1993

Gas phase thermochemistry of organogermanium compounds

John Paul Engel
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Gas phase thermochemistry of organogermainium compounds

Engel, John Paul, Ph.D.
Iowa State University, 1993
Gas phase thermochemistry of organogermanium compounds

by

John Paul Engel

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa
1993
DEDICATION

To my wife, Amy.
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INTRODUCTION

Since its inception a little over a hundred years ago, germanium chemistry has developed at a much slower pace than that of its Group IV counterparts silicon and carbon.\textsuperscript{1} This apparent neglect is due in part to the prohibitive cost of organogermanium compounds and their limited industrial applications. It is little wonder than that the chemistry of divalent germanium compounds (germylenes) has been only briefly explored as compared to that of its counterparts carbenes\textsuperscript{2} and silylenes.\textsuperscript{3}

Even more limited are examples of free germylene formation in the gas phase.\textsuperscript{21,26,28} The work described in this dissertation involves the thermally-induced, gas phase generation of germylenes. Of particular interest has been the formation of germylenes from germyl-acetylene precursors. Kinetic data is used to support the relative rates of germylene formation and to compare these rates to those of the analogous silicon compounds.

This study also explores the mechanism of germylene formation from germyl-acetylene precursors. The discussion section of this thesis examines in detail a mechanistic proposal involving a germacyclopentene intermediate.

In the process of this investigation, a unique rearrangement between germanium and silicon was discovered. This rearrangement is helpful in theorizing a mechanism for
the generation of germylenes and the analogous silylenes. Finally, it is necessary to emphasize the breadth of the syntheses outlined here. The synthetic strategy used is an economical although somewhat labor intensive approach toward the preparation of mixed silylgermanes.
LITERATURE SURVEY

To fully understand the magnitude of the research presented in this dissertation, one must first take a look at the history of divalent germanium chemistry. Early gemylene chemistry centered on the dihalogermylenes. Since these compounds can be isolated and therefore easily characterized, a great deal of attention was directed toward their formation and subsequent reactions. Early studies reporting gemylene formation are, however, questionable; often limited by the characterization techniques available at the time. This review focuses on alkyl- and aryl-gemylene chemistry reported over the past decade with special attention paid to the limited examples of gemylenes formed thermally, while in the gas phase.

Methods of Gemylene Generation

Reduction of Organogermapanes

The earliest examples of gemylene formation are reductions of organogermapanes. The reduction of dihalodiorganogermapanes with metals was one method used to produce diorganogermylenes. For example, the reduction of dimethyl dichlorogermapane with lithium in THF gave dodecamethylcyclohexagermane, 3, and poly(dimethylgermane).
Dimethylgermylene is believed to be an intermediate in this reaction.

\[
\begin{align*}
\text{Me}_2\text{GeCl}_2 + \text{Li} & \xrightarrow{\text{THF}} \text{Me}_2\text{Ge}: \\
2 & \rightarrow (\text{Me}_2\text{Ge})_6 + \text{polymer} \\
\end{align*}
\]

Diethyl-,\textsuperscript{7} dibutyl-,\textsuperscript{8} and diphenyl-\textsuperscript{9-13} germylene were also reported to be produced in this manner. Lei and Gaspar\textsuperscript{15} modified this procedure to sonochemically produce germacyclopent-3-enes. Riviere et al. reported using a strong base such as DBU to dehydrohalogenate organogermandes thus producing germylenes.\textsuperscript{16} This procedure was further extended for a number of nucleophilic bases such as triethylamine and pyridine.\textsuperscript{17,18}

![Germylene Formation via Alpha-eliminations](image)

Germylene Formation via Alpha-eliminations

Following the lead of silicon chemistry,\textsuperscript{3} alpha-elimination of alcohols from hydrido-alkoxygermanes is another early method used to produce germylenes.\textsuperscript{16,19,23} Riviere and Satge\textsuperscript{20} reported several examples of this type of elimination.
Again paralleling silicon chemistry,\(^3\) the alpha-elimination of halogermanes (silanes) is another effective means of producing germynes.\(^4,16,24-27\) Satge et al.\(^16\) reported the thermal formation of germyl-germylene \(^9\) and its subsequent reaction with a trapping agent, 2,3-dimethyl-1,3-butadiene, \(^10\), to form germacyclopent-3-ene \(^11\).

In a more detailed study, Bulten and Noltes\(^26\) studied the thermal decomposition of chloropentaethyldigermane, \(^12\), at 230–250°C. Their kinetic study showed this decomposition to be unimolecular. This conclusion was supported by the formation of mixed methyl- and ethyl- germanes when the
pyrolysis was conducted in the presence of trimethylchlorogermaine.

\[
\begin{align*}
\text{Et}_3\text{GeGeEt}_2 & \quad \text{230 - 250°C} \quad \text{Me}_3\text{GeCl} \\
\text{12} & \quad \text{Et}_2\text{Ge} + \text{Me}_2\text{GeGeEt}_2 \\
\text{14} & \quad \text{Me}_3\text{GeGeGeEt}_2 \\
\end{align*}
\]

The thermal alpha-elimination of hydridodigermanes has also been shown to be an effective germylene generator.\(^\text{16,28,29}\) After observing the thermal formation of germylene upon pyrolysis of digermane and the subsequent formation of trigermane,\(^\text{16}\) Sefcik and Ring studied the relative rates of germylene and silylene insertion into various hydrido-germanes and silanes.\(^\text{30}\) Surprisingly they were not able to trap the germylene formed with 1,3-butadiene.\(^\text{29}\) It is interesting to note the differences in pyrolysis temperatures between digermane (280°C) and disilane (350°C). This relative facility with which germylene formation occurs relative to silylene is reiterated in the context of this dissertation.

\[
\begin{align*}
\text{H}_3\text{GeGeH}_3 & \quad \text{280°C} \\
\text{18} & \quad \text{GeH}_4 + \text{H}_3\text{GeGeGeH}_3 + \text{polymer} \\
\text{19} & \quad \text{H} \\
\text{20} & \quad \text{H}
\end{align*}
\]

Gaspar et al. thermally prepared dimethylgermylene using this same route.\(^\text{31}\) Upon pyrolyzing pentamethyldigermane at
250°C they found the exclusive products to be trimethylgermane, 22, and heptamethyltrigermane, 23.

\[
\begin{array}{c}
\text{H} \\
\text{Me}_3\text{GeGeMe}_2 \\
\text{21}
\end{array}
\xrightarrow{250°C}
\begin{array}{c}
\text{Me}_3\text{GeH} + \\
\text{Me}_3\text{GeGeGeMe}_2 \\
\text{22}
\end{array}
\]

In a later study, Caspar found the dimethylgermylene formed to add stereospecifically to substituted butadienes thus demonstrating the singlet nature of free germylene. Taking this study one step further, Caspar et al. prepared the first example of a thermally generated silylgermylene with the flow pyrolysis of bis(trimethylsilyl)methylgermane, 24.

\[
\begin{array}{c}
\text{H} \\
(\text{Me}_3\text{Si})_2\text{GeMe} \\
\text{24}
\end{array}
\xrightarrow{}\begin{array}{c}
\text{Me}_3\text{SiH} + \\
\text{Me}_3\text{SiGe:} \\
\text{25}
\end{array}
\text{26}
\]

330°C, 57% conversion
410°C, >95% conversion

In addition to these alpha-eliminations, Ring et al. proposed that a germylene intermediate is involved in the CVD process of depositing germanium metal on surfaces from germane (GeH₄)³⁴ and methylgermane (CH₃GeH₃).³⁵
Cyclic Germanes as Germylene Precursors

In a related alpha-elimination to form germylenes, Barrau et al. demonstrated that cyclic thiogermaines can be thermally and photolytically treated to form germylenes. For instance, 2,2,3,3-tetramethyl-2,3-digerma-1,4-dithiane, 27, when heated to 200°C in the presence of 2,3-dimethyl-1,3-butadiene gives the resultant extrusion product, 2,2-dimethyl-2-germa-1,3-dithiane, 28, (60%), and trapped germylene (1,1-dimethyl-1-germacyclo-pent-3-ene, 29, 20%) as the major products with a small amount of hexamethylcyclotrisilthiane, 30, (5%).

Ando et al. demonstrated how 3-alkyldenethiagermirane, 31, can be thermally decomposed to extrude dimesitylgermylene and subsequently trapped with 2,3-dimethyl-1,3-butadiene.
Illustrating the reversible nature of the germylene-1,3-butadiene reaction, Lei and Caspar\textsuperscript{15} used germacyclopent-3-enes to thermally produce dimethylgermylene. For example, the flow pyrolysis of 1,1,3-trimethyl-1-germacyclopent-3-ene, 33, at 470°C in the presence of a 10-fold excess of 2,3-dimethyl-1,3-butadiene produced 29 in 83% yield.

\[
\begin{align*}
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\hline
\end{align*}
\]

Ando and Tsumuraya demonstrated that cyclotrigermanes (e.g. 34) can thermally, as well as photolytically extrude germylenes in addition to the corresponding digermenes.\textsuperscript{38}

\[
\begin{align*}
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\hline
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\text{Mes} & \quad \text{Mes} \\
\hline
\end{align*}
\]

Baines and Cooke showed that a similar siladigermirane, 37, when thermolyzed will selectively extrude germylene leaving the resultant germasilene, 38.\textsuperscript{39}
This group has also reported the digermene formed by Ando as being capable of rearranging to a germyl-germylene in the absence of a compound reactive toward the digermene. A similar rearrangement occurs for the silagermene thus demonstrating the relative stability of germylenes versus silylenes.

\[
\text{Mes}_2M \equiv \text{GeMes}_2 \xrightarrow{\Delta} \text{Mes}_2\text{Ge}:
\]

\[
\text{M = Si or Ge}
\]

This observation is supported by theoretical studies recently reported by Grev and coworkers. Silylgermylene was calculated to be 6 Kcal/mol lower in energy than germasilene. Germylsilylene was calculated to be 9 Kcal/mol higher in energy than germasilene.

Generation of Germylenes from 7-Germanorbornadienes

The first examples of 7-germanorbornadienes were reported in the 1960's. A number of derivatives were subsequently
reported. These compounds have the versatility of being both thermal and photochemical precursors to germynes. However, unlike the thermal precursors in this work, germyn extrusion is believed to go through a diradical intermediate.\(^\text{52}\)

![Diagram of 2,3-dibenzo-7,7-dialkyl-7-germanorbornadiene](image)

The germynes evolved from these precursors have received a large amount of attention as attested by the number of papers published in the past decade.\(^\text{52,75}\)

**Photochemically Generated Germynes**

Although many of the germyn precursors previously presented are capable of extruding germynes upon photolysis, a few additional examples must be mentioned. In 1983, Sakurai and co-workers reported the formation of dimethylgermylene upon photolysis of dibenzo-1,1,2,2-tetramethyl-1,2-germacyclohexa-3,5-diene.\(^\text{76}\) Similarly, dibenzo-1,1,2,2,3,3-hexamethyl-1,2,3-trigermacyclohepta-4,6-diene also extrudes germyn upon irradiation.\(^\text{77}\)
Cyclic germanes have also been shown to be facile germlylene precursors. Cyclics from 3-membered to 6-membered rings have been recently reported to extrude germlylene upon photolysis.

In addition, aryl-digermanes, trigermanes, and mixed silylgermanes have also been shown to act as photochemical precursors to germlyenes.
Finally, West et al. reported geminal diazide 40 as a photochemical source of dimethylgermylene.

\[ \text{Me}_2\text{Ge} (\text{N}_3)_2 \xrightarrow{\text{hv (254 or 248 nm)}} \text{Me} \text{Ge} \]  

Reactions of Germynes

Several examples of germylene reactions have been demonstrated above. However, a general overview of germylene reactions seems necessary and appropriate. In general there are three basic germylene reactions: 1. Polymerization. 2. Insertion into σ-bonds. 3. Addition to unsaturated systems. Each of these will be touched upon here with special emphasis given to germylene additions to unsaturated systems.

In the absence of an appropriate trapping agent, germylenes will generally react with each other to form cyclics and/or polygermanes. In most cases, these polymers have not been characterized. It is assumed that a dimerization is the first step in this process, followed by additional germylene insertion.

\[ 2 \text{R}_2\text{Ge} \rightarrow \text{R}_2\text{Ge} = \text{GeR}_2 \rightarrow \text{R}_2\text{Ge} \rightarrow (\text{GeR}_2)^{n+2} \]
Early examples of thermally produced germylenes were detected by the insertion of germylenes into σ-bonds. As previously demonstrated, Ge-Ge\textsuperscript{16,26,28,29} bonds are efficient germylene traps. In many of these examples, however, there is a question as to whether the actual insertion is into a Ge-H, Ge-halogen, or Ge-Ge bond. One study showed insertion of germylenes into Ge-H bonds to be more facile than Si-H bonds.\textsuperscript{30} However, Mochida reported a detailed study of dimethylgermylene insertion into Si-H bonds\textsuperscript{68} and Baines trapped dimesitylgermylene with triethylsilane.\textsuperscript{40} Several examples of germylene insertion into C-halogen bonds have also been reported.\textsuperscript{55,94,95} Insertion into C-S and C-O bonds is also known.\textsuperscript{94}

\[
\begin{align*}
M - X + R_2Ge &\rightarrow M - Ge - X \\
M &= Si \text{ or Ge} \\
X &= H, Ge, \text{halogen} \\
C - X + R_2Ge &\rightarrow C - Ge - X \\
X &= O, S, \text{halogen}
\end{align*}
\]

In general, simple alkenes are inert toward free germylenes.\textsuperscript{94} However, a number of examples of germylene addition to conjugated dienes exist. The most common example of this reaction is the addition of germylenes to
1,3-butadienes. A debate has raged over the mechanism for this addition. Neumann contests that germylene addition to conjugated dienes precedes via a [2+4] cycloaddition. He cites several examples of stereospecific addition of germylenes to dienes to support his view. However, Gaspar has presented kinetic data which strongly suggests a [2+2] addition of germylene to an alkene followed by a rapid sigmatropic rearrangement of the vinyl germacyclop propane to form germacyclopent-3-ene.

Examples of germylene addition to 1-aza and 1,4-diazabutadienes, vinyl ketones, and orthoquinones have also been reported.

Addition of germylenes to alkynes occurs at a much slower rate than addition to dienes. Where the reaction does occur, it is believed that a germacyclop propane is involved in the first step. Subsequently, this intermediate reacts with another alkyne to form a germacyclopenta-2,4-diene.
or it dimerizes to form a 1,4-digermacyclohexa-2,5-diene. Palladium has been shown to catalyze this reaction, suggesting that a straightforward [2+2] cycloaddition is not taking place.\textsuperscript{72}

\[
\text{R}_2\text{Ge:} + \text{R}^1-\text{C}=\text{C}-\text{R}^2 \rightarrow \text{dimerize}
\]

To this point, only one example of a germacyclopropene has been isolated.\textsuperscript{102,103} Dialkylgermylene was produced thermally from a 7-norbornadiene precursor in the presence of 3,3,6,6-tetramethyl-1-thiacycloheptene, \textit{42}, giving the trapped germylene, \textit{43}. 

\[
\text{Me}_2\text{Ge:} \rightarrow \text{Me}_2\text{GeH}
\]
Calculations by Gordon and coworkers estimate that germacycloprenes are thermodynamically less stable than silacycloprenes by approximately 30 Kcal/mol. This large difference is thought to be due to the stability of the elimination product (silylene < germylene) in addition to the ring strain of the cyclopropene.
RESULTS AND DISCUSSION

With silylene research over the past decade proving to be such a challenging and rewarding field, it was natural to wonder what exciting discoveries awaited us in germylene chemistry. The major drawback to performing germanium chemistry has been the prohibitive cost of the few available starting materials and the challenge of synthesizing the appropriate germylene precursors.

