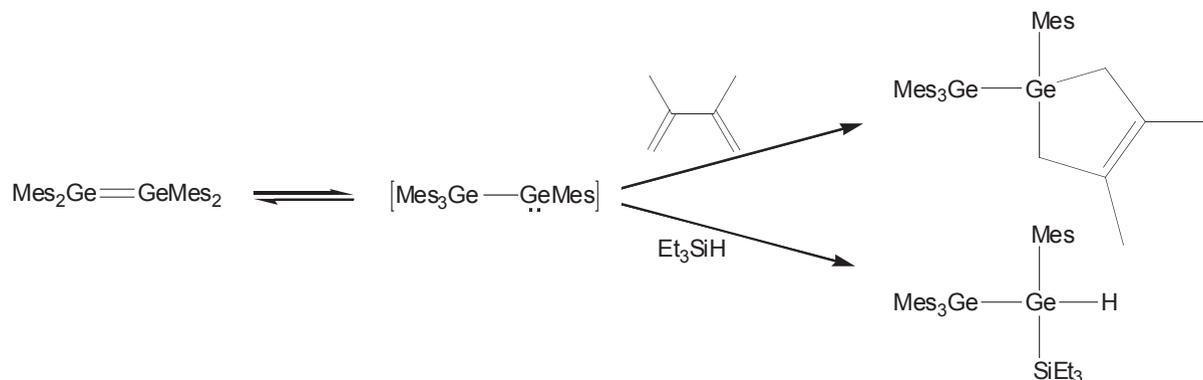
Scheme 20

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 $\text{Ge}=\text{Ge}$ double bond of halogen substituted cyclotrigermenes has an effect on selectivity in the reaction with dimethyl butadiene. Thus, the dimethylbutadiene attacks the $\text{Ge}=\text{Ge}$ double bond from the side having the bulkier $t\text{Bu}_3\text{Si}$ and only one stereoisomer is formed during the reactions. This is opposite to the selectivity of mesityl substituted cyclotrigermenes.^{61,62,52}



Scheme 21

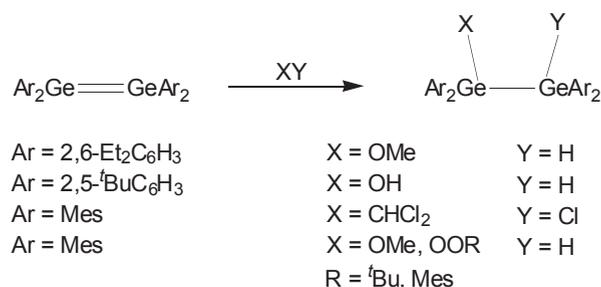
When $\text{Mes}_2\text{Ge}=\text{GeMes}_2$ was reacted with 1,3-butadiene, formation of mesityl(trimesitylgermyl)-germacyclopentene was observed. This was explained on the basis of a 1,2 shift of one mesityl group from one to the second germanium atom followed by trapping with the diene. A trapping reaction using Et_3SiH led to the same result.⁷



Scheme 22

Reactions with Protic Lewis Acids and Halogen Reagents

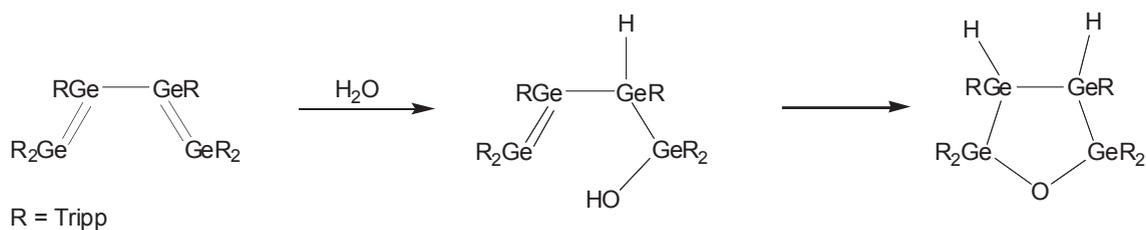
Reactions of digermenes with protic reagents can either lead to addition products or eliminations. For example, the reaction of digermenes with alcohols has been investigated by several groups. Masamune and coworker observed the addition of methanol to tetra(diethylphenyl)digermene ($\text{Ar}_2\text{GeGeAr}_2$).¹⁸ The same reactivity was found for $\text{Mes}_2\text{GeGeMes}_2$ 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.⁷



