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Review

Singly Bonded Catenated Germanes: Eighty Years of Progress

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Singly Bonded Catenated Germanes: Eighty Years of Progress

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Contents

1. Introduction

Catenated compounds of the group 14 elements which contain single element−element bonds are of interest, since they represent the heavier analogues of alkanes. The electrons in the element−element bonds are not localized between two atoms in these molecules but rather are delocalized across the entire backbone. This attribute is referred to as σ-delocalization[1–3] and imparts physical properties to these systems that resemble conjugated unsaturated hydrocarbons, despite the fact that the heavier silicon, germanium, and tin catenates are held together by single element−element bonds. The HOMO−LUMO transition in these systems, which corresponds to promoting an electron from the σ to the σ^* molecular orbital, gives rise to interesting optical attributes. Furthermore, the heavier group 14 catenates exhibit other useful physical characteristics such as conductivity, thermochromism, and nonlinear optical properties.

Although the synthesis, properties, and chemistry of silicon-[4–14] and tin-containing[15–32] catenates have been well developed, those of the related germanium congeners have received less attention. Although germanium lies between silicon and tin on the periodic table, the purported similarity of organogermanium compounds to those of its lighter and heavier neighbors has been overstated. Many differences in the chemistry of organogermanium compounds exist, and in the case of catenated germanium compounds, this is demonstrated by the difficulties encountered in reactions involving the formation of germanium−germanium bonds. While compounds containing Si−Si and Sn−Sn bonds can be obtained in good to excellent yields by several facile methods, general routes to the germanium congeners are complicated by low yields and/or the formation of product mixtures. The relative difficulty in preparing discrete oligogermanium compounds has precluded a detailed investigation into the relationship between the composition of these materials and their physical properties, while such investigations have been conducted in detail for the aforementioned silicon and tin catenates.

Until recently, methods for the formation of germanium−germanium bonds have included Wurtz-type coupling reactions involving germanium(IV) halides and alkali metals, the insertion of germylenes:GeR_2 into Ge−X bonds (X = N, O, or a halogen), thermal decomposition of germylmercury compounds, or treatment of germanium halides with organolithium or Grignard reagents. The latter method provided a series of perphenylated linear oligogermanes $Ph(GePh_2)_nPh$ ($n = 2-5$) as well as the cyclic derivatives $(Ph_2Ge)_n$ ($n = 4-6$), although the desired products were obtained in low yields in all cases. The hydrogermolysis reaction has also been employed for the formation of Ge−Ge bonds,[33] and recently this process has proven to be a versatile method for the preparation of oligogermanes in drastically improved yields.[34–37] Significant improvements in yield have also been recently achieved using SmI_2 for the coupling of organohalogermanes.[38,39]

The presence of organic functional groups or halogens is necessary to stabilize the germanium−germanium bond. For example, the parent germanium analogue of ethane H_3GeGeH_3 is highly pyrophoric.[40–44] The first compound described as having a germanium−germanium bond, $Ph_3GeGePh_3$ (**1**), was reported in 1925,[45] 39 years after the discovery of germanium itself by Winkler in 1886[46,47] and 38 years after the preparation of the first organometallic germanium derivative Et_4Ge.[48] In the subsequent 80 years, significant progress has been made in the preparation and characterization of oligomeric germanium compounds bearing organic substituents, but the scope of these investigations has not approached the magnitude of those directed at the related silicon- and tin-containing compounds.

The focus of this review is the synthesis, structures, and reactivity of discrete oligogermanes containing Ge−Ge single bonds, where normal Ge−Ge single bond distances in these systems are regarded to be within the range 2.43−2.47 Å.[49] In addition, the synthesis and characterization of polygermanes (i.e., mixtures of compounds with a molecular weight distribution), that have been the subject of several reviews,[50–58] will also be briefly discussed here. A number of reviews on

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Monika L. Amadoruge was born in Colombo, Sri Lanka. She received her B.Sc. degree in Chemistry from the University of Kelaniya (Sri Lanka) in 2003, where she worked as an undergraduate researcher with Professor S. Wimalasena, investigating the presence of heavy metals in fresh water fish taken from Sri Lankan waters. After graduation, she served as an Assistant Lecturer at the University of Kelaniya. She began her doctoral studies in Chemistry at Oklahoma State University in 2005, and she is currently a third year graduate student in the laboratory of Professor Scott Weinert. Her doctoral research to date has focused on the synthesis and characterization of linear and branched oligogermanes, which focuses on developing correlations between their optical and electronic attributes and their composition.

Charles S. (Scott) Weinert was born in Detroit in 1971. He attended the University of Michigan (B.S. 1995), where he was an undergraduate researcher in the laboratory of Dr. Arthur J. Ashe, III. He spent a year working for Selective Technologies, Inc. with Dr. Glenn Martin and Dr. Mark E. Meyerhoff before attending the University of Chicago (M.S. 1997), where he studied under the direction of Prof. Lawrence R. Sita. Scott then attended Northwestern University, and received his Ph.D. in 2000 under the supervision of Prof. Du Shriver, where his thesis focused on the ligand substitution chemistry and physical properties of octahedral tungsten chloride clusters. He was a postdoctoral research fellow with Prof. Ian Rothwell at Purdue University from 2001 to 2004, where his research focused on the synthesis and characterization of germanium(II) aryloxide and binaphthoxide complexes, as well as the development of chiral tantalum(V) binaphthoxide complexes for asymmetric hydrogenation. He began his independent career at Oklahoma State University in 2004, where his research has focused on the rational synthesis, structures, and properties of oligogermanes. His research also currently explores the synthesis of germanium calixarene complexes and their potential use as support platforms for electrochemically or magnetically active transition metal complexes.

the chemistry of digermenes, that contain Ge═Ge double bonds ranging in length from 2.21−2.35 Å, have recently appeared, and these species will not be discussed herein.[59–66] In addition, the preparation, characterization, and properties of ionic germanium clusters[67–80] will not be covered here.

2. Digermanes

The first digermane, $Ph_3GeGePh_3$ (**1**), was prepared in modest yield by the Wurtz-type coupling of Ph_3GeBr with sodium metal (eq 1).[81] Similarly, $Et_3GeGeEt_3$, which represents the first hexaalkyldigermane, was prepared from Et_3GeBr and sodium metal in 1932.[82] The synthesis of the hexamethyl derivative, $Me_3GeGeMe_3$, from Me_3GeBr and potassium was described in 1958,[83] and an alternate method for its preparation was reported in 1976.[84]

$$2Ph_3GeBr + 2Na \xrightarrow[\Delta,\ 3\ h]{\text{xylene}} \underset{\substack{\mathbf{1} \\ 24\%}}{Ph_3Ge{-}GePh_3} + 2NaBr \tag{1}$$

Grignard reactions directed at the preparation of Ph_4Ge from $GeCl_4$ can have a number of different outcomes depending on the reaction conditions and stoichiometry employed.[45,85–88] Compound **1** was not obtained when $GeBr_4$ was treated with a large excess of PhMgBr in Et_2O[81] but was isolated in 69% yield from the reaction of $GeCl_4$ with 7.8 equiv of PhMgBr in THF that contained a 20 mol % excess of magnesium metal.[89] The isolation of **1** in 59% yield using a 14:4 molar ratio of PhMgBr:$GeCl_4$ also has been reported.[90]Under similar conditions again using THF as the solvent, it was found that the trigermane $Ph_3GeGePh_2GePh_3$ (**2**) and the tetragermane $Ph_3GeGePh_2GePh_2GePh_3$ (**3**) also are formed as minor products.[86]

Hexaphenyldigermane (**1**) was the first compound with a Ge−Ge bond to be structurally characterized, and it can adopt three different morphologies depending on the crystallization conditions. Crystallization from CH_2Cl_2 at 25 °C furnished a hexagonal form (**1a**),[91] crystallization at −15 °C from CH_2Cl_2 produced a triclinic form (**1b**),[91] and crystallization at 25 °C from benzene yielded a rhombohedral form (**1c**) that contains two molecules of benzene in the unit cell.[92] The structures of the latter two species have been fully determined, and structural data for these compounds are collected in Table 1, along with crystallographic data for several other digermanes that are discussed below. The geometries of the germanium atoms in both **1b** and **1c** are nearly tetrahedral, and the Ge−Ge bond lengths differ slightly between **1b** and **1c**. The Ge−Ge bond length in the unsolvated triclinic form (**1b**) is 2.437(2) Å, and in the solvated rhombohedral form (**1c**), it is elongated to 2.446(1) Å. The structure of the digermane in **1c** is shown in Figure 1.[92,93]

The formation of the three oligomers **1**−**3** has been rationalized by considering the reaction pathway involved in the formation of Ph_4Ge from $GeCl_4$ and PhMgBr (Schemes 1 and 2). The formation of Ph_4Ge likely occurs in a stepwise fashion (Scheme 1), and upon generation of Ph_3GeCl, the presence of excess magnesium generates the germyl Grignard reagent $Ph_3GeMgCl$, which also can be obtained from the reaction of Ph_3GeCl with PhMgBr itself (Scheme 2). This species then reacts with the other phenylchlorogermanes present as intermediates in the stepwise formation of Ph_4Ge to generate the three oligomeric products. The three oligogermanes can be formed in the presence or absence of excess magnesium metal in the Grignard reaction, and the choice of solvent is also of

Scheme 1

$$GeCl_4 \xrightarrow[\text{- MgClBr}]{\text{PhMgBr}} PhGeCl_3 \xrightarrow[\text{- MgClBr}]{\text{PhMgBr}} Ph_2GeCl_2 \xrightarrow[\text{- MgClBr}]{\text{PhMgBr}}$$

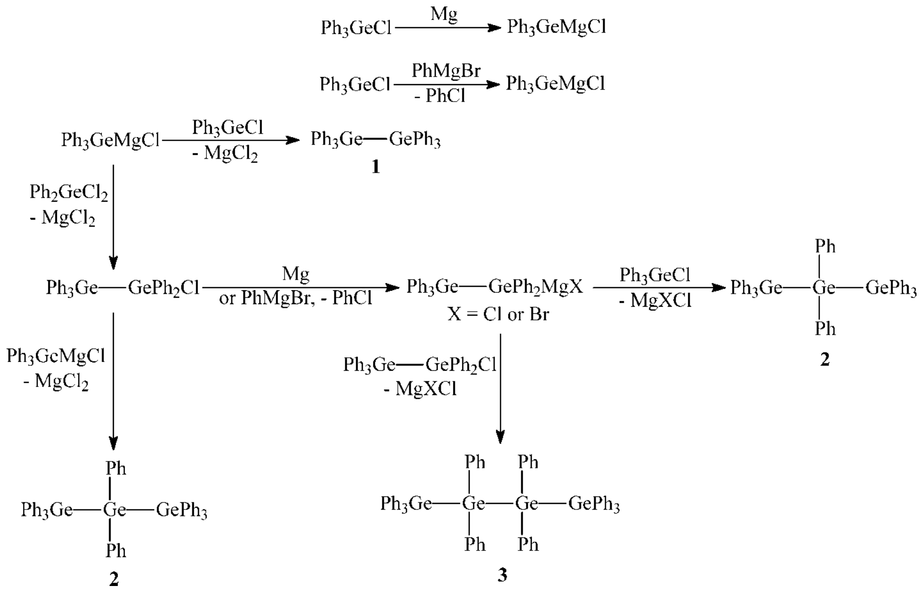
$$Ph_3GeCl \xrightarrow[\text{- MgClBr}]{\text{PhMgBr}} Ph_4Ge$$

Table 1. Selected Distances (Å) and Angles (deg) in Digermanes

compound	d Ge^1−Ge^2	d_{avg} Ge−C	$\angle_{avg}$ C−Ge−Ge	$\angle_{avg}$ C−Ge−C	ref
$Ph_3Ge^1{-}Ge^2Ph_3$ (**1b**)	2.437(2)	1.96(1) Ge^1	110.8(3)	108.6(5)	91
$Ph_3Ge^1{-}Ge^2Ph_3 \cdot 2C_6H_6$ (**1c**)	2.446(1)	1.97(2)	110.9(3)	108.1(3)	92
$Cl_3CCOOPh_2Ge{-}GePh_2OOCCCl_3$ (**8**)	2.393(2)	1.942(4)	121.6(1)	116.4(2)	100
$Ph_4Ge_2O_3Si_2Ph_4$ (**10**)	2.4586(3)	1.947(2)		109.1(1)	102
$Ph_4Ge_2O_2GeBu^t_2$ (**11**)	2.430(3)	1.97(2)		112.9(7)	103
$Cl_2PhGeGePhCl_2$ (**13**)	2.413(1)	1.924(5)	119.0(1)		104
$Ph_8Ge_4O_2$ (**14**)	2.448(1)	1.942(3)			105
$Ph_6Ge_3Se_2$ (**16**)	2.415(1)	1.954(4)			105
$K_2[C_{12}H_8Ge]_2$ (**24**)	2.569(1)	1.988(5)	100.0(1)	84.0(2)	110
$ArH_2Ge{-}GeH_2Ar$ (**26**)[a]	2.402(1)	1.975(5)	114.9(2)		111
$Ar_2HGe{-}GeAr_2N_3$ (**28**)	2.4637(4)	1.990(3)	115.62(7)		112
$(C_6H_3Mes_2\text{-}2,6)Ge{-}GeBu^t_3$ (**29**)	2.5439(7)	2.011(5)	114.9(1)		113
$(Me_3Si)_3SiCl_2Ge{-}GeCl_2Si(SiMe_3)_3$ (**30**)	2.42(1) [b]				114
$(Me_3Si)_3Ge{-}Ge(SiMe_3)_3$ (**31**)	2.4787(7)				117
$Pr^i_3Ge{-}GePh_3$	2.4637(7)	1.974(2)	110.51(6)	108.33(9)	35
$Bu^t_3Ge{-}GeBu^t_3$ (**32**)[c]	2.710(1)	2.076(6)	112.1(2)	107.2(1)	118
$Ph_3Ge{-}GeBu^n_3$ (**33**)[c]	2.421(8)	1.953(4) Ge^1	110.7(1)	108.0(2)	34
$Ph_3Ge{-}GeEt_3$ (**34**)	2.4253(7)	1.957(2)	110.15(8)	108.77(8)	34
$Ph_3Ge{-}GeMe_3$ (**36**)	2.418(1)	1.950(3)	110.3(1)	108.7(1)	123
$[C_6H_2(CF_3)_3\text{-}2,4,6]_2HGe{-}GeH[C_6H_3(CF_3)_2\text{-}3,5]_2$ (**37**)	2.4352(3)	1.977(2)		110.7(1)	124
$[(Et_3P)_2HPt]Ar_2Ge{-}GeAr_2[PtH(PEt_3)_2]$ (**38**)	2.466(1)	2.001(4)	102.0(2)	102.1(2)	125
$[(OC)_5Cr]I_2Ge{-}GeI_2[Cr(CO)_5]$ (**40a**)	2.448(1)				126
$[(OC)_5W]I_2Ge{-}GeI_2[W(CO)_5]$ (**40b**)	2.456(2)				126
$[(Me_3SiNCPh)_2(Me_3Si)Ge]_2$ (**42**)	2.4340(5)	2.004(3)	106.29(7)		128

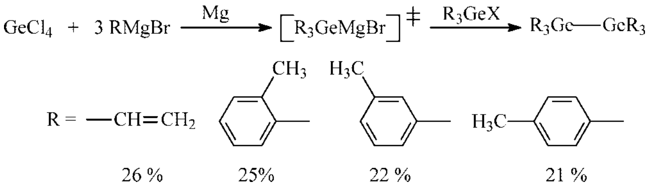
[a] Values are the average of three crystallographically independent molecules. [b] Complete refinement of the structure was not achieved for **30**. [c] Values are the average of two crystallographically independent molecules.

Scheme 2



importance, since yields of the tri- and tetragermanes are diminished if Et_2O/toluene is used instead of THF as the reaction medium. Generation of intermediate germyl Grignard reagents due to the presence of an excess of magnesium has been reported to result in the isolation of various other digermanes, including hexavinyldigermane[88] and three isomeric hexatolyldigermanes[87] (Scheme 3).

Scheme 3



Halogenated digermanes are useful, since they can serve as functionalized precursors for the preparation of larger oligogermanes. The 1,2-dibrominated digermane (**4**) was prepared in 1960 (eq 2)[94] and was converted to the dihydride **5** by reaction with $LiAlH_4$, and also to the 1,4-dioxatetragermacyclohexane **6** by reaction of **4** with sodium hydroxide (Scheme 4).[95] Hexabromodigermane, $Br_3GeGeBr_3$, was prepared by the insertion of $GeBr_2$ into the Ge−Br bond of $GeBr_4$ in 25% yield.[96,97] The tetrahalogenated digermanes $Cl_2PhGeGePhCl_2$ and $Br_2PhGeGePhBr_2$ were obtained from **1** in near quantitative yields using anhydrous HCl or HBr.[97]

$$Ph_2GeBr_2 \xrightarrow[Et_2O,\ 40\ h]{1\ equiv\ of\ Li/Hg} \underset{\underset{\mathbf{4}}{60\%}}{BrPh_2Ge{-}GePh_2Br} + LiBr + Hg \tag{2}$$

Several additional reports concerning the synthesis of digermanes bearing one or more functional groups subsequently followed. The reaction of $Et_3GeGeEt_3$ with $GeCl_4$ at 200 °C can selectively provide the monochlorinated derivative $ClEt_2GeGeEt_3$ or the dichlorinated species $ClEt_2GeGeEt_2Cl$, depending on the stoichiometric ratio of the reactants (Scheme 5).[98] Other tetrahalides ECl_4 (E = C,

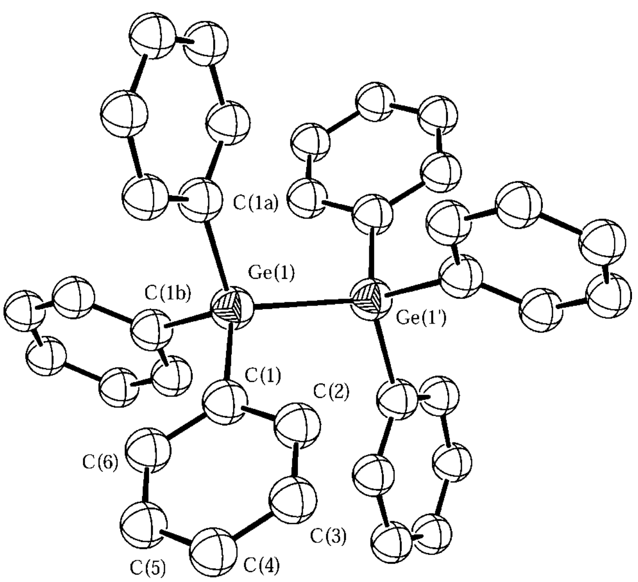
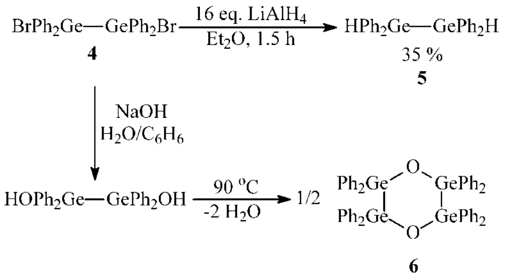


Figure 1. ORTEP diagram of **1c** with the benzene solvates omitted. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(1′), 2.446(1); Ge(1)−C(1), 1.963(1); C(1)−Ge(1)−C(1a), 108.11(1); C(1)−Ge(1)−Ge(1′), 110.80(1).

Scheme 4



Scheme 5

$$\mathrm{Et_3Ge{-}GeEt_3 + GeCl_4 \xrightarrow[6\ h]{} \underset{88\ \%}{Et_3Ge{-}GeEt_2Cl} + EtGeCl_3}$$

$$\mathrm{Et_3Ge{-}GeEt_3 + 2\,GeCl_4 \xrightarrow[6\ h]{cat.\ GeI_2} \underset{86\ \%}{ClEt_2Ge{-}GeEt_2Cl} + EtGeCl_3}$$

Si, or Sn) react similarly with $Et_3GeGeEt_3$, with the tin(IV) chloride being the most efficient halogenation reagent, and other alkylated digermanes R_3GeGeR_3 (R = Pr^n, Bu^n) also can be halogenated by these methods.[98]

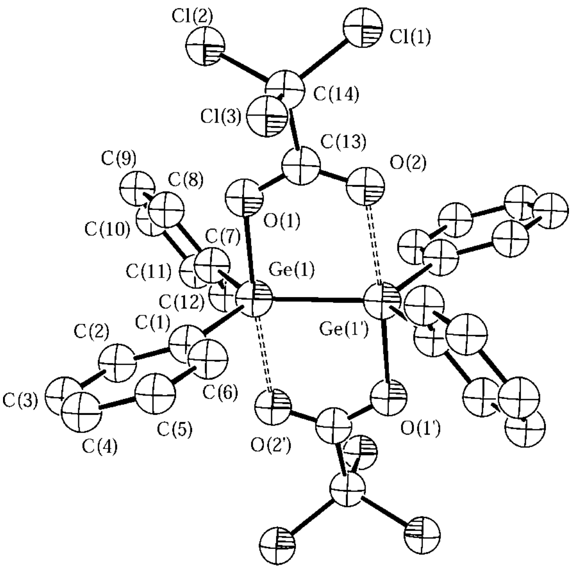


Figure 2. ORTEP diagram of **8**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(1′), 2.393(2); Ge(1)−O(1), 2.073(3); Ge(1)−O(2′), 2.314(3); Ge(1)−C(1), 1.935(4); Ge(1)−C(7), 1.219(5); C(1)−Ge(1)−C(7), 116.4(2); C(1)−Ge(1)−O(1), 91.1(2); C(1)−Ge(1)−O(2′), 89.5(2); C(1)−Ge(1)−Ge(1′), 120.2(1); C(7)−Ge(1)−O(1), 93.5(2); C(7)−Ge(1)−O(2′), 90.3(2); C(7)−Ge(1)−Ge(1′), 123.0(1); O(1)−Ge(1)−O(2′), 175.4(1); O(1)−Ge(1)−Ge(1′), 91.9(1); O(2′)−Ge(1)−Ge(1′), 83.8(1).

The dichlorination of $Me_3GeGeMe_3$ to give **7** can be achieved using sulfuric acid and NH_4Cl (Scheme 6).[84] Reaction of **7** with Bu^tLi at low temperatures resulted in the formation of a polymeric material, small amounts of $Bu^tMe_2GeGeMe_2Bu^t$ and $HMe_2GeGeMe_2Bu^t$, and traces of other products (Scheme 6). The formation of the polymer presumably results from dechlorination of **7** to yield $Me_2Ge{=}GeMe_2$, which then immediately polymerizes. The *tert*-butyl species $Bu^tMe_2GeGeMe_2Bu^t$ can also be obtained as shown in eq 3, and reaction of this material with sulfuric acid results in the formation of a polymer.[84]

$$\mathrm{Bu^tMe_2GeCl \xrightarrow[cyclohexane,\ reflux\ for\ 1\ h]{10\ equiv\ of\ K} \underset{43\%}{Bu^tMe_2Ge{-}GeMe_2Bu^t}} \tag{3}$$

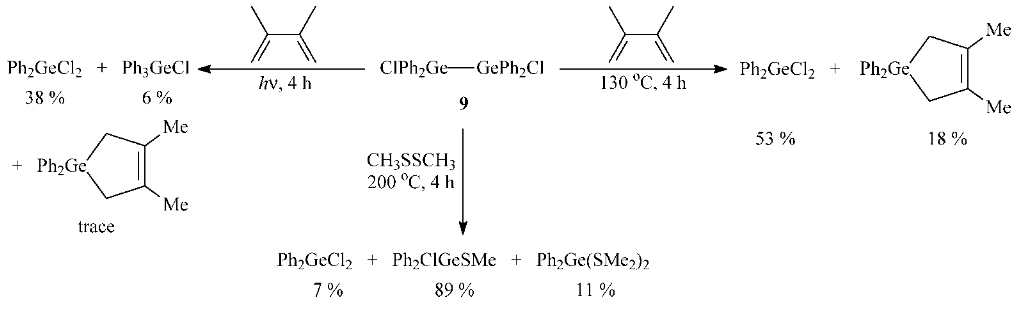
The direct functionalization of $Ph_3GeGePh_3$ using trihaloacetic acids was first accomplished in 1973,[99] and the resulting

Scheme 6

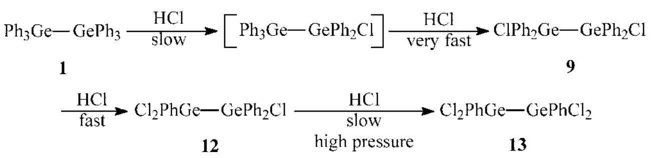
$$\mathrm{Me_3Ge{-}GeMe_3 \xrightarrow[2).\ NH_4Cl,\ 30\ min]{1).\ H_2SO_4,\ 25\ ^{\circ}C,\ 30\ h} \underset{\underset{87\ \%}{7}}{ClMe_2Ge{-}GeMe_2Cl}}$$

$$\mathrm{\underset{7}{ClMe_2Ge{-}GeMe_2Cl} \xrightarrow[\substack{or\ Et_2O \\ -40\ ^{\circ}C\ to\ -60\ ^{\circ}C}]{\substack{Bu^tLi \\ petroleum\ ether}} polymer + Bu^tMe_2Ge{-}GeMe_2Bu^t + HMe_2Ge{-}GeMe_2Bu^t}$$
$$\mathrm{+\ Bu^tMe_2Ge{-}GeMe_2Cl\ (trace) + HMe_2Ge{-}GeMe_2H\ (trace)}$$

Scheme 7



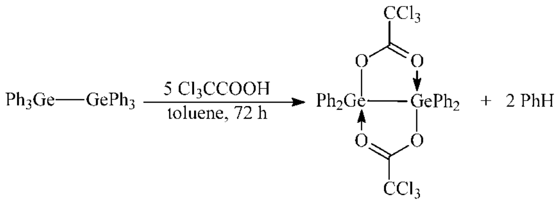
Scheme 8



$$\underset{\mathbf{1}}{Ph_3Ge{-}GePh_3} \xrightarrow[\text{slow}]{HCl} \left[Ph_3Ge{-}GePh_2Cl\right] \xrightarrow[\text{very fast}]{HCl} \underset{\mathbf{9}}{ClPh_2Ge{-}GePh_2Cl}$$

$$\xrightarrow[\text{fast}]{HCl} \underset{\mathbf{12}}{Cl_2PhGe{-}GePh_2Cl} \xrightarrow[\substack{\text{slow}\\ \text{high pressure}}]{HCl} \underset{\mathbf{13}}{Cl_2PhGe{-}GePhCl_2}$$

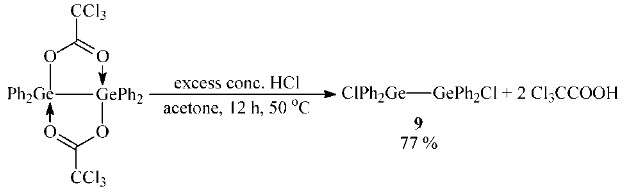
products were subsequently used for the preparation of several different compounds.[99,100] Reaction of 5 equiv of trichloroacetic acid with **1** in toluene results in the selective cleavage of two of the phenyl groups, providing the functionalized digermane **8** (eq 4).[100] In Figure 2 is shown



8
56 %

(4)

the structure of **8**, which contains a relatively short Ge−Ge bond measuring 2.393(2) Å. The contraction of this bond from the normal Ge−Ge bond length (2.43−2.47 Å) is a result of the bridging interactions of the acetate groups with each germanium atom, which involves coordination of the two carbonyl oxygen atoms. Compound **8** can subsequently be converted to the dichloride species **9** by reaction with concentrated HCl in acetone (eq 5).[100] The resulting product

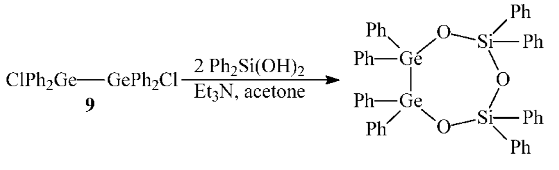


9
77 %

8

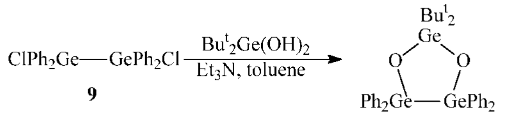
(5)

9 undergoes several thermal and photolytic reactions that proceed through the formation of intermediate germylenes (Scheme 7).[101] Compound **9** reacts with 2 equiv of $Ph_2Si(OH)_2$ (eq 6) to furnish the seven-membered cyclic species **10**[102] or with 1 equiv of $Bu^t_2Ge(OH)_2$ (eq 7) to yield the nearly planar five-membered heterocycle **11**.[103]



10
48 %

(6)



11

(7)

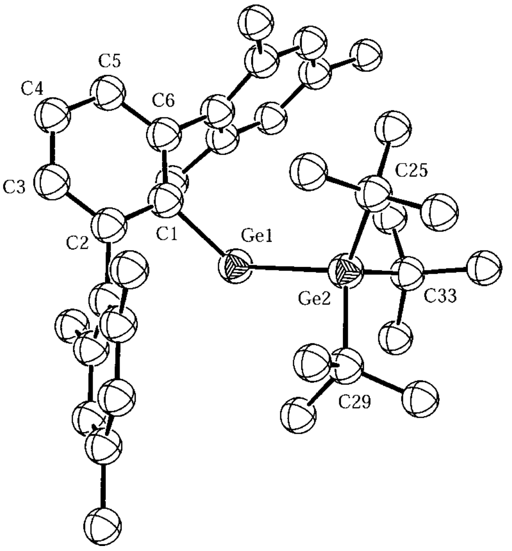
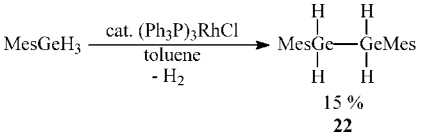


Figure 3. ORTEP diagram of **29**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.5439(7); Ge(1)−C(1), 2.011(5); Ge(2)−C(25), 2.014(5); Ge(2)−C(29), 2.025(5); Ge(2)−C(33), 2.033(5); C(1)−Ge(1)−Ge(2), 114.9(1); Ge(1)−Ge(2)−Ge(25), 120.93(9); Ge(1)−Ge(2)−C(29), 104.87(9); Ge(1)−Ge(2)−C(33), 97.62(9).

Compound **1** can also be directly halogenated to give **9** by reaction with liquid HCl under pressure (Scheme 8).[104] The yields of the more highly halogenated species **12** and **13** increase as the pressure is increased, and **13** can be formed exclusively from **1** in quantitative yield using a 44:1 ratio of HCl to **1** as shown in eq 8. The structure of **13** contains a short Ge−Ge bond length of 2.413(1) Å, resulting from the presence of two electronegative Cl atoms bound to each Ge center in compound **13**.[104] Both **8** and **9** can be converted to chalcogen-containing five- and six-membered heterocycles (Schemes 9 and 10), where compound **14** adopts a chairlike conformation while **16** adopts a half-chair conformation.[105]

$$\underset{\mathbf{1}}{Ph_3Ge{-}GePh_3} \xrightarrow[\text{8 h, 47 atm}]{\text{44 equiv of HCl}} \underset{\substack{\mathbf{13}\\ 100\%}}{Cl_2PhGe{-}GePhCl_2} \qquad (8)$$

The synthesis of a number of sterically encumbered digermanes has been reported. Three different functionalized tetramesityl-substituted digermanes (**19**−**21**)[106,107] were prepared starting with either Mes_2GeCl_2 or Mes_2GeHCl (Scheme 11).[107] The related dimesityl derivative **23** can be obtained from the corresponding hydride **22** and can be used for the synthesis of three additional digermanes bearing fluorenyl substituents, including a difluorinated derivative (Scheme 12).[108] The tetrahydride precursor **22** was obtained via the catalytic coupling of $MesGeH_3$ using Wilkinson's catalyst (eq 9).[109]



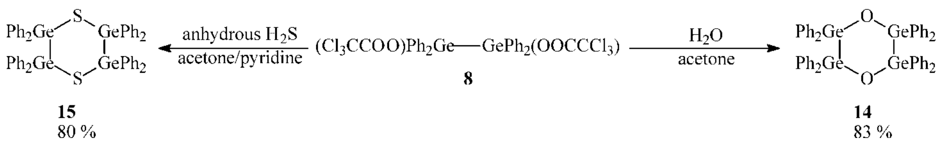
$$MesGeH_3 \xrightarrow[\substack{\text{toluene}\\ -H_2}]{\text{cat. }(Ph_3P)_3RhCl} MesGeH_2{-}GeH_2Mes$$

15 %
22

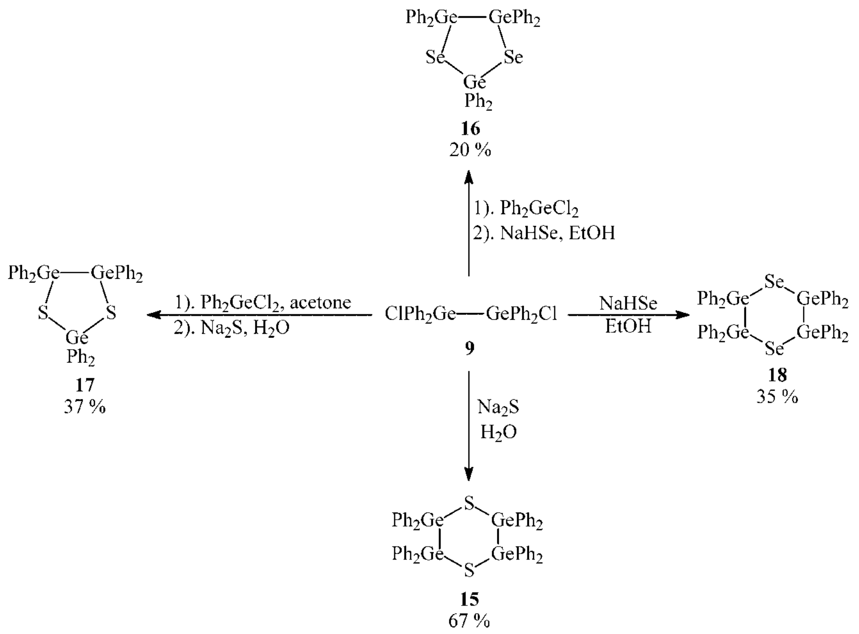
(9)

A digermane dihydride containing germafluorene moieties (**25**) was prepared according to Scheme 13. A long Ge−Ge single bond distance of 2.569(1) Å was observed in the solid-state structure of the dianion precursor **24**, and the lone electron

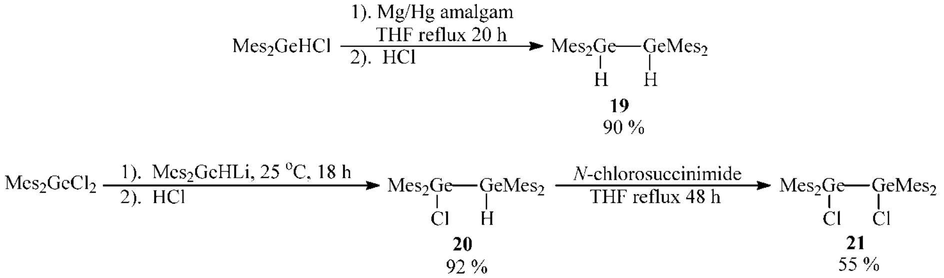
Scheme 9



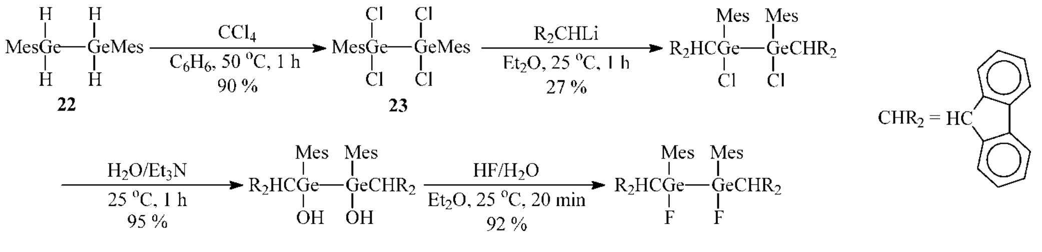
Scheme 10



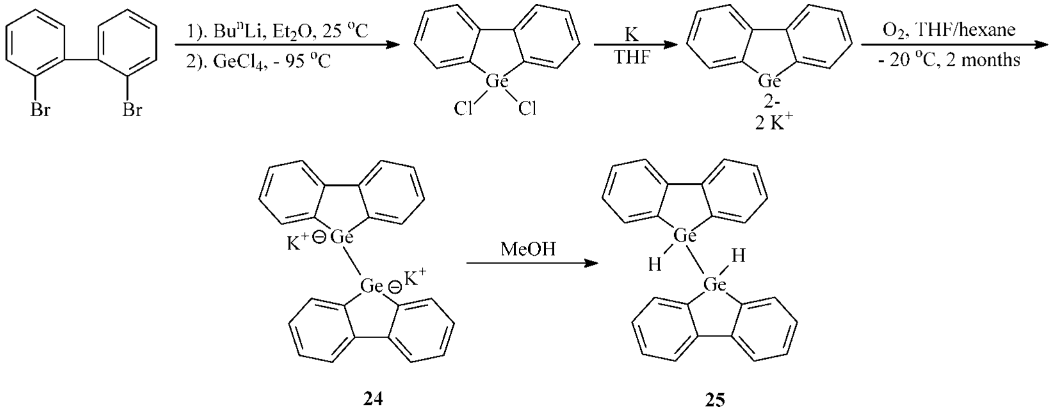
Scheme 11



Scheme 12



Scheme 13

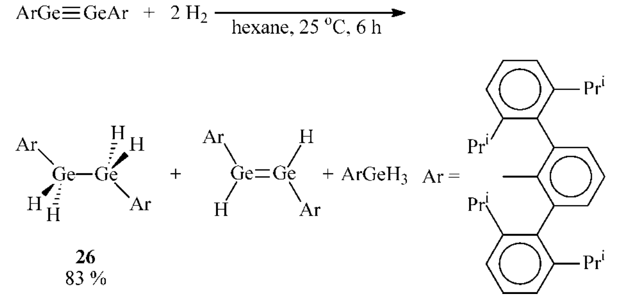


Scheme 14

$$\mathrm{GeCl_4} + 3\,\mathrm{LiCu(CN)Bu^t} \xrightarrow[-25\,^{\circ}\mathrm{C}]{\mathrm{THF}} \underset{25\,\%}{\mathrm{Bu^t_3GeCl}} + 3\,\mathrm{LiCl} + 3\,\mathrm{CuCN}$$

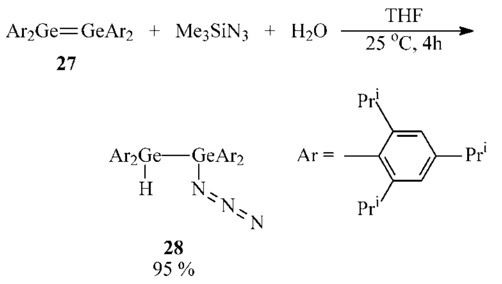
$$2\,\mathrm{Bu^t_3GeCl} + 2\,\mathrm{Li/C_{10}H_8} \xrightarrow[25\,^{\circ}\mathrm{C},\ 12\ \mathrm{h}]{\mathrm{THF}} \underset{\substack{\mathbf{32}\\ 16\,\%}}{\mathrm{Bu^t_3Ge{-}GeBu^t_3}} + 2\,\mathrm{LiCl} + 2\,\mathrm{C_{10}H_8}$$

pairs at the germanium centers of **24** remain localized, thus rendering both germafluorenyl ring systems nonaromatic.[110] A digermane containing two extremely bulky aryl ligands (**26**) was prepared by the carefully controlled hydrogenation of the corresponding digermyne (eq 10). Compound **26** contains a normal Ge−Ge bond distance despite the presence of the large aryl groups, since this species also has two sterically unencumbering hydrogen atoms attached to each germanium center.[111] Reaction of the digermene **27** with hydrazoic acid, generated *in situ* from trimethylsilylazide and water, results in a 1,2-addition of $\mathrm{HN_3}$ to furnish the azide-substituted digermane **28** in near-quantitative yield (eq 11).[112] The two N−N distances in the azide ligand of **28** are nearly identical (1.14 Å), which contrasts with the case of organic molecules containing a $\mathrm{N_3}$ group.