The results and discussion of the research presented here has been divided into four major areas. The first section describes the work done in extending previous examples of germylene formation. This is followed by the bulk of our research, the thermochemistry of germyl-acetylenes. In the process of studying this chemistry, an unexpected, apparent dyatropic rearrangement between germanium and silicon was discovered and studied. Finally, results of the thermochemistry of other organogermainium compounds is reported.

Germylenes Formed via Alpha-Eliminations

As mentioned earlier, Caspar and coworkers were the first to thermally prepare a silylgermyle. The major products were the expected butadiene-trapped silyl-germyle (18.8%) and trapped dimethylgermyle (5.6%). No less than 7 others
products were identified, all found in low yield. A variety of methyl and proton shifts were hypothesized to explain this plethora of pyrolysis products.

In an attempt to extend Caspar's work, tris(trimethyl-silyl)germane, 48, was prepared (Scheme 1) in 32% yield from germanium tetrachloride following the procedure of Brook, Abdesaken and Söllradl. When pyrolyzed in a flow pyrolysis apparatus heated to 330°C and 380°C with 1,3-butadiene as the carrier gas, the major germanium containing product was the expected trapped germylene, 49, in yields of 25% and 35%, respectively. A number of minor products were also present. GC-IR-MS analysis suggested hydrogenylation had occurred to a small extent. When 2,3-dimethyl-1,3-butadiene (DMB) was used as the trapping agent, trapped germylene, 50, was the exclusive product.

Contrary to Caspar's work, rearrangement of the germylene was not observed. Germylene rearrangements of this type were not observed in any appreciable amount in the work described in this thesis.

Hydrido-germane 48 can be converted quantitatively to the corresponding chlorogermane, 53 (Scheme 2), by slowly adding it to carbon tetrachloride in the presence of sunlight. Alternatively, treatment of tris(trimethylsilyl)methylgermane, 52, with tin (IV) chloride afforded 53 in 60% yield.

Flow pyrolysis of 53 in the presence of a 20-fold excess
Scheme 1

\[
\text{GeCl}_4 + 4 \text{Me}_3\text{SiCl} \xrightarrow{\text{Li, THF}} (\text{Me}_3\text{Si})_4\text{Ge} \xrightarrow{\text{MeLi}} (\text{Me}_3\text{Si})_3\text{GeLi} \xrightarrow{\text{H}_2\text{O}^+} (\text{Me}_3\text{Si})_3\text{GeH}
\]

32% overall yield

\[330, 380\,^\circ\text{C flow pyrolysis}\]

\[\text{(Me}_3\text{Si)}_3\text{GeH} \xrightarrow{290-350\,^\circ\text{C}} \text{Me}_3\text{Si} \longrightarrow \text{Ge} \rightarrow (\text{25, 35\% yield}) + \text{Me}_3\text{SiH}
\]

54 - 82% decomposition

Scheme 2

\[
\text{Cl}_3\text{GeMe} + 4 \text{Me}_3\text{SiCl} \xrightarrow{\text{Li, THF}} (\text{Me}_3\text{Si})_3\text{GeMe} \xrightarrow{\text{SnCl}_4} (\text{Me}_3\text{Si})_3\text{GeH}
\]

51 45 (77\% yield) 52 (60\%)

54 - 82% decomposition

\[\text{DMB gave exclusive formation of the desired 50 and the elimination product, trimethylchlorosilane, 45. A kinetic study of this decomposition in a pulsed-stirred flow reactor (SFR) gave Arrhenius parameters of Log(A/s\(^{-1}\)) = 10.9 \pm 0.2 and } E_{\text{act}} = 33.4 \pm 0.6 \text{ Kcal/mol. (Scheme 3, figure 1) This data}\]
suggests that a concerted process involving an α-elimination of germylene is taking place, evidenced by the Log A near 11.\textsuperscript{107} The activation energy is some 7-8 Kcal/mol lower in energy than a typical α-elimination on silicon. This was the first kinetic data supporting the belief that germylenes are more easily formed than silylenes.

**Scheme 3**

\[
\begin{align*}
\text{(Me}_3\text{Si)}_3\text{GeCl} & \quad \xrightarrow{\text{SFR, 310 - 380°C, 10 - 80% decomposition}} \\
\text{Me}_3\text{SiGeCl} & \quad + \quad \text{Me}_3\text{SiCl}
\end{align*}
\]

\begin{align*}
\text{Log}(A/s^{-1}) &= 10.9 \pm 0.2 \\
E_{\text{act}} &= 33.4 \pm 0.6 \text{ Kcal/mol}
\end{align*}

Bis(trimethylsilyl)methylchlorogermane, 55, was prepared as previously reported\textsuperscript{33} (Scheme 4) by the tin(IV) chloride cleavage of a methyl group from bis(trimethylsilyl)-dimethylgermane, 54, in a yield of 89%. Compound 54 was obtained in 77% yield by the lithium coupling of trimethylchlorosilane, 45, and dimethyldichlorogermane, 1. A variation of a direct process reactor described by Gaspar et al.\textsuperscript{108} was used to produce 1 in 80% yield.

Flow pyrolysis of 55 (Scheme 5) at 300°C with a 20-fold excess of DMB as trapping agent yielded the trapped germylene, 56, and TMSCl as the exclusive products. A total of 15%
Log (A/s^-1) = 10.9 ± 0.2

E_{act} = 33.4 ± 0.6 Kcal/mol

Figure 1, Arrhenius plot for the thermal decomposition of 53 following the formation of 50.
Scheme 4

\[
\text{Me}_2\text{GeCl}_2 + 2 \text{Me}_3\text{SiCl} \xrightarrow{\text{Li, THF}} \text{Me}_2\text{Ge(SiMe}_3\text{)}_2 \xrightarrow{\text{SnCl}_4} \text{MeGe(SiMe}_3\text{)}_2
\]

Starting material remained at this temperature.

Scheme 5

To finish this series, (trimethylsilyl)dimethylchlorogername, 68, was prepared (Scheme 6) in a fashion similar to that described by Kumada et al. A germanium-catechol salt, 60, was prepared in 88% yield following Corriu's procedure. Tetraphenylgermane, 61, was prepared in 91% yield by the reaction of phenyl Grignard with this salt, 60, or germanium tetrachloride, 44, in 51% yield. Compound 61 was subsequently converted to dibromodiphenylgermane, 62, with the addition of two equivalents of bromine in a yield of 88%. Dimethyldiphenylgermane, 63, which was prepared in 81% yield by the Grignard coupling of 1 or 62 (90%); was treated with bromine to give 64 in 95% yield. Alternatively, 63 was
reacted with HCl in the presence of AlCl₃ to form 65 in 74% yield. Addition of 64 or 65 to 1 mm lithium chunks in THF formed the germyl anion 66. Quenching this anion with trimethylchlorosilane yielded 67, 65% yield from 64 or 65. Finally, 67 underwent electrophilic aromatic substitution with HCl (AlCl₃ as catalyst) in chloroform to afford 68 in 74% yield.

Kinetic data was obtained for the pyrolysis of 68 (Scheme 7) employing the SFR and DMB as a trap. The Arrhenius parameters obtained were: \( \log(A/s^{-1}) = 12.8 \pm 0.1 \) and \( E_{\text{act}} = 40.1 \pm 0.3 \) Kcal/mol. (figure 2) This data is consistent with an \( \alpha \)-elimination and demonstrates the facility of germylene extrusion as compared to the analogous silylene. A kinetic study of the analogous silicon system, 69, reported by Davidson, Hughes and Ijadi-Maghsoodi was found to have Arrhenius parameters of: \( \log(A/s^{-1}) = 11.7 \pm 0.3 \) and \( E_{\text{act}} = 50.1 \pm 1.1 \) Kcal/mol.¹⁰⁷

A comparison of these kinetic parameters with those obtained for 53 also demonstrates a substituent effect for germylene formation. This effect is supported by a comparison of rate constants for each system at the same temperature. For example, \( k_{350} = 5.4 \times 10^{-2} \) for 68 and \( k_{350} = 1.3 \times 10^{-1} \) for 53. By comparison, \( k_{350} = 1.3 \times 10^{-6} \) for 69.

The literature shows no examples of a bromogermane as a thermal germylene precursor. By treating 67 with bromine, bromo(trimethylsilyl)dimethylgermane, 70, was prepared.
Figure 2, Arrhenius plot for the thermal decomposition of 68 following the formation of 29.

Log (A/s$^{-1}$) = 12.8 ± 0.1
$E_{\text{act}} = 40.1 \pm 0.3$ Kcal/mol
Scheme 6

\[ \text{GeO}_2 + \text{HO-} + \text{KOCH}_3 \rightarrow 2\text{K}^+ \text{Ge}^+ \text{(88% yield)} \]

\[ \text{2Bp} + \text{GePh}_4 \rightarrow \text{Ph}_2\text{GeBr}_2 \text{(88%)} \]

\[ \text{Me}_2\text{GeCl}_2 + 2 \text{Ph-MgX} \rightarrow \text{Me}_2\text{GePh} \rightarrow \text{Br} \rightarrow \text{Me}_2\text{GePh} \rightarrow \text{Br} \rightarrow \text{Me}_2\text{GePh} \]

\[ \text{HCl/AlCl}_3 \rightarrow \text{Cl} \]

\[ \text{Me}_3\text{SiGeMe}_2 \rightarrow \text{HCl/AlCl}_3 \rightarrow \text{Me}_3\text{SiGeMe}_2 \rightarrow \text{Me}_3\text{SiCl} \rightarrow \text{Me}_2\text{GePh} \]
Scheme 7

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me}_3\text{SiGeCl} & \quad \text{SFR}, \quad \text{340 - 390°C} \\
\text{Me} & \quad \text{Me}_2\text{SiGe} + \text{Me}_3\text{SiCl} \\
\text{68} & \quad 20 - 75\% \text{ decomposition} \\
\end{align*}
\]

\[\log(A/s^{-1}) = 12.8 \pm 0.1\]
\[E_{\text{act}} = 40.1 \pm 0.3 \text{ Kcal/mol}\]

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me}_3\text{SiSiCl} & \quad \text{SFR} \\
\text{Me} & \quad \text{Me}_2\text{Si} + \text{Me}_3\text{SiCl} \\
\text{69} & \quad \log(A/s^{-1}) = 11.7 \pm 0.3\]
\[E_{\text{act}} = 50.1 \pm 1.1 \text{ Kcal/mol}\]

Pyrolysis of 70 in the presence of DMB gave the expected 29. Arrhenius parameters (Scheme 8) were also obtained for this compound. \[\log(A/s^{-1}) = 9.9 \pm 0.6\] and \[E_{\text{act}} = 32.2 \pm 1.8 \text{ Kcal/mol}\] at pyrolysis temperature ranging from 330-380°C (15-50% decomposition). The range of pyrolysis temperatures is very close to that of its chlorine analog, 68, and \[k_{350} = 4.5 \times 10^{-2}\] for 70 is also similar to the \[k_{350} = 5.4 \times 10^{-2}\] of 68. However, the differences in \(\log A\) suggests a drastically different transition state. A value of 10 for the \(\log A\) suggests that a heterogeneous process may be involved. The Arrhenius plot (figure 3) shows a large deviation from the best-fit line, thus accounting for the large variance in the \(\log A\) value.
$\log (A/s^{-1}) = 9.9 \pm 0.6$

$E_{\text{act}} = 32.2 \pm 1.8 \text{ Kcal/mol}$

Figure 3, Arrhenius plot for the thermal decomposition of 70 following the formation of 29.
Additional experiments were conducted using a 40-fold excess of DMB replacing the 20-fold excess normally used. Identical rate constants were obtained. This large deviation cannot be explained except by instrument error.

\[ \text{Scheme 8} \]

\[
\begin{align*}
\text{Me} & \quad \text{SFR,} \\
\text{Me} & \quad \text{330 - 380°C} \\
\text{Me} & \quad 15 - 50\% \text{ decomposition}
\end{align*}
\]

\[ \log(A/s^{-1}) = 9.9 \pm 0.6 \]
\[ E_{\text{act}} = 32.2 \pm 1.8 \text{ Kcal/mol} \]

In order to see if a germyl group would have an effect on the rate of silylene extrusion by \( \alpha \)-elimination, (trimethylgermyl)dimethylchlorosilane, 76, was prepared as shown in Scheme 9.\textsuperscript{109} Commercially available 1,2-dichloro-1,1,2,2-tetramethyldisilane, 72, was coupled with two equivalents of phenyl Grignard to give 1,2-diphenyl-1,1,2,2-tetramethyldigermane, 73, in 93% yield. When 73 was added to additional lithium while stirring in THF, silyl anion 74 was formed. Quenching 74 with trimethylchlorogermane, 13, yielded 75 in 67%. Trimethylchlorogermane, 13, was obtained via a redistribution reaction of tetramethylgermane, 71, with tin(IV) chloride in 75% yield. In turn, compound 71 was obtained in 80% yield by adding four equivalents of methyl
Grignard to 60. (Note: Compound 71 was also prepared from tris(butane-2,3-diolato)germinate, 77). Finally, treatment of 75 in chloroform with HCl in the presence of a catalytic amount of AlCl₃ produced 76 in 65% yield.

Pyrolysis of 76 in the SFR (Scheme 10) demonstrated the stability of this compound. At 500°C, where germylene formation was complete, no decomposition was observed. By 550°C only 5% decomposition of starting material was evident. Finally, at 600°C 60% decomposition was observed. Among a large variety of other products was observed 29 (20%) and trapped dimethylsilylene, 78 (15%).

At these high temperatures it is evident that germylene
extrusion through some other type of mechanism is competitive with silylene extrusion. A number of examples of germylene extrusion by an alternative mechanism are given in the last section of this discussion. More detail will be given to the possible mechanism there.

**Thermochemistry of Germyl-Acetylenes**

In studying the thermal rearrangement of ethynyl silanes, Petrich\textsuperscript{112} found that ethynyl disilanes were convenient thermal precursors to silylenes. A mechanism was developed (Scheme 11) incorporating a vinylidene transition state and a silacyclopentene intermediate.

Given the stability of germylenes relative to silylenes,\textsuperscript{96} it was hypothesized that one could thermally produce germylenes from germyl-acetylenes. The hope was that
germylenes would be produced at lower temperatures, thus making it possible to isolate germacyclopentene intermediates similar to those reported by Krebs and Berndt.\textsuperscript{102,103} Assuming germanium behaved similar to silicon, it was also proposed that the germanium would act as a labeling tool in exploring Petrich’s mechanism.

As shown in Scheme 12, addition of lithium trimethylsilylacetylene, \textbf{80}; prepared by the addition of MeLi to trimethylsilylacetylene; to \textbf{53} gave [tris(trimethylsilyl)-germyl]trimethylsilylacetylene, \textbf{81}, in 64\% yield.