Scheme 23

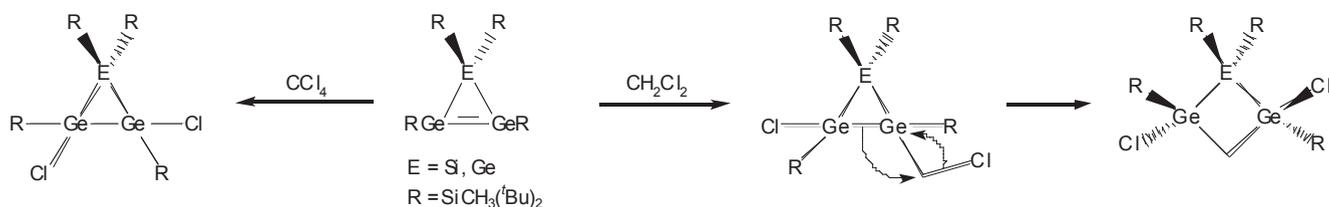
The reaction of R_2GeGeR_2 ($\text{R} = 2,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3$) with water resulted in a digermanol.⁵⁵ This is in contrast to reactions of $(\text{Dis})_2\text{GeGe}(\text{Dis})_2$ with ethanol or $\text{Tbt}(\text{Mes})\text{GeGe}(\text{Mes})\text{Tbt}$ with methanol, respectively, which provided the corresponding alkoxides via an elimination reaction.^{24,63}

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.³⁰



Scheme 24

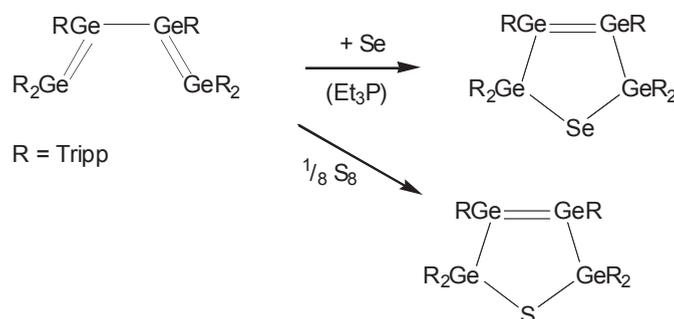
Ring compounds featuring GeGe double bonds also react with methylene dichloride and tetrachloro methane at room temperature. In the case of CCl_4 a 1,2-addition occurs and the resulting cyclodigermene can be isolated using an excess of dichloromethane the product of a ring expansion is obtained. For chloroform only formation of a mixture of products was obtained.^{25,26}



Scheme 25

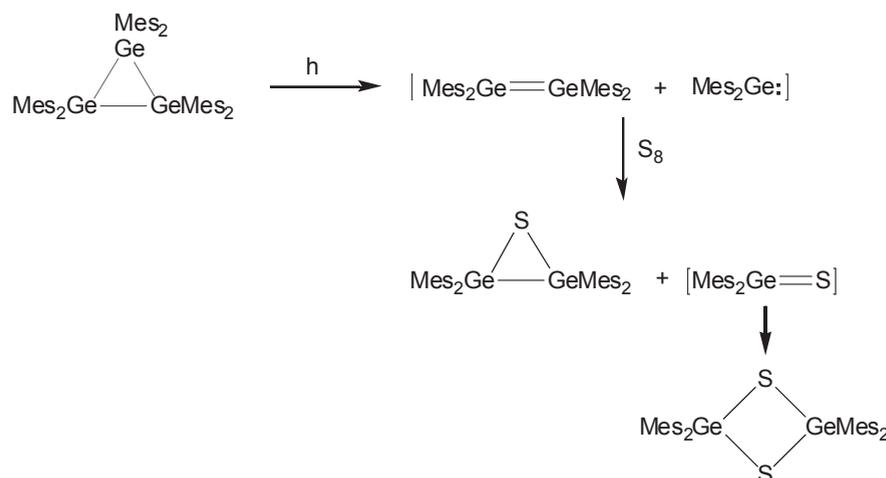
Reactions with Heavier Chalcogens

Heating of tetramerma-1,3-butadiene with excess of selenium in the presence of a small amount of Et_3P 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 thiotetragermacyclopentane.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 \AA are typical for GeGe single bonds, but the Ge2Ge3 bonds, which are $2.2841(5)$ and $2.2975(5) \text{ \AA}$ are typical for a GeGe double bond.