26
83 %

(10)



27

28
95 %

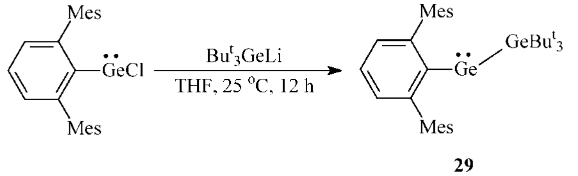
(11)

The reaction of 2,6-dimesitylphenylchlorogermanium(II) with $\mathrm{Bu^t_3GeLi}$ furnishes the tri-*tert*-butylgermyl-substituted germylene **29** (eq 12, Figure 3).[113] The Ge(II)−Ge(IV) bond length in **29** is outside the normal range for Ge−Ge single bonds (2.5439(7) Å), due to the mixed oxidation states of the two germanium atoms, and the environment about Ge(1) approaches trigonal with a C−Ge−Ge angle of 114.9(1)°. The UV/visible spectrum of **29** exhibits an absorption maximum at 719 nm, resulting from an n → p transition from the Ge(IV) fragment to the vacant p-orbital of the germylene fragment.

Scheme 15

$$\mathrm{R_3GeNMe_2} + \mathrm{R'_3GeH} \xrightarrow[85\,^{\circ}\mathrm{C},\ 48\ \mathrm{h}]{\mathrm{CH_3CN}} \mathrm{R_3Ge{-}GeR'_3}$$

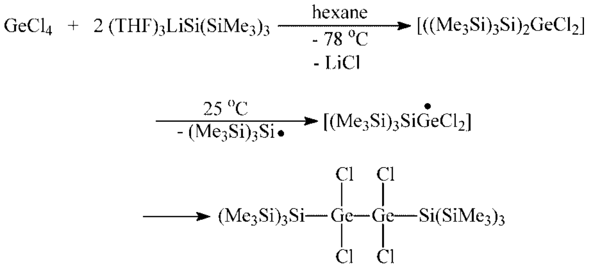
33: R = Bu, R' = Ph, 83 %
34: R = Et, R' = Ph, 84 %
35:R = Bu, R' = Me, 86 %



29
9 %

(12)

The tris(trimethylsilyl)silyl-substituted digermane **30** was obtained in 49% yield according to eq 13,[114] while the coupling of $(\mathrm{Me_3Si})_3\mathrm{GeLi}$ in the presence of 1,2-dibromoethane[115] or $\mathrm{PbCl_2}$[116] provides the related digermane $(\mathrm{Me_3Si})_3\mathrm{GeGe(SiMe_3)_3}$ (**31**), where the yield via the latter preparative route was 45% (eq 14). The structure of **31** (Figure 4) contains a slightly elongated Ge−Ge bond length of 2.4787(7) Å due to the presence of the bulky $-\mathrm{SiMe_3}$ groups, and the three $-\mathrm{SiMe_3}$ groups on each Ge atom adopt a staggered conformation with torsion angles of 43.2° and 76.8°.[117] The related digermane $\mathrm{Bu^t_3GeGeBu^t_3}$ (**32**) was prepared from $\mathrm{GeCl_4}$ in two steps as shown in Scheme 14, and was also characterized by X-ray diffraction (Figure 5).[118] The unit cell of **32** contains two crystallographically independent molecules with Ge−Ge bond distances of 2.705(1) Å and 2.714(1) Å (average = 2.710(1) Å), that represent two of the longest reported Ge−Ge single bond lengths to date.[118] Each molecule of **32** contains a 2-fold axis of symmetry which bisects the Ge−Ge bond. The longer Ge−Ge distances in **32** versus that of the related species **31** are due to the increased steric repulsion of the three $\mathrm{Bu^t}$-groups versus the three $-\mathrm{SiMe_3}$ groups, since the Ge−Si bonds in **31** are longer than the Ge−C bonds in **32**. This results in less steric crowding about the germanium centers in **31**, therefore resulting in a shorter Ge−Ge distance.



$$\mathrm{GeCl_4} + 2\,(\mathrm{THF})_3\mathrm{LiSi(SiMe_3)_3} \xrightarrow[\substack{-78\,^{\circ}\mathrm{C}\\ -\mathrm{LiCl}}]{\text{hexane}} [((\mathrm{Me_3Si})_3\mathrm{Si})_2\mathrm{GeCl_2}] \xrightarrow[-(\mathrm{Me_3Si})_3\mathrm{Si}\bullet]{25\,^{\circ}\mathrm{C}} [(\mathrm{Me_3Si})_3\mathrm{Si}\dot{\mathrm{Ge}}\mathrm{Cl_2}] \longrightarrow (\mathrm{Me_3Si})_3\mathrm{Si{-}GeCl_2{-}GeCl_2{-}Si(SiMe_3)_3}$$

30
49 %

(13)

$$(\mathrm{Me_3Si})_3\mathrm{GeLi(THF)_{2.5}} + \mathrm{PbCl_2} \xrightarrow[-78\,^{\circ}\mathrm{C},\ 6\ \mathrm{h};\ 25\,^{\circ}\mathrm{C},\ 6\ \mathrm{h}]{\mathrm{Et_2O}} \underset{\substack{\mathbf{31}\\ 45\%}}{(\mathrm{Me_3Si})_3\mathrm{Ge{-}Ge(SiMe_3)_3}} + \mathrm{Pb} + 2\mathrm{LiCl} \quad (14)$$

The synthesis of unsymmetrical digermanes having sterically undemanding substituents has been described using several methods, including the preparation of the methyl-substituted compounds $\mathrm{Me_3GeGeR_3}$ (R = Et, Bu) by nucleophilic substitution reactions involving trialkylgermyl anions (eq 15).[119] The hydrogermolysis reaction involving a germanium hydride and germanium amide also is a useful reaction for the formation of Ge−Ge bonds, and several unsymmetrical digermanes have also been prepared using this method. The reaction of $(\mathrm{C_6F_5})_3\mathrm{GeH}$ with $\mathrm{Et_3GeNEt_2}$ yielded the digermane $(\mathrm{C_6F_5})_3\mathrm{GeGeEt_3}$ (eq 16),[33] and three

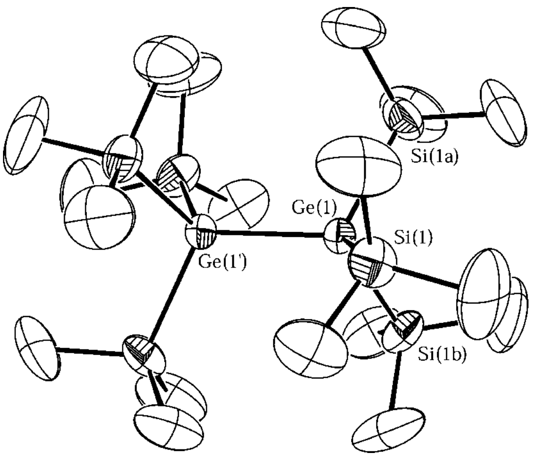
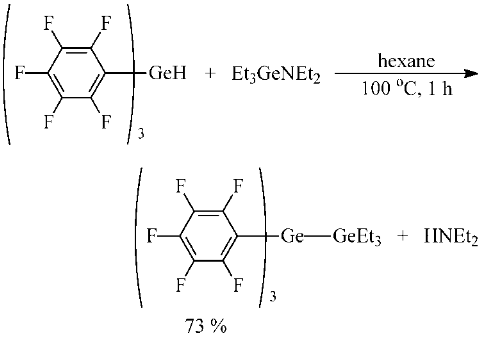


Figure 4. ORTEP diagram of **31**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(1′), 2.4787(7); Ge(1)−Si(1), 2.4062(6); Si(1)−Ge(1)−Si(1a), 105.65(2); Si(1)−Ge(1)−Ge(1′), 113.07(2).

digermanes **33**−**35** were obtained from the corresponding amide and hydride using acetonitrile as the reaction medium (Scheme 15).[34]

$$R_3GeCl + 2K \xrightarrow{HMPT} \underset{\substack{R=Et,Bu\\ yield=60\%}}{R_3GeK + KCl} \xrightarrow{Me_3GeCl} R_3Ge-GeMe_3 + KCl \quad (15)$$

The hydrogermolysis reaction is generally regarded to require "activated" germanium hydrides, such as the perfluorophenyl species $(C_6F_5)_3GeH$ mentioned above, for the generation of germanium−germanium bonds. However, this was circumvented in the syntheses of compounds **33**−**35** (Scheme 15), where the CH_3CN solvent used as the reaction medium reacts with the germanium amides to produce α-germyl nitriles.[120−122] These species contain a labile Ge−C bond that undergoes reaction with the Ge−H bond of Ph_3GeH to yield the digermanes, and therefore CH_3CN is not only a solvent but also a reagent in this process.



(16)

The presence of an α-germyl nitrile as a reactive intermediate was confirmed by the direct preparation of Bu_3GeCH_2CN. Subsequent reaction of this material with Ph_3GeH (Scheme 16) yielded the digermane **33** in approximately 1 h instead of 48 h.[34] The shorter reaction time is not general, however, as indicated by the reactions of $Pr^i_3GeCH_2CN$ and $Bu^t_3GeCH_2CN$ with Ph_3GeH.[35] In the former case, complete conversion to the desired digermane $Pr^i_3GeGePh_3$ required a reaction time of 36 h, while in the latter case generation of $Bu^t_3GeGePh_3$ via the hydrogermolysis reaction did not occur. Rather, a 3-amidocrotononitrile compound was isolated in low yield as the only product (Scheme 16). This arises from the insertion of a molecule of acetonitrile into the Ge−C bond of the α-germyl nitrile via a process similar to the Thorpe reaction, and the same 3-amidocrotononitrile product was obtained starting with the amide $Bu^t_3GeNMe_2$. Therefore, the general lability of the Ge−C bond previously reported[120,121] seems suspect, and the reactivity of the α-germyl nitriles with germanium hydrides appears to depend on the other substituents attached to germanium.

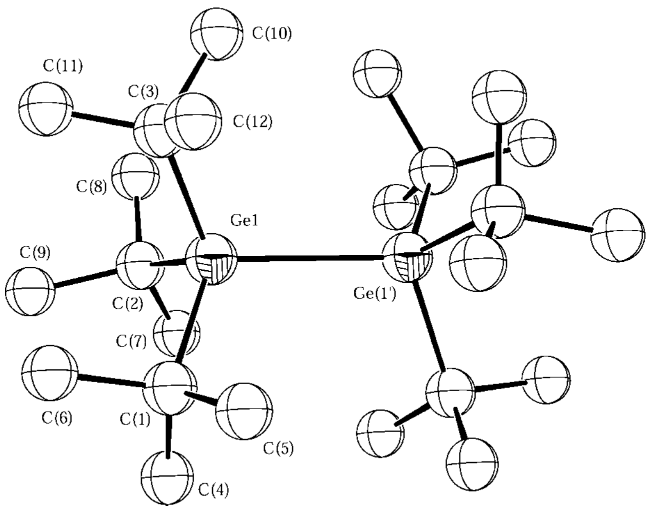


Figure 5. ORTEP diagram of one molecule of **32**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(1′), 2.705(1); Ge(1)−C(1), 2.085(5); Ge(1)−C(2), 2.047(8); Ge(1)−C(3), 2.048(4); C(1)−Ge(1)−C(2), 109.0(3); C(1)−Ge(1)−C(3), 106.3(2); C(2)−Ge(1)−C(3), 108.4(3); C(1)−Ge(1)−Ge(1′), 112.7(1); C(2)−Ge(1)−Ge(1′), 110.1(3); C(3)−Ge(1)−Ge(1′), 112.7(1).

The structures of three digermanes $Ph_3Ge-GeR_3$ (R = Me (**36**), Et (**34**), Bu^n (**33**)) bearing different substituent sets on one of the germanium atoms have been determined. The structures of the methyl- and ethyl-containing derivatives **36**[123] and **34**[34] each exhibit 3-fold symmetry about the Ge−Ge bond, while this symmetry element is absent in the *n*-butyl derivative **33**.[34] Compound **33** contains two crystallographically independent but chemically identical mol-

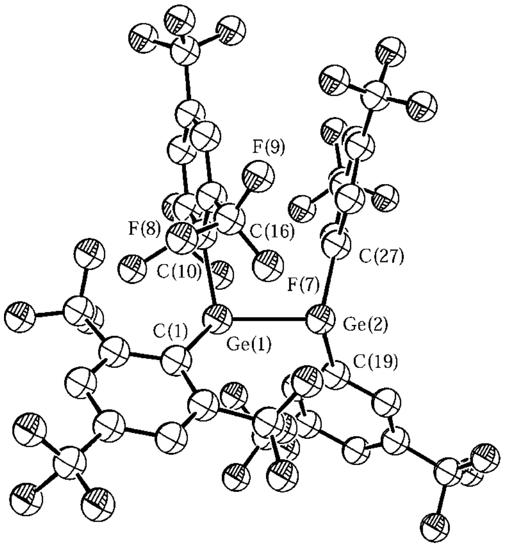
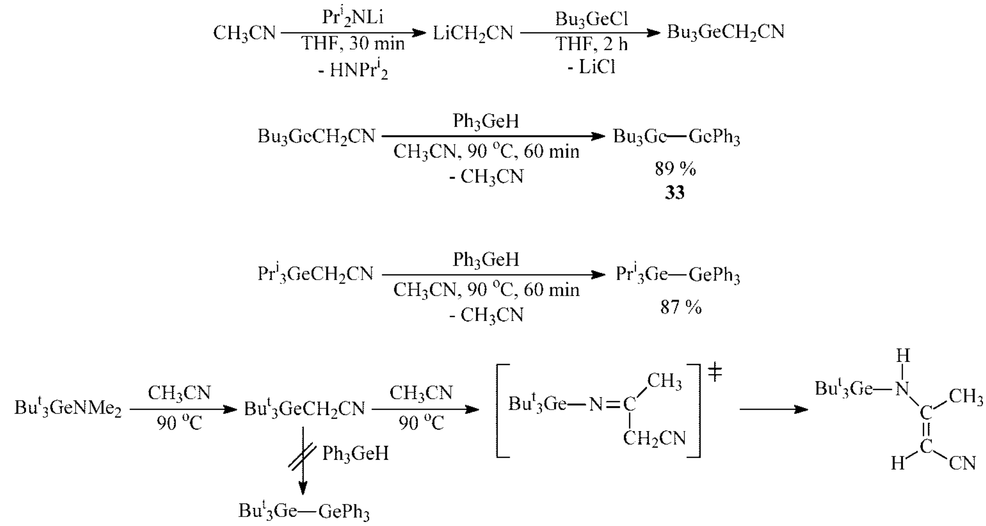
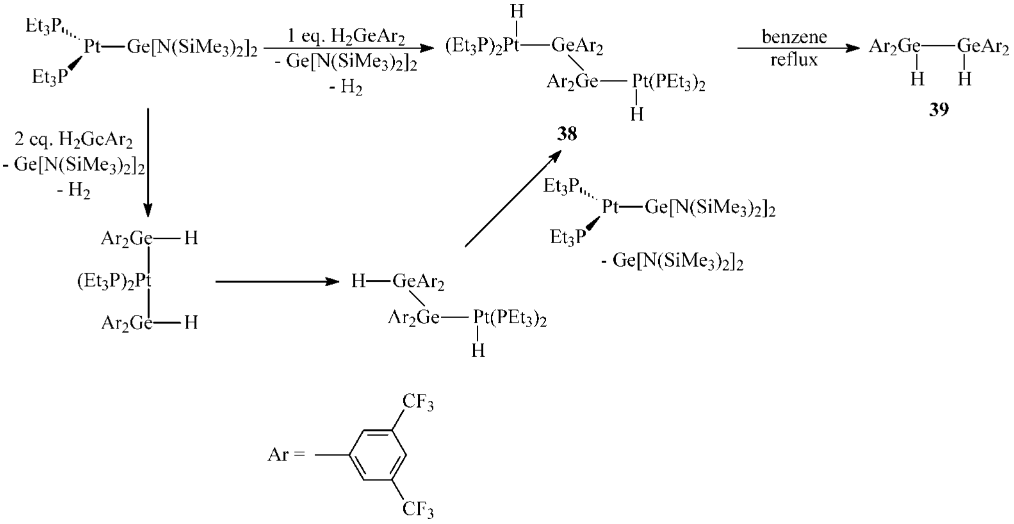


Figure 6. ORTEP diagram of **37**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.4352(3); Ge(1)−C(1), 2.012(2); Ge(1)−C(10), 2.001(2); Ge(1)−F(7), 2.837(2); Ge(2)−C(19), 1.942(2); Ge(2)−C(27), 1.952(2); C(1)−Ge(1)−C(10), 112.42(9); C(19)−Ge(2)−C(27), 109.0(1).

Scheme 16

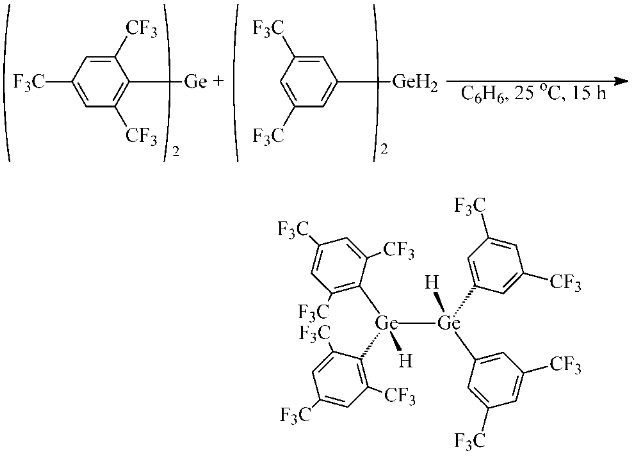


Scheme 17



ecules in the unit cell. The environment of the germanium atoms in both **36** and **34** approaches tetrahedral, while the Ge atom of **33** bearing the *n*-butyl substituents deviates slightly from this idealized geometry. The Ge–Ge bond lengths in these digermanes are very similar, owing to the fact that methyl or methylene groups attached to the germanium atom in each case are similar in terms of steric bulk.

The synthesis of several digermanes with unusual substituents has also been described. In an interesting reaction, the unsymmetrical trifluoromethylphenyl-substituted germane **37** was obtained via the insertion of a germylene into a Ge–H bond (eq 17).[124] The structure of **37**, shown in Figure 6, is unusual in that there are several weak Ge–F contacts between the germanium atoms and the aryl-CF_3 groups, the shortest of which is 2.837(2) Å, occurring between Ge(1) and F(7). Digermanes having transition metal complexes as substituents have been prepared and characterized, including a platinum complex–substituted digermane (**38**). Compound **38** was obtained by the displacement reaction shown in Scheme 17, and the mechanism for its formation was elucidated by variation of the stoichiometric ratio of the reactants.[125] The structure of **38** exhibits a *trans*-disposition of the two platinum substituents about the Ge–Ge bond, where the two Ge–Pt bond distances are 2.4363(5) Å and the two Pt–Ge–Ge angles are 116.86(3)°. Heating **38** in refluxing benzene results in the loss of the platinum ligands to furnish the digermane **39**.[125]

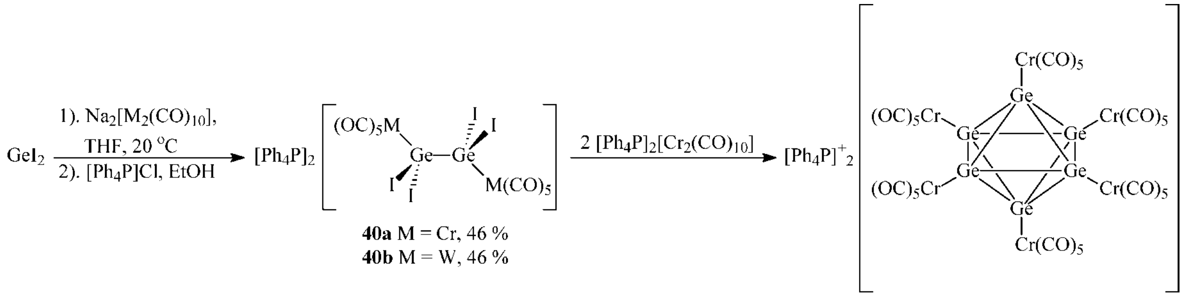


37
67 %

(17)

Reductive coupling of germanium(II) iodide with dimetallic group 6 carbonyl anions provides the digermanes **40**

Scheme 18

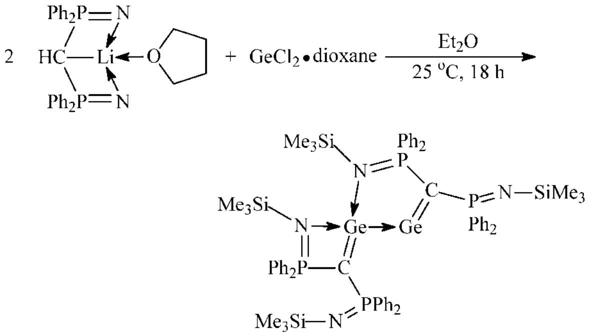


40a M = Cr, 46 %
40b M = W, 46 %

41

that formally contain germanium in the unusual +1 oxidation state (Scheme 18).[126] The structures of the $[Ph_4P]^+$ salts of **40a** and **40b** were obtained, and these contain normal Ge−Ge bond lengths and Ge−M distances of 2.468(1) Å (**40a**, M = Cr) and 2.606(1) Å (**40b**, M = W). The chromium containing species can be further reacted with $[Cr_2(CO)_{10}]^{2-}$ to yield the cluster **41**, which contains an octahedral Ge_6^{2-} core.[126] The structure of **41** has been determined, and the molecule exhibits D_4 symmetry with long Ge−Ge bond distances of 2.525(2) Å among the germanium atoms in the equatorial Ge_4 plane, and even more elongated bond distances of 2.541(1) Å between the germanium atoms in the equatorial plane and those at the apexes.[127]

Two other digermanes having uncommon substituents have also been recently reported. The digermane **42** was obtained from the reaction of the 3-germa-β-diketiminate complex **43** with palladium chloride (Scheme 19).[128] The formation of **42** from **43** is presumed to occur via reduction of the intermediate chloride **44** by finely divided palladium metal formed in the reaction. The digermane **45** was obtained from $GeCl_2$·dioxane (eq 18), and is formally a dimer containing two bis(germavinylidene) moieties bound together in a head to head fashion via a dative Ge−Ge bond measuring 2.483(1) Å,[129] which is slightly outside the 2.43−2.47 Å range of normal Ge−Ge single bond lengths.



45
42 %

(18)

UV-absorption data for a number of digermanes, as well as numerous higher oligomers, has been reported, and λ_{max} values for these compounds are collected in Table 2. It can be seen that subtle variation of the substituents attached to the germanium centers in various digermanes, including replacement of methyl groups with phenyl groups, replacement of phenyl groups with chloride atoms, and variation of the attached halogens, has a measurable effect on the position of the absorption maxima of these species. The observed absorption features correspond to the HOMO−LUMO

Table 2. UV/Visible Data for Oligogermanes with Absorbance Maxima (λ_{max}) in Nanometers

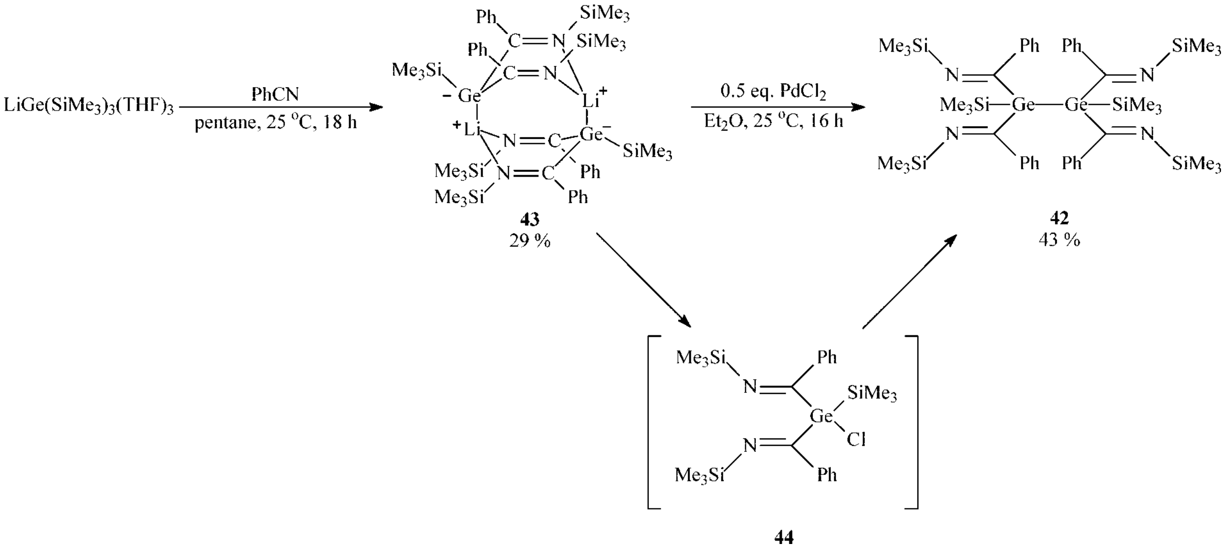
compd	λ_{max}	ref	compd	λ_{max}	ref
Digermanes			**Trigermanes**		
$Me_3GeGeMe_3$	197	207	Me_8Ge_3	218	208
$PhMe_2GeGeMe_3$	228	131	Et_8Ge_3	218	189
$PhMe_2GeGeMe_2Ph$	233	131	$Ph(GeEt_2)_3Ph$	241	131
$Ph_3GeGeMe_3$	233	131	$Ph_3Ge(GeEt_2)GePh_3$ (**46**)	247	131
$Ph_3GeGeMe_2Ph$	234	131	$Ph_3Ge(GeMe_2)GePh_3$ (**49**)	245	131
$Ph_2MeGeGeMe_2Ph$	237	131	$Ph_3Ge(GePhMe)GePh_3$	250	131
$Ph_3GeGePh_3$ (**1**)	241	131	$Ph_3Ge(GePh_2)GePh_3$ (**2**)	250	131
$Ph_3GeGeClPh_2$	236	131	Mes_6Ge_3 (**62b**)	273	206
$Ph_2FGeGeFPh_2$	226	131			
$Ph_2ClGeGeClPh_2$ (**9**)	225	131	**Tetragermanes**		
$Ph_2BrGeGeBrPh_2$ (**4**)	231	131	$Me_{10}Ge_4$	233	208
$Ph_2IGeGeIPh_2$	240	131	$Et_{10}Ge_4$	234	189
$PhCl_2GeGeCl_2Ph$ (**13**)	230	131	$Ph(GeEt_2)_4Ph$	248	131
$Et_3GeGeEt_3$	202	189	$Ph_3Ge(GeEt_2)_2GePh_3$	256	131
$(Me_3Si)_3GeGe(SiMe_3)_3$ (**31**)	209	117	$Ph_3Ge(GeEt_2)_3CH_2CH_2OEt$ (**96a**)	235	34
$Ph(GeEt_2)_2Ph$	233	131	$Ph_3Ge(GeBu_2)_3CH_2CH_2OEt$ (**96b**)	241	34
			$(Pr^i{}_2Ge)_4$	280	206
Pentagermanes			$(Ph_2Ge)_4$ (**103**)	280	206
$Me_{12}Ge_5$	246	208			
$Et_{12}Ge_5$ (**112**)	248	189	**Hexagermanes**		
$Ph_3Ge(GeEt_2)_3GePh_3$ (**113**)	269	131	$Me_{14}Ge_6$	255	208
$Ph(GeEt_2)_5Ph$	256	131	$Et_{14}Ge_6$	258	189
$(Me_2Ge)_5$	270	206	$Ph(GeEt_2)_6Ph$	264	131
$(Ph_2Ge)_5$ (**115**)	272	206	$Ph_3Ge(GeEt_2)_4GePh_3$	278	131
			$(Me_2Ge)_6$	250	206
			$(Ph_2Ge)_6$ (**116**)	270	206

Table 3. Selected Distances (Å) and Angles (deg) in Linear Trigermanes

compd	*d* Ge^1−Ge^2	*d* Ge^2−Ge^3	d_{avg} Ge−Ge	d_{avg} Ge−C	∠Ge^1−Ge^2−Ge^3	ref
$Ph_3Ge^1-Ge^2Ph_2-Ge^3Ph_3$ (**2**)	2.438(2)	2.441(2)	2.440(2)	1.96(1)	121.3(1)	86
$Ph_3Ge^1-Ge^2Me_2-Ge^3Ph_3$ (**49**)	2.429(1)	2.429(1)	2.429(1)	1.951(6)	120.3(1)	133
$ClPh_2Ge^1-Ge^2Ph_2-Ge^3Ph_2Cl$ (**53**)[a]	2.425(2)	2.421(2)	2.418(2)	1.95(5)	113.6(1)	135
$IBu^t_2Ge^1-Ge^2Bu^t_2-Ge^3Bu^t_2I$ (**56**)	2.660(1)	2.622(1)	2.641(1)		115.4(1)	137
$BrBu^t_2Ge^1-Ge^2Bu^t_2-Ge^3Bu^t_2Br$ (**57**)	2.623(1)	2.595(1)	2.609(1)	2.050(6)	113.5(1)	138
$MeBu^t_2Ge^1-Ge^2Bu^t_2-Ge^3Bu^t_2Me$ (**58**)	2.620(1)	2.620(1)	2.620(1)	2.027(7)	118.6(1)	138

[a] Values are the average of two crystallographically independent molecules.

Scheme 19



electronic transition in these systems, which is typically regarded as promotion of an electron from the σ to the σ* molecular orbital, and are related to the number of atoms present in the Ge−Ge backbone as well as the identity of the attached organic substituents.

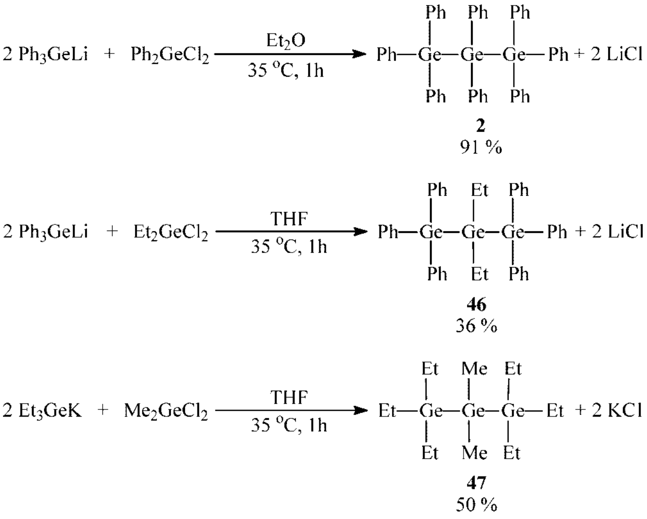
As shown in the data for the digermanes collected in Table 2, the presence of phenyl substituents has a pronounced effect on the relative energies of the frontier orbitals in these molecules. The phenyl group is a better σ-donor and is more sterically encumbering than alkyl substituents, and therefore is expected to raise the energy of the HOMO.[36] The phenyl groups in these digermanes result in the LUMO being primarily composed of combinations of the phenyl π* orbitals, rather than being a germanium-based σ* orbital, and thus the λ_{max} values are red-shifted in these systems versus those for the digermanes having only alkyl groups as the substituents.

3. Trigermanes

3.1. Linear Trigermanes

The preparation of the linear trigermane $Ph_3GeGePh_2GePh_3$ (**2**) was originally achieved by the nucleophilic substitution reaction of Ph_3GeNa with Ph_2GeCl_2, although the yield was not reported.[130] Compound **2** was later obtained in high (91%) yield by the reaction of Ph_3GeLi with Ph_2GeCl_2,[131] and the trigermanes $Ph_3GeGeEt_2GePh_3$ (**46**)[131] and $Et_3GeGeMe_2GeEt_3$ (**47**)[132] were also prepared using similar methods (Scheme 20).