Flow pyrolysis of \textbf{81} (Scheme 13) in the presence of DMB cleanly afforded 1,1-bis(trimethylsilyl)-3,4-dimethyl-1-germacyclopent-3-ene, \textbf{50}, and bis(trimethylsilyl)acetylene, \textbf{82}. The Arrhenius parameters for this reaction were obtained
Scheme 12

\[
\begin{align*}
\text{Scheme 12} & \\
\text{HCC} & - \text{SiMe}_3 \\
\text{79} & \\
\text{MeLi} & \\
\text{53} & + \text{LiC} & - \text{SiMe}_3 \\
\text{80} & \rightarrow \text{(Me}_3\text{Si)}_3 \text{Ge} & - \text{C} & - \text{C} & - \text{SiMe}_3 \\
\text{81} & \\
\end{align*}
\]

employing the SFR: \( \log(A/s^-1) = 10.5 \pm 0.4, E_{\text{act}} = 33.8 \pm 1.0 \) Kcal/mol. (figure 4)

Scheme 13

flow pyrolysis at 355°C

\[
\begin{align*}
\text{Scheme 13} & \\
\text{(Me}_3\text{Si)}_3 \text{GeC} & - \text{C} & - \text{SiMe}_3 \\
\text{81} & \\
\text{SFR, 330 - 390°C} & \rightarrow & \text{Me}_3\text{Si} & + \text{Me}_3\text{SiC} & - \text{C} & - \text{SiMe}_3 \\
\text{50} & & \text{82} & \\
\text{15-65% decomposition} & \\
\end{align*}
\]

\[\log(A/s^-1) = 10.5 \pm 0.4\]

\[E_{\text{act}} = 33.8 \pm 1.0 \text{ Kcal/mol}\]

In a similar fashion, the analogous silicon compound, 83, was also prepared and pyrolyzed (Scheme 14) in the SFR to give Arrhenius parameters of \( \log(A/s^-1) = 11.1 \pm 0.1 \) and \( E_{\text{act}} = 42.8 \pm 0.5 \) Kcal/mol. (figure 5) Clearly it can be seen that less energy is required to extrude bis(trimethylsilyl)-germylene as compared to bis(trimethylsilyl)silylene. By comparing rate constants at 430°C, it can be seen that the germylene is
Log (A/s⁻¹) = 10.5 ± 0.4  
Eₐₜₙ = 33.8 ± 1.0 Kcal/mol

Figure 4, Arrhenius plot for the thermal decomposition of 81 following the formation of 82.
Figure 5, Arrhenius plot for the thermal decomposition of 83 following the formation of 82.

\[
\text{Log (A/s}^{-1}) = 11.1 \pm 0.1
\]

\[
\text{E}_{\text{act}} = 42.8 \pm 0.5 \text{ Kcal/mol}
\]
extruded at a rate 160 times greater than that of the silylene.

Scheme 14

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{SiC≡CSiMe}_3 & \xrightarrow{460 - 530^\circ C} \text{Me}_3\text{SiSiMe}_3 + \text{Me}_3\text{SiC≡CSiMe}_3 \\
\text{20-70\% decomposition}
\end{align*}
\]

\[
\begin{align*}
\text{Log}(A/s^{-1}) &= 11.1 \pm 0.1 \\
E_{\text{act}} &= 42.8 \pm 0.5 \text{ Kcal/mol}
\end{align*}
\]

For 81: \(k_{430} = 0.90 \text{ s}^{-1}\)

For 83: \(k_{430} = 0.0056 \text{ s}^{-1}\)

None of the proposed germacyclopene intermediate, 86, was detected. The following mechanism is suggested: (Scheme 15)

Petrich had obtained the Arrhenius parameters for the thermal decomposition of [(trimethylsilyl)dimethylsilyl]-trimethylsilylacetylene, 83:

\[
\begin{align*}
\text{Log}(A/s^{-1}) &= 11.5 \pm 0.3, \quad E_{\text{act}} = 40.8 \pm 1.1 \text{ Kcal/mol}.
\end{align*}
\]

(Scheme 16) These kinetic parameters match those obtained for 83 closely. This suggests that there is little or no substituent effect in silylene formation. This begged the question for germylenes. Would there be any substantial effect on the rate of germylene formation if two trimethylsilyl groups on germanium were replaced with methyl groups?
Scheme 15

![Chemical Diagram]

Scheme 16

(Ref. 112)

![Chemical Diagram]

Log(A/s⁻¹) = 11.5 ± 0.3

Eₜₐₓ = 40.8 ± 1.1 Kcal/mol

To answer this question, [(trimethylsilyl)dimethylgermyl]trimethylsilylacetylene, 89, was prepared (Scheme 17) by the addition of lithio-acetylene 80 to chlorogermane 68 in 40% yield.

Flow pyrolysis of 89 (Scheme 18) at 400°C in the presence of DMB gave the expected 29 and 82. Arrhenius parameters were
obtained for the unimolecular, thermal decomposition of 89 employing two different SFR techniques. The first, and most widely used, technique involves the gas phase introduction of the starting material and trap directly into the reaction vessel. A second technique uses a heated vaporization chamber to vaporize a solution of starting material and trapping agent. This alternative technique was devised to overcome the problem of obtaining Arrhenius parameters of compounds with low volatility. Both methods were used to obtain Arrhenius parameters for compound 89 in order to substantiate the validity of using the solution injection technique. Identical Arrhenius parameters were obtained using both techniques: Log(A/s⁻¹) = 11.5 ± 0.4 and E_{act} = 40.9 ± 1.2 Kcal/mol. (figure 6)

These kinetic parameters are identical to those obtained for its silicon analog, 88. This would suggest identical energy surfaces and points toward a substituent effect affecting germylene formation. It would appear that silicon bonded to germanium lowers the energy barrier associated with germylene formation. To test this hypothesis further,
Figure 6, Arrhenius plot for the thermal decomposition of 89 following the formation of 82.

Log (A/s\(^{-1}\)) = 11.5 \pm 0.4

E\(_{\text{act}}\) = 40.9 \pm 1.2 Kcal/mol
Scheme 18

\[
\begin{array}{c}
\text{Me} \\
\text{Me}_3\text{SiGeC≡CSiMe}_3 \\
\text{Me}
\end{array}
\xrightarrow{\text{SFR}}
\begin{array}{c}
\text{Me} \\
\text{Me}_3\text{SiGeC≡CSiMe}_3 \\
\text{Me}
\end{array}
\rightarrow
\begin{array}{c}
\text{Me} \\
\text{Me}_3\text{SiGeC≡CSiMe}_3 \\
\text{Me}
\end{array}
\]

Log\((A/s^{-1}) = 11.5 \pm 0.4\)

\(E_{\text{act}} = 40.9 \pm 1.2\) Kcal/mol

[bis(trimethylsilyl)methylgermyl]trimethylsilylacetylene, 90, was prepared from 55 and 80 in 20% yield as shown in Scheme 19.

Scheme 19

\[
\begin{array}{c}
\text{Me} \\
\text{(Me}_3\text{Si})_2\text{GeCl} \\
\text{Me}
\end{array}
\xrightarrow{\text{THF} \quad -78^\circ\text{C}}
\begin{array}{c}
\text{Me} \\
\text{Me}_3\text{SiGeC≡CSiMe}_3 \\
\text{Me}
\end{array}
\]

Flow pyrolysis of 90 (Scheme 20) at 420°C with a 20-fold excess of DMB gave as expected the trapped germylene, 91, and the eliminated acetylene, bis(trimethylsilyl)acetylene. Pyrolysis of 90 in the SFR yielded Arrhenius parameters of

Log\((A/s^{-1}) = 11.8 \pm 0.2\) and \(E_{\text{act}} = 38.6 \pm 0.6\) Kcal/mol. (figure 7)

To conclude this comparison, [bis(trimethylsilyl)methylsilyl]trimethylsilylacetylene, 92, was prepared. SFR pyrolysis of this compound (Scheme 21) gave Arrhenius
Figure 7, Arrhenius plot for the thermal decomposition of 90 following the formation of 82.

Log (A/s\(^{-1}\)) = 11.8 \pm 0.2

\(E_{\text{act}} = 38.6 \pm 0.6 \text{ Kcal/mol}\)
Log\((A/s^{-1})\) = 11.8 ± 0.2  
\(E_{\text{act}} = 38.6 ± 0.6\) Kcal/mol

parameters of Log\((A/s^{-1})\) = 11.6 ± 0.2 and \(E_{\text{act}} = 42.2 ± 0.5\) Kcal/mol. (figure 8) By comparing rate constants at 400°C and 420°C, it can be seen that germylene extrusion takes place at a rate 16 times greater than the corresponding silylene extrusion.

Log\((A/s^{-1})\) = 11.6 ± 0.2  
\(E_{\text{act}} = 42.2 ± 0.5\) Kcal/mol

For \(92\): \(k_{400} = 1.1 \times 10^{-2} \text{ s}^{-1}\) \(k_{420} = 2.6 \times 10^{-2} \text{ s}^{-1}\)  
For \(90\): \(k_{400} = 1.8 \times 10^{-1} \text{ s}^{-1}\) \(k_{420} = 4.2 \times 10^{-1} \text{ s}^{-1}\)

Scheme 22 summarizes the Arrhenius parameters just discussed. Clearly as trimethylsilyl groups are replaced with
Figure 8, Arrhenius plot for the thermal decomposition of 92 following the formation of 82.

Log (A/s⁻¹) = 11.6 ± 0.2

Eₜₐₓ = 42.2 ± 0.5 Kcal/mol
methyl groups there is an increase in the energy required to extrude the corresponding germynes.

Scheme 22

<table>
<thead>
<tr>
<th>M=</th>
<th>Ge</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>R¹ = R² = SiMe₃</td>
<td>Log (A/s⁻¹) = 10.5 ± 0.4</td>
<td>Log (A/s⁻¹) = 11.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>E_{act} = 33.8 ± 1.0 Kcal/mol</td>
<td>E_{act} = 42.8 ± 0.5 Kcal/mol</td>
</tr>
<tr>
<td></td>
<td>330 - 390°C</td>
<td>460 - 530°C</td>
</tr>
<tr>
<td>R¹ = Me</td>
<td>Log (A/s⁻¹) = 11.8 ± 0.2</td>
<td>Log (A/s⁻¹) = 11.6 ± 0.2</td>
</tr>
<tr>
<td>R² = SiMe₃</td>
<td>E_{act} = 38.6 ± 0.6 Kcal/mol</td>
<td>E_{act} = 42.2 ± 0.5 Kcal/mol</td>
</tr>
<tr>
<td></td>
<td>360 - 430°C</td>
<td>440 - 500°C</td>
</tr>
<tr>
<td>R¹ = R² = Me</td>
<td>Log (A/s⁻¹) = 11.5 ± 0.4</td>
<td>Log (A/s⁻¹) = 11.5 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>E_{act} = 40.9 ± 1.2 Kcal/mol</td>
<td>E_{act} = 40.8 ± 1.1 Kcal/mol</td>
</tr>
<tr>
<td></td>
<td>430 - 490°C</td>
<td>440 - 500°C</td>
</tr>
</tbody>
</table>

To demonstrate the relative ease of silyl-substituted germylene formation as compared to silylenes, a molecule capable of an internal competition between silylene and germylene extrusion was desired. Compound 97 was chosen due to the facility with which bis(trimethylsilyl)germylene was shown to be thermally extruded. This material was prepared (Scheme 23) from the appropriate lithio-acetylene, 96, and chlorogermane 53 in 64% yield. Ethynyl disilane 95 was obtained by adding ethynyl Grignard to 94 in 82% yield.
As expected, SFR pyrolysis of 97 (Scheme 24) in the 330-420°C temperature range (20-90% decomposition) with a 20-fold excess of DMB gave trapped bis(trimethylsilyl)germylene, \(50\), and the corresponding trisilylacetylene, \(98\), as the exclusive products.

At this point, we wished to understand the effect of silyl-substitution on germylene formation. By looking at our proposed mechanism for this process, one explanation was a
preferential vinylidene insertion into a germanium-silicon bond. Since there were no examples of germyl-acetylene elimination to form a silylene, compound 104 was prepared as shown in Scheme 25. Silyl anion 100 was easily formed, following the procedure of Kumada et al.,\textsuperscript{109} by the addition of lithium to methyldiphenylchlorosilane. Addition of this anion to commercial trimethylbromogermane, 101, cleanly afforded 102 in 87\% yield. Electrophilic aromatic substitution replacing one of the phenyl groups using HCl with AlCl\textsubscript{3} as catalyst produced 103 in 79\% yield. Finally, addition of 80 leads to our target molecule, 104, in 57\% yield.

\textbf{Scheme 25}

\begin{center}
\begin{tabular}{c c c c}
\textbf{Me} & \textbf{Me} & \textbf{Me} \\
\textbf{Ph\textsubscript{2}SiCl} + Li & \textbf{Ph\textsubscript{2}SiLi} + \textbf{Me\textsubscript{3}GeBr} & \textbf{Ph\textsubscript{2}SiGeMe\textsubscript{3}} \\
\textbf{99} & \textbf{100} & \textbf{101} & \textbf{102} \\
& & (87\% yield) & \\
& & \textbf{Ph\textsubscript{2}GeSiC\equivCSiMe\textsubscript{3}} \\
& & \textbf{104} (57\%) & \\
& & LiC\equivCSiMe\textsubscript{3} & \\
& & \textbf{80} & \\
& & \textbf{PhSiGeMe\textsubscript{3}} & \\
& & Cl & \textbf{103} (79\%) \\
\end{tabular}
\end{center}

Flow pyrolysis of 104 at 530\textdegree C with a 20-fold excess of DMB gave (trimethylgermyl)trimethylsilylacetylene, 106, and the corresponding trapped silylene, 105, as the major products.

SFR pyrolysis of this mixture from 440-500\textdegree C led to
20-85% decomposition of starting material. This is the same temperature range where dimethylgermylene (from compound 89) and dimethylsilylene (from compound 88) were extruded. If preferential insertion of a vinylidene into a germanium-silicon bond was a contributing factor in the relative ease of silyl-germylene formation, one would reasonably expect to see an increase in the rate of silylene extrusion with 104.

With germyl-acetylene elimination demonstrated to be a viable route toward silylene formation, a molecule capable of an internal competition reaction between dimethylsilylene and dimethylgermylene extrusion was designed. The kinetic data for the pyrolysis of 88 and 89 were almost identical, therefore compound 109 was chosen as an appropriate model. This molecule was prepared (Scheme 27) from the appropriate lithio-acetylene, 108, and chlorogermane 68 in 73% yield. Compound 108 was prepared by the addition of MeLi to 107 which was in turn prepared by adding ethynyl Grignard to 76 in 76% yield.
Scheme 27

\[
\begin{align*}
\text{Me}_3\text{GeSiCl} & \quad \text{HC} & \quad \text{C} \quad \text{MgBr} \quad \xrightarrow{76\% \text{ yield}} \quad \text{Me}_3\text{GeSiC} & \equiv & \text{CH} \\
\text{MeLi} & \quad \xrightarrow{108} \quad \text{Me}_3\text{SiGeMe}_2 & + & \text{Me}_3\text{GeSiC} & \equiv & \text{CLi} \\
68 & & & & & \text{Me}_3\text{SiGeC} & \equiv & \text{CSiGeMe}_3 & \quad \xrightarrow{73\% \text{ yield}} & & 109
\end{align*}
\]

SFR pyrolysis of 109 (Scheme 28) with a 20-fold excess of DMB from 430-530°C shows a sequential loss of either a germylene or a silylene followed by loss of the other. Roughly a 4-fold preference is shown for germylene formation over silylene. It is puzzling to note that only trace amounts of the dimethylsilylene presumably produced was trapped by the DMB. This slight preference for germylene formation is consistent with the kinetic data obtained for 88 and 89.

However, we were no closer to understanding the preference for silyl-germylene formation. In an attempt to gain more insight into this mechanism, we replaced the terminal trimethylsilyl group, which had been a fixture in previous examples, with a proton. Petrich\textsuperscript{112} had demonstrated that in the case of disilanes, there was a competition between
an apparent silicon-proton dyotropic rearrangement and extrusion of silylene. A series of ethynyl germanes (112, 113, 114) were prepared as shown in Scheme 29.