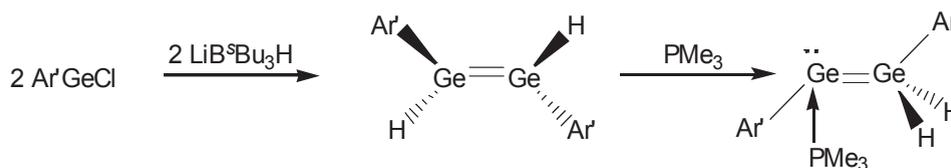
Scheme 26

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, $\text{Mes}_2\text{Ge}=\text{S}$, intermediate that is formed by reaction of sulfur and the corresponding germylene.⁶⁴



Scheme 27

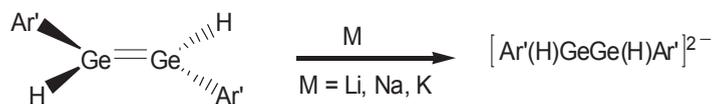
Reaction of digermene dihydride with PMe_3 results in an isomerization reaction to afford a mixed valent species. In this compound the GeGe distance of $2.5304(7) \text{ \AA}$ is at the longer end of the GeGe single bond range.^{28,65}



Scheme 28

Reduction Reactions

Reduction of the dihydrodigermene $\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}'$ with alkaline metals (Li, Na or K) gave highly reactive salts $\text{M}_2[\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}']$ as deep red/black crystals.⁶⁶ Depending on the nature of the alkali metal counterions the nature of the structural type formed differed. In the potassium salt the $[\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}']^{2-}$ 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 $[\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}']^{2-}$ core has bridging hydrogen atoms, the GeGe distance with 2.5904(5) Å is long.⁶⁶ 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.⁶⁷



Scheme 29

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 digermine by this route was described in 2002.⁶⁸ Reduction of $\text{Ar}'(\text{Cl})\text{GeGe}(\text{Cl})\text{Ar}'$ with potassium furnished $\text{Ar}'\text{GeGeAr}'$ as orange-red crystals. This digermine 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)°.

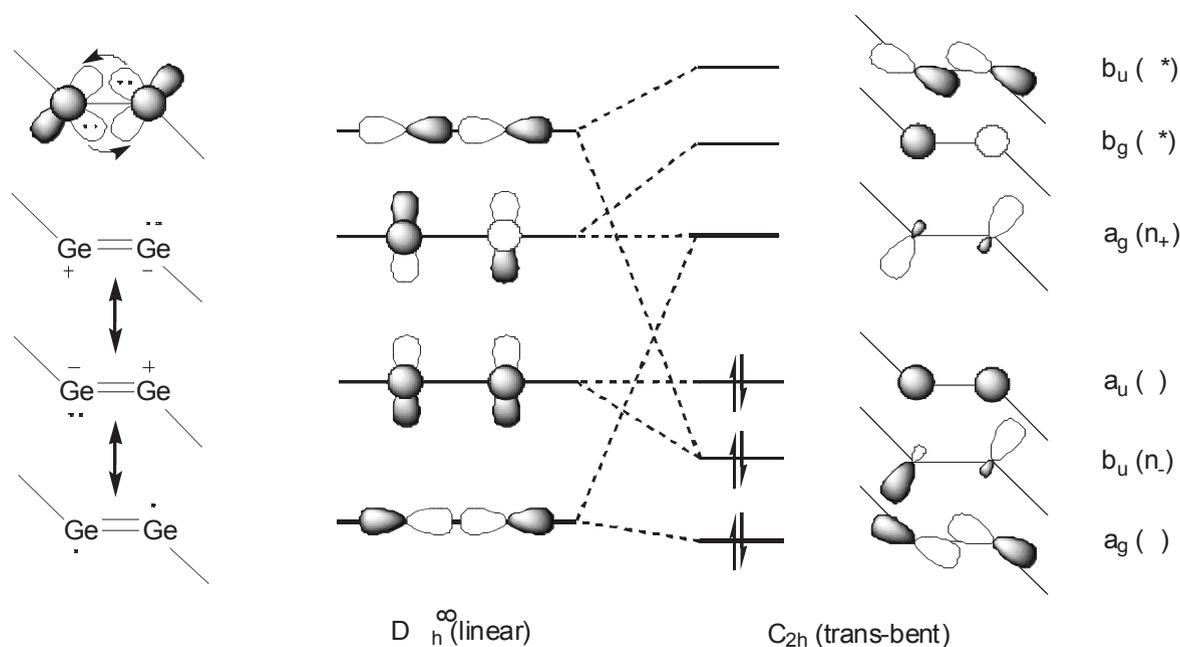


Scheme 30

A similar reaction was also reported in 2006 by Tokitoh and co-workers.⁶⁹ Starting with BbtBrGeGeBrBbt, Bbt = C₆H₂-2,6-(CH(SiMe₃)₂)₂-4-C(SiMe₃)₃, a reduction with KC₈ 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)°).