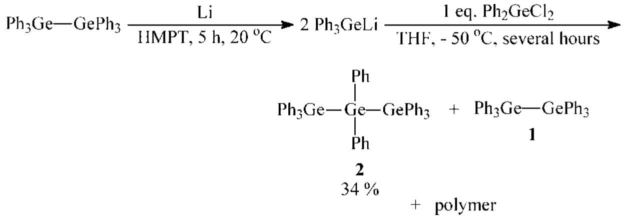
Scheme 20



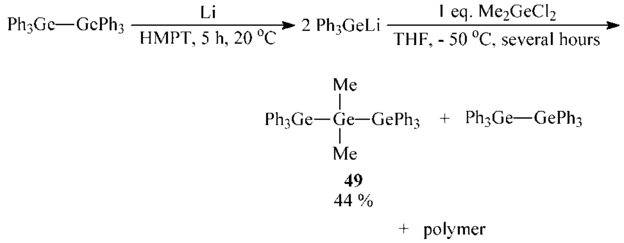
Compound **2** was also isolated from the reaction of PhMgBr with $GeCl_4$ in a maximum yield of 11% with minimal formation of the tetragermane **3** (Scheme 2). This was observed when THF was used as the reaction medium and the excess magnesium metal used to generate PhMgBr from bromobenzene was removed from the reaction mixture by filtration (Scheme 2).[86] The structure of **2** was determined, and the molecule was found to adopt a bent conformation about the central germanium atom with Ge−Ge distances of 2.438(2) and 2.441(2) Å and a Ge−Ge−Ge angle of 121.3(1)°.[86] The phenyl substituents in **2** are arranged in a staggered conformation (Figure 7), and the environment about each of the three germanium atoms approaches tetrahedral (Table 3).

The yield of **2** from the reaction of PhMgBr and $GeCl_4$ was later optimized to 34% yield by using hexamethylphosphorus trisamide (HMPT) as the solvent (eq 19), and the reaction pathway for this process is shown in Scheme 21.[133]

The presence of HMPT in this case suppresses nucleophilic attack of the $\mathrm{Ph_3Ge^-}$ anion at the newly formed Ge−Ge bond of the intermediate species **48**, thus increasing the amount of **2** produced. Under similar conditions, the mixed alkyl/aryl trigermane **49** was obtained in 44% yield (eq 20), and its crystal structure was determined (Table 3). Compound **49** has C_2 symmetry with two identical Ge−Ge bond lengths of 2.429(1) Å, which is shorter than those of **2** due to the presence of two methyl groups at the central germanium atom. Similar to **2**, compound **49** adopts a bent structure with a Ge−Ge−Ge bond angle of 120.3(1)°.[133] A related mixed group 14 analogue of **2**, $\mathrm{Ph_3GeGePh_2SiPh_3}$, has also been synthesized.[134]



$$\mathrm{Ph_3Ge{-}GePh_3} \xrightarrow[\text{HMPT, 5 h, 20 °C}]{\text{Li}} 2\,\mathrm{Ph_3GeLi} \xrightarrow[\text{THF, - 50 °C, several hours}]{\text{1 eq. }\mathrm{Ph_2GeCl_2}} \underset{\substack{\mathbf{2}\\ 34\,\%}}{\mathrm{Ph_3Ge{-}Ge(Ph)_2{-}GePh_3}} + \underset{\mathbf{1}}{\mathrm{Ph_3Ge{-}GePh_3}} + \text{polymer} \qquad (19)$$



$$\mathrm{Ph_3Ge{-}GePh_3} \xrightarrow[\text{HMPT, 5 h, 20 °C}]{\text{Li}} 2\,\mathrm{Ph_3GeLi} \xrightarrow[\text{THF, - 50 °C, several hours}]{\text{1 eq. }\mathrm{Me_2GeCl_2}} \underset{\substack{\mathbf{49}\\ 44\,\%}}{\mathrm{Ph_3Ge{-}Ge(Me)_2{-}GePh_3}} + \mathrm{Ph_3Ge{-}GePh_3} + \text{polymer} \qquad (20)$$

A preparative route for the formation of several discrete trigermanes involves the coupling of organogermanium halides using 10 equiv of $\mathrm{SmI_2}$ as the reducing agent, which provides these compounds in excellent yields in most cases (Table 4, eq 21).[39] When only 2 equiv of $\mathrm{SmI_2}$ are used, polygermanes are obtained as the products. The hydrogermolysis reaction has also been employed for the efficient synthesis of the discrete trigermanes **52** from the digermanes **50** bearing an ethoxyethyl substituent.[34] The ethoxyethyl substituent can be removed with di*iso*butylaluminum hydride (DIBAL-H), to generate a reactive hydride site in the compounds **51** that are subsequently employed for the introduction of an additional germanium atom into the chain (Scheme 22).[34] The phenyl-substituted digermane **50c**, however, could not be converted to the corresponding hydride **51c** using this method, presumably due to the steric and electronic effects of the attached phenyl groups. The Ge−Ge bond forming reactions again proceed by the conversion of the starting amides to α-germyl nitriles by reaction of these compounds with the $\mathrm{CH_3CN}$ solvent. This process is highly useful, since it can be used for the stepwise synthesis of oligogermanes and permits the variation of the organic substituents bound to each of the atoms in the Ge−Ge backbone (*vide infra*).

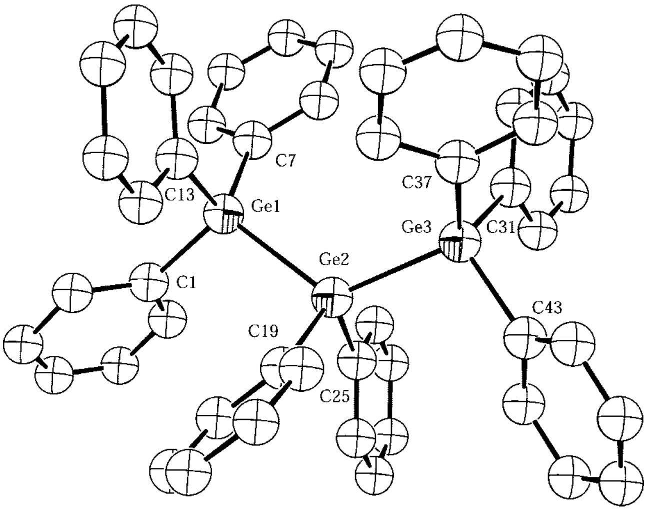
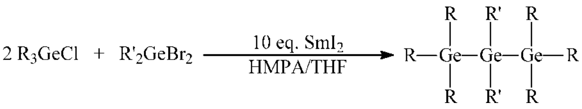


Figure 7. ORTEP diagram of **2**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.438(2); Ge(2)−Ge(3), 2.441(2); Ge−$\mathrm{C_{avg}}$, 1.960(1); Ge(1)−Ge(2)−Ge(3), 121.3(1); Ge−Ge−$\mathrm{C_{avg}}$, 108.7(3); C−Ge−$\mathrm{C_{avg}}$, 108.8(5).

Table 4. Experimental Data for Eq 21

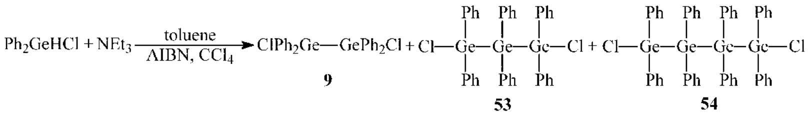
$\mathrm{R_3GeCl}$	$\mathrm{R'_2GeBr_2}$	trigermane product	yield (%)
$\mathrm{Me_3GeCl}$	$\mathrm{Ph_2GeBr_2}$	$\mathrm{Me_3GeGePh_2GeMe_3}$	87
$\mathrm{Et_3GeCl}$	$\mathrm{Ph_2GeBr_2}$	$\mathrm{Et_3GeGePh_2GeEt_3}$	94
$\mathrm{Pr^i{}_3GeCl}$	$\mathrm{Ph_2GeBr_2}$	$\mathrm{Pr^i{}_3GeGePh_2GePr^i{}_3}$	30
$\mathrm{Bu^n{}_3GeCl}$	$\mathrm{Ph_2GeBr_2}$	$\mathrm{Bu^n{}_3GeGePh_2GePh_3}$	87
$\mathrm{Et_3GeCl}$	$\mathrm{MePhGeBr_2}$	$\mathrm{Et_3GeGeMePhGeEt_3}$	70



$$2\,\mathrm{R_3GeCl} + \mathrm{R'_2GeBr_2} \xrightarrow[\text{HMPA/THF}]{\text{10 eq. }\mathrm{SmI_2}} \mathrm{R{-}Ge(R)_2{-}Ge(R')_2{-}Ge(R)_2{-}R} \qquad (21)$$

The functionalized trigermane **53**, which contains a chloride atom at each terminus of the chain, was prepared along with the chlorinated digermane **9** and tetragermane **54** according to Equation 22,[135] and the ratio of the oligomers produced depends on the reaction stoichiometry. The pathway for the formation of **9**, **53**, abd **54** involves elimination of HCl from $\mathrm{Ph_2GeHCl}$ to generate the germylene:$\mathrm{GePh_2}$ (Scheme 23), with subsequent insertion of the germylene into the Ge−Cl bond of $\mathrm{Ph_2GeHCl}$. In a related reaction, the insertion of PhGeCl, generated from $\mathrm{PhGeHCl_2}$ and MeOLi, into the Ge−Cl bonds of $\mathrm{PhGeCl_3}$ followed by treatment with MeMgI results in a mixture of products (Scheme 24), including a trigermane and a branched tetragermane.[136]

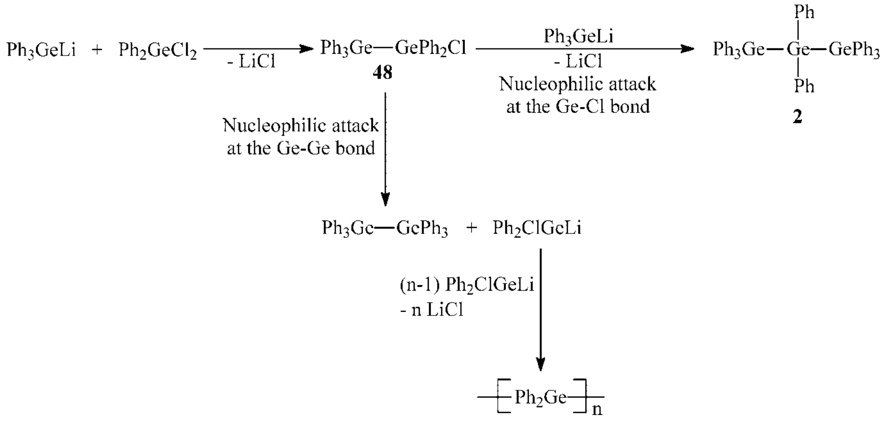
The structure of **53** contains two crystallographically independent molecules where the Cl−$\mathrm{Ge_3}$−Cl chain is arranged in a *gauche−gauche* conformation in one molecule (**53a**) and in a *anti−gauche* conformation in the other (**53b**), as shown in Figure 8. The Ge−Ge bond distances are different in each case, measuring 2.437(2) and 2.419(1) Å in **53a** and 2.413(2) and 2.423(2) Å in **53b**. The Ge−Ge−Ge bond angles are also substantially different among the two molecules, being 110.4(1)° in **53a** and 116.7(1)° in **53b**. The



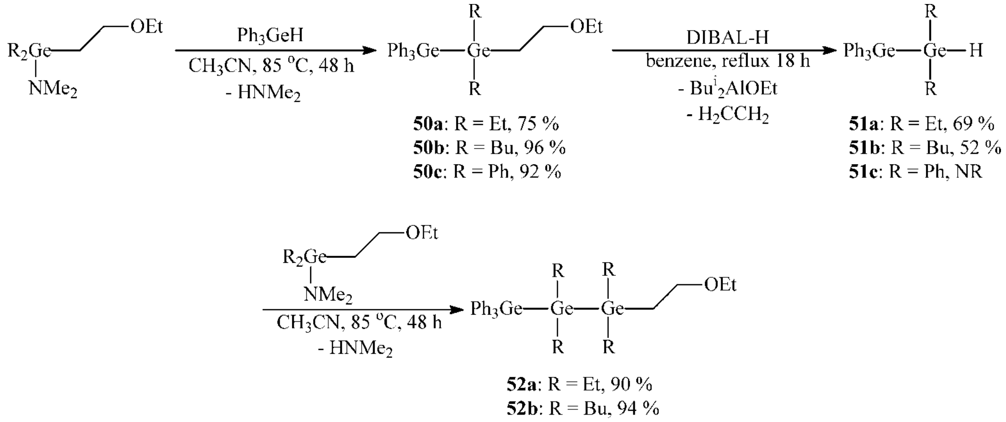
$$\mathrm{Ph_2GeHCl} + \mathrm{NEt_3} \xrightarrow[\text{AIBN, }\mathrm{CCl_4}]{\text{toluene}} \underset{\mathbf{9}}{\mathrm{ClPh_2Ge{-}GePh_2Cl}} + \underset{\mathbf{53}}{\mathrm{Cl{-}Ge(Ph)_2{-}Ge(Ph)_2{-}Ge(Ph)_2{-}Cl}} + \underset{\mathbf{54}}{\mathrm{Cl{-}Ge(Ph)_2{-}Ge(Ph)_2{-}Ge(Ph)_2{-}Ge(Ph)_2{-}Cl}} \qquad (22)$$

Ratio $\mathrm{Ph_2GeHCl/NEt_3}$		Yield:	9	53	54
	3/2		60 %	10 %	0 %
	3/3		26 %	40 %	2 %
	3/6		23 %	21 %	36 %

Scheme 21



Scheme 22

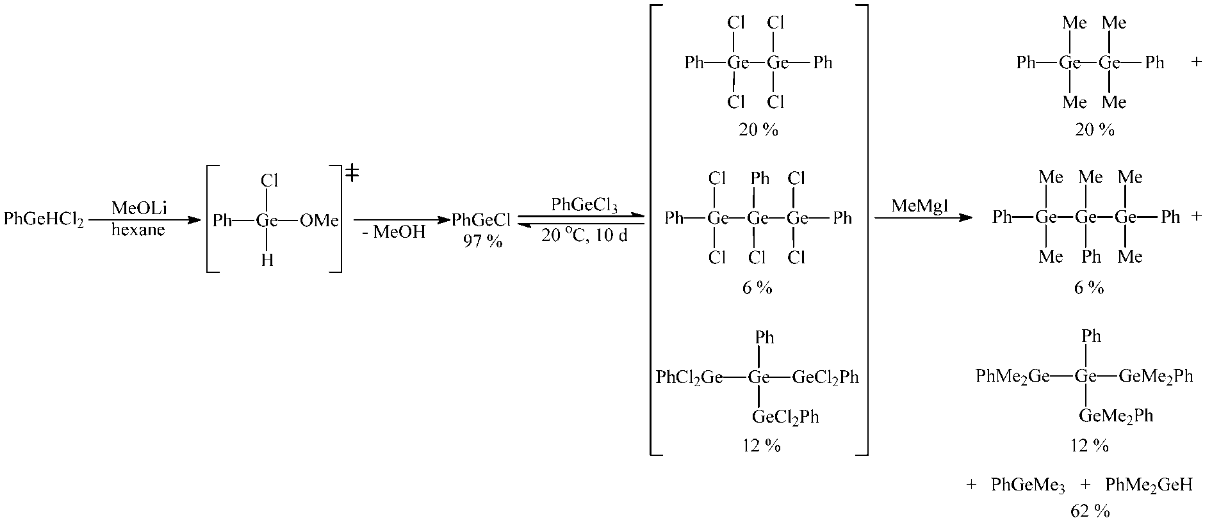


Scheme 23

$$Ph_2GeHCl + NEt_3 \longrightarrow Ph_2Ge + [HNEt_3]Cl$$

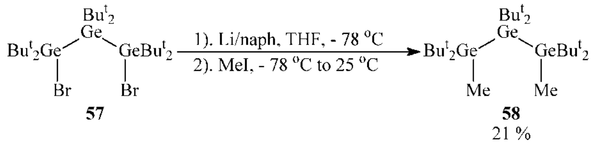
$$(n\text{-}1)\,Ph_2Ge + Ph_2GeHCl \longrightarrow Cl(Ph_2Ge)_nH \xrightarrow[AIBN]{CCl_4} Cl(Ph_2Ge)_nCl + CHCl_3$$

Scheme 24



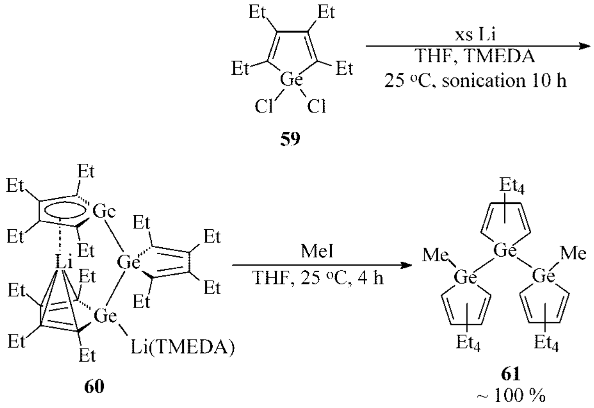
Ge−Ge distances in **53** are all shorter than those in **2** due to the electron withdrawing nature of the chlorine atoms. The bond angles in both molecules of **53** are more acute than those of **2**, since the two chlorine atoms present in **53** are less sterically encumbering than the two phenyl groups in **2**.

The cyclic trigermane **55**[118] undergoes a ring-opening reaction in the presence of I_2,[137] Br_2,[138] or CCl_4[138] to produce three halide-terminated linear trigermanes (Scheme 25). The structures of the diiodo-[137] and dibromo-terminated[138] compounds **56** and **57** have been determined. The structure of **56** adopts a *gauche*−*trans* conformation with long Ge−Ge bond lengths of 2.660(1) and 2.622(1) Å and a Ge−Ge−Ge bond angle of 115.4(1)°,[137] while the dibromo derivative **57** has an identical conformation with slightly shorter Ge−Ge bond distances of 2.623(1) and 2.595(1) Å and a more acute Ge−Ge−Ge bond angle of 113.5(1)°.[138] The relative electronegativities of the attached halogen atoms are manifested in the Ge−Ge bond distances in **56** and **57**, where **57** has shorter Ge−Ge bonds due to the presence of the more electronegative bromine atoms at the termini of the chain. The elongation of these bonds, all of which lie outside the typical range of 2.43−2.47 Å, can be attributed to the steric congestion resulting from the presence of six *tert*-butyl groups in these molecules. These are among some of the longest Ge−Ge single bond lengths that have been reported, although they are significantly shorter than that of the hexa-*tert*butyl derivative **32** (2.710(1) Å).[118] Reaction of lithium naphthalenide with **57** followed by treatment with methyl iodide yields the dimethyl-substituted species **58** (eq 23), which also was structurally characterized and has two identical Ge−Ge bond lengths of 2.620(1) Å and a Ge−Ge−Ge angle of 118.6(1)°.[138]



(23)

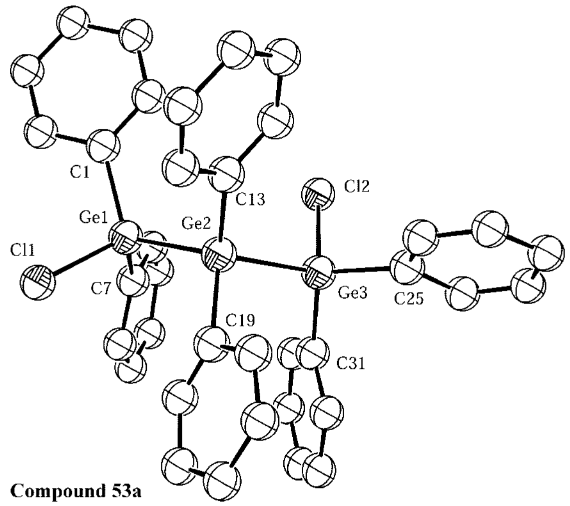
Reduction of the germole **59** with lithium metal followed by quenching with methyl iodide yields the trigermane **61** that contains three germoles linked together via single Ge−Ge bonds (eq 24).[139] The structure of the intermediate TMEDA complex **60** was determined, and this compound contains two different types of bonding modes of the lithium atoms to the germanium heterocycles. In the sandwich-type portion of this complex, one C_4Ge ring is η^5-bound to the central lithium atom while the other C_4Ge ring is η^4-bound to the central lithium atom. The Ge atom in the latter has a formal σ-bond to the second Li atom that is solvated by a TMEDA molecule. The Ge−Ge distances in **60** are longer than typical Ge−Ge single bond lengths and average 2.518(2) Å.



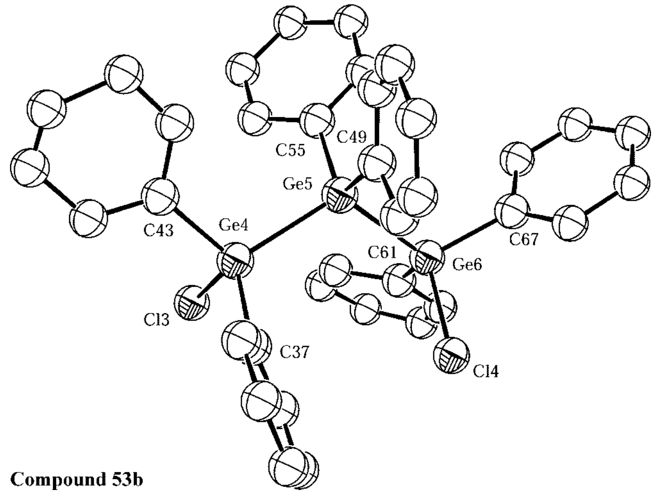
(24)

3.2. Cyclic Trigermanes

Compound **62a** was the first cyclotrigermane to be synthesized and structurally characterized.[140] Compound **62a** was originally obtained via a multistep synthetic route (Scheme 26), and the germanium atoms of **62a** form an approximate equilateral triangle with C_2-symmetry, long Ge−Ge bond distances of 2.543(1) and 2.537(1) Å, and near-ideal Ge−Ge−Ge bond angles of 59.9(1) and 60.1(1)°. Compound **62a** photodissociates into a digermene and a germylene, which is a common reaction motif exhibited by a number of related cyclotrigermanes.[140]



Compound 53a

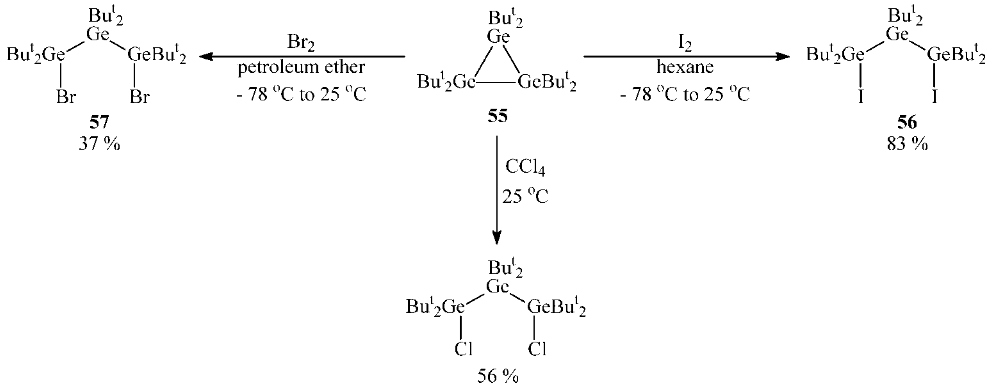


Compound 53b

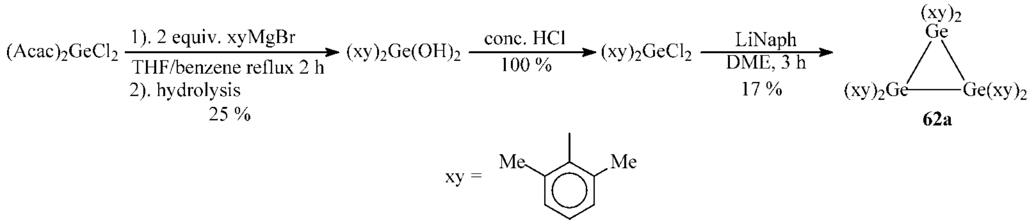
Figure 8. ORTEP diagrams of **53a** and **53b**. Selected bond distances (Å) and angles (deg) for **53a**: Ge(1)−Ge(2), 2.437(2); Ge(2)−Ge(3), 2.419(1); Ge(1)−Cl(1), 2.187(6); Ge(3)−Cl(3), 2.194(4); Ge−C_{avg}, 1.95(1); Cl(1)−Ge(1)−Ge(2), 104.4(2); Ge(1)−Ge(2)−Ge(3), 110.4(1); Ge(2)−Ge(3)−Cl(3), 105.8(1). Selected bond distances (Å) and angles (deg) for **53b**: Ge(4)−Ge(5), 2.413(2); Ge(5)−Ge(6), 2.423(2); Ge(4)−Cl(4), 2.192(6); Ge(6)−Cl(6), 2.196(6); Ge−C_{avg}, 1.95(1); Cl(4)−Ge(4)−Ge(5), 109.9(1); Ge(4)−Ge(5)−Ge(6), 116.7(1); Ge(5)−Ge(6)−Cl(6), 108.1(1).

Several homoleptic cyclotrigermanes **62** and a heteroleptic cyclotrigermane **63** were prepared via the reductive coupling of dichlorogermanes in moderate to low yields (Scheme 27).[141,142] The structure of the C_2-symmetryic mesityl derivative **62b** has been determined (Figure 9) that exhibits Ge−Ge bond distances of 2.539(2) and 2.535(2) Å and two identical Ge−Ge−Ge bond angles of 59.89(6)°.[143] Therefore, the presence of mesityl substituents in **62b** versus the 2,6-xylyl substituents in **62a** results in very little difference in structure. The related silicon-containing derivative Mes_6SiGe_2 has also been crystallographically characterized, and the silicon atom is disordered over all three positions in the ring, giving a mean Si−Ge bond distance of 2.508(3) Å.[143]

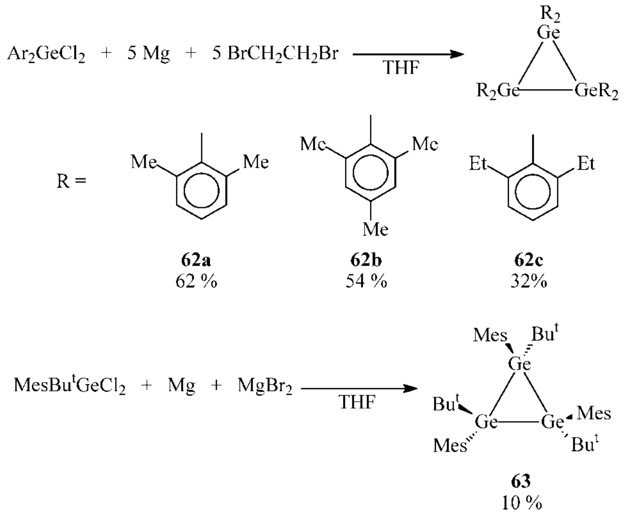
Scheme 25



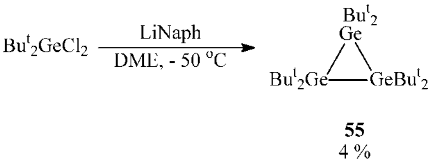
Scheme 26



Scheme 27



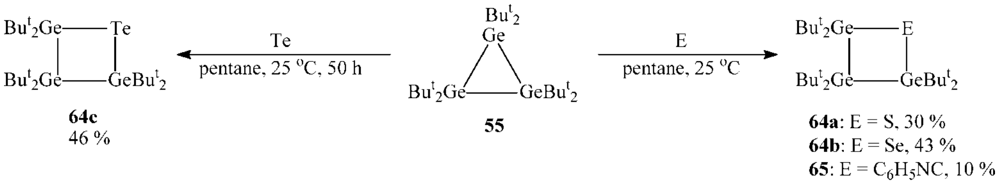
By comparison, the *tert*-butyl-substituted species **55**, that was prepared according to eq 25, has longer Ge−Ge bond distances, measuring 2.563(1) Å, and also has Ge−Ge−Ge bond angles of exactly 60° due to the C_3 symmetry of the molecule.[118] Compound **55** can also be prepared in an improved yield in three steps starting with $Ge(OEt)_4$ (eq 26).[144] Treatment of **55** with elemental sulfur or selenium yields the trigermetanes **64** via a ring expansion reaction, and reaction of **55** with phenylisocyanide generates the related compound **65** (Scheme 28).[144] The structure of the selenium-containing derivative **64b** was determined[144] and exhibits two identical Ge−Ge distances of 2.568(1) Å and two nearly identical Ge−Se distances of 2.394(1) and 2.392(1) Å. The bond angles in **64b** about the selenium and the attached germanium atoms average 91.8(1)°, which is close to the ideal value of 90°, and the Ge−Ge−Ge bond angle is slightly acute, measuring 84.6(1)°. The tellurium analogue **64c** was obtained in a similar fashion from **55** and elemental Te (Scheme 28).[145] The Ge_3Te ring of **64c** is planar, all four bond angles approach the ideal value of 90°, the Ge−Ge bond distances average 2.584(2) Å, and the Ge−Te bond distances average 2.590(1) Å. The two average Ge−E bond distances between **64b** and **64c** differ by 0.20 Å, which is nearly identical to the difference in covalent radius between selenium and tellurium.



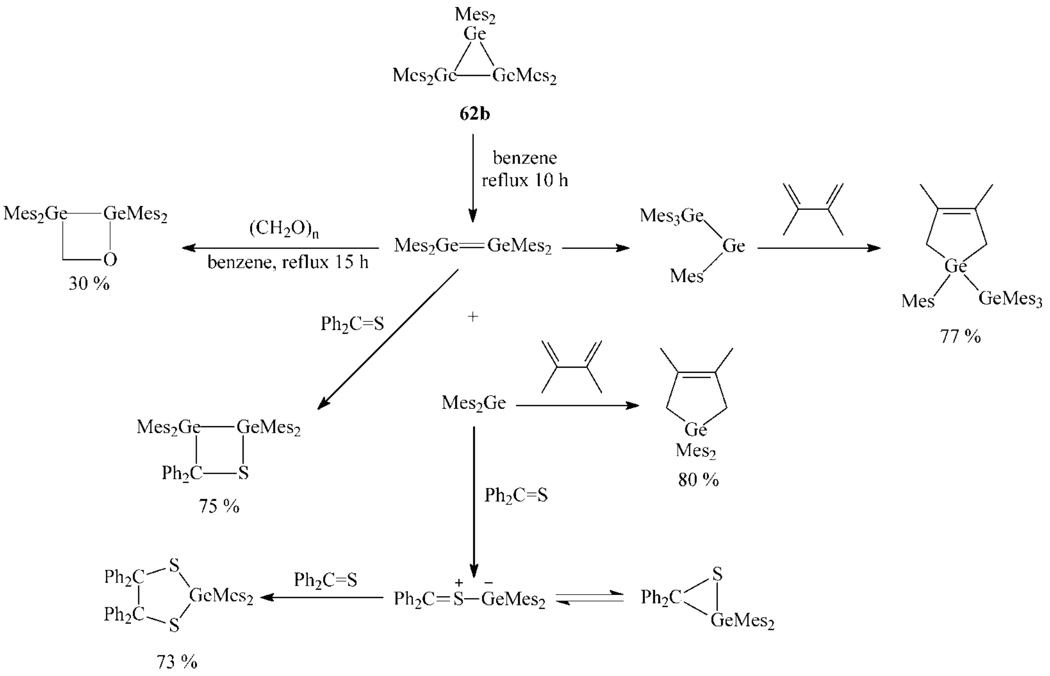
(25)

The mesityl-substituted cyclotrigermane **62b** undergoes a variety of thermal and photochemical reactions. Thermolysis of **62b** produces dimesitylgermylene and tetramesityldigermene, as identified by their trapping products (Scheme 29).[142] The $Mes_2Ge{=}GeMes_2$ fragment undergoes a rearrangement to a germyl-substituted germylene and generates an oxadigermetane in the presence of paraformaldehyde or a thiagermetane in the presence of thiobenzophenone. The germylene Mes_2Ge: generated by the thermal process also reacts with thiobenzophenone to produce a dithiager-

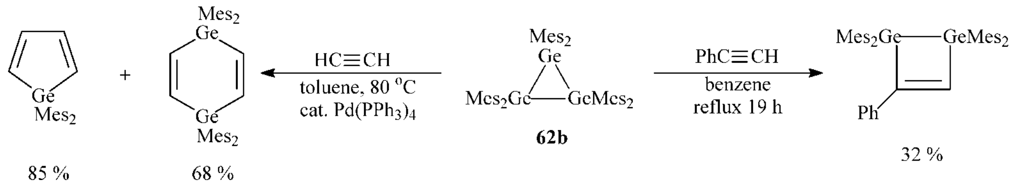
Scheme 28



Scheme 29



Scheme 30



molane.[142] Compound **62b** also reacts thermally with acetylene to give cyclic products or with phenylacetylene to give a 1,2-digermetene (Scheme 30).[142] The rate constants for the quenching of Mes_2Ge: in the presence of O_2 ((7.3 ± 0.8) × 10^6), Et_3SiH ((1.1 ± 0.1) × 10^5), and $C_6H_{11}Br$ ((5.4 ± 0.5) × 10^5) have been determined.[146]

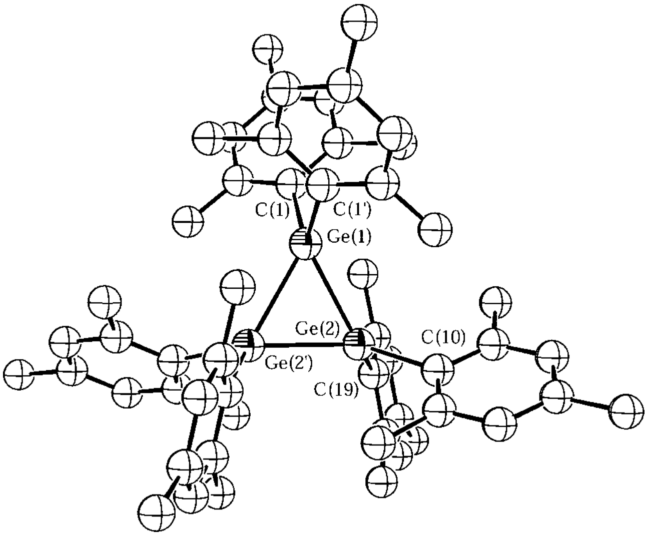
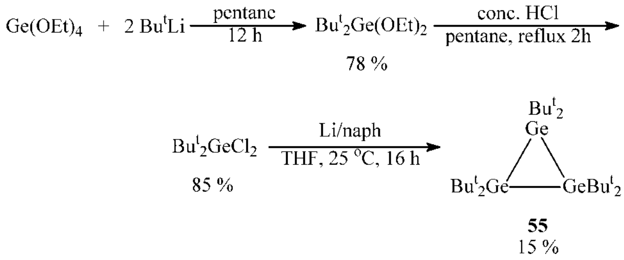
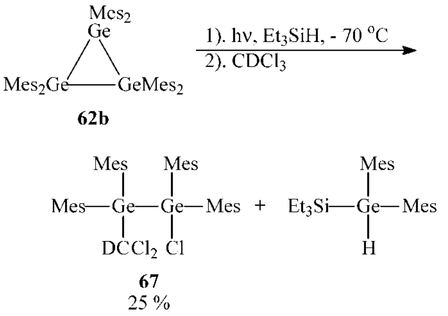


Figure 9. ORTEP diagram of **62b**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.539(2); Ge(2)−Ge(2′), 2.535(2); Ge(1)−C(1), 2.020(7); Ge(2)−C(10), 2.003(8); Ge(2)−C(19), 2.025(7); Ge(1)−Ge(2)−Ge(2′), 59.89(6).