Pyrolysis of these compounds (Scheme 30) in the SFR led to extrusion of the expected germynes, however the dyotropic rearrangement was not observed as no products containing a Ge-H bond were present in the pyrolysate.

The pyrolysis of 112 was conducted at 360°C and 380°C with 70% and 85% decomposition, respectively. The major
product was the trapped germylene, 50. This fits the temperature range for decomposition established earlier with 81. Trimethylsilylacetylene was not detected due to its similarity in GC retention with DMB.

Pyrolysis of 113 in the SFR led to a myriad of products. Major among these was the trapped germylene, 91. Pyrolysis at 320-410°C led to 10-90% decomposition of 113. Again this matches closely the pyrolysis temperature range for its
silylated counterpart 90.

Finally, the pyrolysis of 114 was clean enough to obtain Arrhenius parameters for the elimination of trimethylsilylacetylene. Pyrolysis from 420-470°C (10-50% decomposition) afforded the following parameters: Log(\(A/s^{-1}\)) = 11.4 ± 0.2 and \(E_{\text{act}} = 41.8 ± 0.7\) Kcal/mol. (figure 9) This is very close to the kinetic parameters obtained for 89.

**Scheme 31**

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{GeC}≡\text{CH} & \xrightarrow{\text{SFR}} \text{Me}_3\text{SiGeC}≡\text{CH} + \text{Me}_3\text{SiC}≡\text{CH} \\
112 & \xrightarrow{360, 380^\circ\text{C}} \text{Me}_3\text{SiGeC}≡\text{CH} + \text{Me}_3\text{SiC}≡\text{CH} \\
& \text{70, 85% decomposition} \\
\text{Me} & \text{(Me}_3\text{Si)}_2\text{GeC}≡\text{CH} \xrightarrow{\text{SFR}} \text{Me}_3\text{SiGeC}≡\text{CH} + \text{others} \\
113 & \xrightarrow{320-410^\circ\text{C}} \text{Me}_3\text{SiGeC}≡\text{CH} + \text{Me}_3\text{SiC}≡\text{CH} \\
& \text{10-90% decomposition} \\
\text{Me} & \text{Me}_3\text{SiGeC}≡\text{CH} \xrightarrow{\text{SFR}} \text{Me}_3\text{SiGeC}≡\text{CH} + \text{Me}_3\text{SiC}≡\text{CH} \\
114 & \xrightarrow{420-470^\circ\text{C}} \text{Me}_3\text{SiGeC}≡\text{CH} + \text{Me}_3\text{SiC}≡\text{CH} \\
& \text{10-50% decomposition} \\
\end{align*}
\]

\[
\begin{align*}
\text{Log}(A/s^{-1}) &= 11.4 ± 0.2 \\
E_{\text{act}} &= 41.8 ± 0.7 \text{ Kcal/mol}
\end{align*}
\]

Our research group has recently developed a strong interest in strained cyclic acetylenes.\textsuperscript{113} One approach toward reaching strained rings is to start with larger rings
Figure 9, Arrhenius plot for the thermal decomposition of 114 following the formation of 79.

\[ \log (A/s^{-1}) = 11.4 \pm 0.2 \]
\[ E_{\text{act}} = 41.8 \pm 0.7 \text{ Kcal/mol} \]
and simply extrude members of the ring. With this in mind, we attempted to use the germyl-acetylene chemistry just described to form a highly strained cyclic-diacetylene. Compound 120 was prepared by the addition of dichlorodigermane 119 to the di-Grignard 117 for an isolated yield of 37%. As shown in Scheme 32, the di-Grignard was prepared from 116 which was obtained by adding two equivalents of ethynyl Grignard to 115 in 90% yield. Dichlorodigermane, 119, was prepared from 118 by treatment with HCl and AlCl₃ as catalyst. Compound 118 was prepared by the lithium coupling of two equivalents of 64. Compound 120 was stable upon pyrolysis in the SFR (only 25% decomposition at 550°C) which was consistent with its all-silicon analog. None of the expected trapped silylene or germylene, nor the resultant strained ring were observed.

**Apparent Dyotropic Rearrangement of Silicon and Germanium**

Looking back at our mechanism for germylene extrusion from germylacetylenes (Scheme 33), there are three possible rate-determining steps. In the last section it was shown that vinylidene insertion showed no preference for a Si-Ge bond over a Si-Si bond. This leaves vinylidene formation via a germyl shift or germylene extrusion from the germacyclopentene intermediate as the rate-determining step.

To test whether vinylidene (or germacyclopentene)
Scheme 32

\[ \text{Me}_2\text{SiCl} \xrightarrow{\text{2 HCClMgCl}} \text{Me}_2\text{SiC≡CH} \xrightarrow{\text{2 EtMgCl}} \text{Me}_2\text{SiC≡CMgCl} \]

115 (90% yield)

\[ \text{Me}_2\text{SiCl} \xrightarrow{\text{Ph}} \text{Me}_2\text{SiCHCHMeSiCECMgCl} \xrightarrow{\text{Ph}} \text{Me}_2\text{SiC≡CMgCl} \]

116

117

\[ \text{Ph} \xrightarrow{\text{2 Me}_2\text{GeBr}} \text{Me}_2\text{GeGeMe}_2 \xrightarrow{\text{HCl/AlCl}_3} \text{Cl} \]

118 (75%)

119 (54%)

\[ \text{Me}_2\text{SiC≡CGeMe}_2 \xrightarrow{\text{Me}_2\text{SiC≡CGeMe}_2} \text{Me}_2\text{SiC≡CGeMe}_2 \xrightarrow{\text{Me}_2\text{SiC≡CGeMe}_2} \]

120 (37%)

Scheme 33

\[ \text{Me}_3\text{Si} \xrightarrow{\text{Ge}} \text{C≡C} \text{R} \xrightarrow{\text{not rate determining step}} \text{Me}_3\text{SiC≡C} \text{R} + \text{R}^1\text{R}^2\text{Si} \]

R^1

R^2

not rate determining step

R^1

R^2

SiMe_3

C≡C
formation was rate-determining, a compound designed to extrude silylene with a trimethylgermyl group at the terminal acetylene position was desired. If vinylidene (or germacyclopene) formation was involved in the rate-determining step, one should see an increase in the rate of silylene formation due to the ability of the germyl group to shift at a more facile rate than silicon. Compound 124 (Scheme 34) was prepared in 61% yield by the addition of 101 to lithioacetylene 123. Lithioacetylene 123 was prepared from MeLi treatment of 122 which in turn was obtained by adding ethynyl Grignard to 121 in 76% yield.

Scheme 34

\[
\begin{align*}
\text{(Me}_3\text{Si)}_3\text{SiCl} & \quad + \quad \text{HC}≡\text{CMgCl} & \quad \rightarrow \quad \text{(Me}_3\text{Si)}_3\text{SiC}≡\text{CH} \\
\text{121} & \quad & \quad \text{122 (76% yield)} \\
\text{MeLi} & \quad \downarrow & \quad \text{Me}_3\text{GeBr} \\
& \quad & \quad \text{(Me}_3\text{Si)}_3\text{SiC}≡\text{CGeMe}_3 \\
& \quad & \quad \text{124 (61%)}
\end{align*}
\]

Surprisingly, SFR pyrolysis of 124 in the temperature range 330°-400°C did not produce silylene but instead an apparent dyatropic rearrangement between the trimethylgermyl group on the acetylene and a trimethylsilyl group attached to silicon occurred. (Scheme 35) Flow pyrolysis of 124 in a 20-fold excess of DMB at 400°C gave isomer 125 as the
exclusive product. Arrhenius parameters were obtained for this rearrangement. (figure 10)

Scheme 35

![Scheme 35 Diagram]

Log($A/s^{-1}$) = 10.2 ± 0.1
$E_{act}$ = 32.7 ± 0.2 Kcal/mol

This isomerization, as shown in Scheme 36, can be explained by a 1,2-germyl shift to form vinylidene 126 or silacyclopropene 127, which can undergoing another 1,2-germyl shift from C to Si, to produce 125. Compound 125 is lower in energy than 124 as is evidenced by complete conversion from 124 to 125 at 400°C. Pyrolysis of 125 at higher temperatures results in decomposition with exclusive formation of the germyl substituted silylene, 130.

This data is consistent with Petrich's work in which he used a terminal acetylene in place of a (trimethylgermyl)-ethynyl group. He observed the isomerization of ethynyl-disilanes to bis(silanyl)acetylenes as shown in Scheme 37.
\[ \log(A/s^{-1}) = 10.2 \pm 0.1 \]
\[ E_{\text{act}} = 32.7 \pm 0.2 \text{ Kcal/mol} \]

Figure 10, Arrhenius plot for the thermal isomerization of 124 to 125.
It can be reasonably concluded that extrusion of germylene from a germacyclopene intermediate is the rate-determining step for this reaction. From the examples cited, we can also draw some conclusions as to how substituents affect the stability of these metalocyclopene
intermediates. For example, 2,3-silicon substitution on the ring lowers the barrier to germylene extrusion. Whereas with silacycloprenes there is no substantial substituent effect. These energy differences can be depicted in the form of an energy diagram as shown in Scheme 38.

To further support our conclusions, compound 134 (Scheme 39) was prepared in 63% yield by adding Me₃GeBr to
lithioacetylene 133. Addition of ethynyl Grignard to chlorosilane 131 afforded 132 in 75% yield, which upon treatment with one equivalent of MeLi gave 133.

Scheme 39

Flow pyrolysis of 134 (Scheme 40) at 390°C gave complete conversion to the isomerized product, 135. Arrhenius parameters (Scheme 40) were obtained for both the isomerization [Log(A/s⁻¹) = 11.0 ± 0.1, Eₜₐₜ = 35.7 ± 0.2 Kcal/mol] (figure 11) and the extrusion of silylene [Log(A/s⁻¹) = 10.2 ± 0.4, Eₜₐₜ = 37.8 ± 1.3 Kcal/mol] (figure 12).

Pyrolysis of 135 cleanly led to extrusion of the germysilylene and showed no evidence of reverting to 134.

At first it may appear that an example of a substitution effect on silylene extrusion has been found. However, by comparing rate constants for the decomposition of 135 with those of 92 we see little difference. For example: $^{135}k_{460} = 9.4 \times 10^{-2}$ s⁻¹, $^{92}k_{460} = 1.0 \times 10^{-1}$ s⁻¹, $^{135}k_{480} = 1.6 \times 10^{-1}$ s⁻¹, $^{92}k_{480} =$
Figure 11, Arrhenius plot for the thermal isomerization of 134 to 135.

Log (A/s⁻¹) = 11.0 ± 0.1
E_{act} = 35.7 ± 0.2 Kcal/mol

$Me$ $\text{(Me}_3\text{Si)}_2\text{SiC} \equiv \text{GeMe}_3$
Log (A/s\(^{-1}\)) = 10.2 ± 0.4

\( E_{act} = 37.8 ± 1.3 \text{ Kcal/mol} \)

Figure 12, Arrhenius plot for the thermal decomposition of \( 135 \) following the formation of \( 82 \).
As can be seen, the rate constants at all three temperatures are very close.

Pyrolysis of 137, prepared as shown in Scheme 41, in the SFR with a 20-fold excess of DMB gave two major products: the expected isomer, 138, and the resultant eliminated acetylene, 106. Unexplainably, trapping of silylene by DMB to give 78 was not observed. Due to the competition between isomerization and decomposition, it was not possible to obtain valid Arrhenius parameters. Pyrolysis temperatures and the
corresponding pyrolysate compositions are reported in Scheme 42.

From previous examples, one would reasonably conclude that acetylene 106 was derived from decomposition of 138. However, the possibility that the decomposition of 137 was contributing to the formation of 106 could not be ignored. To answer this question, 138 was prepared in 65% yield by the condensation of 80 and 76 as shown in Scheme 43.

Arrhenius parameters (Scheme 44, figure 13) were obtained for the thermal decomposition of 138. The higher temperatures required for this decomposition clearly shows that 106 is derived primarily from 137.

A graphic representation of this energy surface is
Scheme 42

\[
\begin{array}{c}
\text{Me} \\
\text{Me}_3\text{SiSiC}≡\text{CGeMe}_3 \\
\text{137 Me}
\end{array}
\xrightarrow{\text{SFR}}
\begin{array}{c}
\text{Me} \\
\text{Me}_3\text{GeSiC}≡\text{CSiMe}_3 \\
\text{138 Me}
\end{array}
\]

\[
\begin{array}{c|c|c|c}
\text{Oven Temp.} & \text{137} & \text{138} & \text{106} \\
\hline
410℃ & 95% & 3.5% & 1.5% \\
430℃ & 80% & 10% & 10% \\
450℃ & 60% & 20% & 20% \\
470℃ & 40% & 25% & 35% \\
490℃ & 20% & 30% & 50%
\end{array}
\]

Scheme 43

\[
\begin{array}{c}
\text{Cl} \\
\text{Me}_3\text{GeSiMe}_2 + \text{Li}≡\text{CSiMe}_3 \\
\text{76} \\
\hline
\end{array}
\xrightarrow{(65\% \text{ yield})}
\begin{array}{c}
\text{Me} \\
\text{Me}_3\text{GeSiC}≡\text{CSiMe}_3 \\
\text{138 Me}
\end{array}
\]

difficult to present here due to its 3-dimensional nature. In it's most basic form, we see that with 126 and 134, where it is possible to form bis(trimethylsilyl)acetylene as the elimination product, the apparent dyatropic rearrangement does not compete with silylene extrusion. However, to form 106 as the elimination product, it is evident that this is a higher energy process which is competitive with the apparent
Figure 13, Arrhenius plot for the thermal decomposition of $^{138}$ following the formation of $^{106}$.

$\log (A/s^{-1}) = 10.0 \pm 0.6$

$E_{act} = 42.9 \pm 2.1 \text{ Kcal/mol}$
It was desired to test the universality of this thermal rearrangement. Petrich\textsuperscript{112} had shown that one could perform a ring expansion of 139, thus cleverly converting an exocyclic acetylene compound to endocyclic 141. Pyrolysis of 139 in the presence of an excess of DMB led to the formation of 141, decamethylpentasilacycloheptyne, 144, and trapped silylene 145. Compound 141 was isolated and found to be stable at the temperatures necessary to decompose 139. Petrich did not, however, heat 141 to higher temperature to see if 144 was formed. He explained these results by employing a vinyl-silylene intermediate, 142, as shown in Scheme 45.

We desired to see if germanium would facilitate this rearrangement. Addition of 101 to lithioacetylene 148 afforded 149 in 58\% yield from silylacetylene 139. Compound 139 was prepared following Petrich's\textsuperscript{112} procedure by ethynyl Grignard addition to 147 in 95\% yield. In turn, 147 was
Scheme 45
(ref. 112)

Me₂Si – SiMe₂
Me₂Si 139 Si – C≡CH
Me₂Si – SiMe₂

360°C

Me₂
Si
Me₂
SiMe₂
140
Si
Me₂
Me₂
C ≡ C
Me
H

C ≡ C
Me
H

Me₂Si
Me₂
SiMe₂
141
Si
Me₂
Me₂
Me₂

(69%)

360°C

Me₂
Si
Me₂
SiMe₂
142
Si
Me₂
Me₂

(15%)

Me₂Si
Me₂
SiMe₂
143
Si
Me₂
Me₂

+ MeSiH
DMB

Me
H

(8%)
Scheme 46

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad \text{Me}_2\text{Si} \\
\text{Si} & \quad \text{Si} \\
\text{Me}_2 & \quad \text{Me}_2
\end{align*}
\]

(82% yield)

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad \text{Si} \\
\text{Me}_2 & \quad \text{Me}_2
\end{align*}
\]

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad \text{Si} \\
\text{Me}_2 & \quad \text{Me}_2
\end{align*}
\]

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad \text{Si} \\
\text{Me}_2 & \quad \text{Me}_2
\end{align*}
\]

(95%)

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad \text{Si} \\
\text{Me}_2 & \quad \text{Me}_2
\end{align*}
\]

(58%)
prepared in 82% yield by adding SbCl₅ to 146 as demonstrated by Derczewski and Wojnowski.¹¹⁴

Flow pyrolysis of 149 at 360°C afforded 150 in 57% and 144 in 22% with 12% 149 remaining. SFR pyrolysis of 149 with a 20-fold excess of DMB from 380°-520°C shows a gradual conversion from 149 to 150 with silylene extrusion becoming competitive at higher temperatures. Again selective extrusion of the germylsilylene is observed as evidenced by the formation of 144. Again it was puzzling that only a trace amount of germylsilylene was successfully trapped.