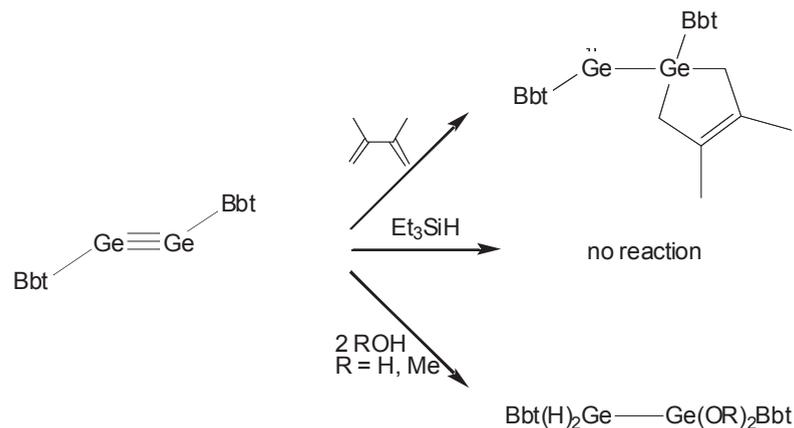


Although Ar'GeGeAr' and BbtGeGeBbt are both digermynes, they show different reactivities which is apparently caused by the different germanium substituents. In Ar'GeGeAr' the bond order is decreased from idealized triply bonded to approximately two and contains some lone-pair character at the germanium atoms. The lower bond order may be accounted for in terms of a second-order Jahn-Teller effect involving the mixing of a σ^* orbital and the in plane π -orbital upon trans bending of the linear skeleton (Scheme 32).^{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.



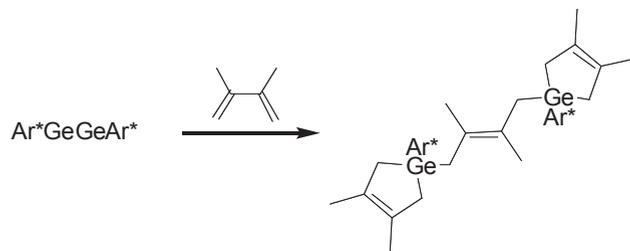
Reactivity of Ar'GeGeAr'

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-dimethoxydigermene and 1,1-dihydroxydigermene, respectively, was observed. Reaction with 2,3-dimethyl-1,3-butadiene yielded the product of a [4+1] addition.⁷⁰



Scheme 33

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.

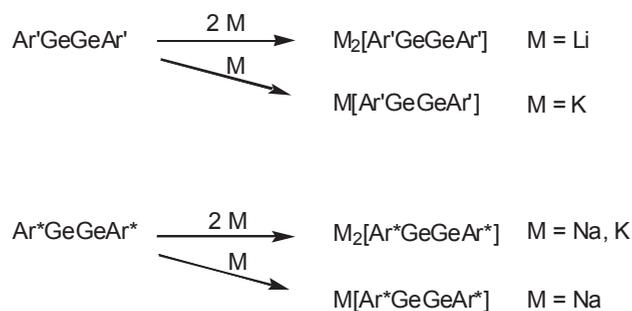


Scheme 34

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* = C₆H₃-2,6-(C₆H₂-2,4,6-Pr^{*i*}₃)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 diarylacetylenes^{76,77} 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 electropositive 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

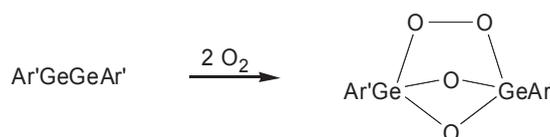
Reaction of Ar'GeCl and Ar*GeCl with an excess of lithium, sodium or potassium afforded the doubly reduced salts.⁷⁹ The alkali metal counteranions are sandwiched between the flanking aryl rings and the structures are very similar. The GeGe distances are somewhat increased (Li: 2.455(9) Å, Na: 2.394(1) 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.⁷⁹ Also the [Ar'GeGeAr']²⁻ is isoelectronic to double bonded Ar'SbSbAr'⁸⁰ and the GeGe bond can be considered a double one.