(26)

The photolysis or thermolysis of **62b** in the presence of various carbonyl compounds yields a variety of products (Scheme 31),[147] and the reaction pathway was shown to involve the formation of radical intermediates. The structure of one of the products (**66**) was determined that has a highly distorted six-membered ring with a slightly elongated Ge−Ge bond distance of 2.456(2) Å. Compound **62b** also reacts with organolithium and Grignard reagents under photolytic or thermal conditions to yield digermane hydrides.[148] The photolytic reaction of **62b** with Et_3SiH has various different outcomes depending on the reagents and conditions employed. Photolysis of **62b** followed by addition of chloroform-*d* yields the digermane **67** (eq 27),[149] while photolysis of **62b** in the presence of Et_3SiH under an inert atmosphere followed by treatment with O_2 yields the digermadioxetane **68** (Scheme 32). When the photolytic reaction with Et_3SiH is conducted under an oxygen atmosphere, a complex mixture of products results (Scheme 32)[150] where the Et_3SiH serves to trap the intermediate germylene generated in the reaction. The structures of **69** and **70** were obtained, and compound **70** has a near-planar Ge_3O_2 ring and a Ge−Ge distance of 2.504(3) Å. The Ge−Ge bond in this case is substantially longer than those in the related five- and six-membered cyclic species **11** (2.430(3) Å)[103] and **14** (2.448(1) Å),[105] and this can be ascribed to the increased steric bulk of the mesityl substituents in **70**.

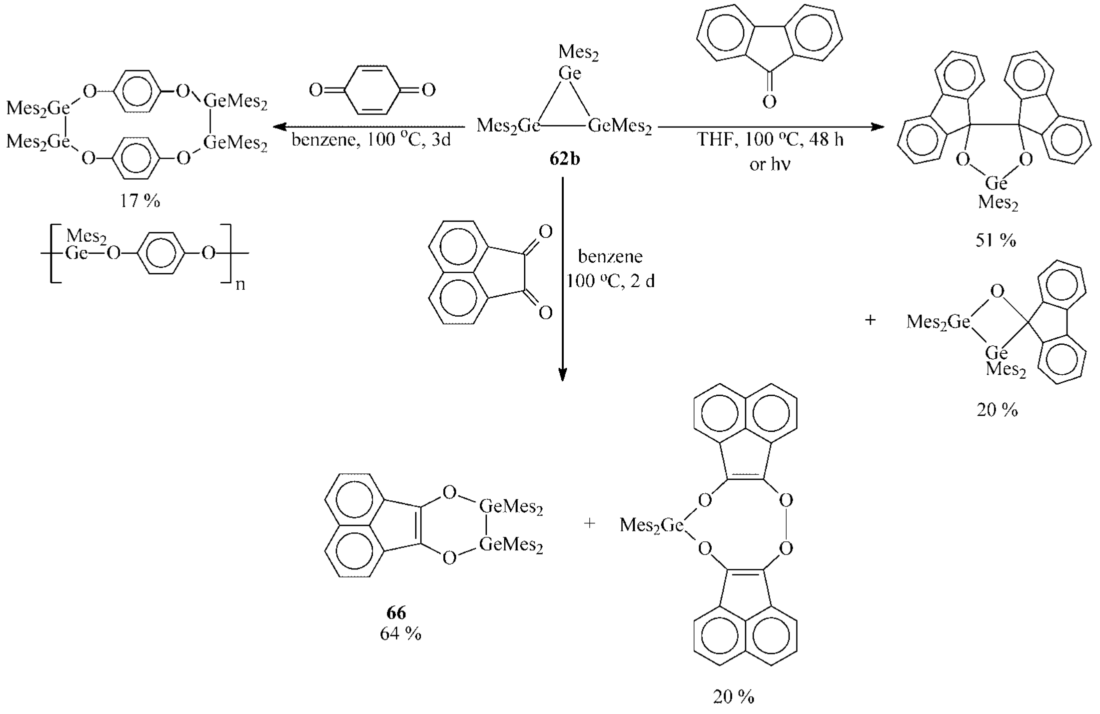


(27)

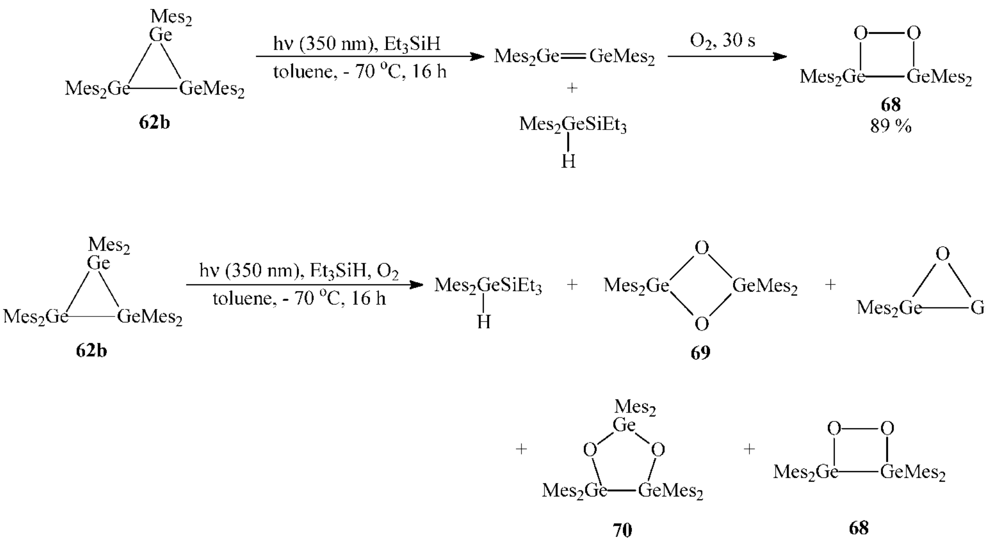
Similar reactions of the related hexamesitylsiladigermirane **71**, prepared according to eq 28,[151] have been investigated as well.[151–158] A dramatic difference in the reactivity of the silicon-containing derivative **71** and **62b** was illustrated by the photolytic reaction of each of these materials with Et_3SiH, followed by addition of *trans*-2-phenylcyclopropane carbaldehyde or *trans,trans*-2-methoxy-3-phenylcyclopropane carbaldehyde (Scheme 33).[159] The reaction results in a [2 + 2] cycloaddition reaction of the carbonyl to the Ge=Ge double bond in the case of **62b**, which differs from the reactivity observed upon photolysis of **71**, where ring opening of the cyclopropane moiety occurs.[156,157]

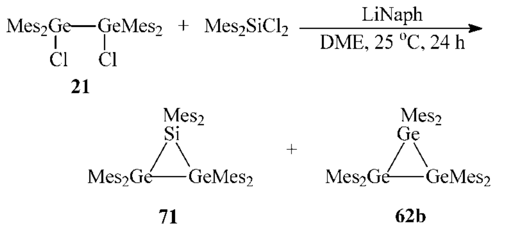
Photolysis of **62b** in the presence of elemental sulfur generates the thiadigermirane **72** in 26% yield (Scheme 34), which proceeds through the formation of a digermene intermediate.[160] A short Ge−Ge bond distance of 2.376(2) Å was found in **72**, suggesting that there is substantial contribution to the overall structure from the π-complex shown in Scheme 34. The germylene fragment Mes_2Ge: generated in the reaction also reacts with the elemental sulfur

Scheme 31



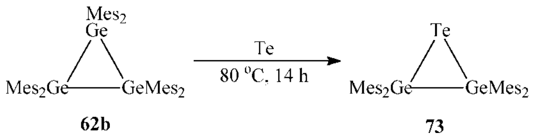
Scheme 32





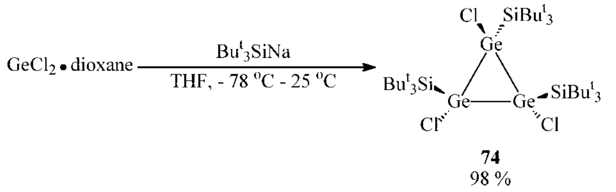
(28)

present to generate a thiagermone that subsequently dimerizes. The selenium-containing analogue of **72** can also be prepared by an analogous reaction,[160] and the tellurium analogue **73** was obtained by thermolysis of **62b** in the presence of elemental Te (eq 29).[161] The structure of **73** was determined and exhibits a Ge−Ge bond length of 2.435(2) Å, a Ge−Te distance of 2.597(2) Å, and an acute angle about Te which measures 55.9(4)°. Despite the fact that both Ge atoms in **73** are in a planar geometry, the presence of a normal Ge−Ge distance in **73** versus that in **72** suggests that the contribution of the π-complex form to the overall structure of **73** may be diminished.

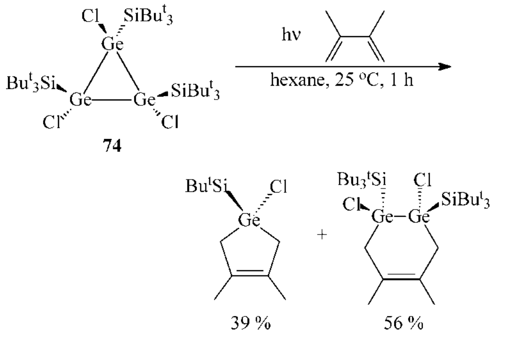


(29)

The sterically encumbered cyclotrigermane **74** was prepared from the reaction of $GeCl_2 \cdot$dioxane with Bu^t_3SiNa (eq 30), and only one of the possible stereoisomers was formed in this reaction, as confirmed by NMR spectroscopy and X-ray diffraction.[162] In the single isomer of **74** generated in this reaction, one of the Bu^t_3Si groups is disposed on the opposite side of the central Ge_3 triangle from the other two.[162] This results in a distortion from an equilateral triangular geometry, as the Ge−Ge bond distances in **74** are 2.4883(5), 2.4931(5), and 2.5306(4) Å, and the Ge−Ge−Ge bond angles measure 59.56(1), 59.38(1), and 61.06(1)°. As observed for compound **62b** and other cyclotrigermanes, compound **74** undergoes photolytic cleavage to yield a digermene and a germylene, as confirmed by trapping studies in the presence of 2,3-dimethylbutadiene (eq 31).[163] Photolysis of **74** in the presence of Et_3SiH yields the expected germylene trapping product, but the digermene generated in the reaction undergoes a digermene−germylgermylene rearrangement to yield a substituted digermane end product (Scheme 35).[163]



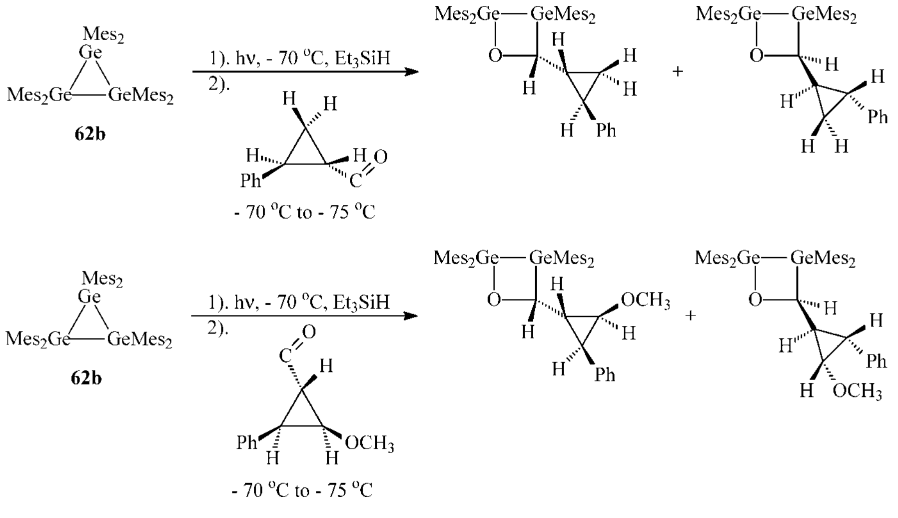
(30)



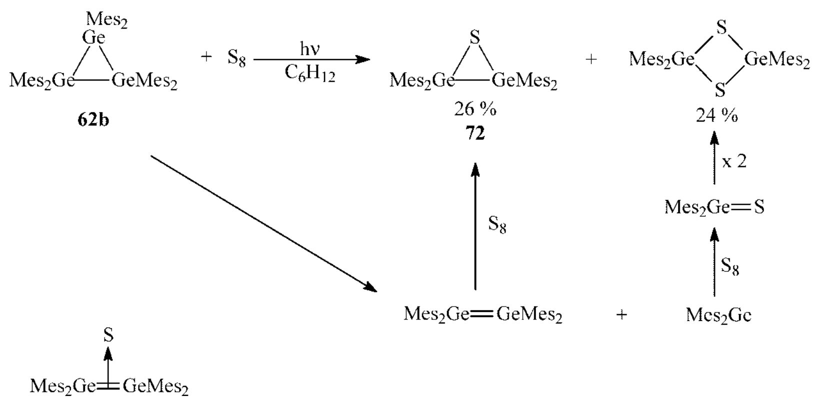
(31)

The synthesis and structures of three other sterically congested cyclotrigermanes have also been recently described. The synthesis of **75** was achieved by the reaction of $LiGe(SiMe_3)_3$ with $GeCl_2 \cdot$dioxane (eq 32),[164] and the structure of this compound is not as sterically crowded as those of **55** or **74**, as indicated by the shorter Ge−Ge bond length of 2.460(1) Å in **75**. The steric effects of the two $-SiMe_3$ substituents are not as significant as those of the *tert*-butyl substituents of **55**, as indicated by the longer Ge−Si bonds in **75** (2.388(4) Å) versus the Ge−C bonds in **55** (2.085(5) Å).[118] The tri-*tert*butylsilyl- and germyl-substituted cyclotrigermenes **76** were obtained by the metathesis reaction shown in eq 33. The structure of **76b** is highly disordered, but the molecule was determined to be trigonal planar, containing two Ge−Ge single bonds measuring 2.522(4) Å as well as a Ge−Ge double bond measuring 2.239(4) Å.[165] Treatment of **76a** with a trityl fluoroborate reagent generated the cyclotrigermenium cations **77** that

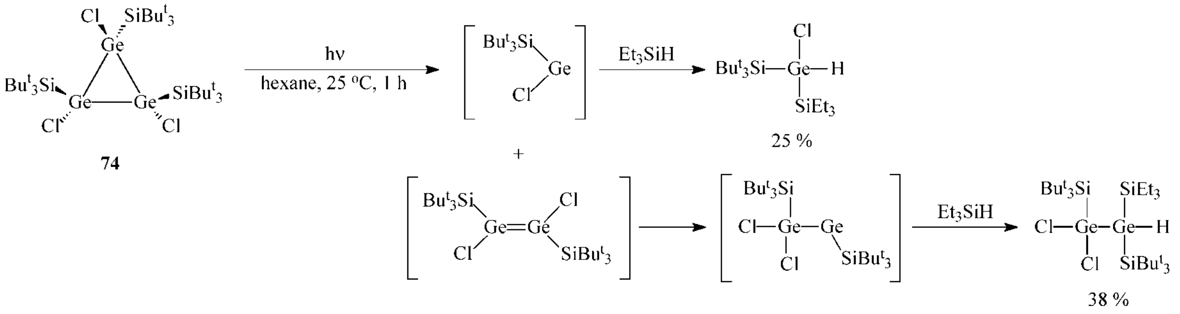
Scheme 33



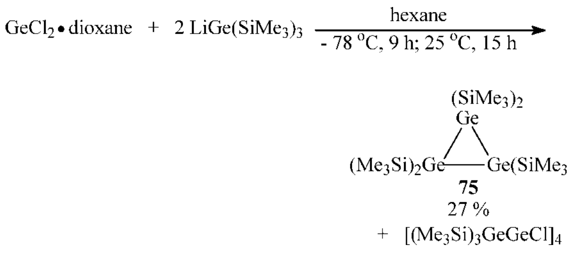
Scheme 34



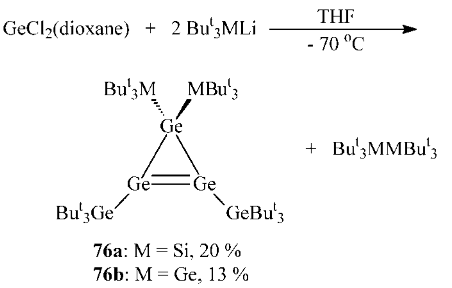
Scheme 35



contain five different tetraarylborate counterions (Scheme 36).[166–168] The structures of **77a**,[166,168] **77d**,[166] and **77e**[167] have been determined, and in each case the structure of the trigermyl cation approximates an equilateral triangle, with similar average Ge–Ge bond lengths of 2.335(2), 2.3325(8), and 2.326(4) Å (respectively). These distances are intermediate between Ge–Ge single (2.43–2.47 Å) and double (2.21–2.35 Å) bond lengths, indicating the 2π-electrons are completely delocalized about the Ge_3 framework.



(32)



(33)

Reaction of **77c** with KX (X = Cl, Br, I) furnishes the halide-substituted cyclotrigermenes **78** (Scheme 36).[169] The bromide derivative **78b** was structurally characterized and contains a *cis*-bent geometry about the Ge–Ge double bond. The two Ge–Ge single bonds in **78b** are 2.4191(9) and 2.4200(9) Å, while the Ge–Ge double bond length is 2.2743(8) Å. All three halide-substituted species react with 2,3-dimethylbutadiene to give the bicyclic compounds **79**,[169] and the geometry about the Ge=Ge double bond in **78a–c** results in face selectivity in this reaction, generating only one stereoisomer of **79 a–c**. Treatment of **79c** with potassium graphite provides the germyl anion **80** (Scheme 36), which contains an unsymmetrical Ge_3 array having one normal Ge–Ge bond (2.4354(5) Å) and two elongated Ge–Ge bonds (2.5003(5) and 2.54333(6) Å).[170] Compound **80** abstracts a proton from cyclopentadiene to give **81**, and it also reacts with MeI to give **82**, where both of these reactions furnish only one stereoisomer of the product.

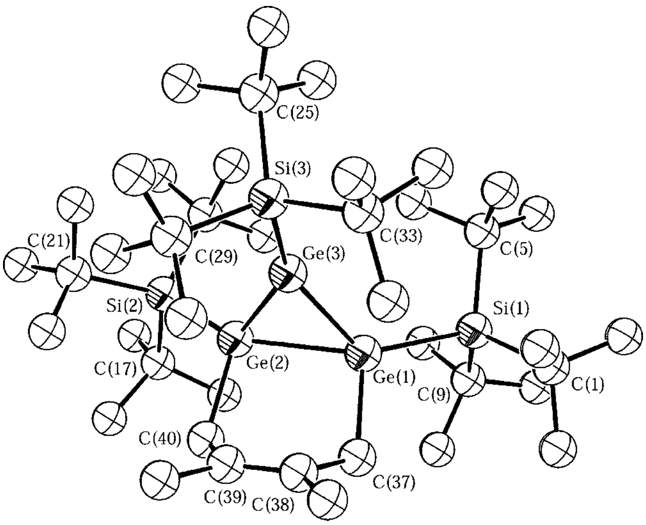
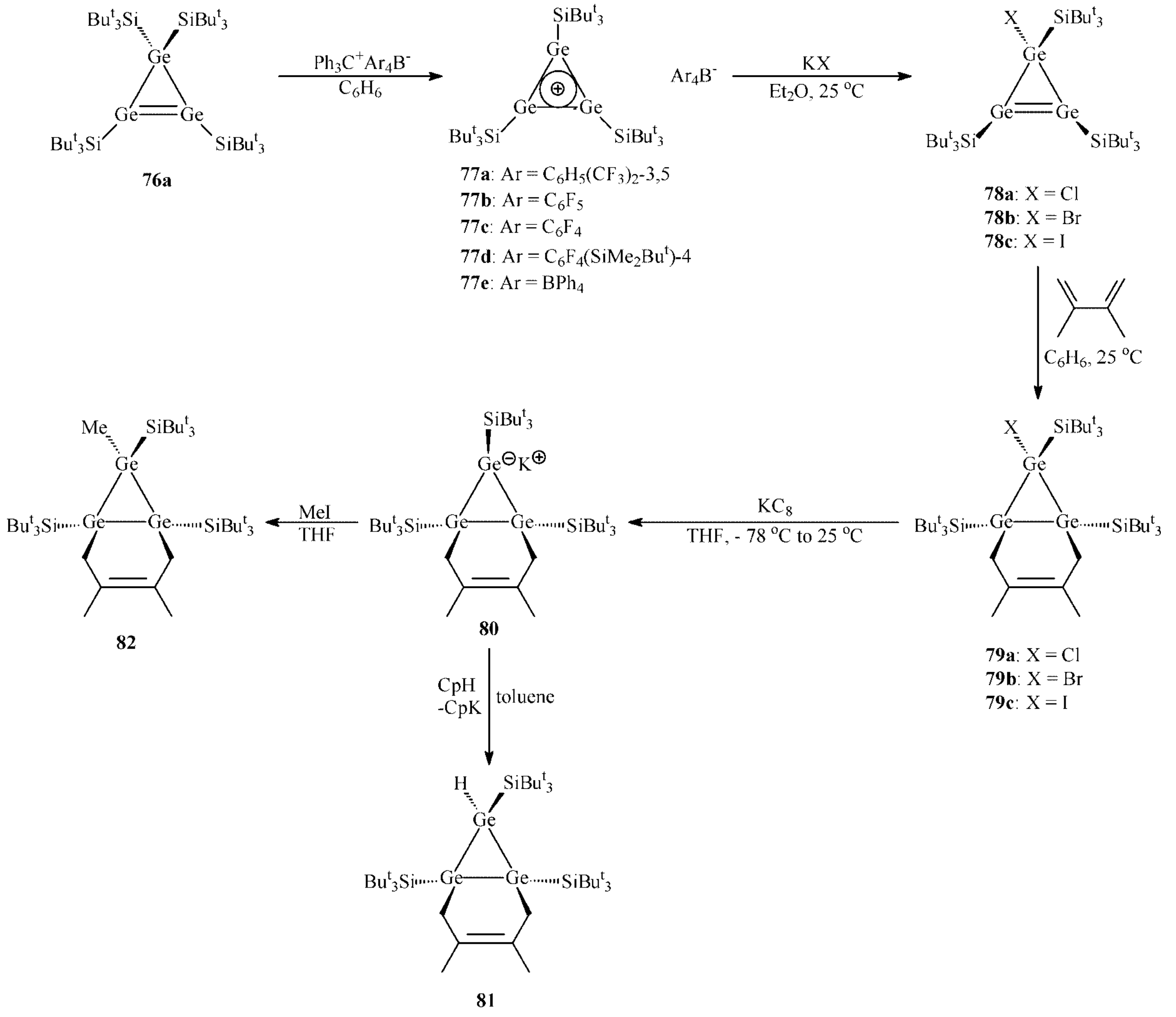


Figure 10. ORTEP diagram of **83**. Selected bond distances (Å) and angles (deg): Ge(1)–Ge(2), 2.4864(4); Ge(1)–Ge(3), 2.4254(5); Ge(2)–Ge(3), 2.4326(4); Ge(1)–Si(1), 2.4302(8); Ge(2)–Si(2), 2.4359(9); Ge(3)–Si(3), 2.4040(9); Ge(1)–C(37), 2.041(1); Ge(2)–C(40), 2.036(1); C(38)–C(39), 1.355(5); Ge(3)–Ge(1)–Ge(2), 59.36(1); Ge(1)–Ge(2)–Ge(3), 59.07(1); Ge(2)–Ge(3)–Ge(1), 61.57(1).

Scheme 36



The anionic compound **80** can be converted to a stable germyl radical **83** by reaction with $B(C_6F_5)_3$ (Scheme 37),[170] which is structurally characterized (Figure 10) and exhibits a nearly planar environment about the radical Ge center. There is a clear interaction between Ge(3) and the π-system of the exocyclic C═C double bond, as shown by the Ge—C close contacts of 3.612 and 3.632 Å. The Ge−Ge distances in the Ge_3 framework measure 2.4864(4), 2.4326(4), and 2.4254(5) Å, with the shorter bonds between the radical Ge center and the other two Ge atoms of the ring. Treatment of **83** with CCl_4 furnishes the chloride species **84**, while reaction with MeI yields both the iodide **79c** and the methylated derivative **82** (Scheme 37).[170]

Bicyclic derivatives **85** and **86** incorporating a cyclotrigermane moiety were prepared according to Scheme 38, and the structures of **85b** and **86a** were obtained.[171] The Ge−Ge bond lengths in **85b** (2.5938(3), 2.6068(3), and 2.4705(3) Å) are elongated due to the presence of the bulky Bu^t_3Si and mesityl substituents, which is also observed in the structure of **86a** (2.5958(5), 2.5592(4), 2.4857(4) Å). As with the other cyclotrigermanes described above, both **85a** and **86b** are thermally converted to a germylene and digermene that react with diphenylacetylene to give a germacyclopropene and a digermane **87a,b** (Scheme 39).[172] The digermane ultimately produced in this reaction consists of a germacyclopropene and a germacyclopentene linked by a Ge−Ge bond that is formed from a ring contraction of the cyclic digermene produced during photolysis.

Dehalogenation of the bicyclic cyclotrigermane **88** furnishes a germanium cyclopropenylium cation complex (**89**) that has been structurally characterized (eq 34).[173] The structure of the cation of **89** is a highly strained fused bicyclic housene-type structure containing a Ge_3 equilateral triangle and a Ge_2C_2 four membered ring. The bonding in the Ge_2C_2 ring consists of two short Ge—C distances from the apical germanium atom of the Ge_3 triangle to the carbon atoms of the double bond, measuring 2.415(7) and 2.254(7) Å, and a long C═C bond between the two carbons measuring 1.411(9) Å. This bonding-type interaction is (3c, 2e) in nature and results from donation of the π-electrons of the C═C double bond to the vacant p-orbital on the apical germanium atom, thus rendering it five-coordinate. The Ge_3 ring in the cation of **89** is a near equilateral triangle with each of the Ge−Ge−Ge bond angles being very close to 60°.

4. Tetragermanes

4.1. Linear Tetragermanes

The phenyl-substituted tetragermane $Ph_3Ge(GePh_2)_2GePh_3$ (**3**) was obtained in 18% yield by a variation of the process shown in Scheme 2, in which excess magnesium metal was not removed by filtration. In this case, the yield of the

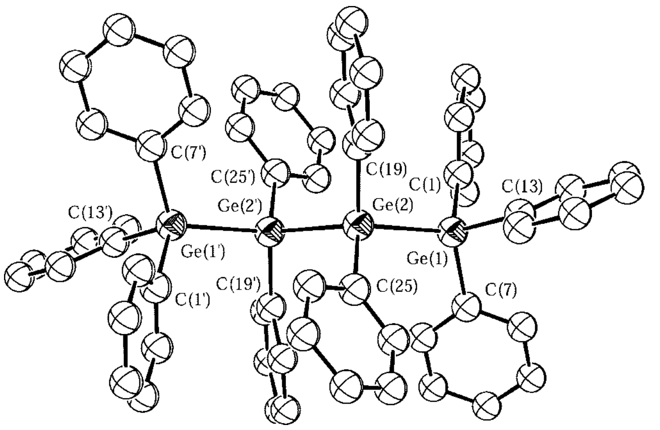
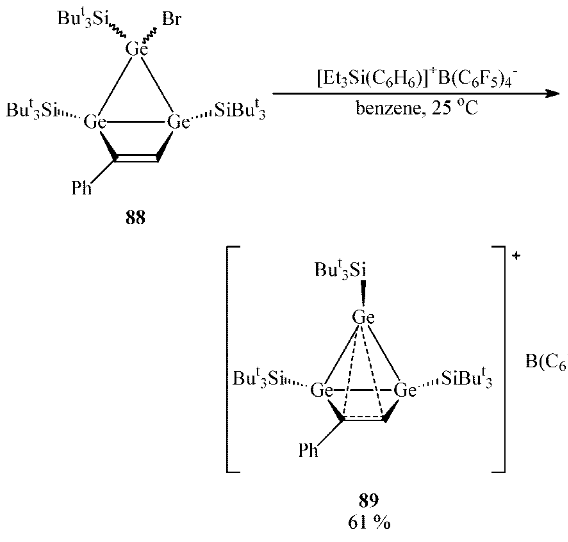
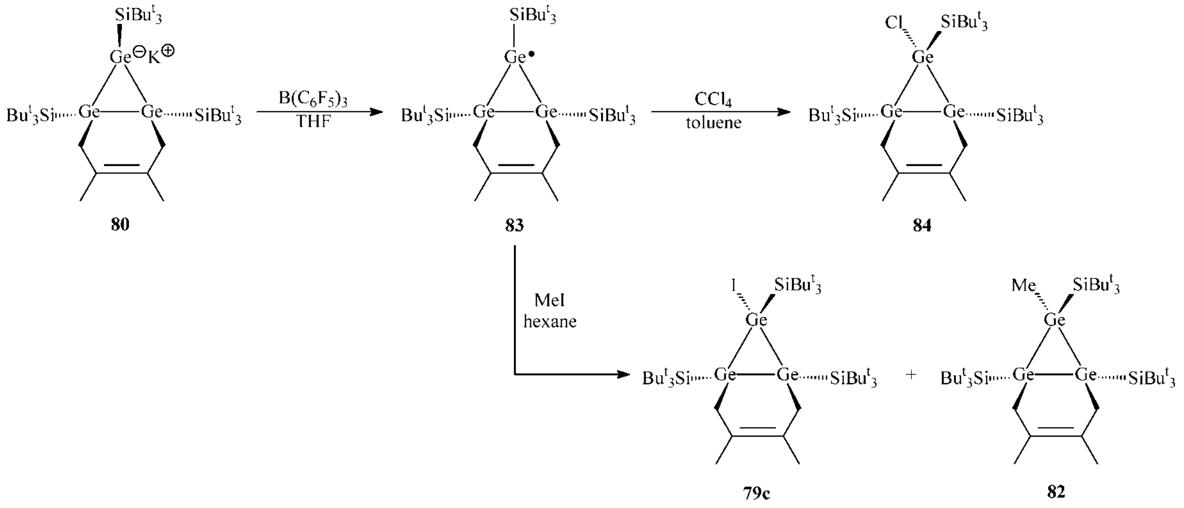


Figure 11. ORTEP diagram of **3**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.463(2); Ge(2)−Ge(2′), 2.461(1); Ge−C_{avg}, 1.968(5); Ge(1)−Ge(2)−Ge(2′), 117.8(1); Ge−Ge−C_{avg}, 109.5(2); C−Ge−C_{avg}, 107.1(5).



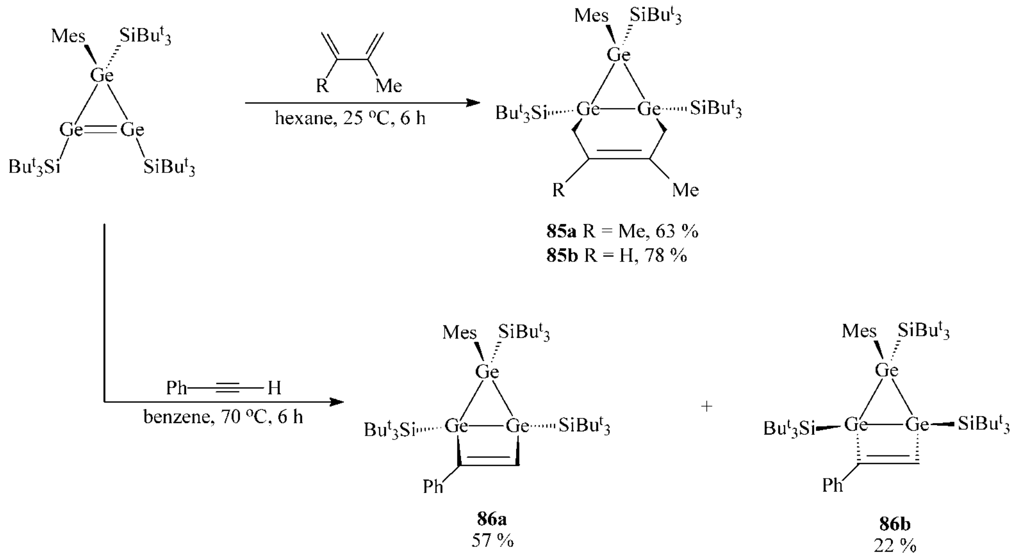
(34)

Scheme 37

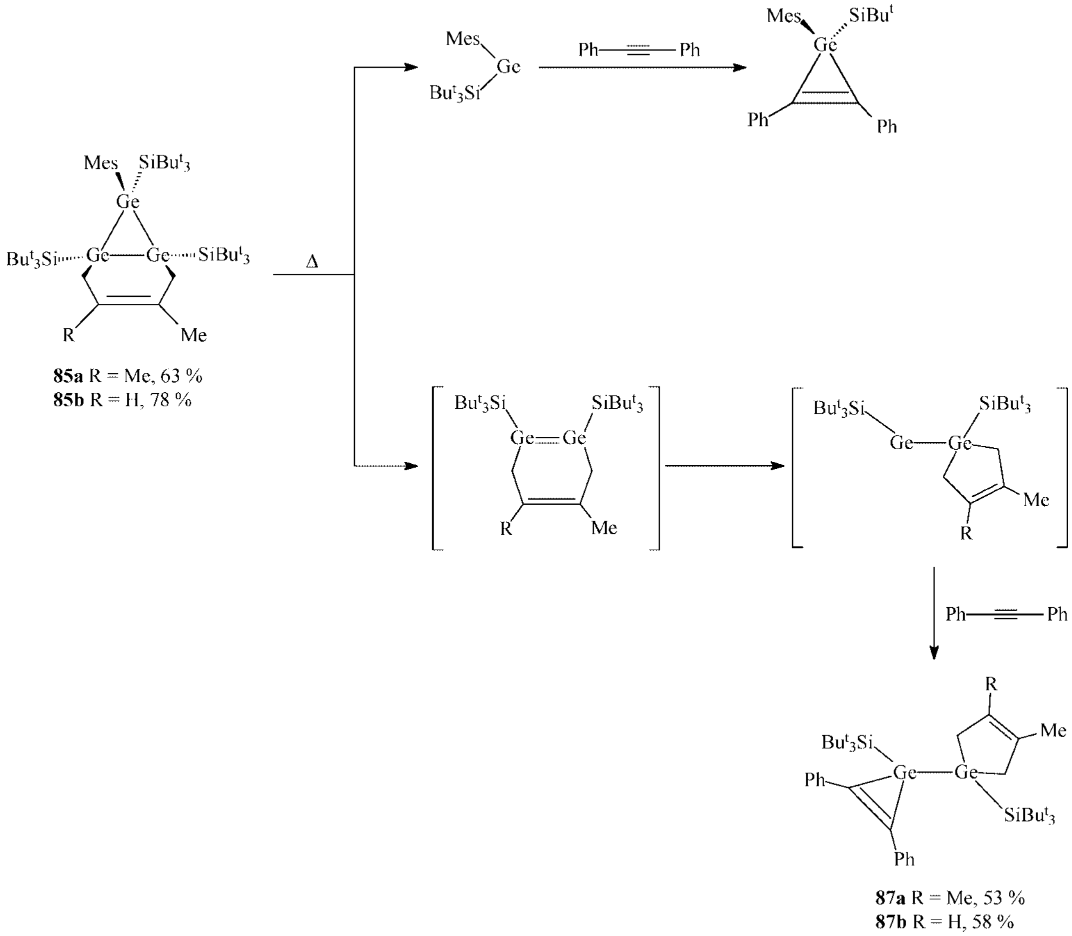


trigermane **2** was 11%, and the digermane **1** and Ph_4Ge were produced in yields of 17% and 53%, respectively.[86] The structure of **3** (Figure 11) is similar to that of the trigermane **2**, in that the molecule adopts a staggered conformation among the four germanium atoms and the two halves of the molecule are related by a center of symmetry. The Ge−Ge distances are nearly identical, measuring 2.463(2) and 2.461(3) Å, and the Ge−Ge−Ge angle is 117.8(1)°.[86] The related tetragermane $Ph_3Ge(GeEt_2)_2GePh_3$ was obtained in 25% yield from Ph_3GeLi and $ClEt_2GeGeEt_2Cl$,[131] and the