These results are completely consistent with the linear model. However, in order to account for the selective extrusion of germylsilylene it becomes necessary to adopt Petrich's vinylsilylene mechanism.

Clearly silylene extrusion from ethynyl disilanes warrants a closer look. Using the germyl group as a labeling tool will be useful in studies of this sort.

**Thermochemistry of Other Germanes**

As mentioned earlier in this dissertation, there have been a few examples of pyrolyses of organogermainium compounds that are not believed to follow the pathways of α-elimination or extrusion of germylene via a germacyclopropene. One example was presented earlier. Compound 76 was designed to extrude dimethylsilylene via an α-elimination of
Scheme 47

trimethylchlorogermane. It was observed that both dimethylgermylene and silylene were detected. This was disturbing, till several other examples came to light of germylene extrusion through an alternative mechanism.

Again to test the effect of germanium substitution on
the α-elimination of silylene, compounds 151 and 152 were prepared from 76 as shown in Scheme 48. Compound 151 was prepared by adding a 1:1 molar mixture of n-butanol and pyridine to 76. Compound 152 was obtained as a by-product from partial hydrolysis of 76.

As shown in Scheme 49, SFR pyrolysis of 151 from 540°-600°C in the presence of a 20-fold excess of DMB lead to the formation of trapped germylene, 29, and the resultant butoxytrimethylsilane, 153.
Following this trend, pyrolysis of \textbf{152} (Scheme 50) in the same temperature range afforded \textbf{154} and \textbf{155}. For example, pyrolysis at 580°C produced \textbf{154} in 20% and \textbf{155} in 60% with 20% \textbf{152} remaining. The driving force here is obviously the bond strengths (Ge-O vs. Si-O, Ge-Si vs. C-Si) and the relative stability of the germylene formed versus a silylene. The mechanism for this decomposition is not so obvious.

\textbf{Scheme 50}

Pyrolysis of \textbf{151} and \textbf{152} was also conducted in the presence of a 20-fold excess of methylene chloride to trap any radicals formed. Only unreacted starting material and the corresponding siloxane were detected. This leads us to believe that germylene extrusion is occurring through a concerted mechanism as depicted in Scheme 51. These would be the first examples of a thermal α-elimination of an alkylsilane to form germylene.

Another puzzling thermal decomposition was that of allyltrimethylgermane, \textbf{156}. In order to compliment the
Scheme 51

\[
\begin{align*}
\text{Me}_2\text{Ge'} & \rightarrow \text{Me} \quad \text{SiMe}_2 \rightarrow \text{Me}_2\text{Ge} : + \text{Me}_3\text{SiX} \\
X &= \text{OR, Cl}
\end{align*}
\]

pyrolysis study of allyltrimethylsilane reported by Barton et al.\textsuperscript{116} compound 156, prepared as shown in Scheme 52, was pyrolyzed in anticipation of germylene formation.

Scheme 52

\[
\begin{align*}
\text{Me}_3\text{GeCl} + & \quad \text{MgCl} \quad \rightarrow \quad \text{Me}_3\text{Ge} \quad 156
\end{align*}
\]

SFR pyrolysis of 156 (Scheme 53) at 580°C with a 20-fold excess of DMB resulted in the formation of trimethylgermane, 157 (33%), and trapped dimethylgermylene, 29 (21%), as the major products with 38% 156 recovered. Flow pyrolysis at 530°C gave similar results.

The formation of 157 (Scheme 53) can simply be explained by bond homolysis of the weakest bond in the molecule, the Ge-allyl bond, followed by proton abstraction by the resultant radical. However, the formation of dimethylgermylene is more difficult to explain. It is possible that the trimethylgermyl
radical has lost a methyl group to form the more stable germylene. Conversely, it is possible a concerted mechanism is involved.

Our interest in strained cyclic compounds\textsuperscript{117} led us to one final example of organogermanium thermochemistry.
Compound 165 was prepared as shown in Scheme 55 by the addition of 160 to dilithioallene 164. Compound 160 was prepared in 66% yield by replacing the phenyl groups of 159 with chlorines using HCl/AlCl₃. Addition of two equivalents of germyl anion 66 to dimethyldichlorosilane, 158, afforded 159 in 86% yield. Dilithioallene was prepared as previously reported¹¹⁷ by the addition of two equivalents of n-BuLi to bis(trimethylsilyl)propyne, 163. In turn, compound 163 was prepared from propargyl bromide as shown.

Scheme 55
Pyrolysis of \( 165 \) (Scheme 56) at 550°C in the SFR showed no ring contracted products. The major product was \( 163 \) (36%) with minor amounts of tris(trimethylsilyl)propyne, \( 166 \) (7.2%), and tris(trimethylsilyl)allene, \( 167 \) (9.6%). No germanium containing products were detected.

Scheme 56

These results parallel those of its all-silicon analog.\(^{117}\) Obviously, this is a very complex decomposition. With the relatively large amount of \( 163 \) formed, a radical mechanism is the logical choice, but such a variety of choices and such little data doesn't warrant postulation.
EXPERIMENTAL

Instrumentation

High resolution $^1$H (300 MHz), $^{13}$C (75.5 MHz), and $^{29}$Si (59.6 MHz) NMR spectra were recorded on a Varian VXR-300 spectrometer. Chemical shifts for $^1$H and $^{13}$C NMR are reported as parts per million using the stated solvent as standard (i.e. chloroform = 7.22 ppm, benzene = 7.15 ppm). Tetramethylsilane was added as an internal standard for all $^{29}$Si NMR spectra. Standard abbreviations are used to designate proton splitting. Mass spectra were recorded using a Hewlett Packard 5970B (GC/MS) operating at 70 eV and are reported as m/e (% relative intensity). Infrared (IR) spectra were recorded on a Hewlett Packard 5965A (GC/IR) and are reported as wave numbers (cm$^{-1}$). Quantitative gas chromatography (GC) analyses were performed on a Hewlett Packard 5890A equipped with a flame ionization detector; using a 30 meter, 0.25 mm i.d. capillary column with a 0.25 um DB-5 stationary phase. Helium was used as the carrier gas.

Preparative gas chromatographic separations were performed on a Varian 1720 gas chromatograph using 9 to 15 foot 1/4 inch copper columns packed with 15-25% SE-30 on Chromosorb W. The instrument was equipped with a thermal conductivity detector and a chart recorder. Again helium was used as the carrier gas.
Column chromatography used silica gel as the support and hexane as the eluent. All solvents were distilled over calcium hydride or lithium aluminum hydride.

A pulsed stirred-flow reactor (SFR) modeled after the design of Baldwin et al.\textsuperscript{106} was used for kinetic studies. The SFR was calibrated by following the well-established thermal isomerization of cyclopropane to propylene. The quartz reaction chamber had a volume of 3 cm\textsuperscript{3} and a $\tau$ of 2.39 s. The reaction chamber was heated by an oven regulated by a Digi-Sense temperature controller. The SFR system used a 60 ml per minute flow of helium to sweep the sample through the reactor and into a Varian 6000 GC fitted with a 30 meter DB-5 megabore column. The GC (FID) signals were recorded on a Hewlett Packard 3390A integrator as well as a Magnum XT/Mark 2 microcomputer for determination of the reactant and product areas. Response factors were determined for all the starting materials and products. These were included in the Arrhenius parameters which were obtained. In addition to the SFR used for kinetics, a similar SFR was used in series with the GC-IR-MS system previously described.
Procedures and Results

Synthesis of 2,2,4,4-tetramethyl-3,3-bis(trimethylsilyl)-2,4-disila-3-germapentane, 46.

Following the procedure of Brook et al.,\textsuperscript{105} pentane was used to wash 25.0 g (3.57 mol) of lithium cut into 0.5 cm chunks from 0.5 cm diameter wire. Under stirring and nitrogen flow, 800 ml dry THF was added. To this was added 202 ml (1.60 mol) trimethylchlorosilane over a 20 min. period. The reaction mixture was cooled to -78°C at which time 77.8 g (0.363 mol) germanium tetrachloride was added over a 4 hour period. After stirring for 8 hours, the cold bath was removed and the reaction mixture was allowed to stir at room temperature for an additional 25 hours. At this time the resultant brown/black solution was quenched with 1 M HCl and the organic portion extracted with diethyl ether and left to dry over Na$_2$SO$_4$/MgSO$_4$. The resultant solid was recrystallized from acetonitrile yielding 53.5 g (0.147 mol) of a white crystalline compound, 40.5% yield. $^1$H(C$_6$D$_6$): s 0.365; $^{13}$C(C$_6$D$_6$): 3.494; $^{29}$Si(C$_6$D$_6$): -5.158; MS: 366 (M$^+$, 17), 351(11), 278(50), 219(16), 204(17), 145(13), 131(17), 73(100); IR(cm$^{-1}$): 2956, 2900, 1398, 1252, 840.

Synthesis of 2,2,4,4-tetramethyl-3-trimethylsilyl-2,4-disila-3-germapentane, 48.

Again following Brook's procedure,\textsuperscript{105} a solution of 4.78
g (13.1 mmol) 46 in 80 ml dry THF was purged with argon to remove any air present. To this stirring solution was added 9.1 ml (1.46 M, 13.3 mmol) MeLi. This mixture was allowed to stir at room temperature for 62 hours at which time the reaction was quenched with 1 M HCl and the organic portion extracted with diethyl ether. GC analysis indicated a yield of 80%. Purification was accomplished by preparative gas chromatography (180°C isotherm, flow=29 ml/min., 15 ft. column). $^1$H(C$_6$D$_6$): s 0.281 (27H), s 2.159 (1H); $^{13}$C(C$_6$D$_6$): 2.710; $^{29}$Si(C$_6$D$_6$): -6.067; MS: 294 (M$^+$, 1.9), 292 (1.4), 220 (30), 219 (11), 218 (22), 216 (16), 147 (12), 146 (37), 145 (22), 144 (26), 142 (19), 132 (10), 131 (39), 75 (41), 73 (100), 57 (31); IR(cm$^{-1}$): 2956, 2899, 2125, 1949, 1406, 1253, 841.

Flow pyrolysis of 48 to form 1,1-bis(trimethylsilyl)-1-germacyclopent-3-ene, 49.

A total of 140 mg (0.514 mmol) 48 was added dropwise to a flow pyrolysis apparatus heated to 360° and 380°C with an argon flow of 45 ml/min. The pyrolysate was collected using a dry ice/IPA bath. Characterization of the resultant product mixture was accomplished using GC-IR-MS only, due to the complexity of the pyrolysate mixture. MS: 274 (M$^+$, 12), 272 (8.4), 270 (5.7), 220 (30), 218 (21), 216 (15), 148 (10), 146 (44), 145 (23), 144 (31), 142 (23), 132 (10), 131 (41), 73 (100), 59 (19); IR(cm$^{-1}$): 2957, 2907, 1612, 1405, 1253, 1056, 842.
Synthesis of 2,2,3,4,4-pentamethyl-3-trimethylsilyl-2,4-disila-3-germapentane, 52, and 2,2,3,3,4,4-hexamethyl-2,4-disila-3-germapentane, 54.

Following the lithium coupling procedure reported by Gaspar et al., pentane was used to wash 12.1 g (0.64 mol) Li chunks 0.5 cm in diameter. To this was added 200 ml dry THF followed by 80.4 ml (0.64 mol) trimethylchlorosilane. Upon cooling to -78°C, a 100 ml THF solution containing 23.1 g (0.113 mol) dimethyldichlorogerane and 9.2 g (0.047 mol) methyltrichlorogerane was added over a 3 hour period under high speed stirring. After stirring for 26 hours, the salts and unreacted lithium were removed via filtration through Celite 503. The resultant solution was quenched with 1M HCl and the organic portion extracted with diethyl ether. The lower boiling bis(trimethylsilyl)dimethylgermane was removed by distillation (b.p. = 38°C, 0.2 mm Hg) affording 25.3 g (0.102 mol), 77% yield, of a clear colorless liquid; leaving 8.7 g (0.028 mol) tris(trimethylsilyl)methylgermane, 60% yield, as a clear colorless liquid.

For 52: $^1H(C_6D_6)$: s 0.225 (27H), s 0.261 (3H); $^{13}C(C_6D_6)$: -13.791, 1.213; $^{29}Si(C_6D_6)$: -6.780; MS: 308($M^+$, 7), 293(5), 235(6), 220(23), 145(22), 131(31), 73(100); IR(cm$^{-1}$): 2957, 2902, 1402, 1253, 840, 786.

For 54: $^1H(C_6D_6)$: s 0.160 (18H), s 0.255 (6H); $^{13}C(C_6D_6)$: -7.861, -0.574; $^{29}Si(C_6D_6)$: -9.211; MS: 250($M^+$, 3), 235(6),
Synthesis of 3-chloro-2,2,4,4-tetramethyl-3-trimethylsilyl-2,4-disila-3-germapentane, 53.

Following the procedure of Brook et al., a total of 9.1 g (31.1 mmol) 48 was added dropwise to a stirring solution of 250 ml carbon tetrachloride. This solution was left sitting in the window ledge in direct sunlight. After 1 hour GC-MS analysis showed 85% conversion to the desired chlorogermane. Solvent was removed by vacuum line and the crude product used as is.

Alternatively, following a procedure reported by Gaspar et al., to a frozen slurry of 0.983 g (3.21 mmol) tris(trimethylsilyl)methylgermane in nitromethane was added 0.39 ml (3.3 mmol) SnCl\textsubscript{4}. GC analysis showed complete conversion to the desired product. \textsuperscript{1}H(C\textsubscript{6}D\textsubscript{6}): s 0.327 (27H); \textsuperscript{13}C(C\textsubscript{6}D\textsubscript{6}): 0.082; \textsuperscript{29}Si(C\textsubscript{6}D\textsubscript{6}): -2.456; MS: 328(M\textsuperscript{+}, 1), 313(6), 220(32), 146(37), 131(39), 73(100); IR(cm\textsuperscript{-1}): 2958, 2903, 1403, 1254, 843.

Flow pyrolysis of 53 to give 1,2-bis(trimethylsilyl)-3,4-dimethyl-1-germacyclopent-3-ene, 50.

A solution of 244 mg (0.746 mmol) 53 in 5 ml DMB was added dropwise to a flow pyrolysis apparatus heated to 300\textdegree C.
with an argon flow of 45 ml/min. The pyrolysate was collected using a dry ice/IPA bath. Purification by preparative gas chromatography (160°C isotherm, flow=30 ml/min., 9' column) yielded 46 mg (0.153 mmol) of a clear colorless product, 21% yield. $^1$H(C$_6$D$_6$): s 0.198 (18H), s 1.757 (6H), s 1.891 (4H); $^{13}$C(C$_6$D$_6$): -0.139, 19.642, 22.413, 131.904; $^{29}$Si(C$_6$D$_6$): -8.580; MS: 320 (M$^+$, 14), 300 (10), 229 (19), 228 (11), 227 (16), 225 (11), 220 (18), 218 (13), 216 (10), 148 (11), 146 (51), 145 (24), 144 (35), 142 (26), 131 (34); IR (cm$^{-1}$): 2920, 2900, 1403, 1253, 1112, 841; calc. for C$_{12}$H$_{29}$GeSi$_2$ 298.09726, measured 298.09751.