Scheme 35

Reactions with Unsaturated Molecules

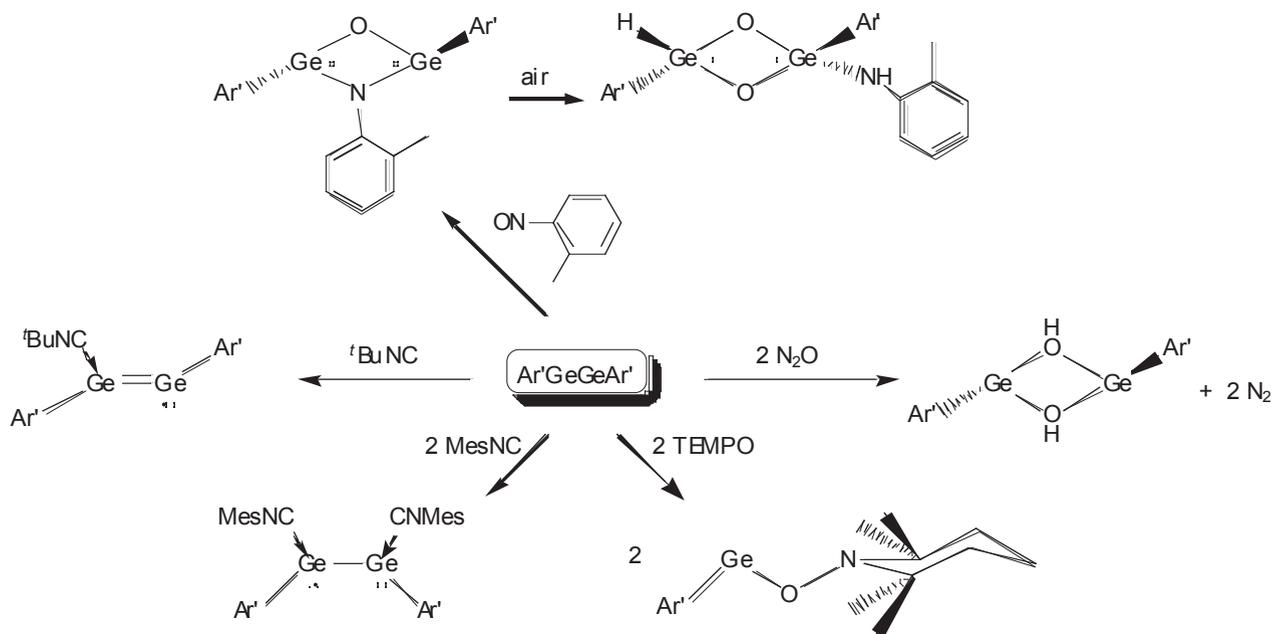
Several of the reactions of Ar'GeGeAr' are suggestive of diradical character (Scheme 36-38). For instance, very recently it has been shown the addition of two equivalents O₂ to a bis terphenyl digermine yielding the unique species {Ar'Ge(μ-O)₂(η₁,η₁:μ₂-O₂)GeAr'}. In this species the two germanium atoms 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.