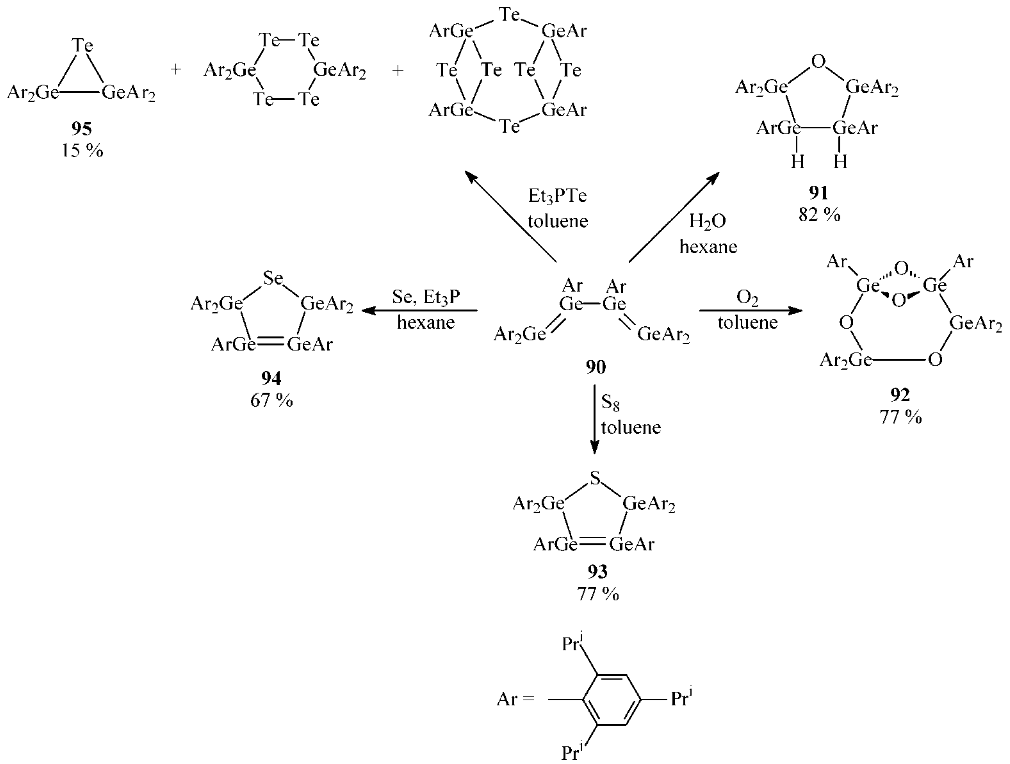
Scheme 38



Scheme 39

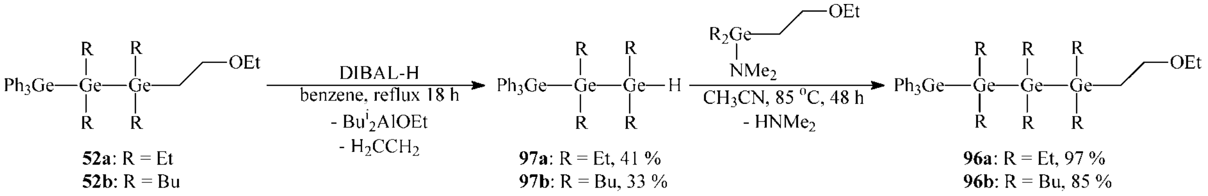


Scheme 40

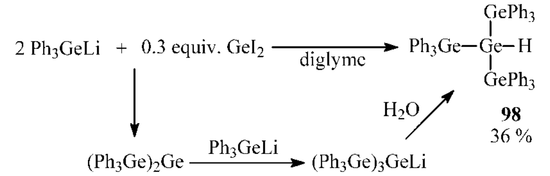


chloride terminated species **54** was prepared and isolated according to eq 22.[135] Similar to the perphenylated derivative **3**, the structure of **54** is centrosymmetric with Ge−Ge distances of 2.450(4) and 2.442(3) Å and a Ge−Ge−Ge angle of 116.2(1)°.[135]

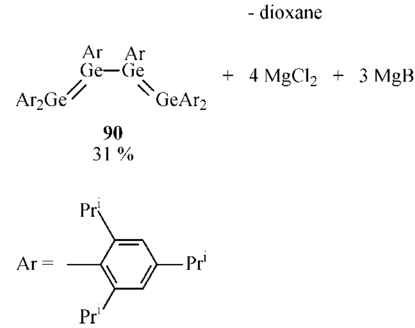
Scheme 41



Scheme 42



A germanium analogue of butadiene **90** was obtained by careful reaction of 2,4,6-triisopropylphenylmagnesium bromide with $GeCl_2$ in the presence of Mg metal, as shown in eq 35.[174] Compound **90** undergoes a number of different reactions with chalcogen-containing reagents to furnish several of cyclic products (Scheme 40).[174,175] The structures of the five-membered heterocylic species **91**, **93**, and **94** were determined, as were those of all three tellurium-containing products. The two types of Ge−Ge distances in the selenium-containing derivative are longer than those in the sulfur-containing congener. For **93**[174] and **94**,[175] the Ge−Ge single bond distances average 2.4504(4) and 2.4661(5) Å (respectively) and the double bonds measure 2.2841(5) and 2.2975(5) Å (respectively). The oxygen-containing species **91** has three Ge−Ge single bonds which measure 2.5494(4), 2.4551(5), and 2.4691(4) Å, and the Ge−Ge distance in **95** is 2.4694(5) Å.[175]



(35)

Two additional tetragermanes **96** (Scheme 41) were obtained by employing the method shown in Scheme 22, which makes use of the hydrogermolysis reaction for the formation of Ge−Ge bonds.[34] The two trigermanes **52** were each reacted with DIBAL-H to furnish the hydrides **97** in modest yields that were isolated and characterized, and these materials were subsequently converted to the tetragermanes **96**. The overall yields of the tetragermanes **96** can be drastically improved if the intermediate hydrides **97** are not isolated but rather reacted directly with the amide synthons $R_2Ge(NMe_2)(CH_2CH_2OEt)$ in a "one pot" reaction. The aluminum-containing byproducts generated along with **97** do not interfere with the Ge−Ge bond forming process, and the formation of **98** from **97** proceeds via the formation of α-germyl nitrile intermediates generated by reaction of the amide synthons with the CH_3CN solvent. Compounds **96a** and **96b** both exhibit absorption bands in their UV/visible spectra resulting from the $\sigma \rightarrow \sigma^*$ electronic transition, appearing at 235 and 241 nm (respectively).[34]

4.2. Branched Tetragermanes

Branched oligogermanes are uncommon, and only a few examples have been reported to date. For example, the tetragermane $(Ph_3Ge)_3GeH$ (**98**) was obtained in 36% yield from the reaction of Ph_3GeLi with GeI_2 and is generated according to the pathway shown in Scheme 42,[176] in which the Ph_3GeLi reagent was prepared *in situ* from $Ph_3GeGePh_3$ and excess (∼7 equiv) Li metal. The presence of excess lithium metal in the reaction mixture likely contributes to the formation of **98**, since hexaphenyldigermane was identified as a component of the crude product mixture. Lithiation of **98** with Bu^nLi followed by reaction with MeI also provided the branched species $(Ph_3Ge)_3GeCH_3$ in 54% yield.[176]

The hydrogermolysis reaction, which proceeds through the conversion of the germanium amides to reactive α-germyl nitrile intermediates, has again been recently employed for the preparation of several new branched tetragermanes.[37] This method was used for the synthesis of $(Ph_3Ge)_3GePh$ (**99**) from Ph_3GeNMe_2 and PhGeH and also for the preparation of the ethoxyethyl-substituted tetragermane **100** (Scheme 43). The structure of **99** was determined, and this represents the first structurally characterized branched oligogermane (Figure 12). The average Ge−Ge bond length in **99** is 2.469(4) Å, and the average Ge−Ge−Ge bond angle is

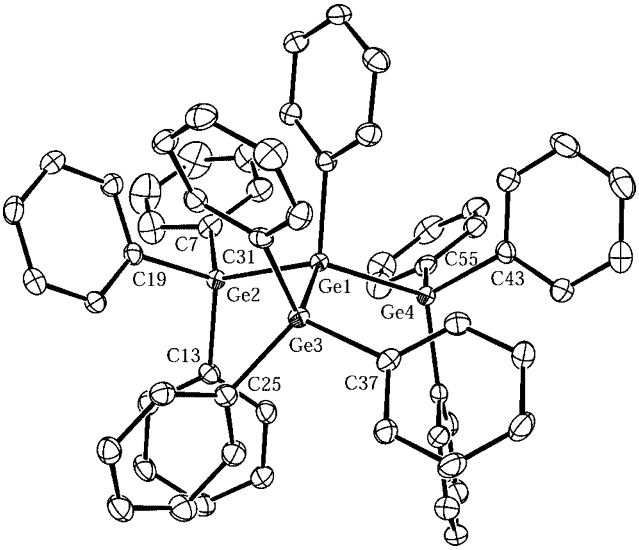
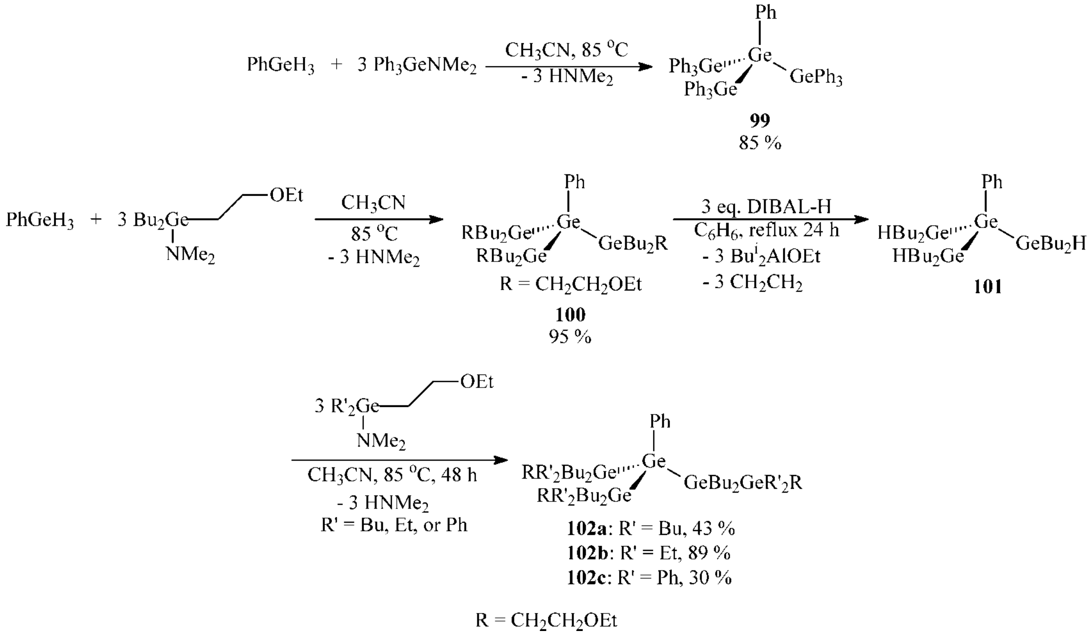


Figure 12. ORTEP diagram of **99**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.4552(4); Ge(1)−Ge(3), 2.4753(4); Ge(1)−Ge(4), 2.4772 (4); Ge(1)−C(1), 1.971(2); Ge(2)−$C_{ipso\ (avg)}$, 1.959(2); Ge(3)−$C_{ipso\ (avg)}$, 1.959(2); Ge(4)−$C_{ipso\ (avg)}$, 1.963(2); Ge(2)−Ge(1)−Ge(3), 107.41(1); Ge(2)−Ge(1)−Ge(4), 115.70(1); Ge(3)−Ge(1)−Ge(4), 115.06(1).

Scheme 43



112.72(1)°. The environment at the central germanium atom is distorted from an idealized tetrahedral geometry due to the steric interactions of the phenyl groups, and the long Ge−C$_{ipso}$ bond length at the central germanium atom (1.971(2) Å) is due to electronic effects resulting from the attachment of the central germanium atom to three other germanium atoms.

This elongated Ge−C bond suggests it might be more reactive than the other Ge−C$_{ipso}$ bonds in **99**, which was confirmed by treatment of **99** with 1 equiv of triflic acid, resulting in the isolation of $(Ph_3Ge)_3Ge(OSO_2CF_3)$, which was reacted with $LiAlH_4$ to yield the branched hydride **98**.[37] In a manner similar to the stepwise construction of linear tetragermanes,[34] compound **100** was employed for the synthesis of three branched heptagermanes **102** by reaction with DIBAL-H to generate the hydride species **101**. This material was not isolated but rather reacted directly with the germanium amide synthons $R'_2Ge(NMe_2)CH_2CH_2OEt$ in CH_3CN solvent.[37]

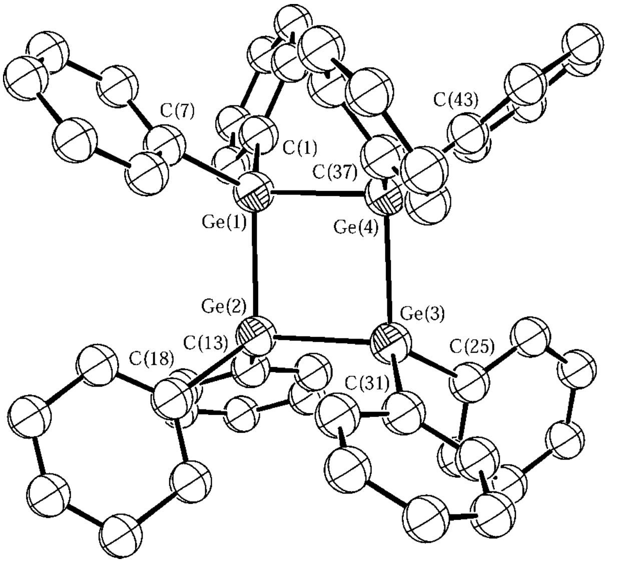


Figure 13. ORTEP diagram of **103**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.458(2); Ge(2)−Ge(3), 2.472(2); Ge(3)−Ge(4), 2.471(2); Ge(4)−Ge(1), 2.461(2); Ge(1)−C(1), 1.958(1); Ge(1)−C(7), 1.951(1); Ge(2)−C(13), 1.961(1); Ge(2)−C(19), 1.976(1); Ge(3)−C(25), 1.962(1); Ge(3)−C(31), 1.971(1); Ge(4)−C(37), 1.959(1); Ge(4)−C(43), 1.959(1); Ge(1)−Ge(2)−Ge(3), 90.3(1); Ge(2)−Ge(3)−Ge(4), 89.4(1); Ge(3)−Ge(4)−Ge(1), 90.2(1); Ge(4)−Ge(1)−Ge(2), 89.9(1).

4.3. Cyclic Tetragermanes

Several cyclic tetragermanes have been prepared and characterized. The first report of the perphenylated cyclotetragermane **103** occurred in 1930 (eq 36) in unspecified yield and was identified by elemental analysis and a molecular weight determination.[130] This compound was later prepared according to eq 37[177,178] and also according to eq 38,[179] where the latter reaction circumvents the use of the toxic diethylmercury compound. The structure of **103** was deter-

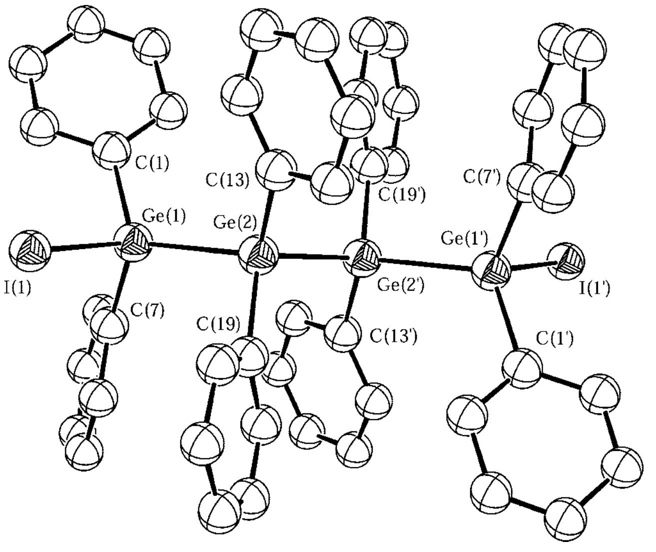
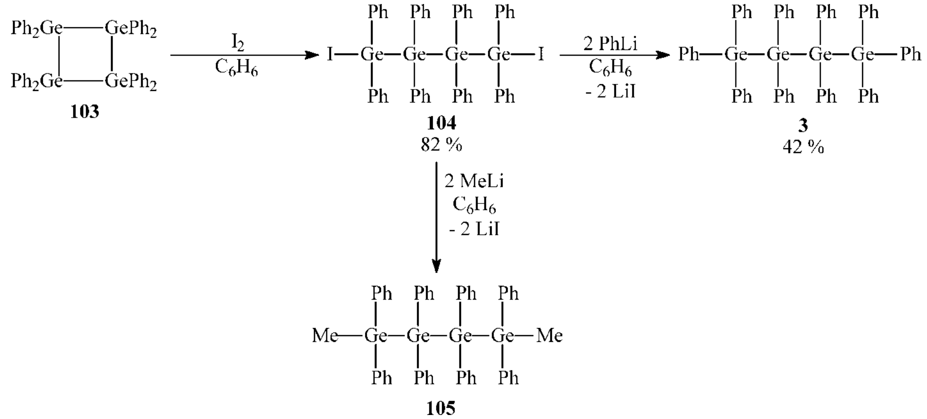
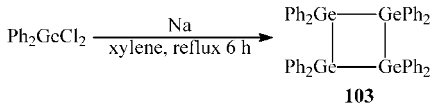


Figure 14. ORTEP diagram of **104**. Selected bond distances (Å) and angles (deg): Ge(1)−I(1), 2.559(1); Ge(1)−Ge(2), 2.451(1); Ge(2)−Ge(2′), 2.459(2); Ge(1)−C(1), 1.935(7); Ge(1)−C(7), 1.951(7); Ge(2)−C(13), 1.961(6); Ge(2)−C(19), 1.950(7); I(1)−Ge(1)−Ge(2), 103.4(1); Ge(1)−Ge(2)−Ge(2′), 114.2(1).

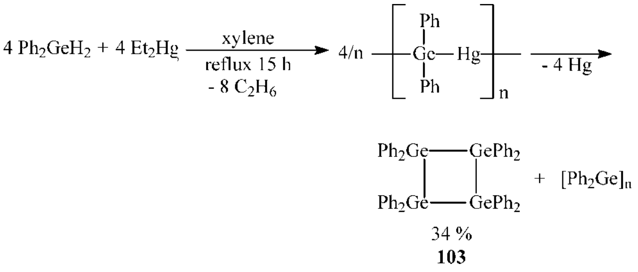
Scheme 44



mined (Figure 13) and contains a nearly square and planar $\mathrm{Ge_4}$ ring with an average Ge−Ge distance of 2.465(5) Å.[179] The structure of the alkyl-substituted species $\mathrm{Pr^i_8Ge_4}$[141] was determined, which contrasts with the planar nature of **103**. The structure of $\mathrm{Pr^i_8Ge_4}$ contains a puckered $\mathrm{Ge_4}$ ring with a dihedral angle of 17°,[180] where this distortion arises due to the presence of the more sterically encumbering isopropyl groups versus the phenyl substituents in **103**.



(36)



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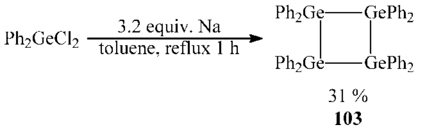


(38)

The reaction of **103** with 1 equiv of I_2 results in a ring-opening reaction to produce the diiodotetragermane **104**, which can subsequently be used for the preparation of **3** or the methyl terminated tetragermane $\mathrm{Me(Ph_2Ge)_4Me}$ (**105**) (Scheme 44).[178] The crystal structure of **104** was also obtained (Figure 14), and this species adopts a hydrocarbon-like all-*trans* geometry with an average Ge−Ge distance of 2.455(1) Å and a Ge−Ge−Ge angle of 114.2(1)°.[181] Crystallographic data for **3**, **54**, and **104** are collected in Table 5, which indicates that the presence of halogen (Cl or I) substituents versus a phenyl group results in contracted Ge−Ge bond lengths, particularly between the two terminal germanium atoms.

The diiodo species **104** also reacts with chalcogenide reagents to furnish the heterocyclic compounds **106a−d** (Scheme 45).[178,182] The tellurium compound **106d** is not stable for long periods of time and decomposes above 50 °C, but the structures of the two lighter congeners **106b−c** have been obtained. The sulfur-containing compound **106b** adopts an envelope-type conformation,[182] while the selenium species **106c** adopts a C_2-symmetric twisted conformation.[183] The average Ge−S distance in **106b** is 2.240(4) Å, and the Ge−Se distance in **106c** is 2.373(1) Å. The average Ge−Ge bond distances in **106b** and **106c** (2.448(3) and 2.443(1) Å, respectively) are slightly shorter than those of the parent pentacyclic species $\mathrm{Ph_{10}Ge_5}$ (2.453(2) Å, *vide infra*)[184] due to the presence of the electronegative chalcogen atoms.

The silyl-substituted cyclotetragermane **107** can be prepared by the reaction of $\mathrm{LiSi(SiMe_3)_3}$ with $\mathrm{GeCl_4}$, which also furnishes a silyl-substituted digermane under slightly different conditions (Scheme 46).[185] The structure of **107** has an average Ge−Ge bond distance of 2.508(1) Å and a slightly puckered $\mathrm{Ge_4}$ ring. The structure of **107** can be compared to the two cyclotrigermanes **75**[164] and **55**.[118] The Ge−Ge bond distances in **107** are shorter than those of the *tert*-butyl substituted compound **55** (2.563(1) Å), since the longer Ge−Si bond relative to the Ge−C bond alleviates some of the steric crowding in the ring system. However, the presence of the bulkier $-\mathrm{Si(SiMe_3)_3}$ groups in **107** versus the two individual $-\mathrm{SiMe_3}$ groups in **75** results in a longer Ge−Ge bond distance in **107** versus that in **75** (2.460(1) Å).[164]

The related mixed-ligand compound **108** was obtained in good yield by the reduction of $\mathrm{PhBu^tGeCl_2}$ as a mixture of isomers and was subsequently converted to the halide-substituted species **109** by selective replacement of the phenyl substituents by chloride atoms (Scheme 47).[186] Only one stereoisomer of **109** was formed in this manner, and the crystal structure of this species was obtained that exhibited Ge−Ge bond lengths of 2.471(2) and 2.445(2) Å and Ge−Ge−Ge bond angles averaging 89.1°. The $\mathrm{Ge_4}$ ring of **109** is puckered, with a dihedral angle of 21°. The tetragermane **110**, which is formed by the reaction of $\mathrm{GeCl_2\cdot dioxane}$ with $\mathrm{NaSiBu^t_3}$ (eq 39), adopts a tetrahedrane-like structure as opposed to a cyclobutane-like geometry and cocrystallizes with $\mathrm{Bu^t_6Si_2}$.[187] The $\mathrm{Ge_4}$ tetrahedron in **110** approaches a nearly idealized geometry with average Ge−Ge distances of 2.441(3) Å.

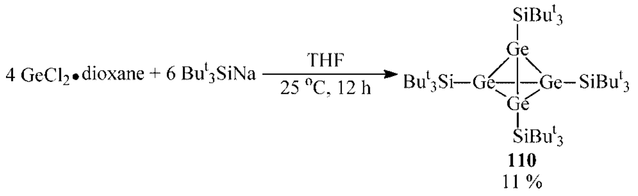
5. Pentagermanes

5.1. Linear Pentagermanes

Several stepwise preparative routes to pentagermanes have been described. The synthesis of **111** involves cleavage of a

Table 5. Selected Distances (Å) and Angles (deg) in Linear Tetragermanes

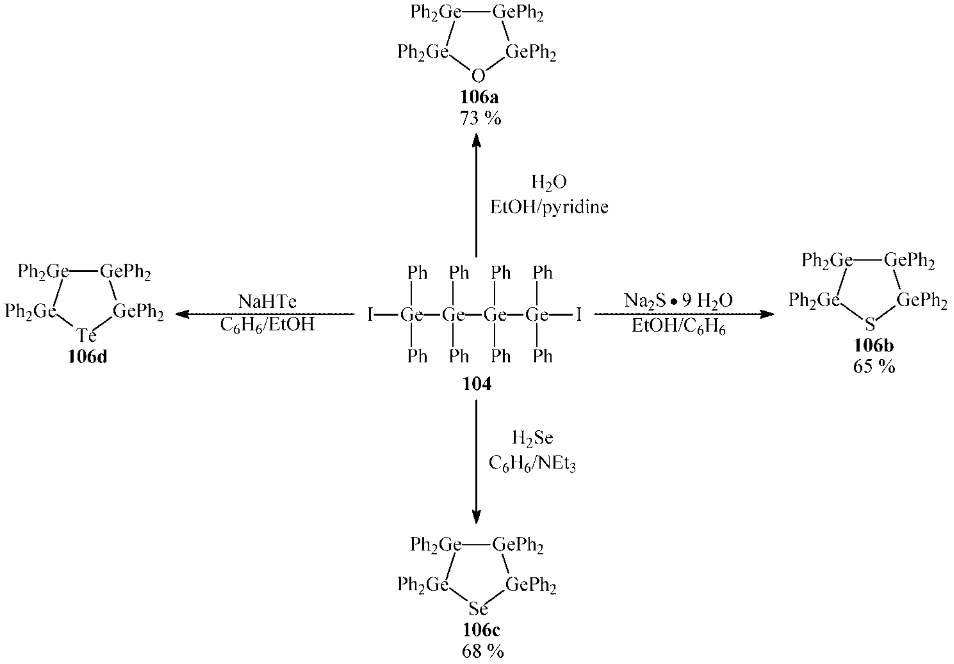
compound	d Ge^1−Ge^2	d Ge^2−Ge^2	d_{avg} Ge−Ge	d_{avg} Ge−C	∠Ge^1−Ge^2−Ge^3	ref
$Ph_3Ge^1Ge^2Ph_2Ge^2Ph_2Ge^1Ph_3 \cdot 2C_6H_6$ (**3**)	2.463(2)	2.461(2)	2.440(3)	1.960(1)	117.8(1)	86
$ClPh_2Ge^1Ge^2Ph_2Ge^2Ph_2Ge^1Ph_2Cl$ (**54**)	2.450(4)	2.442(3)	2.446(3)	1.97(1)	116.2(1)	135
$IPh_2Ge^1Ge^2Ph_2Ge^2Ph_2Ge^1Ph_2I$ (**104**)	2.451(1)	2.459(2)	2.455(2)	1.949(7)	114.2(1)	181



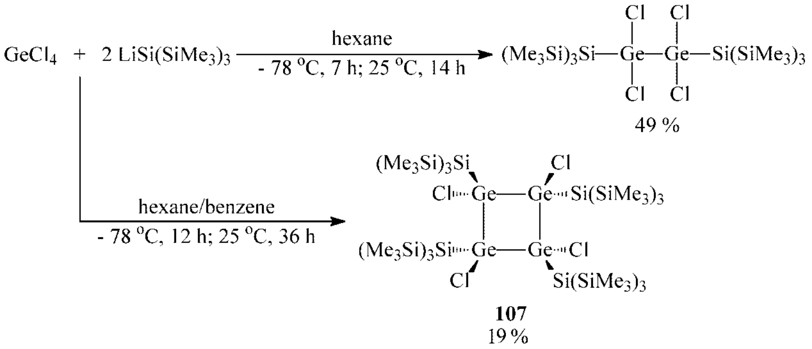
(39)

Ge−Ph bond using HCl and subsequent metathesis with an organogermyllithium reagent (Scheme 48),[188] and the intermediate lower oligomers were isolated and characterized during this study. The perethyl-substituted pentagermane $Et_3Ge(Et_2Ge)_3GeEt_3$ (**112**) was prepared via several stepwise Wurtz-type coupling reactions (Scheme 49).[189,190] In this synthesis, an excess of the chlorodigermane was used to avert Ge−Ge bond cleavage by the alkali metal, and the pentagermane was isolated in 43% yield after separation from the trigermane byproduct by distillation. The related heteroleptic pentagermane $Ph_3Ge(GeEt_2)_3GePh_3$ (**113**) was isolated in 59% yield from the reaction of 2 equiv of Ph_3GeLi and $ClEt_2Ge(GeEt_2)GeEt_2Cl$.[131] The UV/visible spectra (Table 2) of compounds **112** and **113** exhibit absorbance maxima at 248 nm (**112**)[189] and 269 nm (**113**).[131]

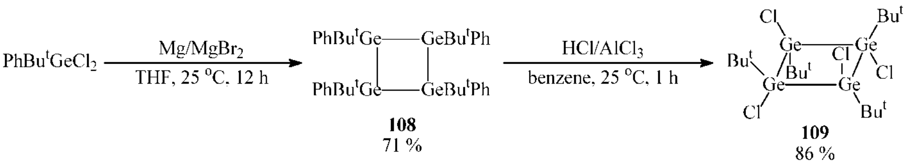
Scheme 45



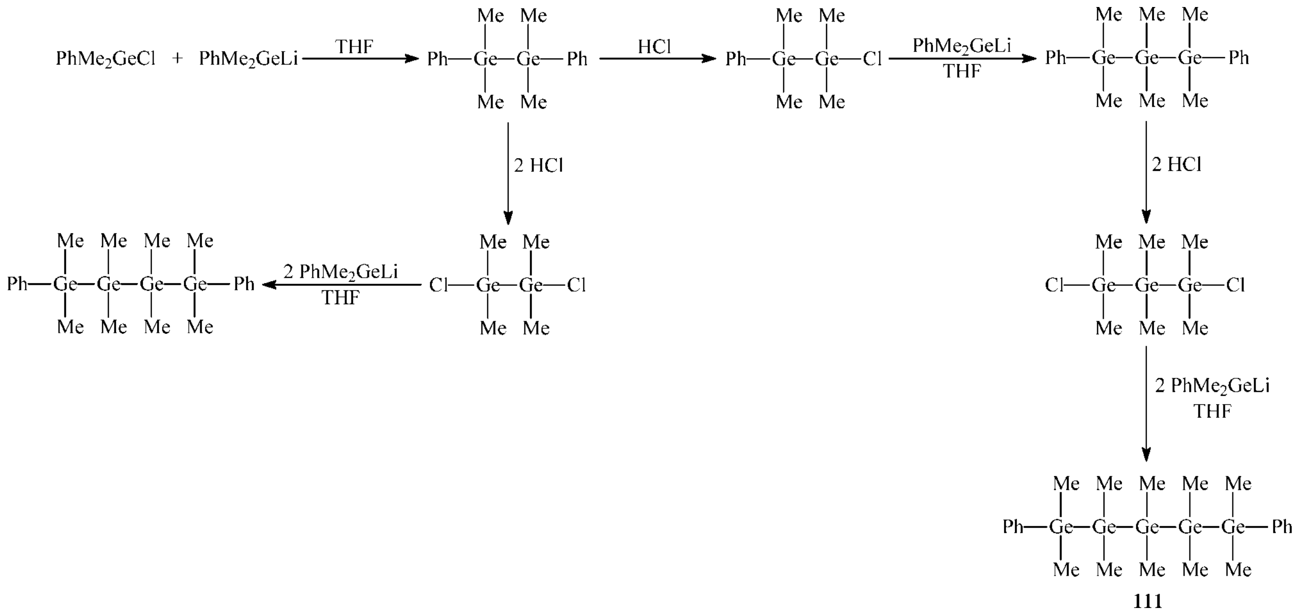
Scheme 46



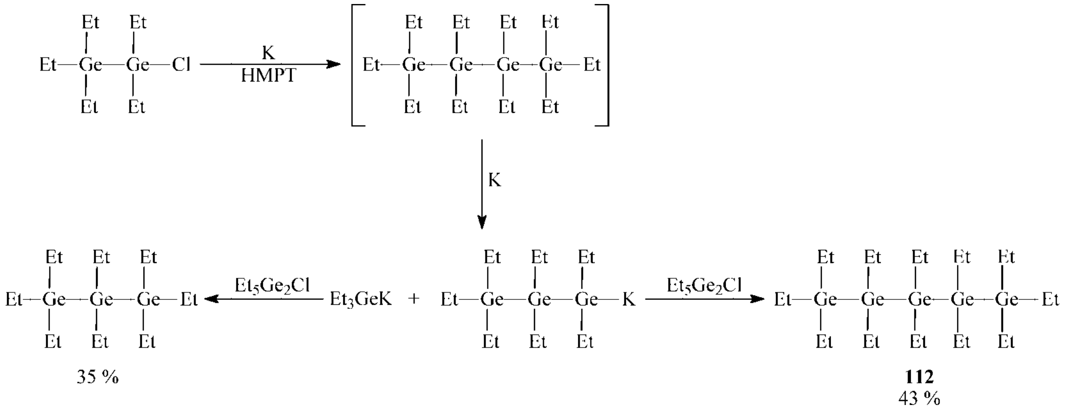
Scheme 47



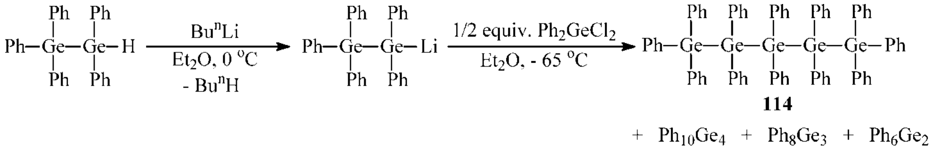
Scheme 48



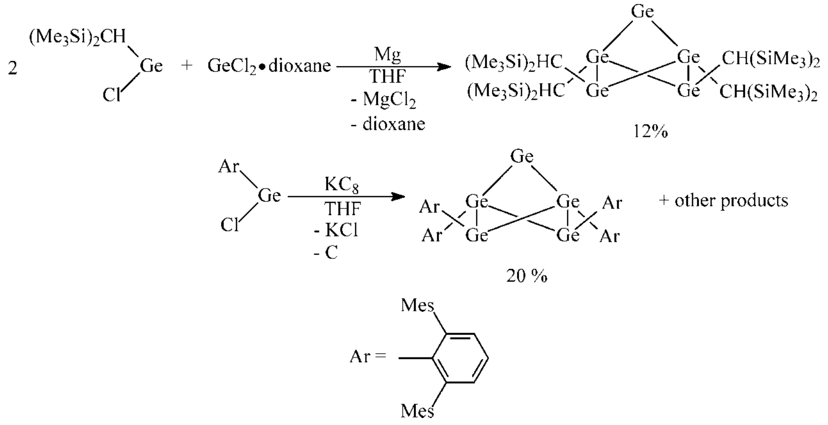
Scheme 49



Scheme 50



Scheme 51



The perphenyl-substituted pentagermane $Ph_3Ge(GePh_2)_3$-$GePh_3$ (**114**) was prepared according to Scheme 50.[191] Compound **114** was isolated in pure form in very low yield (0.2%) using preparative HPLC from the crude product mixture, which also contained Ge_2Ph_6, Ge_3Ph_8, and Ge_4Ph_{10}. The structure of **114** was determined, and this represents the

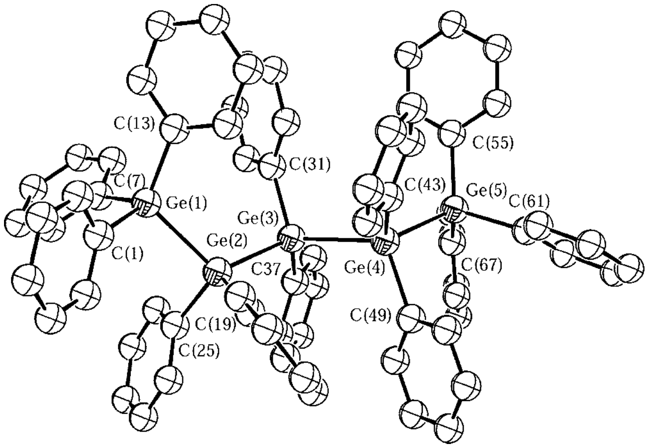


Figure 15. ORTEP diagram of **114**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.447(4); Ge(2)−Ge(3), 2.485(4); Ge(3)−Ge(4), 2.468(4); Ge(4)−Ge(5), 2.439(4); Ge−C$_{avg}$, 1.96(1); Ge(1)−Ge(2)−Ge(3), 116.7(2); Ge(2)−Ge(3)−Ge(4), 114.0(2); Ge(3)−Ge(4)−Ge(5), 116.0(2); Ge−Ge−C$_{avg}$, 109.0(6); C−Ge−C$_{avg}$, 108.1(8).

longest structurally characterized linear oligogermane reported to date (Figure 15). The individual Ge−Ge distances in **114** are 2.447(4) (Ge(1)−Ge(2)), 2.485(4) (Ge(2)−Ge(3)), 2.468(4) (Ge(3)−Ge(4)), and 2.439(4) Å (Ge(4)−Ge(5)), and the average Ge−Ge distance is 2.460(4) Å. The two terminal Ge−Ge bonds are substantially shorter than the two internal Ge−Ge distances, which is likely due to steric effects. The three Ge−Ge angles in **114** measure 116.7(2)° (Ge(1)−Ge(2)−Ge(3)), 114.0(2)° (Ge(2)−Ge(3)−Ge(4)), and 116.0(2)° (Ge(3)−Ge(4)−Ge(5)) with an average value of 115.6(2)°.[191]

The overall shape in the solid state of the Ge$_5$-chain in **114** does not resemble any of the three normal conformations of *n*-pentane (*anti−anti*, *gauche−gauche*, or *antigauche*). One of the torsion angles very closely approaches an antiperiplanar conformation (−179.3(2)°), but the second torsion angle is arranged in an almost ideally anticlinal arrangement (+114.4(2)°). The conformation along only the Ge(3)−Ge(4) bond approaches the expected staggered arrangement of the phenyl groups.