Synthesis of bis(trimethylsilyl)chloromethylgermane, 55.

Following the procedure of Gaspar et al., a solution of 2.6 g (10.5 mmol) 54 in 30 ml CH$_3$NO$_2$ under argon was prepared. To this stirring solution was added 1.3 ml (11.1 mmol) tin(IV) chloride. The reaction mixture was then added to a 50:50 mixture of pentane and concentrated HCl. The organic portion was removed and left to dry over MgSO$_4$/Na$_2$SO$_4$. Removal of the pentane left 2.5 g (9.34 mmol) (89%) of crude product which was not further purified. $^1$H(CDC$_3$): s 0.235 (18H), s 0.671 (3H); $^{13}$C(CDC$_3$): -1.526, 0.116; $^{29}$Si(CDC$_3$): -4.249; MS: 270 (M$^+$, 2), 255 (5), 162 (29), 160 (21), 158 (15), 131 (9), 73 (100); IR (cm$^{-1}$): 2958, 2903, 1405, 1255, 844, 791.
Flow pyrolysis of 55 to forml-trimethyilsilyl-1,3,4-trimethylgermacyclopent-3-ene, 56.

A solution containing 200 mg (0.74 mmol) 55 in 1.5 ml DMB was added dropwise to a flow pyrolysis apparatus heated to 300°C with an argon flow of 45 ml/min. The pyrolysate was collected using a dry ice/IPA bath. Purification by preparative gas chromatography (160°C isotherm, flow=30 ml/min., 9' column) yielded 46 mg (0.111 mmol) of a clear colorless product, 15% yield. $^1$H(C$_6$D$_6$): s 0.135 (9H), s 0.332 (3H), s 1.770 (6H), q 1.59, 1.65, 1.83, 1.89 (4H); $^{13}$C(C$_6$D$_6$): -4.620, -1.179, 19.685, 25.939, 131.270; $^{29}$Si(C$_6$D$_6$): -11.545; MS: 244 (M+, 6.8), 242 (5.0), 240 (3.6), 229 (10), 227 (7), 225 (5), 162 (11), 160 (8), 158 (6), 135 (2), 125 (3), 107 (3), 89 (7), 85 (4), 75 (3), 74 (9), 73 (100), 59 (6); IR(cm$^{-1}$): 2956, 2900, 1644, 1446, 1404, 1254, 1165, 1111, 985, 842, 796.

Synthesis of potassium tris(benzene-1,2-diolato)germinate, 60.

Following the procedure of Corriu et al., a solution of 10.5 g (0.15 mol) KOCH$_3$ in 75 ml MeOH was added to a stirring suspension of 7.83 g (0.075 mol) germanium dioxide in 40 ml methanol under an argon flow. To this was added a solution of 24.75 g (0.225 mol) catechol in 75 ml methanol. This reaction mixture was heated to reflux for 72 hours. After cooling, the methanol was removed by rotory evaporation. The resultant white crystals were washed with diethyl ether.
Upon drying, a total of 31.47 g (0.066 mol) of product was isolated, 88% yield. $^1$H(CD$_3$OD): mult. 6.374-6.418 (6H), mult. 6.538-6.583 (6H); $^{13}$C(CD$_3$OD): 112.646, 118.061, 151.061.

**Synthesis of tetraphenylgermane, 61.**

Following the procedure of Corriu et al, a stirring suspension of 12.34 g (26.0 mmol) of 60 in 150 ml diethyl ether under an argon atmosphere was prepared. To this solution was added 65 ml of a 2M (130 mmol) THF solution of phenylmagnesium bromide. The solution was allowed to stir an additional 2 hours after the addition of the Grignard reagent at which time the reaction was quenched with 100 ml 10% HCl. After repeated washings with demineralized water, 9.0 g (23.6 mmol) of a white crystalline solid (m.p. = 230-235°C) was recrystallized from chloroform and toluene, 91% yield.

Alternatively, to a stirring solution containing 98.82 g (0.460 mol) of 44 in 250 ml dry THF cooled to 0°C while under an argon atmosphere was added 750 ml of 3M (2.25 mol) phenyl grignard (phenylmagnesium chloride or bromide) in a dropwise manner. After completion of the addition of grignard reagent, the reaction mixture was allowed to warm to room temperature at which time the reaction was quenched with 500 ml 1M HCl. The organic portion was extracted with chloroform and recrystallized from benzene affording 89.3 g (0.235 mol) of a white crystalline product (m.p. = 231-233°C), 51 % yield. $^1$H(CDCl$_3$): m 7.305-7.380 (6H), m 7.480-7.520 (4H); $^{13}$C(CDCl$_3$):
Synthesis of dibromodiphenylgermane, 62.

Following the procedure of Mazerolles and Dubac,115 a stirring solution of 51.2 g (0.134 mol) 61 in 500 ml ethylbromide was cooled to 0°C under an argon atmosphere. To this was added 50.0 g (0.313 mol) bromine over a 1 hour period. The reaction mixture was allowed to slowly warm to room temperature and stir under an argon atmosphere for 8 days. GC-MS analysis showed nearly complete conversion to the desired product (88%). The solvent was removed by rotary evaporation and the crude product was not further purified.

Synthesis of dimethyl diphenylgermane, 63.

To a stirring solution of 27.0 g (0.091 mol) 62 in 250 ml THF, cooled to -78°C while under argon, was added 110 ml of 3M (0.33 mol) methylmagnesium chloride. After the addition of grignard, the reaction mixture was allowed to slowly warm to room temperature. The reaction was quenched with 1M HCl, extracted with ether, and left to dry over
Na₂SO₄. Purification by distillation (b.p. = 92-93°C, 0.8 mm Hg) afforded 21.0 g (0.082 mol) of product, 90% yield.

Alternatively, to a stirring solution of 9.86 g (56.8 mmol) 1 in 100 ml dry THF cooled to -78°C while under an argon atmosphere was added 45 ml of a 3M (136 mmol) solution of phenylmagnesium bromide. After the addition of the Grignard reagent, the cold bath was removed and the solution allowed to warm to room temperature. The reaction was quenched with 1M HCl and the organic portion extracted with diethyl ether. Purification by distillation (b.p. = 92-93°C, 0.8 mm Hg) afforded 11.81 g (46.0 mmol) of a clear colorless liquid product, 81% yield. ¹H(C₆D₆): s 0.524 (6H), m 7.15-7.20 (3H), m 7.41 - 7.45 (2H); ¹³C(C₆D₆): -3.131, 128.385, 128.812, 133.969, 140.316; MS: 258(M⁺, 3), 256(2), 254(1.5), 245(21), 244(14), 243(100), 242(32), 241(75), 239(55), 226(11), 151(22), 149(17), 147(13); IR(cm⁻¹): 3061, 3016, 2983, 2914, 2816, 1953, 1882, 1809, 1636, 1578, 1486, 1429, 1303, 1246, 1190, 1091, 1027, 999, 803.

Synthesis of bromodimethylphenylgermane, 64.

To a stirring solution of 20.74 g (80.8 mmol) 63 in 250 ml ethyl bromide under argon was added 4.1 ml (80.8 mmol) bromine. A slight exothermic reaction occurred and over time the reaction mixture turned from a dark red color to a light yellow-orange. After 5 hours of stirring at room temperature the desired product was purified by distillation (b.p. = 58°C,
0.8 mm Hg) to afford 19.95 g (76.8 mmol), of a clear colorless liquid, 95% yield. $^1$H(CDC$_3$): s 1.060 (6H), m 7.39 - 7.44 (3H), m 7.57 - 7.62 (2H); $^{13}$C(CDC$_3$): 4.001, 128.429, 130.096, 132.333, 138.295; MS: 264(1.4), 262(8.0), 261(2.4), 260(M$^+$, 12), 258(8), 249(12), 247(70), 246(20), 245(100), 244(19), 243(73), 241(31), 181(21), 179(15), 177(10), 155(13), 153(24), 151(35), 149(22), 147(12), 91(15), 89(19), 87(14), 85(10), 77(14), 51(28); IR(cm$^{-1}$): 3064, 2996, 2918, 1958, 1885, 1809, 1638, 1576, 1486, 1429, 1303, 1248, 1191, 1092, 1027, 999, 840, 812; calc. for C$_8$H$_{11}$Br$^7$Ge 255.92871, measured 255.92876.

**Synthesis of chlorodimethylphenylgermane, 65.**

A slow (50 ml/min.) flow of HCl was bubbled through a 250 ml solution containing 3.03 g (11.8 mmol) 63 and 0.28 g (2.1 mmol) aluminum trichloride for 4 hours. At this time the product was purified by distillation (b.p. = 43°C, 0.8 mm Hg) to yield 2.3 g (74% yield) of the desired product. $^1$H(CDC$_3$): s 0.909 (6H), m 7.38 - 7.42 (3H), m 7.54 - 7.58 (2H); $^{13}$C(CDC$_3$): 3.111, 128.308, 129.947, 132.126, 138.395; MS: 216(M$^+$, 11.6), 214(9), 212(5), 203(46), 202(13), 201(100), 200(24), 199(76), 197(48), 181(10), 151(10), 111(12), 109(28), 107(21), 105(12), 91(13), 89(13), 77(15), 51(26); IR(cm$^{-1}$): 3064, 2997, 2919, 1958, 1881, 1810, 1638, 1576, 1487, 1428, 1306, 1250, 1190, 1094, 1027, 999, 838, 813.
Synthesis of dimethyl(trimethylsilyl)phenylgermane, 67.

Following the procedure of Kumada et al., a total of 1.58 g (230 mmol) lithium chunks 1 mm in diameter was prepared. To this was added a solution of 17.35 g (66.8 mmol) 64 in 40 ml dry THF. An immediate exothermic reaction occurred. After 5 min. of stirring under argon, the solution turned a dark brown color. After 3 hours of stirring, the germyl anion formed was added to a solution of 17.6 g (162 mmol) trimethylchlorosilane in 30 ml dry THF, cooled to -78°C. The reaction mixture was allowed to slowly warm to room temperature at which time the reaction was quenched with 1M HCl and the organic layer extracted with ether. Purification by distillation (50°C, 0.8 mm Hg) yielded 11.0 g (43.5 mmol) of a clear colorless liquid, 65% yield. ¹H(CDCl₃): s 0.148 (9H), s 0.405 (6H), m 7.24 - 7.34 (3H), m 7.39 - 7.44 (2H); ¹³C(CDCl₃): -4.525, -1.526, 127.582, 127.838, 133.551, 142.362; ²⁹Si(CDCl₃): -11.348; MS: 254(M⁺, 5.4), 252(3.9), 250(2.8), 239(12), 237(9), 181(12), 179(9), 151(12), 149(10), 136(14), 135(100), 89(9), 73(44); IR( cm⁻¹): 3061, 2959, 2905, 1804, 1580, 1484, 1425, 1252, 1086, 1026, 839, 794; calc. for C₁₁H₂₀₇₄GeSi 254.05533, measured 254.05510.

Synthesis of chloro(trimethylsilyl)dimethylgermane, 68.

Following the procedure of Kumada et al., to a stirring solution of 3.255 g (12.9 mmol) 67 in 60 ml CHCl₃ was begun a flow of HCl gas at a rate of 60 ml/min. To this
solution was added 0.1 g (0.75 mmol) aluminum chloride. The HCl flow was maintained for 30 minutes at which time GC analysis indicated complete conversion to the desired chlorosilane. Crude purification was accomplished via vacuum distillation (22°C, 0.8 mm Hg). Final purification by preparative gas chromatography (90°C isotherm, 9’ column, flow rate = 29 ml/min., ret. time = 8 min.) afforded 2.0 g (9.46 mmol) of a clear colorless liquid, 74% yield. $^1$H(CDCl$_3$): s 0.224 (9H), s 0.665 (6H); $^{13}$C(CDCl$_3$): -2.224, 3.636; $^{29}$Si(CDCl$_3$): -5.920; MS: 212 (M$^+$, 3), 210 (2), 208 (1), 197 (2), 195 (1.6), 177 (6), 175 (4), 104 (28), 102 (21), 100 (16), 89 (14), 87 (10), 74 (11), 73 (100); IR (cm$^{-1}$): 2961, 2907, 1408, 1255, 841, 799; calc. for C$_5$H$_{15}$Cl$^3$GeSi 211.98506, measured 211.98540.

Synthesis of bromo(trimethylsilyl)dimethylgermane, 70.

To a stirring solution of 7.59 g (30.0 mmol) 67 in 250 ml ethyl bromide cooled to -78°C under an argon atmosphere was added 1.6 ml (31.1 mmol) bromine over a 2 min. period. The reaction mixture was allowed to slowly warm to room temperature and remained stirring for 3 hours. The solvent was removed by rotary evaporation. Purification by preparative gas chromatography (120°C isothermal, 9’ column, flow = 29 ml/min., ret. time = 6.5 min.) afforded 4.96 g (19.5 mmol) of a clear colorless liquid, 65% yield. $^1$H(C$_6$D$_6$): s 0.159 (9H), s 0.744 (6H); $^{13}$C(C$_6$D$_6$): -2.340, 3.244; $^{29}$Si(C$_6$D$_6$):
Synthesis of tetramethylgermane, 71.

Following the procedure of Corriu et al., to a stirring suspension of 43.30 g (91.23 mmol) 60 in 200 ml butyl ether cooled to 0°C was added 219 ml 3M (0.657 mol) MeMgCl over a 70 min. period. The ice bath was then removed and the reaction mixture was allowed to warm to room temperature while maintaining stirring and an argon flow for 20 hrs.. The salt produced was filtered off and the organic portion distilled (b.p. = 43°C) to give 9.7 g (73.2 mmol) of a clear colorless liquid, 80% yield. $^1$H(CDCl$_3$): s 0.090; $^{13}$C(CDCl$_3$): -0.661; MS: 134(M$^+$, 0.2), 121(21), 119(100), 118(25), 117(74), 115(54), 104(7), 91(16), 89(29), 87(24), 85(12), 75(10); IR(cm$^{-1}$): 3067, 2978, 2913, 1408, 1246, 829.

Synthesis of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, 73.

A total of 200 ml of 3M in THF (0.60 mol) phenylmagnesium bromide was added over a 90 min. period to a stirring solution of 10.0 g (0.054 mol) commercially available 1,2-dichloro-1,1,2,2-tetramethyldisilane in 100 ml THF, cooled
to -78°C while under an argon atmosphere. The reaction mixture was allowed to stir near room temperature for 4 hours. At this time the reaction was quenched with 1M HCl and the organic portion extracted with diethyl ether. After drying over Na₂SO₄/MgSO₄, purification by distillation (b.p. = 111°C, 1 mm Hg) afforded 13.49 g of a white crystalline solid (m.p. = 34°C), 93% yield. \(^1\)H(CDCl₃): s 0.343 (12H), m 7.31-7.33 (6H), m 7.40-7.44 (4H); \(^1^3\)C(CDCl₃): -3.920, 127.682, 128.394, 133.836, 138.972; \(^2^9\)Si(CDCl₃): -21.837; MS: 270 (M⁺, 25), 255(6), 198(6),197(34), 137(22), 135(100), 119(5), 107(12), 105(15); IR(cm⁻¹): 3060, 3016, 2959, 2900, 1950, 1883, 1807, 1638, 1485, 1426, 1253, 1104, 999, 827, 797.