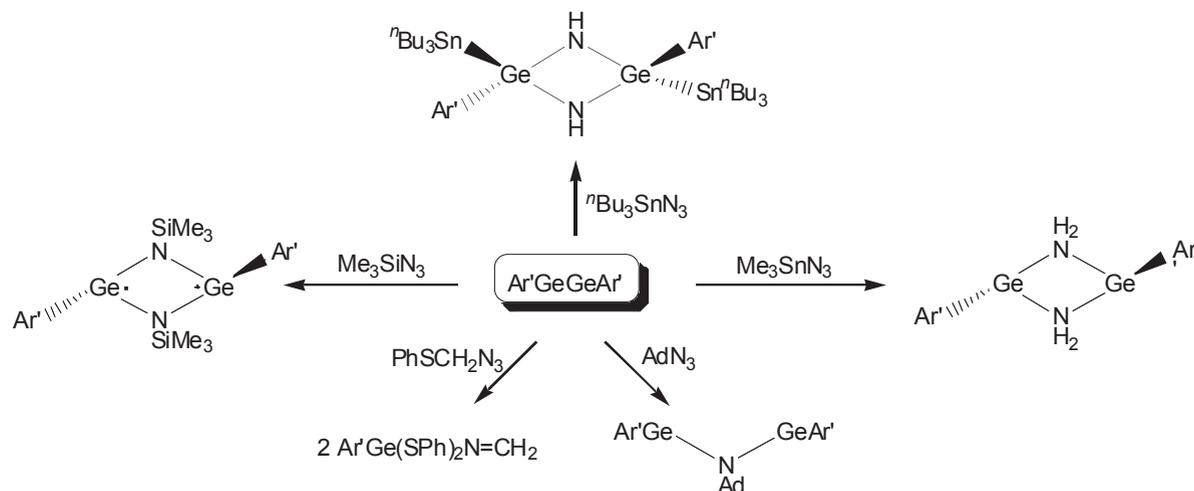
Scheme 36

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.

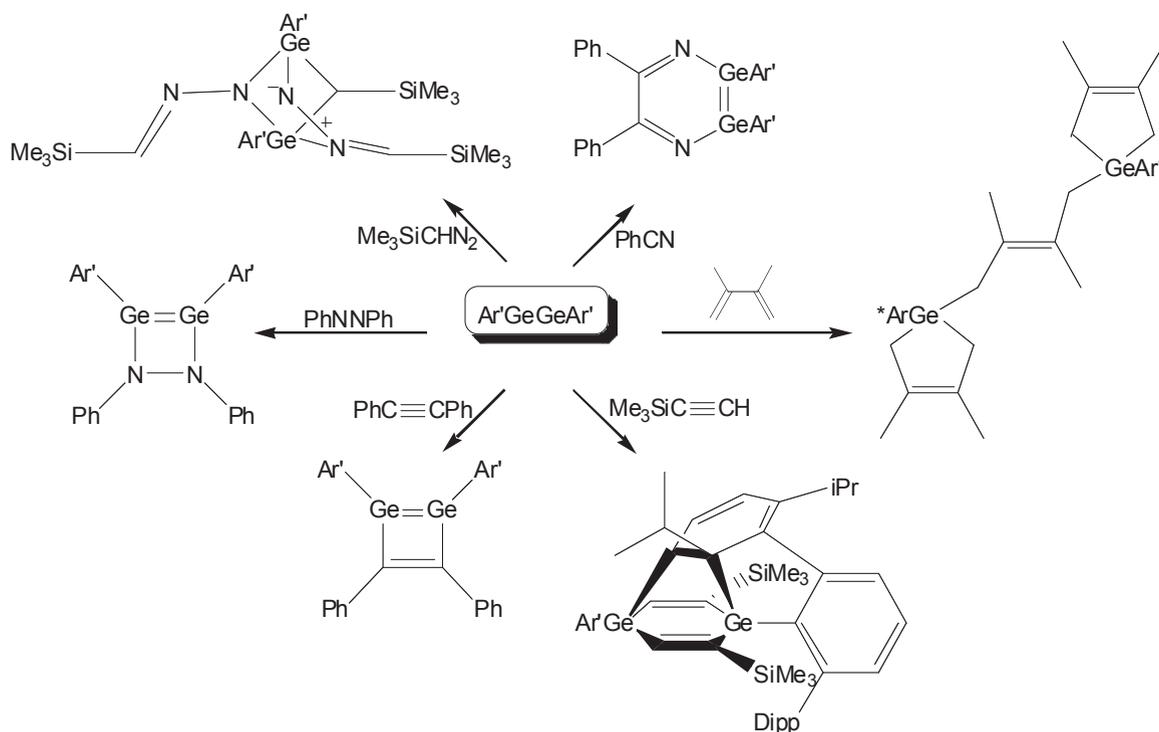
The reaction of $\text{Ar}'\text{GeGeAr}'$ with different isocyanides (Scheme 37) showed different reactivity depending on the nature of the isocyanide. The reaction with ${}^t\text{BuNC}$ afforded a 1:1 adduct in which the isocyanide is coordinated to one of the Ge centers.⁸¹ As a consequence the GeGe 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 ${}^t\text{BuNC}$ as Lewis base but when $\text{Ar}'\text{GeGeAr}'$ was reacted with two equivalents MesNC yielding a digermylene which is characterized by a very long GeGe bond (2.6626(8) Å).⁸²