5.2. Cyclic Pentagermanes

A few cyclic pentagermanes have been prepared and structurally characterized, including the phenyl-substituted cyclopentagermane **115**. This material was synthesized via the sodium naphthalenide reduction of Ph$_2$GeCl$_2$ (eq 40) and was isolated from a product mixture that also included the six-membered cyclohexagermane **116**.[177,178] Compound **115** crystallizes with two independent molecules in the unit cell with average Ge−Ge bond distances of 2.456(2) and 2.450(2) Å and average Ge−Ge−Ge angles of 105.18(1) and 105.27(1)°. The overall conformation of **115** is a slightly twisted envelope.[184] The structure of **115** as its monobenzene solvate was also determined and found to be similar to the unsolvated species.[192]

Two different bicyclic pentagermanes, Ge$_5$[CH(SiMe$_3$)$_2$]$_4$ and Ge$_5$[C$_6$H$_3$-2,6-Mes$_2$]$_4$, were prepared from the corresponding chlorogermylenes as shown in Scheme 51.[193] The structures of both of these materials were determined, and each exhibits a distortion of the four germanium atoms in their cyclic Ge$_4$R$_4$ arrays, but the structures of these species clearly indicate that the unsubstituted germanium atom in both compounds bears a lone pair of electrons and all six Ge−Ge bonds are (2c, 2e) in nature.

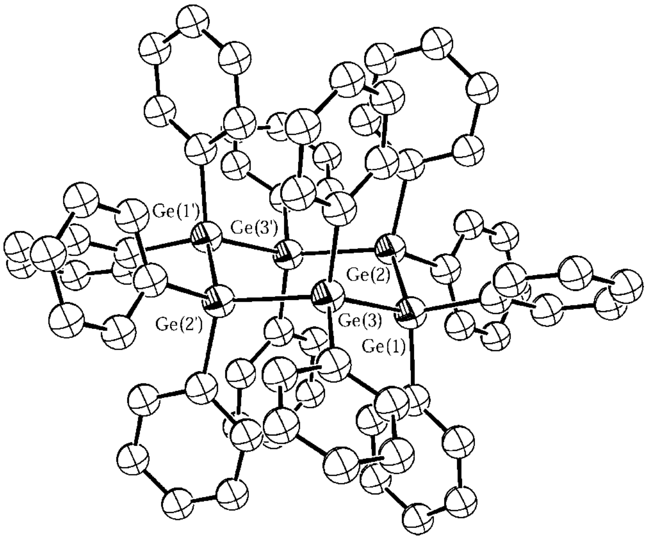
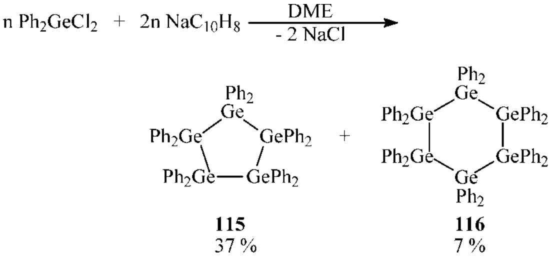


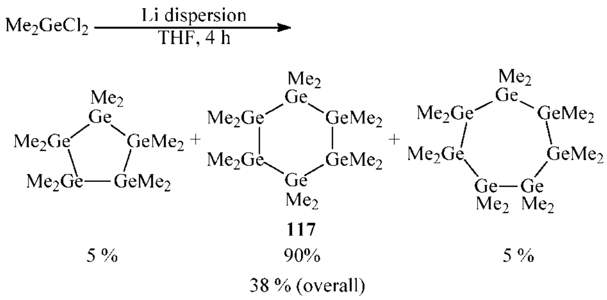
Figure 16. ORTEP diagram of **116**·2C$_7$H$_8$. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.461(2); Ge(2)−Ge(3), 2.466(2); Ge(3)−Ge(1′), 2.461(2); Ge−C$_{avg}$, 1.969(9); Ge(1)−Ge(2)−Ge(3), 114.3(1); Ge(2)−Ge(3)−Ge(1′), 113.9(1); Ge(3) − Ge(1′)−Ge(2′), 111.4(1); C−Ge−C$_{avg}$, 105.1(4); Ge−Ge−C$_{avg}$, 109.6(3).



(40)

6. Cyclic, Cluster, and Cage-Type Hexagermanes

A number of hexagermanes that adopt the common structural motifs expected for an array of six metal atoms have been prepared and characterized, including prismatic and octahedral species as well as the germanium analogues of cyclohexane. The synthesis of permethylcyclohexagermane (Me$_2$Ge)$_6$ (**117**), which was formed as a mixture with (Me$_2$Ge)$_5$ and (Me$_2$Ge)$_7$, was accomplished by the reaction of Me$_2$GeCl$_2$ with lithium metal (eq 41).[194] The perphenyl analogue (Ph$_2$Ge)$_6$ (**116**) was obtained from the product mixture resulting from the reaction of Ph$_2$GeCl$_2$ with sodium naphthalenide (eq 40).[177,178]



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The structure of **116** was shown to adopt three different crystalline forms depending on the solvent of crystallization, and the structure of **117** was determined in 1975[195] and has also recently been reinvestigated.[196] The structures of the

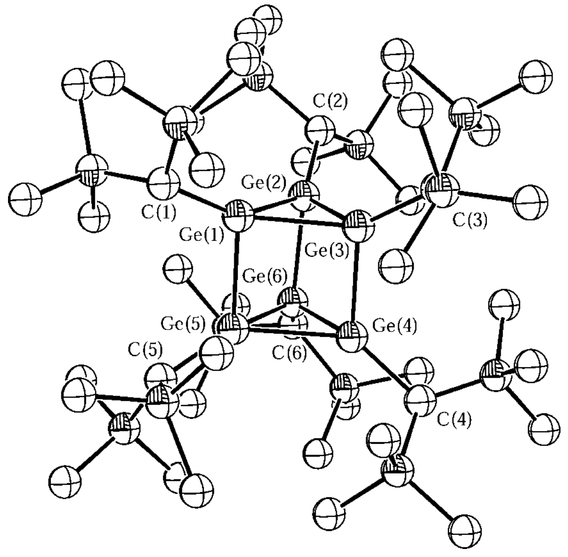


Figure 17. ORTEP diagram of **118**.

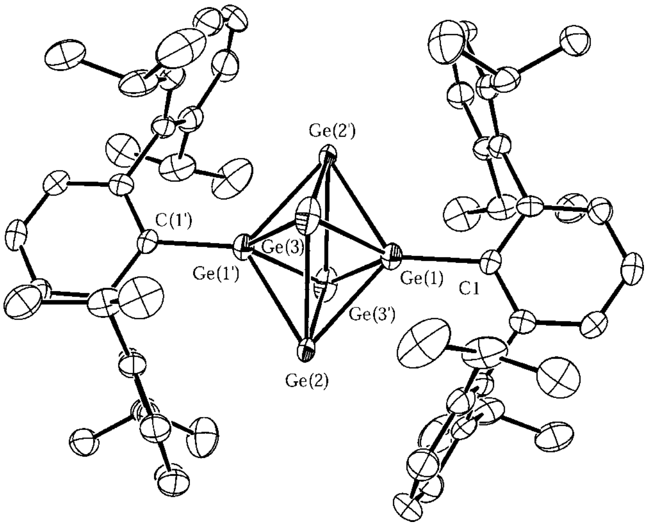


Figure 18. ORTEP diagram of **120**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.546(1); Ge(1)−Ge(3), 2.498(2); Ge(1)−Ge(2′), 2.532(1); Ge(1)−Ge(3′), 2.503(2); Ge(2)−Ge(3), 2.883(2); Ge(2)−Ge(3′), 2.886(2); Ge(1)−C(1), 1.974(6); C(1)−Ge(1)−Ge(2), 126.0(2); C(1)−Ge(1)−Ge(3), 125.0(2); Ge(2)−Ge(1)−Ge(3), 68.70(5); Ge(3)−Ge(2)−Ge(3′), 88.66(5); Ge(2)−Ge(3)−Ge(2′), 91.34(5).

heptabenzene[197] and ditoluene[198] solvates of **116** have been obtained, and the two structures differ only slightly. Similar to cyclohexane, both of the structures of **116** adopt a chairlike conformation with six axial and six equatorial phenyl substituents in both cases. The structure of **116**·2 C_7H_8 is shown in Figure 16. The Ge−Ge distances in **116**·2 C_7H_8 are all similar, with an average value of 2.463(2) Å, and the average Ge−Ge−Ge angles are 113.2(1)°,[198] while in **116**·7 C_6H_6 these values are 2.457(2) Å and 113.8(1)°, respectively.[197]

The structure of **117** adopts a chairlike conformation, and as expected due to the diminished steric effects of methyl-versus phenyl-substitution, the structure of **117** exhibits shorter Ge−Ge bond distances, which average 2.421(1) Å, and slightly more acute Ge−Ge−Ge bond angles, which average 112.00(6)°.[196] The difference in the steric bulk of the substituents is also manifested in the Ge−Ge−Ge−Ge dihedral angles in these two compounds, which are ±49.5° for **116**·2C_7H_8[198] and ±53.0° for **117**.[196] The energy differences among the three possible conformers of **117** were also determined using *ab initio* calculations, which indicated that the twist and boat conformations lie +5.2 and +9.2 kJ/mol (respectively) in energy higher than the chair conformation. The energy for the half-chair conformation for **117** was also calculated to be +10.1 kJ/mol relative to that for the chair conformation. This indicates that the twist to chair interconversion in **117** is substantially less than that of its hydrocarbon analogue C_6Me_6 (70 kJ/mol).[199]

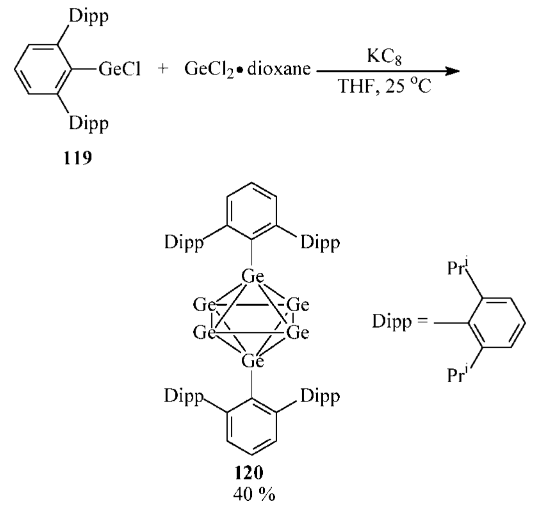
A hexagermaprismane (**118**) was prepared by the reduction $(Me_3Si)_2CHGeCl_3$ (eq 42), and it contains a broad absorption maximum centered at 280 nm in its UV/visible spectrum in hexane solution.[200] Compound **118** also exhibits reversible thermochromism in the solid state, changing from pale yellow at −196 °C to orange at 200 °C. Although the cause for this phenomenon was not described, the change in color at higher temperatures presumably arises from a conformational change that allows the germanium-based orbitals to overlap in such a way to increase the overall *σ*-delocalization in the molecule. This would be analogous to the thermochromic effects observed in polymeric group 14 compounds, where an increase in the number of *trans*-arrangements along the element−element backbone results in a red shift of the absorption maximum.[2,201] The structure of **118**, which was determined at room temperature, is shown in Figure 17 and bond distances and angles for the Ge_6 framework are collected in Table 6. The six Ge−Ge bonds making up the two triangular faces in **118** are nearly identical with an average value of 2.580(6) Å and are longer than the Ge−Ge distances in the three rectangular faces, which have an average value of 2.522(6) Å. The Ge−Ge−Ge bond angles in the triangular faces of **118** are 60°, and the three rectangular faces each have bond angles very close to 90°.

$$(Me_3Si)_2CHGeCl_3 \xrightarrow[\text{THF}\ \ -78\ °\text{C to } 25\ °\text{C, } 18\ \text{h}]{\text{Li}} \underset{\substack{\mathbf{118}\\ 12\%}}{[(Me_3Si)_2CHGe]_6} \qquad (42)$$

Reduction of the bulky germylene **119** in the presence of $GeCl_2$·dioxane using KC_8 generates the octahedral hexagermanium cluster **120** (eq 43).[202] The structure of **120** is shown in Figure 18. The cluster bears only two organic substituents and contains four unsubstituted germanium atoms. The Ge−Ge bond distances among the four unsubstituted Ge atoms are extremely elongated, measuring 2.883(2) Å

Table 6. Selected Bond Distances (Å) and Angles (deg) for 118 (Taken from Ref 200)

Ge(1)−Ge(2)	2.584(6)	Ge(4)−Ge(5)	2.579(6)	Ge(1)−Ge(5)	2.526(6)
Ge(1)−Ge(3)	2.580(6)	Ge(4)−Ge(6)	2.579(5)	Ge(2)−Ge(6)	2.516(6)
Ge(2)−Ge(3)	2.580(5)	Ge(5)−Ge(6)	2.578(6)	Ge(3)−Ge(4)	2.523(4)
Ge(1)−Ge(2)−Ge(3)	60.0(1)	Ge(2)−Ge(1)−Ge(3)	60.0(1)	Ge(3)−Ge(2)−Ge(6)	91.4(1)
Ge(1)−Ge(3)−Ge(2)	60.1(1)	Ge(2)−Ge(1)−Ge(5)	89.9(2)	Ge(3)−Ge(4)−Ge(5)	88.6(2)
Ge(1)−Ge(2)−Ge(6)	89.8(2)	Ge(2)−Ge(3)−Ge(4)	88.5(2)	Ge(3)−Ge(4)−Ge(6)	91.2(2)
Ge(1)−Ge(5)−Ge(4)	91.3(2)	Ge(2)−Ge(6)−Ge(4)	88.7(2)	Ge(4)−Ge(5)−Ge(6)	60.0(2)
Ge(1)−Ge(5)−Ge(6)	89.7(2)	Ge(2)−Ge(6)−Ge(5)	90.3(2)	Ge(4)−Ge(6)−Ge(5)	60.0(2)
Ge(1)−Ge(3)−Ge(4)	91.4(2)	Ge(3)−Ge(1)−Ge(5)	88.5(2)	Ge(5)−Ge(4)−Ge(6)	60.0(2)



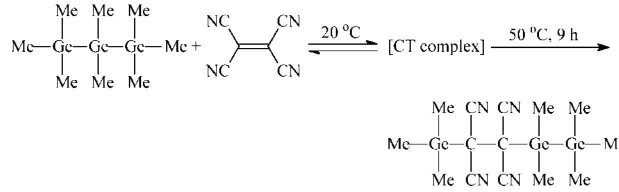
(43)

(Ge(2)−Ge(3)) and 2.886(2) Å (Ge(2)−Ge(3′)), while those from the unsubstituted Ge atoms to the two atoms bearing the aryl groups are closer in length to typical Ge−Ge single bonds with an average value of 2.520(1) Å. Formally, compound **120** has seven electron pairs for bonding within the Ge_6 octahedron and thus has the expected *closo*-structure.

7. Higher Oligomers

To date, no linear oligogermanes with more than five germanium atoms in the backbone have been structurally characterized, but the synthesis of discrete linear oligomers containing six or more Ge atoms has been reported. The action of a large excess of Me_3Al (12.5 equiv) on $GeCl_4$ in the presence of NaCl yielded a mixture of $Me_{14}Ge_6$, $Me_{12}Ge_5$, $Me_{10}Ge_4$, and Me_8Ge_3 as shown by mass spectrometry.[203] Similarly, the reaction of excess Me_3Al (∼ 7 equiv) with GeI_2 furnished a mixture of $Me_{16}Ge_7$, $Me_{14}Ge_6$, and $Me_{12}Ge_5$. The formation of the germanium oligomers was postulated to occur through generation of germanium/aluminum intermediates.[203] The linear hexagermanes $Et_3Ge(GeEt_2)_4GeEt_2$[189] and $Ph_3Ge(GeEt_2)_4GePh_3$[131] have also been reported and exhibit absorbance maxima at 258 and 264 nm, respectively (Table 2).

The Wurtz coupling of Me_3GeCl and Me_2GeCl_2 with lithium metal in THF furnishes the permethylated oligogermanes Me_6Ge_2 (18%), Me_8Ge_3 (20%), $Me_{10}Ge_4$ (10%), and $Me_{12}Ge_5$ (4%)[204] as well as $Me_{22}Ge_{10}$,[205] and the physical properties of these species have been investigated.[204–206] Pulse radiolysis of these oligomers (n = 2, 3, 5, and 10) was shown to generate radical anions for which UV/visible spectra were obtained,[205] while combining these compounds with tetracyanoethylene (TCNE) generated charge transfer complexes at room temperature. The Me_8Ge_3/TCNE charge transfer complex undergoes insertion of TCNE into one of the Ge−Ge bonds to furnish a 1:1 adduct (eq 44).[204] The ionization potentials [204–206] and electrochemical oxidation potentials[207] of these species have also been determined. These data are summarized in Table 7.



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In all cases, the absorption maxima of the parent compounds, the CT complexes, and the radical anions exhibit a bathochromic shift as the length of the Ge−Ge chain increases. Similarly, the ionization and oxidation potentials of these species decrease in energy as the chain length increases. The trends in absorption maxima in these systems, as well as in their ionization and oxidation potentials, are as expected for oligogermanes with varying chain lengths. The decomposition of the permethylated oligogermanes was also investigated by ultraviolet irradiation using a Hg arc lamp, resulting in photodegradation of these species that has been studied by the implementation of trapping reagents.[208] The degradation of these species was shown to proceed by contraction of the Ge−Ge chain via loss of Me_2Ge and homolytic cleavage of the Ge−Ge bond (Scheme 52).

The majority of higher oligomers containing six or more germanium atoms that have been isolated and characterized are polycyclic species, and of these the Ge_8 analogues of cubane are the most common. The preparation of two octagermacubanes (**121** and **122**) in low yields by the methods illustrated in Scheme 53 has been described,[209] and the parent germacubane Ge_8H_8 has been the subject of a theoretical investigation.[210] The 3-methylpentyl derivative **121** was obtained in three steps starting from 3-methylpentylphenylgermanium dichloride, while the 2,6-diethylphenyl derivative **122** was obtained directly from reduction of the corresponding trichloride. Compound **122** was the first germacubane to be structurally characterized, and the Ge−Ge bond distances in **122** average 2.490(1) Å, which is similar to the calculated Ge−Ge bond distance in Ge_8H_8 (2.527 Å),[210] and the Ge−Ge−Ge angles in **122** average 90.0(0)°.

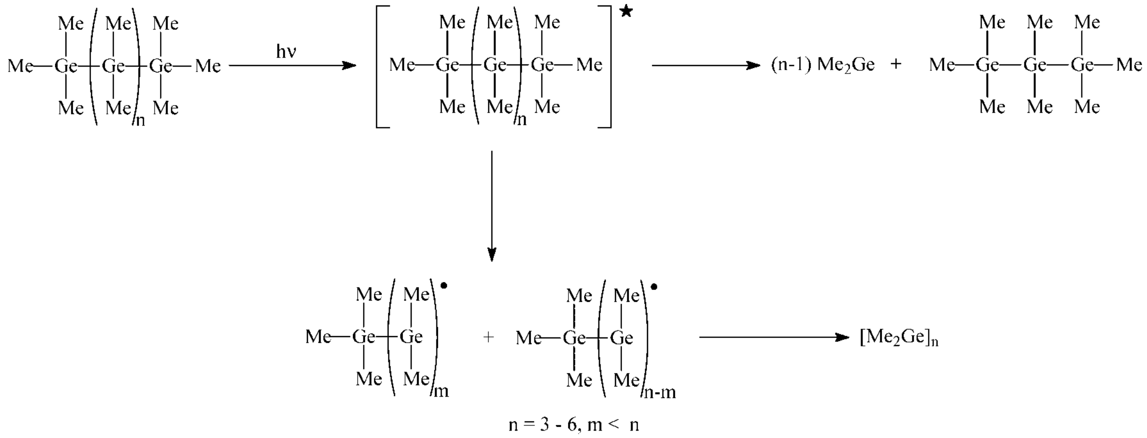
The related octagermacubane **123** was obtained in low yield from $Me_2CHCMe_2GeCl_3$ (Scheme 54),[211] and the structure of **123** contains an inversion center where the average of the four unique Ge−Ge bond distances is 2.516(1) Å, while the Ge−Ge−Ge bond angles again average 90.0(1)°. The UV/visible spectrum of **123** in hexane exhibits an absorption maximum at 235 nm (sh), and **123** can be readily oxidized, as suggested by its oxidation potential, which was determined to be 220 mV (vs SCE). The ease of oxidation of this species was confirmed upon the reaction

Table 7. Physical Data for Permethylated Oligogermanes with Absorbance (λ_{max}) Values Reported in Nanometers

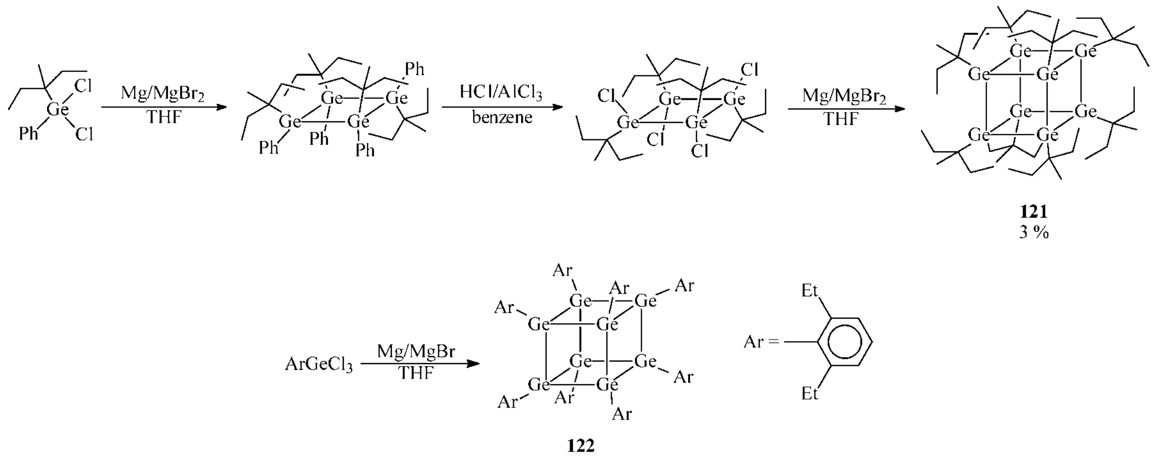
compound	ionization potential (eV)	electrochemical oxidation potential (V)[b]	λ_{max} (neutral oligomer)	λ_{max} (TCNE CT complex)	λ_{max} (radical anion)
Me_6Ge_2	8.58[a]	1.28	197[c]	427[a]	267, 305[d]
Me_8Ge_3	8.15[a]	0.93	217[c]	485[a]	291, 345[d]
$Me_{10}Ge_4$	7.80[a]	0.72	233[c]	550[a]	n/a
$Me_{12}Ge_5$	7.67[a]	0.61	246[c]	565[a]	330, 545[d]
$Me_{22}Ge_{10}$	5.55[d]	n/a	286[c]	n/a	400, 900[d]

[a] Taken from ref 204. [b] Data from ref 207. [c] Data from ref 206. [d] From ref 205.

Scheme 52



Scheme 53



121
3 %

122
1 %

of **123** with PCl_5 (Scheme 54), which furnished **124** as a mixture of isomers.[211] The *exo,exo*-isomer of **124** was obtained as the major product, and treatment of the mixture of isomers with sodium metal resulted in reduction of **124** to regenerate compound **123**.

Two additional octagermacubanes, $Ge_8(C_6H_3(OBu^t)_2\text{-}2,6)_6$ (**125**)[212] and $Ge_8[N(SiMe_3)_2]_6$ (**126**),[213] both can be prepared by a high temperature route involving the intermediate formation of germanium(I) bromide. The synthesis of **125** was achieved according to eq 45, and its structure is illustrated in Figure 19.[212] Both **125** and **126** contain two unsubstituted and six substituted germanium atoms. The Ge−Ge bond distances in **125** are nearly uniform, and the Ge−Ge−Ge bond angles approach 90°, resulting in a near-ideal cubic structure,[212] while the skeleton of **126** is significantly distorted with both relatively acute (75.3° and 81.3°) and obtuse (101.4° and 101.8°) Ge−Ge−Ge angles. The bonds between the substituted germanium centers in **126** are elongated (average value = 2.667 Å) versus those bonds between the substituted and unsubstituted atoms (average value = 2.501 Å).[213]

$$\mathrm{Ge} + \mathrm{HBr} \xrightarrow[\text{2). toluene/NPr}^n_3,\ -196\ ^\circ\text{C}]{\text{1). high vacuum, 1550 }^\circ\text{C}}$$

$$\mathrm{GeBr} \xrightarrow[\text{toluene, - 78 }^\circ\text{C to 25 }^\circ\text{C}]{\mathrm{Li[C_6H_3(OBu^t)_2\text{-}2,6]}} \mathrm{Ge_8(C_6H_3(OBu^t)_2\text{-}2,6)_6} \tag{45}$$

125
10 %

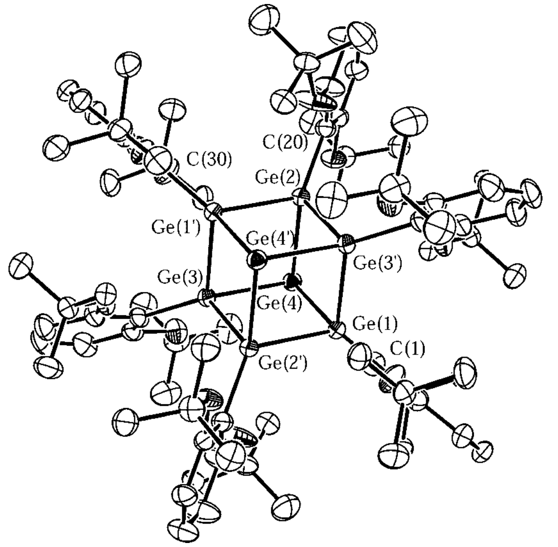
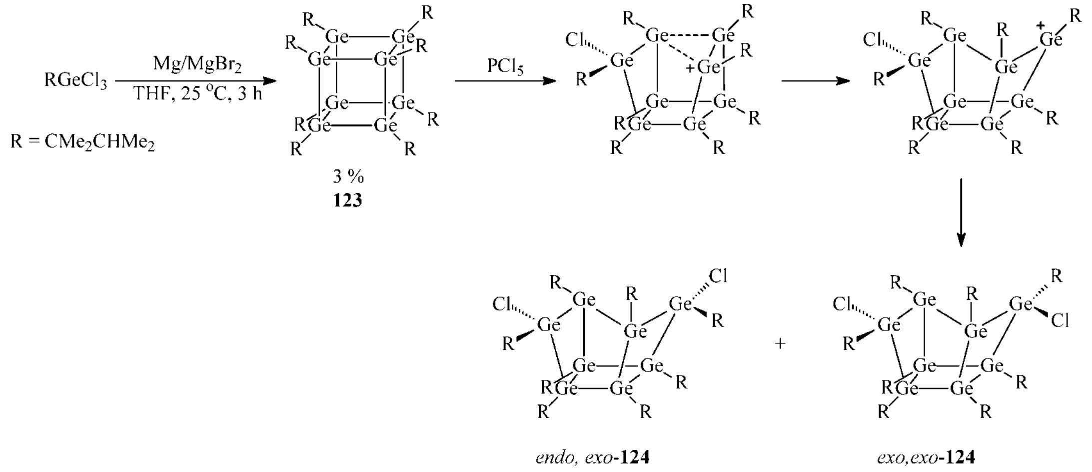


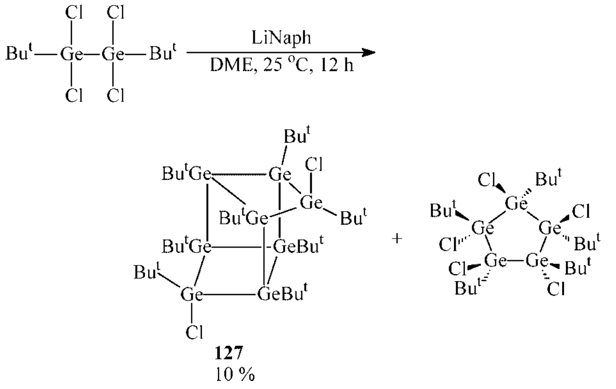
Figure 19. ORTEP diagram of **125**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2′), 2.491(1); Ge(1)−Ge(3′), 2.495(1); Ge(1)−Ge(4), 2.516(1); Ge(2)−Ge(3′), 2.494(1); Ge(2)−Ge(4), 2.529(1); Ge(3)−Ge(4), 2.503(1); Ge(1)−C(1), 1.979(3); Ge(2)−C(10), 1.978(3); Ge(3)−C(20), 1.973(3); Ge(1)−Ge(2′)−Ge(3), 87.67(4); Ge(1)−Ge(2′)−Ge(4′), 91.43(4); Ge(1)−Ge(3′)−Ge(4′), 91.94(4); Ge(1)−Ge(4′)−Ge(2), 88.71(4); Ge(2)−Ge(3′)−Ge(1), 89.97(4); Ge(2)−Ge(3′)−Ge(4′), 92.82(4); Ge(2′)−Ge(1)−Ge(3′), 88.82(4); Ge(2′)−Ge(1)−Ge(4), 92.57(4); Ge(3)−Ge(4)−Ge(1), 86.92(4); Ge(3)−Ge(4)−Ge(2), 87.90(4); Ge(3′)−Ge(1)−Ge(4), 90.80(4).

Scheme 54



The nature of the ligands attached to the germanium atoms therefore exerts a significant influence on the delocalization of the electrons within the Ge_8 cluster framework. When the substituent directly attached to germanium bears a lone pair of electrons, versus substituents which do not, the overall electron delocalization in the cluster framework is increased. This is also manifested in the physical attributes of the cluster systems, as compound **126** is much darker in color than compound **125**.

Two other polycyclic oligogermanes having different overall geometries have been prepared and characterized. The tetracyclic germane **127** was prepared according to eq 46 in low yield, and its structure contains a C_2-symmetric germanium skeleton with two five-membered rings and three four membered rings, and it has Ge—Ge bond distances ranging from 2.442(6) to 2.537(6) Å.[214] The chiral species 4,8-dibromo-octa-*tert*-butyltetracyclo-[3.3.0.0^{2,7}.03,6]octagermane **128** was prepared starting from a digermane (eq 47), which is stable to air and moisture and has Ge—Ge bond distances ranging from 2.443(1) to 2.542(1) Å.[215]

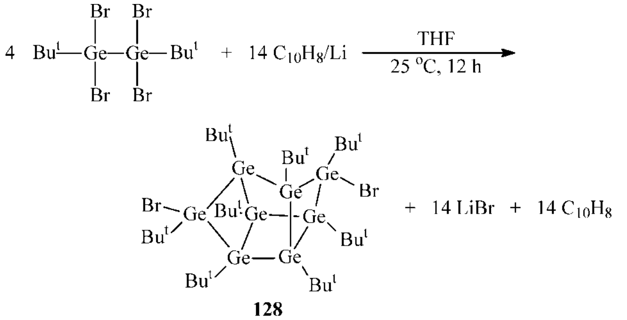


127
10 %

(46)

8. Heterocycles with Ge—Ge Bonds

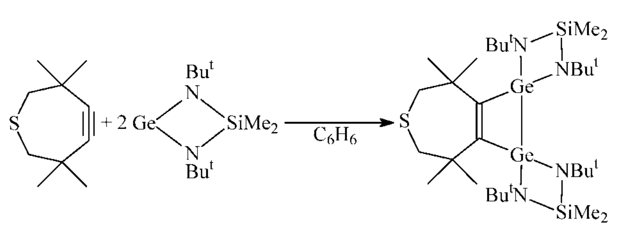
In addition to the digermanes described earlier in this review, a number of cyclic species containing at least one Ge—Ge bond have been prepared and characterized, and several of these types of compounds contain germanium bound to other group 14 elements within the cyclic framework. Structural data for the Ge—Ge bonds for the structurally characterized compounds are collected in Table 8. These include the 1,2-digermacyclobutenes that contain germanium and carbon, which have been prepared by various methods.



128
48 %

(47)

The first example of such a material (**129**) was obtained by the reaction of $GeCl_2$·dioxane with a thiocycloheptyne (Scheme 55),[216] where the formation of **129** was speculated to occur via the formation of one of the two intermediates shown in Scheme 55. A similar fused species (**130**), with the germanium atoms arranged in a spirocyclic fashion, was prepared according to eq 48.[217] The structure of **130** reveals that the Ge_2C_2 ring is slightly puckered and the two GeN_2Si rings are slightly twisted relative to the Ge_2C_2 ring.



130
86 %

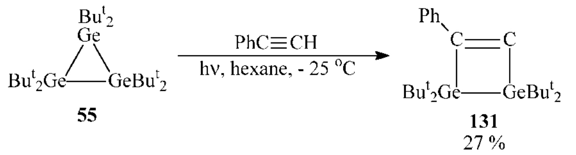
(48)

Several examples of 1,2-digermacyclobutenes having isolated Ge_2C_2 moieties that are not part of fused ring systems are also known, including the sterically unencumbered species **131** that was obtained from the [2 + 2] cycloaddition reaction of **55**[118] with phenylacetylene (eq 49).[137] Three different structurally related digermacyclobutadienes **132** were obtained by the palladium catalyzed insertion of phenylacetylene into the Ge—Ge bond of chloride-substituted digermanes, followed by reduction with sodium metal as shown in Scheme 56.[218] The Ge—Ge bond distance in **132c** measures 2.439(7) Å, and the Ge_2C_2 ring is planar. The ethyl-substituted derivative **132b** undergoes insertion of palladium

Table 8. Germanium−Germanium Bond Distances (in Å) for Structurally Characterized Heterocylic Compounds Containing Ge−Ge Bonds

compound	*d* Ge−Ge (Å)	ref	compound	*d* Ge−Ge (Å)	ref
129	2.380(1)	216	**150**	2.4994(4)	226
130	2.459(1)	217	**151a**	2.389(1)	227
131	2.531(6)	137	**155**	2.429(1),2.429(1)	232
132c	2.439(7)	218	**156**	2.407(1),2.407(1)	232
135	2.514(2)	219	**158**	2.379(1)	231
139	2.513(1)	220	**159**	2.379(1)	233
140	2.422(2)	221	**163a**	2.4237(4)	234
143	2.554(2)	222	**163b**	2.4415(5)	234
145	2.5567(8)	224	**166**	2.441(2)	235
148	2.411(3), 2.406(2)	225	**168b**	2.406(2)	236

into the Ge−Ge bond to give the five-membered heterocycle **133**, which subsequently reacts with phenylacetylene to give the hexacyclic compound **134** in an equal ratio of structural isomers.