**Synthesis of (trimethylgermyl)phenyldimethylsilane, 75.**

A solution of 74 was prepared by adding 30.8 g (0.181 mol) phenyldimethylchlorosilane, 72, to 6.1 g (0.879 mol) Li chunks in 100 ml dry THF cooled to 0°C. After allowing the solution to stir at 0°C for 15 min. the ice bath was removed and the reactants were allowed to warm to room temperature. After stirring for 3 hrs., 35 ml of the silyl lithium solution was added dropwise to 3.56 g (0.014 mol) Me₃GeCl in 45 ml dry THF cooled to -78°C. The reaction was quenched with 1M HCl and the organic portion extracted with ether, washed three times with demineralized water, and left to dry over Na₂SO₄/MgSO₄. Distillation (b.p. = 38-40°C, 0.5 mm Hg) afforded 3.86 g.
(0.121 mol) of a clear, colorless, liquid product, 67% yield. 
$^1$H(CDCl$_3$): s 0.11 (9H), s 0.350 (6H), m 7.286 - 7.308 (3H), m 7.398 - 7.430 (2H); $^{13}$C(CDCl$_3$): -3.392, -3.069, 127.756, 128.504, 133.623, 139.226; $^{29}$Si(CDCl$_3$): -14.664; MS: 254(M$^+$, 8.0), 252(5.7), 250(3.9), 239(18), 237(13), 235(10), 136(14), 135(100), 73(6); IR(cm$^{-1}$): 3061, 3017, 2962, 2904, 1950, 1886, 1807, 1639, 1487, 1426, 1253, 1194, 1105, 1000, 816, 785; calc. for C$_{11}$H$_{20}$GeSi 254.05533, measured 254.05487.

**Synthesis of chloro(trimethylgermyl)dimethylsilane, 76.**

To a stirring solution of 3.11 g (12.3 mmol) 75 in 50 ml CHCl$_3$ was begun a flow of HCl gas at a rate of 60 ml/min. To this solution was added 0.2 g (1.5 mmol) aluminum chloride. The HCl flow was maintained for 24 hours at which time GC analysis indicated complete conversion to the desired chlorosilane. GC yield = 65%. $^1$H(CDCl$_3$): s 0.221 (9H), s 0.492 (6H); $^{13}$C(CDCl$_3$): -3.585, 2.769; $^{29}$Si(CDCl$_3$): 28.199; MS: 214(3.6), 212(M$^+$, 8.1), 210(5.8), 197(15), 195(11), 119(37), 117(28), 115(21), 93(13), 89(17), 87(13) 73(100); IR(cm$^{-1}$): 2975, 2911, 1407, 1255, 831, 802; calc. for C$_7$H$_{15}$Cl$_7$GeSi 211.98506, measured 211.98542.

**Synthesis of potassium tris(butane-2,3-diolato)germinate, 77.**

A solution of 2.8 g (0.04 mol) potassium methoxide in 40 ml methanol was added to a suspension of 2.09 g (0.020 mol) germanium dioxide in 20 ml methanol under an argon flow. To
this was added a solution of 5.4 g (0.06 mol) 2,3-butanediol in 20 ml methanol. The reactant mixture was heated to reflux for 2 hours. The methanol was removed by rotovap and the resultant salt was washed with diethyl ether. A total of 6.34 g (0.0152 mol) of a white powder was obtained, 76% yield.

$^1H(CD_3OD)$: d 1.054, 1.074 (18H), octet 3.118-3.159 (6H) J= 6.6 Hz, 2.0 Hz; $^{13}C(CD_3OD)$: 20.479, 73.70.

**Synthesis of 2,2,6,6-tetramethyl-5,5-bis(trimethylsilyl)-2,6-disila-5-germa-3-heptyne, 81.**

A solution of 24.8 mmol 80 was prepared by adding 12.4 ml of a 2M ethereal solution (24.8 mmol) of MeLi to 3.0 g (30.6 mmol) 79 in 10 ml dry THF cooled to -78°C. After warming to room temperature and then cooling to -78°C, 5.0 g (15.3 mmol) 53 was added. The reaction mixture was allowed to warm to room temperature. Upon quenching with 1M HCl, the organic portion was extracted with Et$_2$O. Purification by preparative GC (180°C isotherm, flow=29 ml/min., 9' column) yielded 3.8 g (9.79 mmol) of a clear colorless liquid, 64% yield. $^1H(C_6D_6)$: s 0.185 (9H), s 0.310 (27H); $^{13}C(C_6D_6)$: 0.530, 1.058, 109.245, 115.107; $^{29}Si(C_6D_6)$: -20.916, -5.326; MS: 390(M$^+$, 8), 388(6), 375(5), 373(4), 220(33), 219(11), 218(24), 216(18), 155(10), 146(38), 145(20), 144(27), 142(20), 131(26), 73(100); IR(cm$^{-1}$): 2960, 2903, 2076, 1404, 1255, 845; calc. for C$_{14}$H$_{36}$GeSi$_4$ 386.11372, measured 386.11374.
Synthesis of 2,2,6,6-tetramethyl-5,5-bis(trimethylsilyl)-2,5,6-trisila-3-heptyne, 83.

A solution of 80 was prepared by adding 3.4 ml of a 1.46M (5.0 mmol) MeLi solution to 20 ml of a 0.5M solution of 79 (10 mmol) at room temperature under argon. This solution was then added to a stirring solution of 0.5 g (1.8 mmol) 53 in 40 ml dry diethyl ether. After stirring for 30 min. the reaction mixture was quenched with 50 ml 1M HCl, washed 3 times with demineralized water and left to dry over Na₂SO₄/MgSO₄. Purification by preparative gas chromatography (190°C isotherm, 15’ column, 15% SE30 on Chromosorb W, flow = 29 ml/min., ret. time = 7 min.) gave 0.36g (1.04 mmol) of a clear, colorless, liquid product, 58% yield. However, GC analysis showed a conversion yield of approximately 95%.

\( ^1H(C_6D_6) : \) s 0.149 (9H), s 0.287 (27H); \( ^{13}C(C_6D_6) : \) 0.224, 0.348, 108.311, 118.320; \( ^{29}Si(C_6D_6) : \) -11.779, -19.994, -100.852; MS: 344 (M⁺, 22), 329 (12), 271 (13), 241 (28), 183 (16), 175 (15), 174 (68), 159 (11), 129 (11), 73 (100); IR (cm⁻¹): 2961, 2905, 2079, 1403, 1256, 846, 786; calc. for C₁₄H₃₆Si₅ 344.16613, measured 344.16635.

Synthesis of 2,2,5,5,6,6-hexamethyl-5-germa-2,6-disilahept-3-yne, 89.

A solution of 80 (3.65 mmol) was prepared by adding 2.5 ml of 1.46 M (3.65 mmol) ethereal MeLi to 10 ml of a 0.5 M
(5.0 mmol) THF solution of 79 cooled to -78°C while under argon flow. The solution was allowed to warm to room temperature to assure complete conversion to the lithioacetylene. Again the reaction mixture was cooled to -78°C at which point a solution of 0.2 g (0.95 mmol) 68 in 1 ml dry THF was added via syringe over a 5 min. period. Upon warming to room temperature the reaction was quenched with 1 M HCl followed by extraction of the organic portion with ether. The product was washed three times with water and left to dry over MgSO4/Na2SO4. Removal to the solvent by vacuum line and subsequent purification by preparative gas chromatography (100°C isotherm for 6.5 min. ramping at 6°C/min. to 230°C, ret. time = 15 min., flow = 28, 15' column) yielded 100 mg (0.048 mmol) purified product (a clear colorless liquid), 50% yield. 1H(C6D6): s 0.158 (9H), s 0.186 (9H), s 0.371 (6H); 13C(C6D6): -2.949, -1.941, 0.302, 113.803, 113.875; 29Si(C6D6): -18.650, -9.021; MS: 274(M+, 21), 272(13), 261(12), 259(54), 258(16), 257(42), 255(29), 171(35), 169(32), 167(15), 156(10), 155(90), 97(14), 89(17), 73(100); IR(cm^−1): 3057, 2965, 2910, 2088, 1416, 1255, 847, 803; calc. for C10H2470GeSi2 270.06596, measured 270.06584.

Synthesis of 2,2,5,6,6-pentamethyl-5-(trimethylsilyl)-5-germa-2,6-disilahept-3-vne, 90.

A solution containing 5.8 mmol 80 was prepared by adding
4.0 ml of 1.46 M (5.8 mmol) ethereal MeLi to 15 ml of a 0.5 M (7.5 mmol) THF solution of 79 cooled to -78°C while under argon flow. The solution was allowed to warm to room temperature to assure complete conversion to the lithioacetylene. Again the reaction mixture was cooled to -78°C at which point a solution of 0.8 g (3.0 mmol) chlorogermaane 55 in 10 ml dry THF was added via syringe over a 15 min. period. Upon warming to room temperature the reaction was quenched with 1 M HCl followed by extraction of the organic portion with ether. The product was washed three times with water and left to dry over MgSO4/Na2SO4. Removal of the solvent by rotovap and subsequent purification by prep GC (180°C isotherm, 6 min. ret. time, 15' column) afforded 0.192 g (0.58 mmol) of a clear colorless liquid, 20% yield. 1H(C6D6): s 0.185 (9H), s 0.242 (18 H), s 0.423 (3H); 13C(C6D6): -7.640, -0.759, 0.424, 112.065, 114.786; 29Si(C6D6): -15.912, -3.188; MS: 332 (M+,9), 317 (4), 229 (5), 213 (3), 162 (26), 160 (19), 158 (14), 73 (100); IR(cm^-1): 2961, 2905, 2083, 1406, 1254, 847, 793; calc. for C12H3070GeSi3 328.08984, measured 328.08955.

Flow pyrolysis of 90 to form 1-(trimethylsilyl)-1,3,4-trimethyl-1-germacyclopent-3-ene 91 and 82.

A solution containing 200 mg (0.60 mmol) 90 in 2 ml DMB was added dropwise to a flow pyrolysis apparatus heated to 420°C with an argon flow of 45 ml/min. The pyrolysate was collected using a dry ice/IPA bath. Purification by
preparative gas chromatography (150°C isotherm, 9' column, flow = 29 ml/min., ret. time = 9.5 min.) yielded 102 mg (0.42 mmol) of a clear colorless liquid, 70% yield. $^1$H(C$_6$D$_6$): s 0.135 (9H), s 0.332 (3H), s 1.770 (6H), d 1.59, 1.65, J = 16 Hz (2H), d 1.83, 1.89, J = 15 Hz (2H); $^{13}$C(C$_6$D$_6$): -4.620, -1.179, 19.685, 25.939, 131.270; $^{29}$Si(C$_6$D$_6$): -11.545; MS: 244 (M+, 6.8), 242 (5.0), 240 (3.6), 229 (10), 227 (7), 225 (5), 162 (11), 160 (8), 158 (6), 135 (2), 125 (3), 107 (3), 89 (7), 85 (4), 75 (3), 74 (9), 73 (100), 59 (6); IR(cm$^{-1}$): 2956, 2900, 1644, 1446, 1404, 1254, 1165, 1111, 985, 842, 796.

**Synthesis of 2,2,5,6,6-pentamethyl-5-(trimethylsilyl)-2,5,6-trisilahept-3-vne, 92.**

A solution of 80 was prepared by adding 7.5 ml of 1.46M (11.0 mmol) ethereal MeLi to 30 ml of a 0.5 M (15 mmol) THF solution of 79 cooled to -78°C while under Ar flow. The solution was allowed to warm to room temperature to assure complete conversion to the lithio-acetylene. Again the reaction mixture was cooled to -78°C at which point a solution of 1.95 g (8.68 mmol) bis(trimethylsilyl)methylchlorosilane in 10 ml dry THF was added via syringe over a 15 min. period. Upon warming to room temperature the reaction was quenched with 1M HCl followed by extraction of the organic portion with ether. The product was washed three times with water and left to dry over MgSO$_4$/Na$_2$SO$_4$. Purification by preparative
gas chromatography (200°C isotherm, flow rate = 30, ret time = 3.1 min., 15’ column) afforded 1.9 g (6.60 mmol) of a clear, colorless, liquid product, 76% yield. $^1$H($C_6D_6$): s 0.145 (9H), s 0.218 (18H), s 0.259 (3H); $^{13}$C($C_6D_6$): -7.953, -1.471, 0.117, 111.282, 118.092; $^{29}$Si($C_6D_6$): -64.592, -19.605, -15.323; MS: 286(M+, 44), 271(24), 215(12), 214(24), 213(96), 197(15), 183(43), 155(20), 117(15), 116(96), 73(100); IR(\text{cm}^{-1}): 2961, 2902, 2086, 1405, 848, 790; calc. for $C_{12}H_{30}Si_4$: measured 286.14247, measured 286.14218.

Synthesis of 3,3,4,4-tetramethyl-3,4-disilapentyne, 95.

To a stirring solution of 4.57 g (27.4 mmol) chloro-pentamethyldisilane in 100 ml dry diethyl ether chilled to -78°C under argon was added 56 ml (28 mmol) 0.5 M ethynyl magnesium bromide over a 20 min. period. After allowing the reaction mixture to stir at -78°C for 10 minutes, the cold bath was removed and the reactants were allowed to slowly warm to room temperature. The reaction was quenched with 1 M HCl and the organic portion was extracted with ether. The product was washed 2X with demineralized water and left to dry over MgSO$_4$/Na$_2$SO$_4$. The ether was distilled off and only a small amount of 95 was purified for spectral characterization. $^1$H($C_6D_6$): s 0.124 (9H), s 0.196 (6H), 2.150 (1H); $^{13}$C($C_6D_6$): -3.131, -2.704, 88.687, 95.832; $^{29}$Si($C_6D_6$): -36.084, -19.012; MS: 156(M+, 14), 141(47), 83(12), 73(100); IR(cm$^{-1}$): 3306, 2962, 2910, 2028, 1406, 1257, 811.
Synthesis of 2,2,6,6,7,7-hexamethyl-3,3-bis(trimethylsilyl)-2,6,7-trisila-3-germaoct-4-yne, 97.

A total of 0.9 ml of 1.46 M MeLi (1.32 mmol) was added to a stirring solution of 0.217 g (1.39 mmol) 95 in 20 ml dry THF while under an argon atmosphere and cooled to -78°C. The reactant mixture was allowed to stir for 20 minutes at which time 0.42 g (1.28 mmol) 53 in 5 ml ether was syringed in. After stirring an additional 10 minutes at -78°C, the cold bath was removed and the reaction flask and contents were allowed to slowly warm to room temperature. The reaction was quenched with 1 M HCl and ether used to extract the product. Solvent was removed by rotovap and final purification was accomplished via preparative gas chromatography (210°C isotherm, flow rate = 31, ret. time = 13 min., 15', 10% Carbowax on Chromosorb W packed column) to give 0.100 g (0.22 mmol) of a clear colorless liquid, 18% yield. \( ^1H(C_6D_6) \): s 0.206 (9H), s 0.251 (6H), s 0.317 (27H); \( ^13C(C_6D_6) \): -2.419, -2.369, 1.100, 110.755, 113.177; \( ^29Si(C_6D_6) \): -36.299, -16.133, -2.696; MS: 448(M\(^+\), 9.5), 446(7), 433(7), 431(4.5), 373(3), 280(26), 279(22), 278(84), 277(30), 276(61), 275(10), 274(41), 220(11), 204(17), 203(14), 202(14), 155(11), 146(26), 145(16), 144(18), 142(14), 131(25), 129(12), 73(100); IR(cm\(^{-1}\)): 2958, 2900, 2068, 1403, 1252, 841; calc. for C\(_{16}H_{42}^{76}GeSi_5\) 444.13760, measured 444.13834.
Synthesis of methyl(trimethylgermyl)diphenylsilane, 102.