Scheme 37



Scheme 38



Scheme 39

Addition of Hydrogen

The digermene $\text{Ar}'\text{GeGeAr}'$ reacts spontaneously with hydrogen under ambient conditions to give, depending on the stoichiometry, differing quantities of germanium hydrides $\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}'$, $\text{Ar}'(\text{H})_2\text{GeGe}(\text{H})_2\text{Ar}'$ and $\text{Ar}'\text{GeH}_3$. These compounds represent germanium hydrides with formal oxidation states at the Ge atom of +2, +3 and +4, respectively.⁸³ This was the first example of a successful addition of hydrogen to a main group molecule at ambient conditions (25 °C and 1 atm).

		$\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}'$	$\text{Ar}'(\text{H})_2\text{GeGe}(\text{H})_2\text{Ar}'$	$\text{Ar}'\text{GeH}_3$
$\text{Ar}'\text{GeGeAr}'$	$\xrightarrow{1 \text{ H}_2}$	21 %	10 %	9 %
	$\xrightarrow{2 \text{ H}_2}$	2 %	85 %	13 %
	$\xrightarrow{3 \text{ H}_2}$	0 %	65 %	35 %

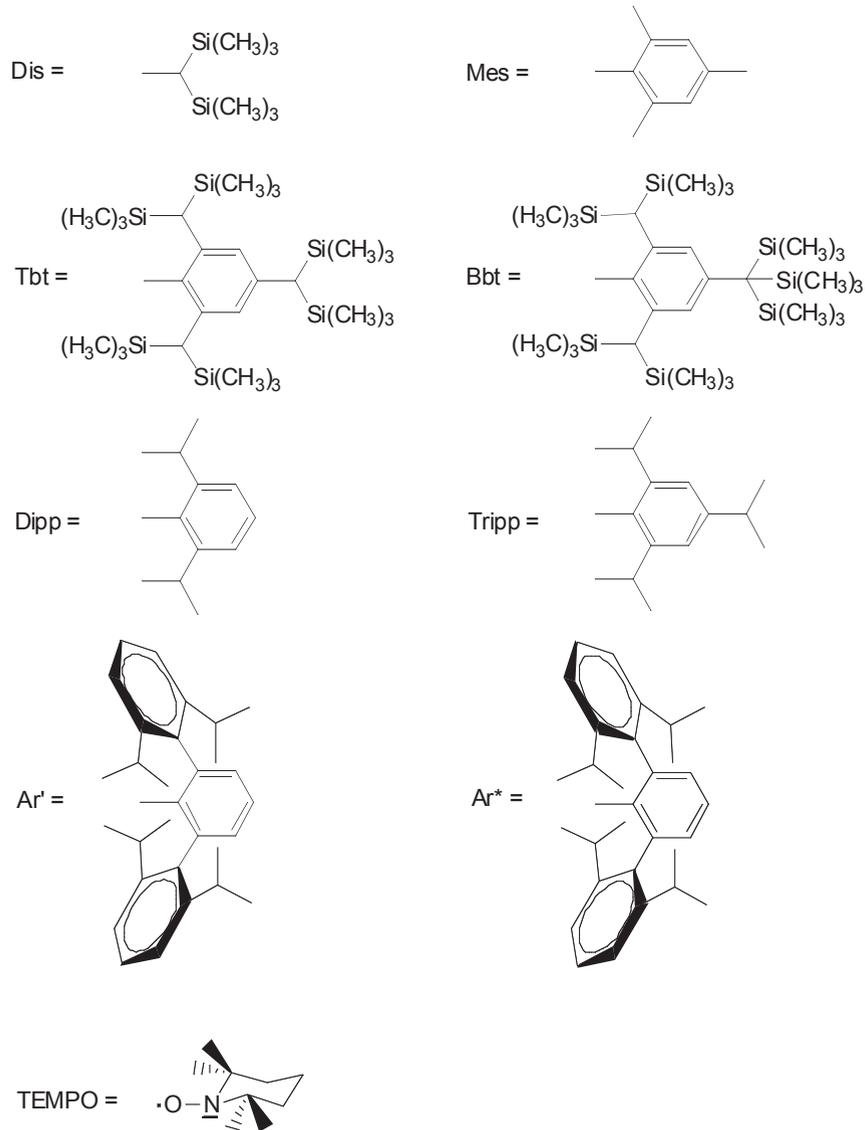
Scheme 40

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

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