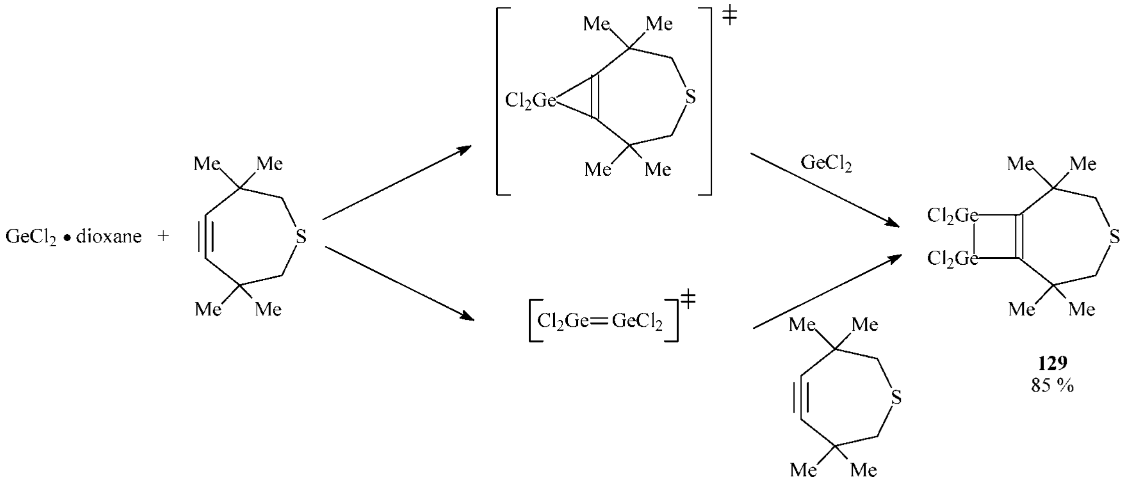


(49)

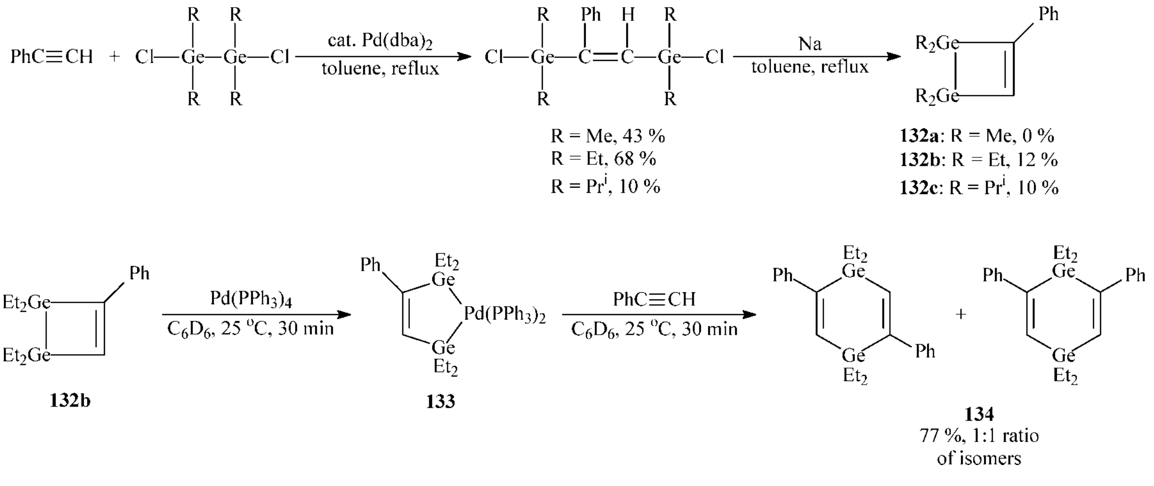
The more sterically hindered digermacyclobutene **135** was synthesized by the reaction of $Br_3GeC(SiMe_3)_3$ and diphenylacetylene, and the tribromogermane precursor also serves for the preparation of the digermabicyclohexane **136** upon reaction with styrene.[219] The formation of **135** results from an initial single-electron transfer from Mg to the halogermane, followed by subsequent coupling of the resulting radical species to give a digermyne that then undergoes a [2 + 2] cycloaddition reaction (Scheme 57).[219] Two additional heterocycles that are similar to **135** and **136** can be prepared by reaction of the germylene $(Me_3Si)_3CGeCl$ with ethylene or phenylacetylene, giving the digermacyclobutene **137** or the digermacyclobutane **138** (Scheme 58),[220] and compound **138** can be converted to the digermabicyclohexane **139** upon addition of a second equivalent of ethylene and magnesium.

In addition to **138**, several digermacyclobutanes have also been reported. A species containing adamantyl groups attached to the ring carbons (**140**) was prepared according

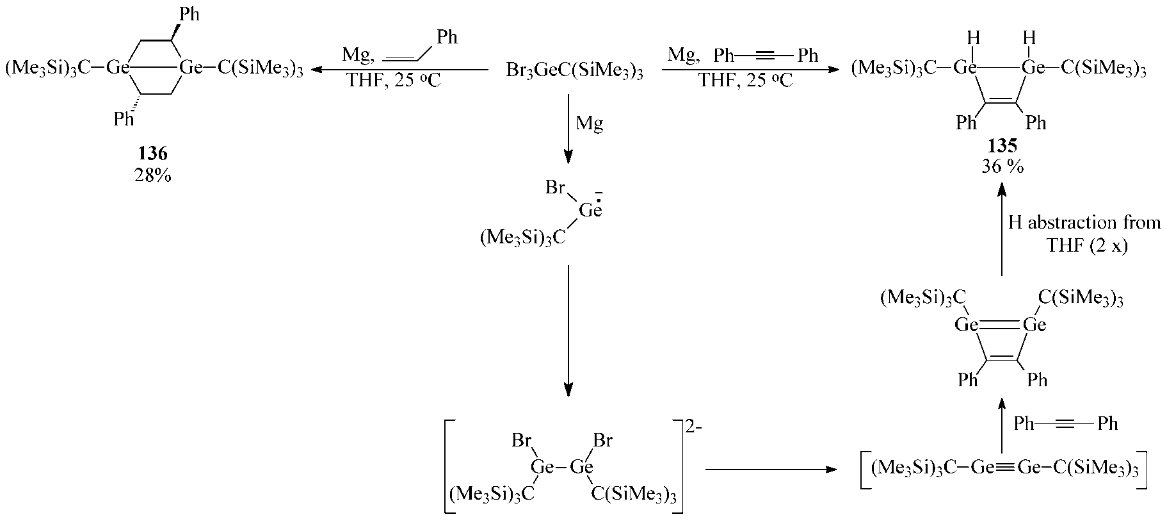
Scheme 55



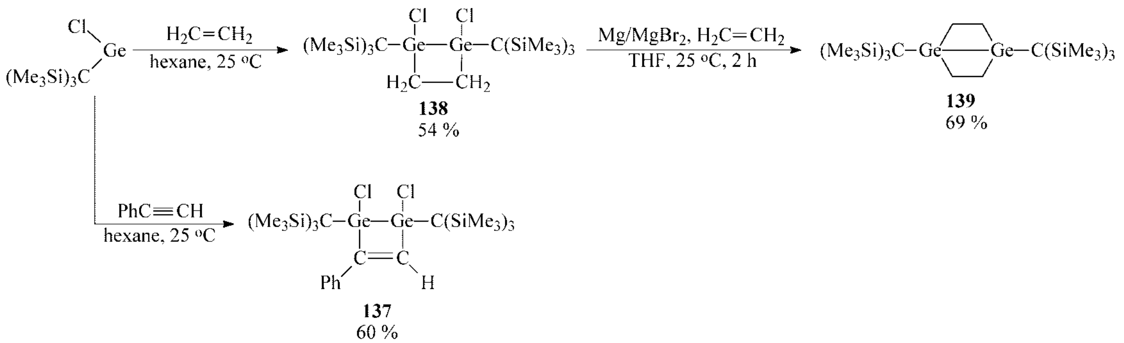
Scheme 56



Scheme 57

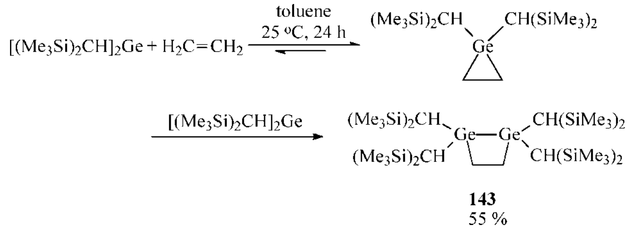


Scheme 58



to Scheme 59,[221] that likely results from dimerization of the intermediate germene **142** that is generated by elimination of $LiOSiMe_3$ from the initially formed alkoxide **141**. The Ge_2C_2 ring in **140** is highly puckered (dihedral angle = 40.7°) due to the presence of the two bulky adamantyl groups.

Three other examples of digermacyclobutanes include **143**−**145**, where the digermacyclobutane **143** was obtained from the germylene $[(Me_3Si)_2CH]_2Ge$ and ethylene (eq 50) and was generated via the initial formation of a germirane intermediate.[222] The silicon-containing germacyclobutane **144** was obtained from the reductive coupling of 1,2-dichlorosilagermane, and reaction of **144** with PCl_5 leads to selective cleavage of the Ge−Ge bond (Scheme 60).[223] The fluorenyl-substituted digermacyclobutane **145** was prepared in several steps as shown in Scheme 61.[224] This species ultimately forms from dimerization of the germaphosphabutadiene **146** and was obtained in 75% yield based on the starting fluoro compound **147**. The structure of **145** contains a trapezoidal Ge_2C_2 ring structure with a long Ge−Ge distance of 2.5567(8) Å.



(50)

In addition to the four-membered systems, five- and six-membered germanium heterocycles are also known. Thermal extrusion of Me_2Ge from a substituted 7-germanorbornadiene in the presence of 1,2-diethynylbenzene furnishes the sterically unencumbered trigermacyclopentene **148** (Scheme 62), which was structurally characterized.[225] The Ge_3C_2 ring of **148** (Figure 20) is approximately planar and has Ge−Ge bonds measuring 2.411(3) and 2.406(2) Å and a C=C double bond length of 1.30(1) Å. The Ge−Ge−Ge bond angle is

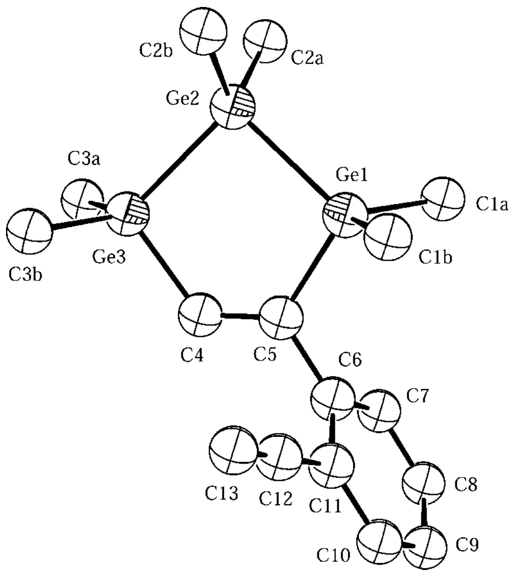
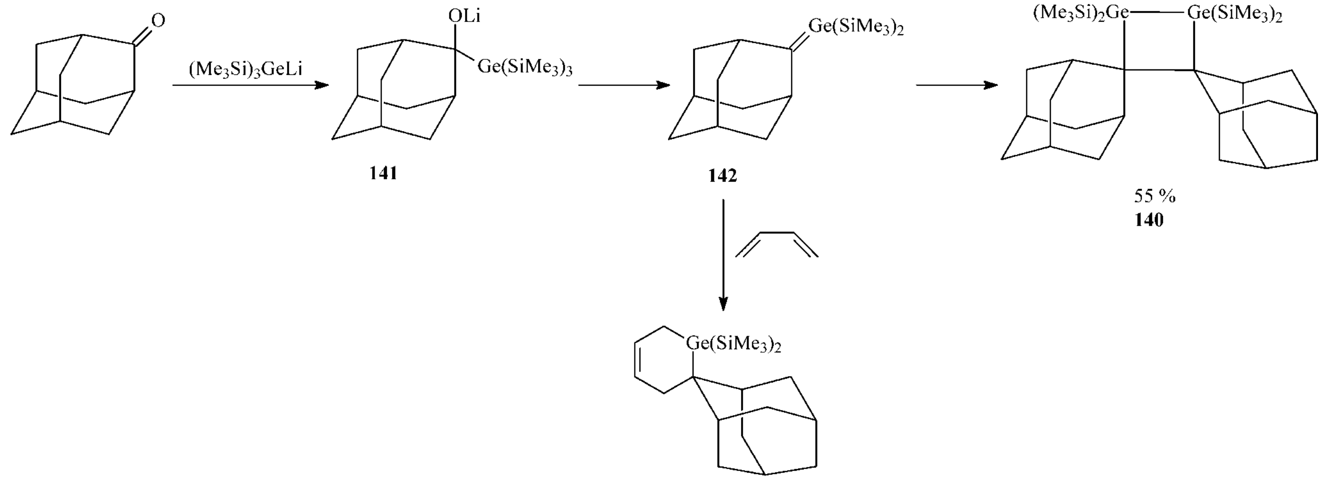
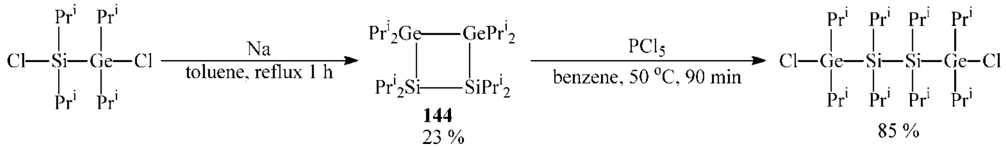


Figure 20. ORTEP diagram of **148**. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2), 2.411(4); Ge(2)−Ge(3), 2.406(2); Ge(1)−C(5), 1.979(9); Ge(3)−C(4), 1.954(8); Ge(1)−Ge(2)−Ge(3), 92.8(1); Ge(2)−Ge(3)−C(4), 99.3(1); Ge(3)−C(4)−C(5), 125.3(7); C(4)−C(5)−Ge(1), 122.4(7); C(5)−Ge(1)−Ge(2), 99.4(3).

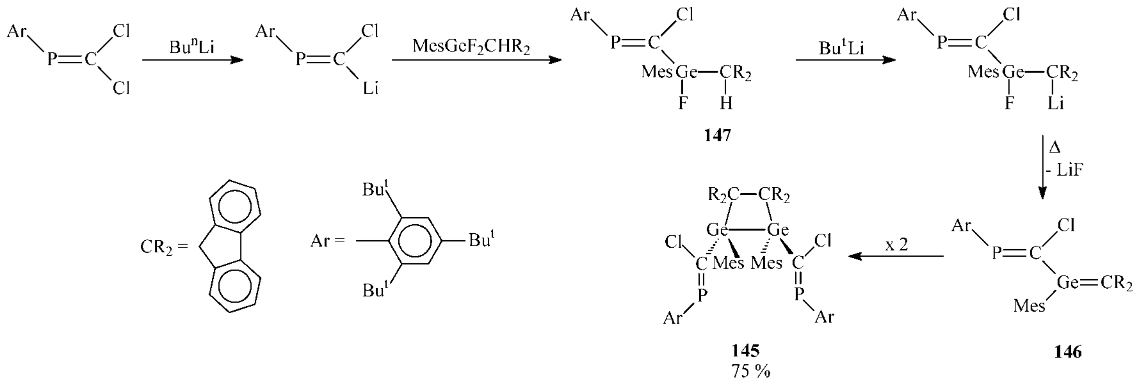
Scheme 59



Scheme 60

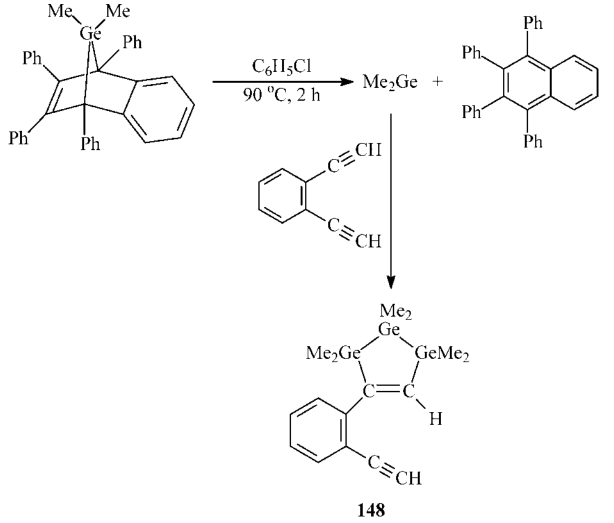


Scheme 61



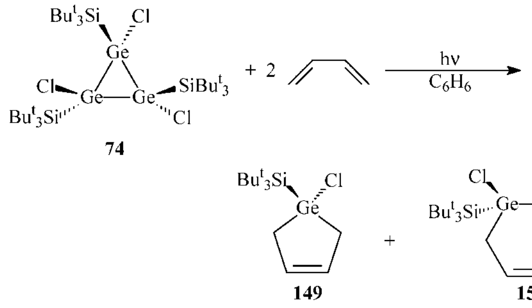
92.8(1)°, and the Ge−Ge−C and Ge−C−C bond angles within the ring average 99.4(3) and 123.8(7)°, respectively.

Scheme 62



Photolysis of the cyclotrigermane **74** in the presence of 2 equiv of butadiene furnishes the [4 + 1] (**149**) and [4 + 2] (**150**) cycloaddition products (eq 51).[226] Several digermacyclohexadienes **151** can be prepared by the metathesis reaction shown in Scheme 63,[227] and all three derivatives of **151** undergo photolytic ring contraction reactions resulting in extrusion of a germylene to furnish stable germoles **152** in near-quanitative or quantitative yields. The reaction of the related 1,2-digermacyclohexa-3,5-diene **153** with TCNE has been investigated, and it results in a mixture of products which contrasts to the reaction of linear oligomers with this substrate (Scheme 64).[228] At elevated temperatures, an additional tricyclic species is formed in the product mixture in 3% yield (Scheme 65).[229]

Some large heterocyclic systems have been prepared, including the tetragermacyclooctadiyne **155**, which was generated from the acetylene-functionalized digermane **154** (Scheme 66)[230,231] The reaction of **155** with tetracycanoethylene (TCNE) results in a charge transfer complex that exhibits an absorption maximum in the visible region at 488 nm. If the mixture of **155** and TCNE is allowed to stand for 2 days, oligomerization of **155** occurs to furnish the twelve-membered and sixteen-membered heterocycles **156** and **157**



(51)

(respectively). Treatment of **155** with the acceptor species DCQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) also yields a charge-transfer complex, which has an absorption maximum at 536 nm that ultimately undergoes a [2 + 6] cycloaddition reaction to yield the product **158** (Scheme 66).[231] The structures of **155** and **156** were determined,[232] and the eight-membered ring of **155** is approximately planar, while the twelve-membered ring of **156** adopts a chairlike conformation with approximately linear GeCCGe fragments.

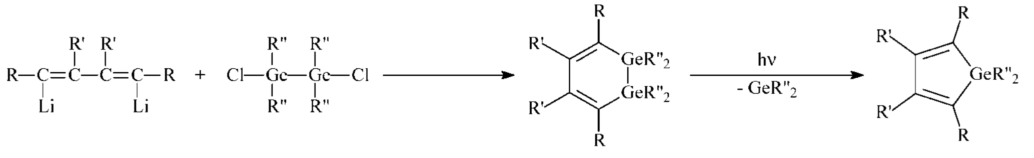
The preparation of several nitrogen-, oxygen-, and sulfur-containing heterocycles has been reported. Photolysis of the cyclotrigermane **62c** in the presence of diazomethane or phenylazide yields the three-membered heterocycles **158** and **159** (Scheme 67).[233] The structures of both of these species have been determined, and these contain identical short Ge−Ge bond distances of 2.379(1) Å and exhibit nearly planar environments at both germanium atoms. These structural attributes, coupled with the reactivity of **158** and **159**, suggest that **152** and **153** have a substantial contribution from the π-complex **160** (Scheme 67), as was suggested for the structure of compound **72**.[160] Curiously, the reaction of the digermene **161**, synthesized from $Ge[N(SiMe_3)_2]_2$ and $Li(C_6H_2Pr^i_3\text{-}2,4,6)$, with diazomethane does not furnish **162**,[233] but rather yields the azadigermirane **163a** via a [2 + 1] cycloaddition (Scheme 68).[234] This indicates that the digermene **161** retains its structure in solution and does not completely dissociate to two discrete germylene fragments. The trimethylsilyl derivative **163b** was prepared by a similar reaction, and the structures of both derivatives were determined and found to contain nearly planar Ge_2N rings.

Two oxygen-containing heterocycles were prepared according to Scheme 69. The addition of nitrous oxide to the digermene **164** furnishes the digermoxirane **165** via a [2 + 3] addition, while reaction of **164** with dioxygen yields the 1,2-digermadioxetane **166**, which undergoes thermal rearrangement to the digermanol **167**.[235] Thermal extrusion of either Me_2Ge or Ph_2Ge from the corresponding germanorbornadiene in the presence of di-*tert*-butylthioketene provides the digermathietanes **168** (eq 52), which were presumed to be generated via an ylide-type intermediate.[236]

9. Polygermanes

The synthesis, chemistry, and properties of polygermanes have received a significant amount of recent attention. Polygermanes, in contrast to oligogermanes, are significantly

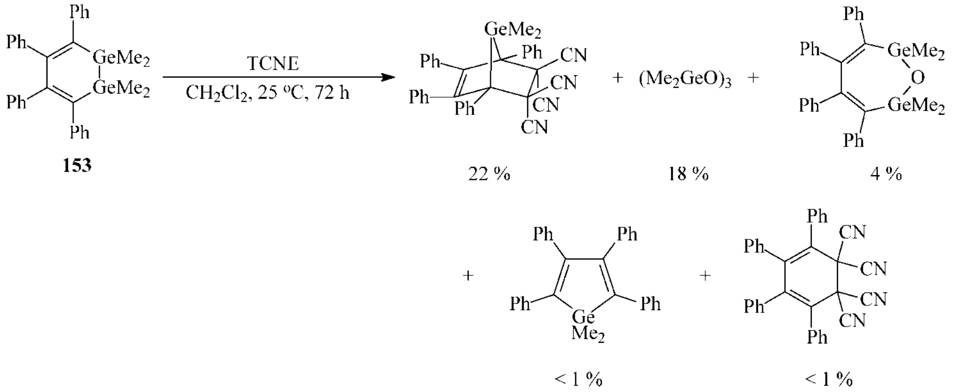
Scheme 63



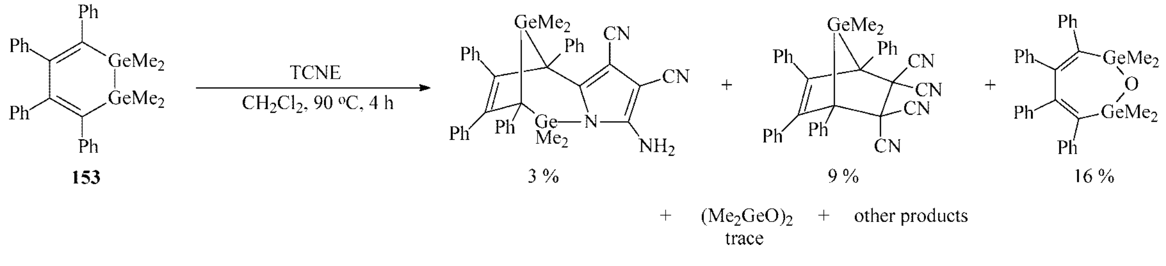
151a R = R' = Ph, R'' = Me, 25 %
151b R = R' = Ph, R'' = Et, 25 %
151c R = R' = R'' = Me, 38 %

152a R = R' = Ph, R'' = Me, 100 %
152b R = R' = Ph, R'' = Et, 98 %
152c R = R' = R'' = Me, 100 %

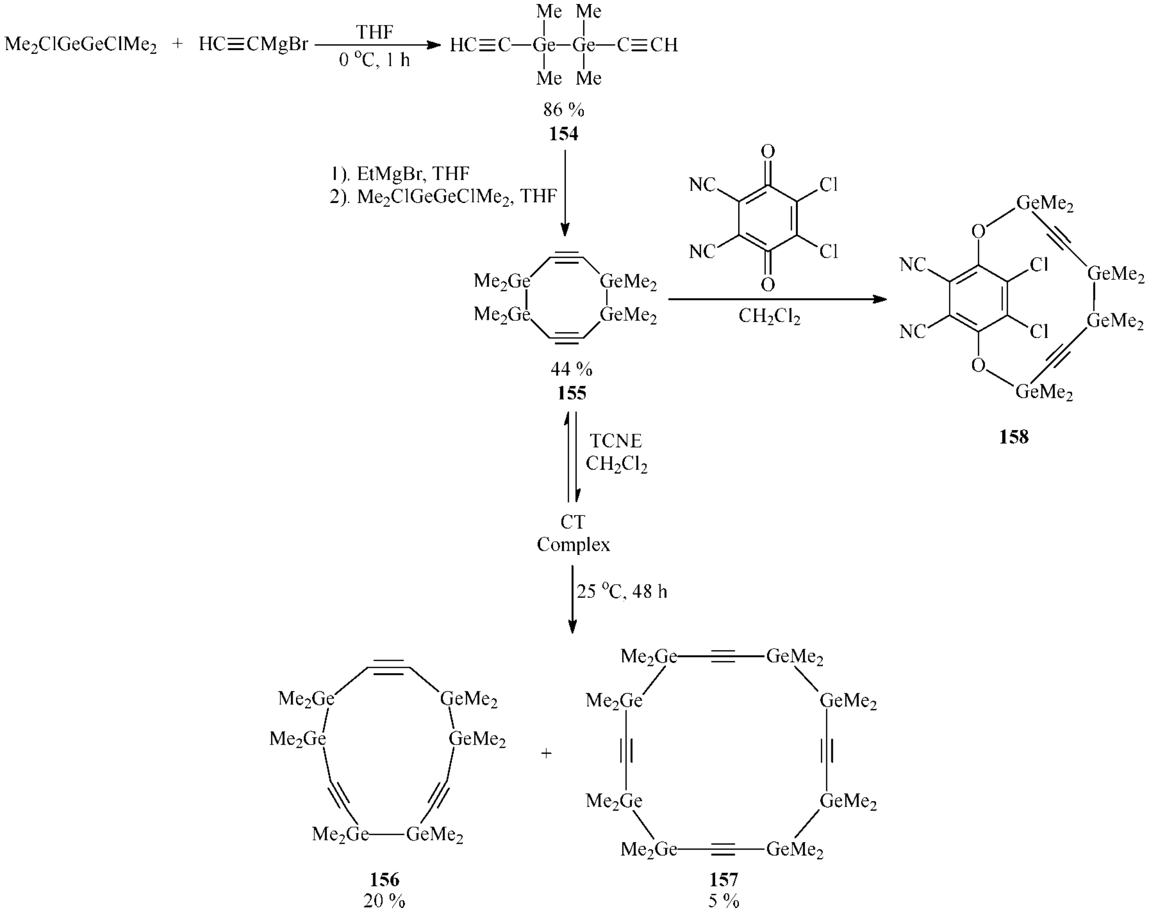
Scheme 64

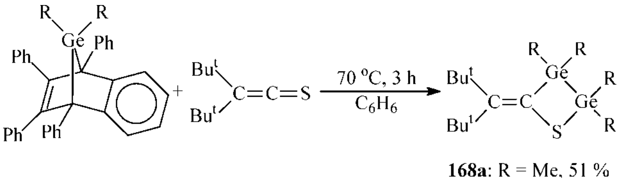


Scheme 65



Scheme 66





168a: R = Me, 51 %
168b: R = Ph, 32 %

(52)

larger molecules which have a molecular weight distribution analogous to their carbon-containing polymeric congeners. Early methods for the synthesis of these systems involved the Wurtz-type coupling of diorganogermanium dihalides, which furnished high molecular weight polygermanes in low yields,[201,237,238] while the use of germanium(II) iodide as a precursor afforded lower molecular weight polygermanes with higher yields.[201,239] The reaction of $GeCl_2 \cdot$dioxane with organolithium reagents has also been employed for the syntheses of three different high molecular weight polygermanes in moderate to good yields (eq 53, Table 9).[240]

$$GeCl_2(dioxane) + RLi \xrightarrow[Et_2O]{} -\!\!(GeR_2)_n\!\!- \qquad (53)$$

Dehydrogenative coupling is a versatile technique for the synthesis of polysilanes, but it cannot be used for the preparation of the analogous germanium-containing polymers.[241] Attempts at obtaining high molecular weight poly(diphenyl)germane by the catalytic dehyrogenative coupling of Ph_2GeH_2 yielded only a tetrameric oligomer.[242] However, catalytic demethanitive coupling of triorganogermanium hydrides has proven to be an excellent method for the synthesis of polygermanes. The room temperature coupling of Me_3GeH using a ruthenium catalyst yields poly(dimethyl)germane in excellent yields (eq 54), in which the molecular weight distribution varies with the amount and type of catalyst used (Table 10).[243] Both linear and branched polygermanes are generated in the reaction, and the reaction pathway for the formation of each type of species has been suggested (Schemes 70 and 71), in which the generation of branched polymers results from a 1,3-methyl migration during the course of the reaction (Scheme 71).

Table 9. Experimental Data for Eq 53

R	temp (°C)	time (h)	yield (%)	M_w ($\times 10^3$)	M_w/M_n
Me	−78	2	45	31.0	7.76
Bu^n	0	2	95	1.3	1.09
Bu^n	0	2	39	1.5	1.31
Bu^n	−78	1	98	17.9	2.88
Ph	0	1	83	0.7	1.17
Ph	−78	3	58	1.0	1.21

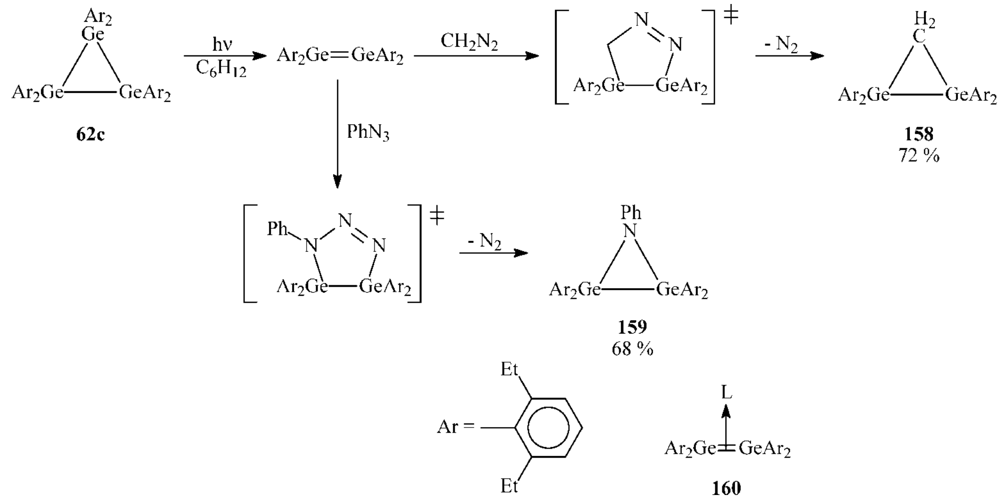
Demethanative coupling has also been employed for the preparation of heteroleptic polygermanes in which the

Table 10. Experimental Data for Eq 54

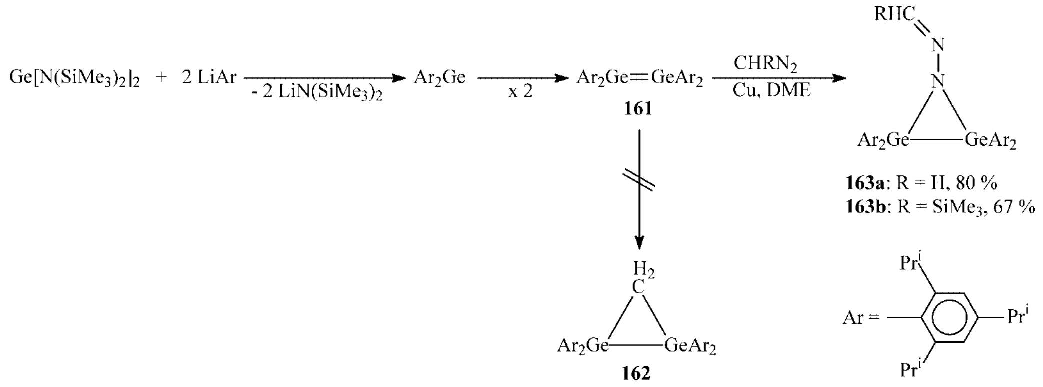
catalyst (mol %)	yield (%)	M_w (GPC)	M_n (GPC)
$Ru(PMe_3)_4(GeMe_3)_2$ (1.0)[a]	85	5.4×10^4	2.8×10^4
$Ru(PMe_3)_4(GeMe_3)_2$ (0.1)	97	6.6×10^4	1.8×10^4
$Ru(PMe_3)_4Me_2$ (1.0)	82	3.8×10^4	1.9×10^4
$Ru(PMe_3)_4Me_2$ (0.1)	92	7.4×10^4	3.7×10^4
$Ru(PMe_3)_4Me_2$ (1.0)[b]	81	2.0×10^4	0.9×10^4

[a] Reaction time = 1 day. [b] T = 60 °C.

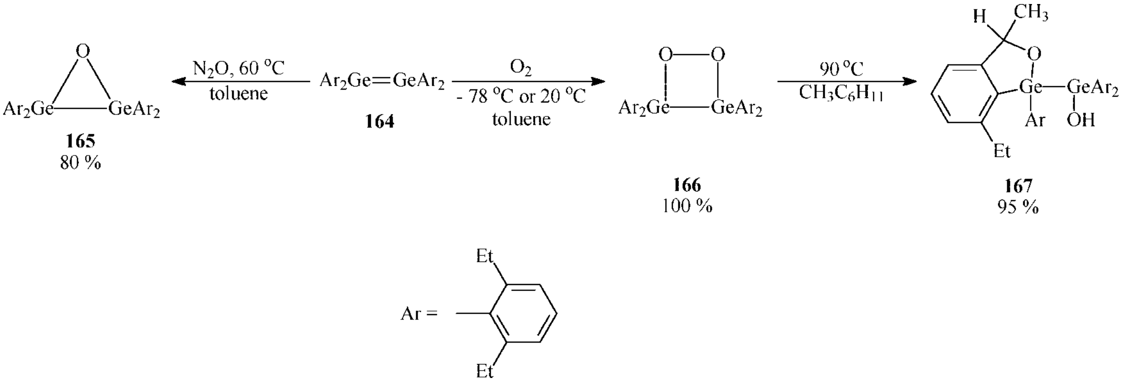
Scheme 67

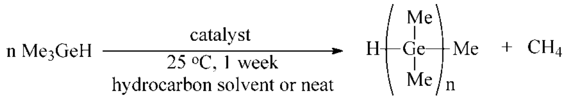


Scheme 68

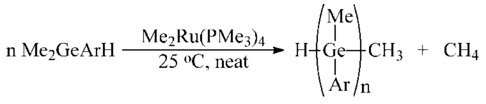


Scheme 69





$$n\ Me_3GeH \xrightarrow[\substack{25\ ^{\circ}C,\ 1\ week\\ hydrocarbon\ solvent\ or\ neat}]{catalyst} H\left(\begin{array}{c} Me\\ |\\ Ge\\ |\\ Me \end{array}\right)_n Me + CH_4 \tag{54}$$



$$n\ Me_2GeArH \xrightarrow[25\ ^{\circ}C,\ neat]{Me_2Ru(PMe_3)_4} H\left(\begin{array}{c} Me\\ |\\ Ge\\ |\\ Ar \end{array}\right)_n CH_3 + CH_4$$

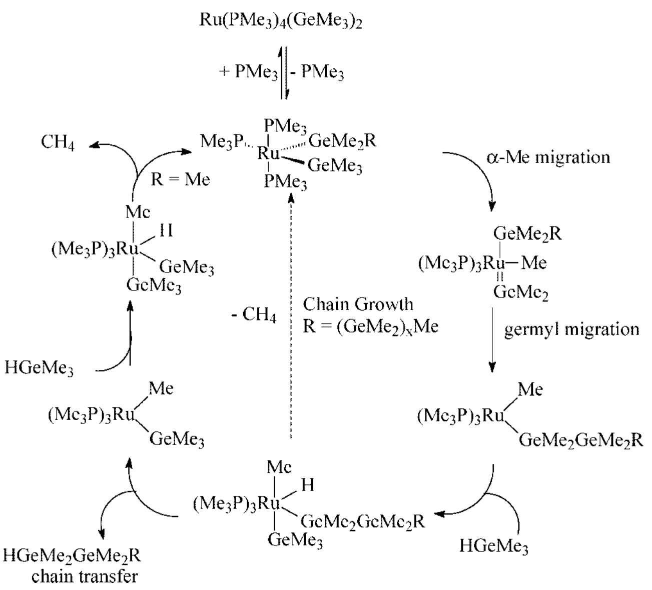
Ar = Ph, *p*-tolyl, *p*-FC_6H_4, *p*-$F_3CC_6H_4$, *m*-$(H_3C)_2C_6H_3$, *p*-$H_3COC_6H_4$

(55)

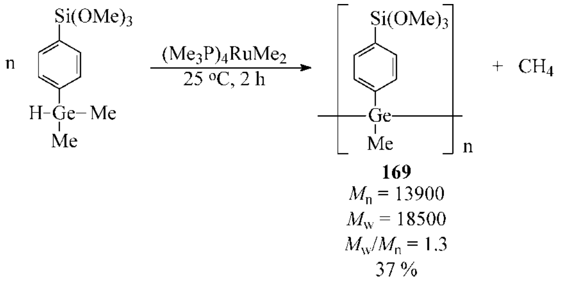
organic substituents attached to the germanium centers are different (eq 55).[244] The molecular weights determined by light scattering techniques and absorption data for the polymers obtained by this method are collected in Table 11. The absorption values show very little dependence on the nature of the aryl groups attached to the germanium centers in the polymer, and unlike the permethylated polygermane described above, no significant branching was detected in these poly(methylaryl)germanes.

The same method can be used for the preparation of the polygermane **169**, which contains a cross-linkable aryl substituent (eq 56).[245] Polygermanes are light sensitive and undergo photodegredation, which is significantly enhanced in the presence of oxygen.[246] The $-Si(OMe)_3$ group in **169** allows for attachment of the polygermane to a tetraethoxysilane or *β*-acetoxyethylsilsesquioxane matrix, resulting in a organic/inorganic material. These materials were determined to increase the thermal and photolytic stability of the

Scheme 70



polygermane without disruption of the σ-conjugation along the Ge−Ge backbone.



169
$M_n = 13900$
$M_w = 18500$
$M_w/M_n = 1.3$
37 %

(56)

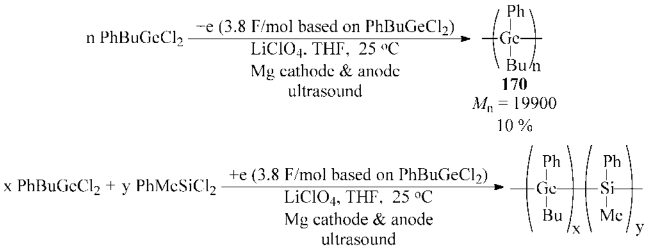
A second useful route to polygermanes involves the electroreductive conversion of organogermanium dihalides using a magnesium[247] or platinum[248] electrode. Poly(butylphenyl)germane (**170**) and a mixed germanium/silicon polymer (**171**) were obtained by this method (Scheme 72),[247] where the composition of compound **171** was dependent on the molar ratio of the germane to the silane as shown in Table 12. Increasing the amount of germane starting material increases the amount of PhBuGe units incorporated to the polymer, and this in turn has an influence on the absorption maximum of the material.

Table 11. Experimental Data for the Polygermanes Prepared According to Eq 55

Ar	yield (%)	M_w	M_n	DP[a]	λ_{max} (nm)	ϵ (L mol^{-1} cm^{-1})
Ph	52	7900	6500	40	332	8000
p-tolyl	54	5500	4700	26	326	7500
p-FC_6H_4	51	10100	8800	48	336	5100
p-$F_3CC_6H_4$	7	6900	6100	26	332	3000
m-$(H_3C)_2C_6H_3$	61	6000	4900	25	330	7100
p-$H_3COC_6H_4$	19	6000	5500	28	338	10100

[a] DP = M_n/(MW of repeat unit).

Scheme 72



170
$M_n = 19900$
10 %

171

Table 12. Composition and Properties of the Germane/Silane Copolymer 171

ratio of $PhBuGeCl_2/PhMeSiCl_2$	yield (%)	Ge content in copolymer (R = $x/(x + y)$)	M_n	λ_{max}
0.39	34	0.16	17000	330
1.04	33	0.45	20600	335

Electroreductive polymerization of a number of germanium monomers was also investigated using a platinum electrode (eq 57, Table 13).[248] Of the monomers employed in this investigation, the dialkyl-substituted germanes ($R^1 = R^2 = C_4H_9$, C_5H_{11}, or C_6H_{13}) resulted in high molecular weight polymers, while the phenyl-substituted monomers typically resulted in low molecular weights. The proposed pathway for the electroreductive synthesis was described, and it was suggested that a chain degradation reaction that involves attack of anions generated in the reaction on newly formed Ge−Ge bonds results in diminished molecular weights and lower yields.

$$nR^1R^2GeX_2 \xrightarrow[\text{DME, voltage = 20 V}]{\text{Pt cathode + }2ne^-} (R^1R^2Ge)_n + 2nX^- \qquad (57)$$

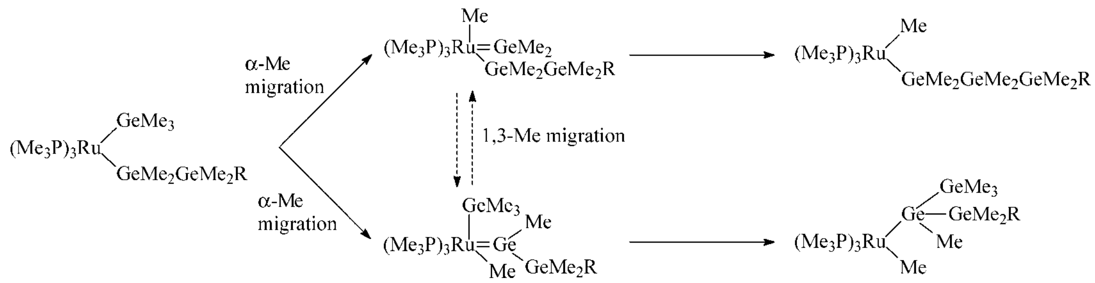
Table 13. Experimental Data for Eq 57

monomer	yield (%)	λ_{max} (nm)	M_w	M_n	M_w/M_n
Et_2GeCl_2	18	293	860	220	4.0
$Pr^n{}_2GeCl_2$	6.8	312	1600	1300	1.2
$Bu^n{}_2GeCl_2$	31	325	14000	2000	7.1
$(C_5H_{11})^n{}_2GeCl_2$	20	327	11000	3900	2.8
$(C_6H_{13})^n{}_2GeCl_2$	41	325	10000	6100	1.7
$PhMeGeCl_2$	11	327	9400	1700	5.7
$PhBuGeCl_2$	16	337	3900	1600	2.5

10. Summary and Outlook

The results summarized in this review clearly indicate that there has been and continues to be substantial interest in the

Scheme 71



synthesis, structures, and properties of oligomeric and polymeric germanium catenates. The advent of new methods for the preparation of these materials that circumvent common difficulties, including low yields and the formation of product mixtures, is an important endeavor, and much work remains to be done in this regard. Discrete oligogermanes undergo a wide variety of interesting transformations, and recently developed methods for their synthesis should permit a detailed investigation of the relationship between their composition and their physical and chemical properties.

The properties of these oligomeric and polymeric systems are tunable, since their physical attributes are dependent on the number of germanium atoms present in the molecule, as well as on the type of organic groups attached to the Ge−Ge backbone. It is expected that continued research in the area of germanium catenates will produce a significant amount of new compounds in pure form with potential applications in electronics, optics, and materials science.

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12. References

(1) Balaji, V.; Michl, J. *Polyhedron* **1991**, *10*, 1265.
(2) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
(3) Ortiz, J. V. *Polyhedron* **1991**, *10*, 1285.
(4) Jones, R. G.; Benfield, R. E.; Cragg, R. H.; Swain, A. C.; Webb, S. J. *Macromolecules* **1993**, *26*, 4878.
(5) Benfield, R. E.; Cragg, R. H.; Jones, R. G.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1022.
(6) Kimata, Y.; Suzuki, H.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1994**, 1163.
(7) Bratton, D.; Holder, S. J.; Jones, R. G.; Wong, W. K. C. *J. Organomet. Chem.* **2003**, *685*, 60.
(8) Shankar, R.; Saxena, A.; Brar, A. S. *J. Organomet. Chem.* **2002**, *650*, 223.
(9) Zuev, V. V.; Skvortsov, N. K. *J. Polym. Sci., A: Polym. Chem.* **2003**, *41*, 3761.
(10) Kimata, Y.; Suzuki, H.; Satoh, S.; Kuriyama, A. *Organometallics* **1995**, *14*, 2506.
(11) Hengge, E. F. *J. Inorg. Organomet. Polym.* **1993**, *3*, 287.
(12) Kashimura, S.; Ishifune, M.; Yamashita, N.; Bu, H.-B.; Takebayashi, M.; Kitajima, S.; Yoshiwara, D.; Kataoka, Y.; Nishida, R.; Kawasaki, S.; Murase, H.; Shono, T. *J. Org. Chem.* **1999**, *64*, 6615.
(13) Miller, R. D.; Jenkner, P. K. *Macromolecules* **1994**, *27*, 5921.
(14) Lacave-Goffin, B.; Hevesi, L.; Devaux, J. *J. Chem. Soc., Chem. Commun.* **1995**, 769.
(15) Sita, L. R. *Organometallics* **1992**, *11*, 1442.
(16) Sita, L. R.; Terry, K. W.; Shibata, K. *J. Am. Chem. Soc.* **1995**, *117*, 8049.
(17) Sommer, R.; Schneider, B.; Neumann, W. P. *Justus Liebigs Ann. Chem.* **1966**, *692*, 12.
(18) Sita, L. R. *Acc. Chem. Res.* **1994**, *27*, 191.
(19) Sita, L. R. *Adv. Organomet. Chem.* **1995**, *38*, 189.
(20) Adams, S.; Dräger, M. *J. Organomet. Chem.* **1985**, *288*, 295.
(21) Adams, S.; Dräger, M.; Mathiasch, B. *J. Organomet. Chem.* **1987**, *326*, 173.
(22) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931.
(23) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607.
(24) Choffat, F.; Smith, P.; Caseri, W. *J. Mater. Chem.* **2005**, *15*, 1789.
(25) Deacon, P. R.; Devylder, N.; Hill, M. S.; Mahon, M. F.; Molloy, K. C.; Price, G. J. *J. Organomet. Chem.* **2003**, *687*, 46.
(26) Thompson, S. M.; Schubert, U. *Inorg. Chim. Acta* **2004**, *357*, 1959.
(27) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 12481.
(28) Lu, V.; Tilley, T. D. *Macromolecules* **1996**, *29*, 5763.
(29) Lu, V. Y.; Tilley, T. D. *Macromolecules* **2000**, *33*, 2403.
(30) Holder, S. J.; Jones, R. G.; Benfield, R. E.; Went, M. J. *Polymer* **1996**, *37*, 3477.
(31) Mochida, K.; Hayakawa, M.; Tsuchikawa, T.; Yokoyama, Y.; Wakasa, M.; Hayashi, H. *Chem. Lett.* **1998**, 91.
(32) Okano, M.; Matsumoto, N.; Arakawa, M.; Tsuruta, T.; Hamano, H. *Chem. Commun.* **1998**, 1799.
(33) Bochkarev, M. N.; Vyazankin, N. S.; Bochkarev, L. N.; Razuvaev, G. A. *J. Organomet. Chem.* **1976**, *110*, 149.
(34) Subashi, E.; Rheingold, A. L.; Weinert, C. S. *Organometallics* **2006**, *25*, 3211.
(35) Amadoruge, M. L.; DiPasquale, A. G.; Rheingold, A. L.; Weinert, C. S. *J. Organomet. Chem.* **2008**, *693*, 1771.
(36) Amadoruge, M. L.; Gardinier, J. R.; Weinert, C. S. *Organometallics* **2008**, *27*, 3753.
(37) Amadoruge, M. L.; Golen, J. A.; Rheingold, A. L.; Weinert, C. S. *Organometallics* **2008**, *27*, 1979.
(38) Azemi, T.; Yokoyama, Y.; Mochida, K. *J. Organomet. Chem.* **2005**, *690*, 1588.
(39) Yokoyama, Y.; Hayakawa, M.; Azemi, T.; Mochida, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2275.
(40) Glockling, F. *The Chemistry of Germanium*; Academic Press: London, 1969.
(41) Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*; Wiley Interscience: London, 1971.
(42) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2, pp 399.
(43) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 2, pp 137.
(44) Weinert, C. S. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. 3, pp 699.
(45) Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc., Trans.* **1925**, *127*, 1760.
(46) Winkler, C. A. *Chem. Ber.* **1886**, *19*, 210.
(47) Winkler, C. A. *J. Prakt. Chem.* **1886**, *142*, 177.
(48) Winkler, C. A. *J. Prakt. Chem.* **1887**, *177*, 1887.
(49) Dräger, M.; Ross, L.; Simon, D. *Rev. Silicon Germanium Tin Lead Cmpds.* **1983**, *7*, 299.
(50) Gates, D. P. In *Annual Reports on the Progress of Inorganic Chemistry, Section A: Inorganic Chemistry*; Royal Society of Chemistry: London, 2005; Vol. 101, pp 452.
(51) Carraher, C. E., Jr., Pittman, C. U., Jr., Zeldin, M., Abd-El-Aziz, A. S., Eds.; *Organogermanium Polymers*; John Wiley and Sons: New York, 2005; Vol. 4.
(52) Jurkschat, K.; Mehring, M. In *Chemistry of Organic Germanium, Tin, and Lead Compounds*; Rappaport, Z., Ed.; John Wiley and Sons: Chichester, 2002; Vol. 2, pp 1543.
(53) Rehahn, M. In *Synthesis of Polymers*; Schlüter, A.-D., Ed.; Wiley-VCH Verlag GmbH: Weinheim, 1999; Vol. 20, pp 319.
(54) Majoral, J.-P.; Caminade, A.-M. *Chem. Rev.* **1999**, *99*, 845.
(55) Manners, I. In *Annual Reports on the Progress of Inorganic Chemistry, Section A: Inorganic Chemistry*; Royal Society of Chemistry: London, 1997; Vol. 93, pp 129.
(56) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603.
(57) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.
(58) Mochida, K. *Main Group Met. Chem.* **1994**, *17*, 25.
(59) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Anselme, G.; Delpon-Lacaze, G.; Chaubon, M.-A.; Kandri Rodi, A.; Satgé, J. *Main Group Met. Chem.* **1994**, *17*, 33.
(60) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113.
(61) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427.
(62) Chaubon, M.-A.; Ranaivonjatovo, H.; Escudié, J.; Satgé, J. *Main Group Met. Chem.* **1996**, *19*, 145.
(63) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.
(64) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.
(65) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283.
(66) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.
(67) Goicoechea, J. M.; Sevov, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 4155.
(68) Goicoechea, J. M.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 4026.
(69) Yong, L.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1149.
(70) King, R. B.; Silaghi-Dumitrescu, I.; Lupan, A. *Dalton Trans.* **2005**, 1858.
(71) Yong, L.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1977.
(72) Ugrinov, A.; Sevov, S. C. *Chem.*−*Eur. J.* **2004**, *10*, 3727.
(73) Downie, C.; Mao, J.-G.; Parmar, H.; Guloy, A. M. *Inorg. Chem.* **2004**, *43*, 1992.
(74) Hauptmann, R.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2266.

(75) King, R. B.; Silaghi-Dumitrescu, I.; Kun, A. *J. Chem. Soc., Dalton Trans.* **2002**, 3999.
(76) Li, S.-D.; Zhao, Z.-G.; Wu, H.-S.; Jin, Z.-H. *J. Chem. Phys.* **2001**, *115*, 9255.
(77) Deutsch, P. W.; Curtiss, L. A.; Blaudeau, J.-P. *Chem. Phys. Lett.* **2001**, *344*, 101.
(78) Downie, C.; Mao, J.-G.; Guloy, A. M. *Inorg. Chem.* **2001**, *40*, 4721.
(79) Bobev, S.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1507.
(80) Queneau, V.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1754.
(81) Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc.* **1925**, *127*, 1760.
(82) Kraus, C. A.; Flood, E. A. *J. Am. Chem. Soc.* **1932**, *54*, 1635.
(83) Brown, M. P.; Fowles, G. W. A. *J. Chem. Soc.* **1958**, 2811.
(84) Triplett, K.; Curtis, M. D. *J. Organomet. Chem.* **1976**, *107*, 23.
(85) Glockling, F.; Hooton, K. A.; Kotz, J. C.; Laubengayer, A. W. *Inorg. Synth.* **1966**, *8*, 31.
(86) Roller, S.; Simon, D.; Dräger, M. *J. Organomet. Chem.* **1986**, *301*, 27.
(87) Glockling, F.; Hooton, K. A. *J. Chem. Soc.* **1962**, 3509.
(88) Seyferth, D. *J. Am. Chem. Soc.* **1957**, *79*, 2738.
(89) Glockling, F.; Hooton, K. A. *Inorg. Synth.* **1966**, *8*, 31.
(90) Harris, D. M.; Nebergall, W. H.; Johnson, O. H.; Rochow, E. G.; Tolivaisa, N. *Inorg. Synth.* **1957**, *5*, 72.
(91) Dräger, M.; Ross, L. *Z. Anorg. Allg. Chem.* **1980**, *460*, 207.
(92) Dräger, M.; Ross, L. *Z. Anorg. Allg. Chem.* **1980**, *469*, 115.
(93) Marsh, R. E. *Acta Crystallogr.* **2002**, *B58*, 893.
(94) Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1960**, *82*, 3321.
(95) Kühlein, K.; Neumann, W. P. *Liebigs Ann. Chem.* **1967**, *702*, 17.
(96) Curtis, M. D.; Wolber, P. *Inorg. Chem.* **1972**, *11*, 431.
(97) Höfler, F.; Brandstätter, E. *Monatsh. Chem.* **1975**, *106*, 893.
(98) Bulten, E. J.; Noltes, J. G. *Tetrahedron Lett.* **1966**, 3471.
(99) Glockling, F.; Houston, R. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1357.
(100) Simon, D.; Häberle, K.; Dräger, M. *J. Organomet. Chem.* **1984**, *267*, 133.
(101) Rivière, P.; Castel, A.; Satgé, J.; Guyot, D. *J. Organomet. Chem.* **1984**, *264*, 193.
(102) Puff, H.; Kök, T. R.; Nauroth, P.; Schuh, W. *J. Organomet. Chem.* **1985**, *281*, 141.
(103) Puff, H.; Heisig, H.; Schuh, W.; Schwab, W. *J. Organomet. Chem.* **1986**, *303*, 343.
(104) Häberle, K.; Dräger, M. *Z. Naturforsch.* **1987**, *42B*, 323.
(105) Dräger, M.; Häberle, K. *J. Organomet. Chem.* **1985**, *280*, 183.
(106) Rivière, P.; Castel, A.; Guyot, D.; Satgé, J. *J. Organomet. Chem.* **1985**, *290*, C15.
(107) Cooke, J. A.; Dixon, C. E.; Netherton, M. R.; Kollegger, G. M.; Baines, K. M. *Synth. React. Inorg. Met.-Org. Chem.* **1996**, *26*, 1205.
(108) Chaubon-Deredempt, M. A.; Escudie, J.; Couret, C. *J. Organomet. Chem.* **1994**, *467*, 37.
(109) Castel, A.; Rivière, P.; Satgé, J.; Ahbala, M.; Abdennadher, C.; Desor, D. *Main Group Met. Chem.* **1993**, *16*, 291.
(110) Liu, Y.; Ballweg, D.; Müller, T.; Guzei, I. A.; Clark, R. W.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 12174.
(111) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232.
(112) Schäfer, H.; Saak, W.; Weidenbruch, M. *J. Organomet. Chem.* **2000**, *604*, 211.
(113) Setaka, W.; Sakamoto, K.; Kira, M.; Power, P. P. *Organometallics* **2001**, *20*, 4460.
(114) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1991**, *30*, 1480.
(115) Brook, A. G.; Abdesaken, F.; Söllradl, H. *J. Organomet. Chem.* **1986**, *299*, 9.
(116) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1993**, *32*, 5623.
(117) Baumgartner, J.; Fischer, R.; Fischer, J.; Wallner, A.; Marschner, C.; Flörke, U. *Organometallics* **2005**, *24*, 6450.
(118) Weidenbruch, M.; Grimm, F.-T.; Herrndorf, M.; Schäfer, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1988**, *341*, 335.
(119) Bulten, E. J.; Noltes, J. G. *Tetrahedron Lett.* **1966**, 4389.
(120) Rivière-Baudet, M.; Rivière, P. *J. Organomet. Chem.* **1976**, *116*, C49.
(121) Rivière-Baudet, M. *Main Group Met. Chem.* **1995**, *18*, 353.
(122) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivatava, R. C. *Metal and Metalloid Amides*; Ellis Horwood Ltd.: Chichester, England, 1980.
(123) Párkányi, L.; Kálmán, A.; Sharma, S.; Nolen, D. M.; Pannell, K. H. *Inorg. Chem.* **1994**, *33*, 180.
(124) Bender, J. E., IV; Banaszak Holl, M. M.; Mitchell, A.; Wells, N. J.; Kampf, J. W. *Organometallics* **1998**, *17*, 5166.
(125) Bender, J E., IV; Litz, K. E.; Giarikos, D.; Wells, N. J.; Banaszak Holl, M. M.; Kampf, J. W. *Chem.—Eur. J.* **1997**, *3*, 1793.
(126) Renner, G.; Kircher, P.; Huttner, G.; Rutsch, P.; Heinze, K. *Eur. J. Inorg. Chem.* **2000**, 879.
(127) Kircher, P.; Huttner, G.; Heinze, K.; Renner, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1664.
(128) Farwell, J. D.; Fernandes, M. A.; Hitchcock, P. B.; Lappert, M. F.; Layh, M.; Omondi, B. *Dalton Trans.* **2003**, 1719.
(129) Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Mak, T. C. W. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2501.
(130) Kraus, C. A.; Brown, C. L. *J. Am. Chem. Soc.* **1930**, *52*, 4031.
(131) Castel, A.; Rivière, P.; Saint-Roch, B.; Satgé, J.; Malrieu, J. P. *J. Organomet. Chem.* **1983**, *247*, 149.
(132) Bulten, E. J.; Noltes, J. G. *Tetrahedron Lett.* **1967**, 1443.
(133) Dräger, M.; Simon, D. *J. Organomet. Chem.* **1986**, *306*, 183.
(134) Charissé, M.; Mathes, M.; Simon, D.; Dräger, M. *J. Organomet. Chem.* **1993**, *445*, 39.
(135) Häberle, K.; Dräger, M. *J. Organomet. Chem.* **1986**, *312*, 155.
(136) Rivière, P.; Satgé, J. *Synth. React. Inorg. Met.-Org. Chem.* **1971**, *1*, 13.
(137) Weidenbruch, M.; Hagedorn, A.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1085.
(138) Weidenbruch, M.; Hagedorn, A.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1996**, *129*, 401.
(139) Hong, J.-H.; Pan, Y.; Boudjouk, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 186.
(140) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.
(141) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514.
(142) Tsumuraya, T.; Kabe, Y.; Ando, W. *J. Organomet. Chem.* **1994**, *482*, 131.
(143) Baines, K. M.; Cooke, J. A.; Payne, N. C.; Vittal, J. J. *Organometallics* **1992**, *11*, 1408.
(144) Weidenbruch, M.; Ritschl, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1992**, *438*, 39.
(145) Weidenbruch, M.; Ritschl, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1992**, *437*, C25.
(146) Toltl, N. P.; Leigh, W. J.; Kollegger, G. M.; Stibbs, W. G.; Baines, K. M. *Organometallics* **1996**, *15*, 3732.
(147) Valentin, B.; Castel, A.; Rivière, P.; Mauzac, M.; Onyszchuk, M.; Lebuis, A. M. *Heteroat. Chem.* **1999**, *10*, 125.
(148) Fujdala, K. L.; Gracey, D. W. K.; Wong, E. F.; Baines, K. M. *Can. J. Chem.* **2002**, *80*, 1387.
(149) Samuel, M. S.; Jennings, M. C.; Baines, K. M. *Organometallics* **2001**, *20*, 590.
(150) Samuel, M. S.; Jennings, M. C.; Baines, K. M. *J. Organomet. Chem.* **2001**, *636*, 130.
(151) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419.
(152) Dixon, C. E.; Netherton, M. R.; Baines, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 10365.
(153) Samuel, M. S.; Baines, K. M.; Hughes, D. W. *Can. J. Chem.* **2000**, *78*, 1474.
(154) Dixon, C. E.; Liu, H. W.; Vander Kant, C. M.; Baines, K. M. *Organometallics* **1996**, *15*, 5701.
(155) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487.
(156) Samuel, M. S.; Jenkins, H. A.; Hughes, D. W.; Baines, K. M. *Organometallics* **2003**, *22*, 1603.
(157) Dixon, C. E.; Hughes, D. W.; Baines, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 11049.
(158) Baines, K. M.; Cooke, J. A.; Dixon, C. E.; Liu, H. W.; Netherton, M. R. *Organometallics* **1994**, *13*, 631.
(159) Samuel, M. S.; Baines, K. M. *J. Am. Chem. Soc.* **2003**, *125*, 12702.
(160) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, *7*, 2015.
(161) Tsumuraya, T.; Kabe, Y.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1990**, 1159.
(162) Ichinohe, M.; Sekiyama, H.; Fukaya, N.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 6781.
(163) Fukaya, N.; Sekiyama, H.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2002**, 802.
(164) Mallela, S. P.; Hill, S.; Geanangel, R. A. *Inorg. Chem.* **1997**, *36*, 6247.
(165) Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 8025.
(166) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Ishida, Y. *Eur. J. Inorg. Chem.* **2000**, 1155.
(167) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60.
(168) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998**, 1045.
(169) Sekiguchi, A.; Ishida, Y.; Fukaya, N.; Ichinohe, M.; Takagi, Z.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 1158.
(170) Ishida, Y.; Sekiguchi, A.; Kobayashi, K.; Nagase, S. *Organometallics* **2004**, *23*, 4891.
(171) Fukaya, N.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3881.
(172) Fukaya, N.; Ichinohe, M.; Kabe, Y.; Sekiguchi, A. *Organometallics* **2001**, *20*, 3364.
(173) Ishida, Y.; Sekiguchi, A.; Kabe, Y. *J. Am. Chem. Soc.* **2003**, *125*, 11468.
(174) Ramaker, G.; Schäfer, A.; Saak, W.; Weidenbruch, M. *Organometallics* **2003**, *22*, 1302.

(175) Ramaker, G.; Saak, W.; Haase, D.; Weidenbruch, M. *Organometallics* **2003**, *22*, 5212.
(176) Glockling, F.; Hooton, K. A. *J. Chem. Soc.* **1963**, 1849.
(177) Neumann, W. P.; Kühlein, K. *Tetrahedron Lett.* **1963**, *4*, 1541.
(178) Neumann, W. P.; Kühlein, K. *Liebigs Ann. Chem.* **1965**, *683*, 1.
(179) Ross, L.; Dräger, M. *J. Organomet. Chem.* **1980**, *199*, 195.
(180) Mochida, K.; Kawajiri, Y.; Goto, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2773.
(181) Dräger, M.; Simon, D. *Z. Anorg. Allg. Chem.* **1981**, *472*, 120.
(182) Ross, L.; Dräger, M. *J. Organomet. Chem.* **1980**, *194*, 23.
(183) Ross, L.; Dräger, M. *Z. Anorg. Allg. Chem.* **1981**, *472*, 109.
(184) Ross, L.; Dräger, M. *Z. Naturforsch.* **1983**, *38B*, 665.
(185) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1994**, *33*, 1115.
(186) Sekiguchi, A.; Yatabe, T.; Naito, H.; Kabuto, C.; Sakurai, H. *Chem. Lett.* **1992**, 1697.
(187) Wiberg, N.; Hochmuth, W.; Nöth, H.; Appel, A.; Schmidt-Amelunxen, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1333.
(188) Kumada, M.; Sakamoto, S.; Ishikawa, M. *J. Organomet. Chem.* **1969**, *17*, 235.
(189) Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1969**, *16*, P8.
(190) Bulten, E. J.; Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1041.
(191) Roller, S.; Dräger, M. *J. Organomet. Chem.* **1986**, *316*, 57.
(192) Ross, L.; Dräger, M. *Z. Anorg. Allg. Chem.* **1984**, *519*, 225.
(193) Richards, A. F.; Brynda, M.; Olmstead, M. M.; Power, P. P. *Organometallics* **2004**, *23*, 2841.
(194) Carberry, E.; Dombek, B. D.; Cohen, S. C. *J. Organomet. Chem.* **1972**, *36*, 61.
(195) Jensen, W.; Jacobson, R.; Benson, J. *Cryst. Struct. Commun.* **1975**, *4*, 299.
(196) Hölbling, M.; Flock, M.; Baumgartner, J.; Hassler, K. *Eur. J. Inorg. Chem.* **2007**, 4952.
(197) Dräger, M.; Ross, L.; Simon, D. *Z. Anorg. Allg. Chem.* **1980**, *466*, 145.
(198) Dräger, M.; Ross, L. *Z. Anorg. Allg. Chem.* **1981**, *476*, 95.
(199) Fitjer, L.; Scheuermann, H.-J.; Wehle, D. *Tetrahedron Lett.* **1984**, *25*, 2329.
(200) Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55.
(201) Mochida, K.; Chiba, H. *J. Organomet. Chem.* **1994**, *473*, 45.
(202) Richards, A. F.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 4071.
(203) Glockling, F.; Light, J. R. C. *J. Chem. Soc. A* **1967**, 623.
(204) Mochida, K.; Hodota, C.; Hata, R.; Fukuzumi, S. *Organometallics* **1993**, *12*, 586.
(205) Mochida, K.; Hata, R.; Chiba, H.; Seki, S.; Yoshida, Y.; Tagawa, S. *Chem. Lett.* **1998**, 263.
(206) Mochida, K.; Hata, R.; Shimoda, M.; Matsumoto, F.; Kurosu, H.; Kojima, A.; Yoshikawa, M.; Masuda, S.; Harada, Y. *Polyhedron* **1996**, *15*, 3027.
(207) Okano, M.; Mochida, K. *Chem. Lett.* **1990**, 701.
(208) Mochida, K.; Chiba, H.; Okano, M. *Chem. Lett.* **1991**, 109.
(209) Sekiguchi, A.; Yatabe, T.; Kamatani, H.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6260.
(210) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.
(211) Unno, M.; Higuchi, K.; Furuya, K.; Shioyama, H.; Kyushin, S.; Goto, M.; Matsumoto, H. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2093.
(212) Schnepf, A.; Drost, C. *Dalton Trans.* **2005**, 3277.
(213) Schnepf, A.; Köppe, R. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 911.
(214) Sekiguchi, A.; Naito, H.; Nameki, H.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Organomet. Chem.* **1989**, *368*, C1.
(215) Weidenbruch, M.; Grimm, F.-T.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 198.
(216) Espenbetov, A. A.; Struchkov, Y. T.; Kolesnikov, S. P.; Nefedov, O. M. *J. Organomet. Chem.* **1984**, *275*, 33.
(217) Krebs, A.; Jacobsen-Bauer, A.; Haupt, E.; Veith, M.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 603.
(218) Mochida, K.; Karube, H.; Nanjo, M.; Nakadaira, Y. *J. Organomet. Chem.* **2005**, *690*, 2967.
(219) Ohgaki, H.; Fukaya, N.; Ando, W. *Organometallics* **1997**, *16*, 4956.
(220) Ohtaki, T.; Ando, W. *Organometallics* **1996**, *15*, 3103.
(221) Bravo-Zhivitivskii, D.; Zharov, I.; Kapon, M.; Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1625.
(222) Ohgaki, H.; Kabe, Y.; Ando, W. *Organometallics* **1995**, *14*, 2139.
(223) Hashimoto, H.; Yagihashi, Y.; Ignatovich, L.; Kira, M. *Heteroat. Chem.* **2001**, *12*, 398.
(224) Pailhous, I.; Ranaivonjatovo, H.; Escudié, J.; Declercq, J.-P.; Dubourg, A. *Organometallics* **1999**, *18*, 1622.
(225) Preut, H.; Weisbeck, M. P.; Neumann, W. P. *Acta Crystallogr.* **1993**, *C49*, 182.
(226) Lerner, H.-W.; Dürner, G.; Bolte, M. *Acta Crystallogr.* **2003**, *E59*, m816.
(227) Mochida, K.; Akazawa, M.; Goto, M.; Sekine, A.; Ohashi, Y.; Nakadaira, Y. *Organometallics* **1998**, *17*, 1782.
(228) Mochida, K.; Shimizu, H.; Nanjo, M. *Chem. Lett.* **2000**, 1226.
(229) Mochida, K.; Shimizu, H.; Kugita, T.; Nanjo, M. *J. Organomet. Chem.* **2003**, *673*, 84.
(230) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K.; Tonogaki-Kubota, M.; Kobayashi, K. *J. Organomet. Chem.* **1995**, *499*, 123.
(231) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K.; Tonogaki-Kubota, M.; Kobayashi, T. *Chem. Lett.* **1994**, 1439.
(232) Nakadaira, Y.; Komoriya, H.; Kakuma, S.; Kako, M.; Mochida, K.; Yasui, M.; Iwasaki, F.; Shimoda, M.; Matsumoto, F.; Yashikawa, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1403.
(233) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1990**, *9*, 2061.
(234) Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159.
(235) Masamune, S.; Batcheller, S. A.; Park, J.; Davis, W. M.; Yamashita, O.; Ohta, Y.; Kabe, Y. *J. Am. Chem. Soc.* **1989**, *111*, 1888.
(236) Ando, W.; Tsumuraya, T.; Goto, M. *Tetrahedron Lett.* **1986**, *27*, 5105.
(237) Miller, R. D.; Sooriyakumaran, R. *J. Polym. Sci., A: Polym. Chem.* **1987**, *25*, 111.
(238) Hayashi, T.; Uchimaru, Y.; Reddy, N. P.; Tanaka, M. *Chem. Lett.* **1992**, 647.
(239) Glockling, F.; Light, J. R. C.; Walker, J. *J. Chem. Soc., Chem. Commun.* **1968**, 1052.
(240) Kobayashi, S.; Cao, S. *Chem. Lett.* **1993**, 1385.
(241) Koe, J. R. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. 3, pp 549.
(242) Aitken, C.; Harrod, J. F.; Malek, A.; Samuel, E. *J. Organomet. Chem.* **1988**, *349*, 285.
(243) Reichl, J. A.; Popoff, C. M.; Gallagher, L. A.; Remsen, E. E.; Berry, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 9430.
(244) Katz, S. M.; Reichl, J. A.; Berry, D. H. *J. Am. Chem. Soc.* **1998**, *120*, 9844.
(245) Huo, Y.; Berry, D. H. *Chem. Mater.* **2005**, *17*, 157.
(246) Mochida, K.; Nagano, S.; Kawata, H.; Wakasa, M.; Hayashi, H. *J. Organomet. Chem.* **1997**, *542*, 75.
(247) Kashimura, S.; Ishifune, M.; Yamashita, N.; Bu, H.-B.; Takebayashi, M.; Kitajima, S.; Yoshiwara, D.; Kataoka, Y.; Nishida, R.; Kawasaki, S.; Murase, H.; Shono, T. *J. Org. Chem.* **1999**, *64*, 6615.
(248) Okano, M.; Takeda, K.; Toriumi, T.; Hamano, H. *Electrochim. Acta* **1998**, *44*, 659.

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