A flask was charged with 1.04 g (149 mmol) pentane washed Li chunks and 5.0 g (12.7 mmol) 1,2-dimethyl-1,1,2,2-tetraphenyldisilane. To this stirring mixture was added 100 ml THF distilled over LiAlH₄. Shortly after the addition of solvent the reaction mixture turned a yellow color and gradually deepened in color to a brown. This solution was decanted into a 80 ml THF solution containing 6.28 g (31.8 mmol) Me₂GeBr at -78°C. After the addition of silyl anion, the reaction mixture was allowed to warm to room temperature. The reaction was quenched with 1 M HCl. The organic portion was extracted with ether, washed two times with demineralized water, and left to dry over MgSO₄/Na₂SO₄. Removal of the solvent by rotovap and vacuum line left the desired product, 8.7 g (27.7 mmol) of a clear colorless liquid, in >97% purity so no further purification was necessary, 87% yield. \( ^1H(CDCl_3) \):
s 0.254 (9H), s 0.668 (3H), m 7.340-7.362 (6H), m 7.478-7.510 (4H); \( ^13C(CDCl_3) \): -4.411, -2.402, 127.867, 128.871, 134.684, 137.020; \( ^29Si(CDCl_3) \): -14.143; MS: 316 (M⁺, 6), 314 (4.5), 301 (10), 299 (7), 197 (100), 135 (16); IR (cm⁻¹): 3062, 3017, 2973, 2908, 1957, 1886, 1811, 1644, 1570, 1487, 1427, 1253, 1193, 1103, 1029, 999, 830, 787; calc. for C₁₆H₂₂⁷⁰GeSi 312.07338, measured 312.07336.
Synthesis of chloromethyl(trimethylgermyl)phenylsilane, 103.

A 250 ml, 3-neck round bottom flask equipped with a stirrer was charged with 3.80 g (12.1 mmol) 102, 0.5 g (3.7 mmol) AlCl₃, and 150 ml chloroform. A flow of 45 ml/min of anhydrous HCl was bubbles through this solution for 12.5 hours. The reaction mixture was allowed to stir at room temperature for an additional 10 hours. A total of 10 ml dry acetone was added to the reaction mixture to complex with the AlCl₃. Solvent was removed by rotary evaporation, followed by addition of diethyl ether. The resultant salt was filtered out and the solvent was again removed. This impure product (79% pure by GC) was used as is in the following experiment.

MS: 274(M⁺,2.7), 272(2.3), 270(1.2), 261(2.1), 259(4.9), 257(3.5), 255(1.9), 155(19), 136(14), 135(100), 119(32), 117(22), 115(16), 91(23), 89(16), 87(12), 65(15), 63(35).

Synthesis of 2,2,5,6,6-pentamethyl-5-phenyl-6-germa-2,5-disilahexan-3-ylene, 104.

A solution of 80 was prepared by adding 10.3 ml of 1.46M (15.0 mmol) ethereal MeLi to 40 ml of a 0.5 M (20 mmol) THF solution of 79 cooled to -78°C while under argon flow. The solution was allowed to warm to room temperature to assure complete conversion to the lithio-acetylene. An additional 50 ml dry THF was added. Again the reaction mixture was cooled to -78°C at which point a solution of 2.0 g (7.3 mmol)
chlorosilane 103 in 10 ml dry THF was added via syringe over a 15 min. period. Upon warming to room temperature the reaction was quenched with 1 M HCl followed by extraction of the organic portion with ether. The product was washed three times with water and left to dry over MgSO4/Na2SO4. The organic extract was filtered through activated carbon to remove some of the dark brown color. Purification by preparative gas chromatography (200°C isotherm, flow rate = 30, ret time = 11 min., 15’ column) afforded 1.36 g (4.1 mmol) of purified product, a clear colorless liquid, in 57% yield.

1H(C6D6): s 0.163 (9H), s 0.309 (9H), s 0.507 (3H), m 7.143-7.192 (3H), m 7.679-7.711 (2H); 13C(C6D6): -3.501, -3.003, -0.089, 110.399, 119.324, 128.342, 129.460, 134.361, 135.558; 29Si(C6D6): -30.699, -16.083; MS: 336(M+, 13), 334(9), 321(24), 319(18), 317(12), 218(23), 217(100), 159(17), 151(10), 135(35), 73(19); IR(cm⁻¹): 3062, 2970, 2908, 1427, 1255, 1105, 857, 797, 766; calc. for C15H2670GeSi2 332.08161, measured 332.08174.

Flow pyrolysis of 104 to give 1,3,4-trimethyl-1-phenyl-1-silacyclopent-3-ene 105 and (trimethylsilyl)trimethyl-germylacetylene, 106.

A 2 ml dimethylbutadiene solution containing 150 mg 104 was pyrolyzed in a packed quartz flow tube maintained at 530°C with argon flowing at the rate of 60 ml/min. The 104 solution was added via syringe over a 15 minute period as the
pyrolysate was trapped with a dry ice/IPA bath. GC-MS analysis indicated the trapped silylene and the eliminated (trimethylsilyl)trimethylgermylacetylene were the major products. GC analysis showed the trapped silylene to starting material ratio to be approximately 0.8 : 1. The trapped silylene was purified by prep GC (185°C isotherm, flow rate = 28, ret time = 5 min., 15' column) isolating 45 mg (0.49 mmol) of 99. An authentic sample of (trimethylsilyl)-(trimethylgermylacetylene was prepared to compare the MS and IR data with that obtained in this experiment. \[^1H(\text{CDCl}_3)\]: s 0.390 (3H), s 1.530 (2H), s 1.565 (2H), s 1.708 (6H), m 7.310-7.332 (3H), m 7.502-7.534 (2H); \[^{13}C(\text{CDCl}_3)\]: -3.770, 19.259, 25.029, 127.767, 129.021, 130.716, 133.665, 135.815; \[^{29}\text{Si}(\text{CDCl}_3)\]: 11.275; MS: 203 (M+1\(^+\), 19), 202 (M\(^+\), 100), 188 (16), 187 (88), 159 (10), 145 (22), 125 (10), 124 (63), 121 (23), 109 (54), 105 (49), 59 (10), 53 (11); IR (cm\(^{-1}\)): 3061, 2966, 2896, 1955, 1886, 1808, 1644, 1431, 1257, 1171, 1114, 988, 815, 779.

Synthesis of 2,2,5,5-tetramethyl-2-sila-5-germahex-3-vne, 106. A solution of 80 was prepared by adding 7.0 ml of 1.46M (10.2 mmol) ethereal MeLi to 25 ml of a 0.5 M (12.5 mmol) THF solution of 79 cooled to -78°C while under argon flow. The solution was allowed to warm to room temperature to assure complete conversion to the lithio-acetylene. Again the reaction mixture was cooled to -78°C at which point a solution
of 1.55 g (7.8 mmol) Me₃GeBr in 20 ml dry THF was added via syringe over a 15 min. period. Upon warming to room temperature the reaction was quenched with 1M HCl followed by extraction of the organic portion with ether. The product was washed two times with water and left to dry over MgSO₄/Na₂SO₄. Purification by preparative gas chromatography (80°C isotherm, flow rate = 26, ret time = 11 min., 15’ column) afforded 1.32 g (6.2 mmol) of purified product (a white solid), 78% yield.

H(C₆D₆): s 0.171 (9H), s 0.251 (9H); C(C₆D₆): -0.346, 0.117, 112.251, 114.217; Si(C₆D₆): -18.564; MS: 216(M⁺, 2.4), 214(1.6), 203(24), 202(13), 201(100), 200(30), 199(71), 197(50), 97(19), 73(17); IR(cm⁻¹): 2969, 2915, 1414, 1255, 842, 771.

Synthesis of ethynyl(trimethylgermyl)dimethylsilane, 107.

To a stirring solution of 2.0 g (9.5 mmol) 76 in 50 ml THF cooled to 0°C under an argon atmosphere was added 30 ml of a 0.5M (15 mmol) THF solution of ethynylmagnesium chloride over a 15 min. period. Upon warming to room temperature, the reaction mixture was quenched with 1M HCl and the organic portion extracted with diethyl ether. After washing 3 times with demineralized water, the crude product was left to dry over Na₂SO₄/MgSO₄. Approximately 250 mg of a clear colorless liquid was obtained by purification of 20% of the crude product (preparative gas chromatography, 90°C isothermal, 9’ column, 27 ml/min. flow rate, ret. time = 7 min.). The
remainder of the crude product was used as is. This translates into a rough yield of 66%. \( ^1H(CDCl_3) \): s 0.190 (9H), s 0.238 (6H), s 2.458 (1H); \( ^1^3C(CDCl_3) \): -3.188, -2.917, -1.956, -1.934, 111.852, 116.859; \( ^2^9Si(CDCl_3) \): -30.803; MS: 202(M\(^+\), 11), 200(8), 198(6), 187(28), 185(21), 183(15), 119(18), 117(15), 115(13), 104(20), 102(16), 100(12), 89(26), 87(20), 85(15), 83(32), 74(10), 73(100); IR(cm\(^{-1}\)): 3305, 2971, 2908, 2028, 1408, 1319, 1253, 809; calc. for C\(_7\)H\(_{16}\)\(^74\)GeSi 202.02403, measured 202.02459.

**Synthesis of 2,2,3,3,6,6,7,7-octamethyl-2,6-digerma-3,7-disilaoct-4-yne, 109.**

A total of 1.2 ml of 1.7M in THF (2.04 mmol) t-butyl lithium was added to a stirring solution of 0.716 g (3.57 mmol) \( 107 \) in 3 ml dry THF cooled to -78°C under an argon atmosphere. The reaction mixture was allowed to stir for 15 min. at cold conditions and an additional 15 min. near room temperature to ensure complete conversion to the lithio-acetylene. This solution was again cooled to -78°C at which time 0.774 g (3.63 mmol) \( 68 \) was added dropwise. The reaction mixture was then allowed to slowly warm to room temperature at which point the reaction was quenched with 1M HCl. The organic portion was extracted with diethyl ether and dried over Na\(_2\)SO\(_4\). Purification by preparative gas chromatography (180°C isothermal, 9’ column, 27 ml/min. flow
rate, ret. time = 5 min.) yielded 563 mg (1.50 mmol) of a clear colorless liquid, 73% yield. $^1$H(C$_6$D$_6$): s 0.165 (9H), s 0.293 (6H), s 0.334 (9H), s 0.373 (6H); $^{13}$C(C$_6$D$_6$): -3.188, -2.917, -1.956, -1.934, 111.852, 116.859; $^{29}$Si(C$_6$D$_6$): -10.407, -33.044; MS: 380 (1.2), 378 (M$^+$, 1.7), 376 (1.4), 374 (0.7), 365 (6.9), 363 (8.8), 361 (8.0), 262 (13), 260 (46), 258 (34), 256 (24), 171 (15), 169 (15), 155 (32), 119 (11), 97 (16), 89 (14), 87 (10), 73 (100); IR(cm$^{-1}$): 2966, 2907, 2081, 1408, 1253, 838, 801; calc. for C$_{12}$H$_{30}$Ge$_2$Si$_2$: 376.03221, measured 376.03302.

Synthesis of 3,3-bis(trimethylsilyl)-4,4-dimethyl-3-germa-4-silaheptyne, 112.

To a stirring solution of 3.0 g (9.2 mmol) 53 in 40 ml dry THF cooled to -78°C under argon was added 70 ml 0.5M (35 mmol) ethynylmagnesium bromide. Upon addition of the grignard reagent, the reaction mixture was allowed to warm to room temperature. After stirring for 3 hours the reaction was quenched with 1M HCl and the organic portion extracted with ether. Purification by preparative gas chromatography (180°C isotherm, 9' column, 15% SE-30 on Chromosorb W, ret. time = 6 min., flow = 29 ml/min.) yielded 2.16 g of a clear colorless liquid with a melting point near 40-50°C, 72% yield. $^1$H(C$_6$D$_6$): s 0.371 (27H), s 2.140 (1H); $^{13}$C(C$_6$D$_6$): 1.029, 83.701, 94.443; $^{29}$Si(C$_6$D$_6$): -5.281; MS: 303 (M$^+$, 0.9), 244 (25), 242 (16), 240 (11), 229 (19), 227 (13), 216 (5), 155 (7), 146 (25), 145 (14), 144 (18), 142 (10), 131 (25), 73 (100), 59 (10); IR(cm$^{-1}$): 3308,
2958, 2904, 1402, 1257, 842; calc. for C_{11}H_{28}^{70}GeSi_{3} 314.07419, measured 314.07363.

**Synthesis of 3-(trimethylsilyl)-3,4,4-trimethyl-3-germa-3-silapentyne, 113.**

To a stirring solution of 1.7 g (6.4 mmol) 55 in 30 ml dry THF cooled to -78°C under an argon atmosphere was added 20 ml, 0.5M (10 mmol) ethynylmagnesium bromide. The reaction mixture was allowed to warm to room temperature before being quenched with 1M HCl. The organic portion was extracted with diethyl ether, washed with demineralized water and left to dry over Na_{2}SO_{4}. Purification by preparative gas chromatography (140°C isotherm, flow rate = 30, ret time = 4 min., 8' 15% SE-30 on Chromosorb W column) afforded 980 mg (3.79 mmol) (61 % yield) of pure product, a clear colorless liquid. \(^1\)H(C\(_6\)D\(_6\)): s 0.226 (18H), s 0.427 (3H), s 2.125 (1H); \(^13\)C(C\(_6\)D\(_6\)): -8.233, -1.324, 86.434, 93.956; \(^29\)Si(C\(_6\)D\(_6\)): -7.713; MS: 260(M\(^+\), 1.5), 258(1.0), 256(0.8), 245(0.8), 243(0.6), 162(13), 160(9), 153(1.2), 141(1.3), 131(1.1), 89(2.4), 87(18), 73(100); IR(cm\(^{-1}\)): 3306, 2957, 2903, 2014, 1404, 1254, 843, 793; calc. for C\(_7\)H\(_{22}\)^{70}GeSi\(_2\) 256.05031, measured 256.05023.

**Synthesis of 3,3,4,4-tetramethyl-3-germa-4-silapentyne, 114.**

To a stirring solution of 1.40 g (5.5 mmol) 70 in 20 ml dry THF cooled to -78°C under argon was added 30 ml 0.5M (15
mmol) ethynylmagnesium chloride over a 15 minute period. Upon addition of the grignard reagent, the cold bath was removed and the reaction mixture was allowed to warm to room temperature. After 1 hour of stirring at room temperature the reaction mixture was quenched with 1M HCl and the organic portion extracted with diethyl ether. Purification by preparative gas chromatography (90°C isotherm, 9’ column, flow = 29 ml/min., ret. time = 4.5 min.) afforded 780 mg (3.90 mmol) of a clear colorless liquid, 71% yield. $^1$H(C₆D₆): s 0.094 (9H), s 0.316 (6H), s 2.076 (1H); $^{13}$C(C₆D₆): -3.124, -2.048, 89.008, 93.659; $^{29}$Si(C₆D₆): -10.415; MS: 202 (M⁺, 6.4), 200(4.6), 198(3.2), 187(9), 104(27), 102(21), 100(16), 89(17), 87(13), 85(10), 83(11), 74(9), 73(100); IR(cm⁻¹): 3304, 2960, 2909, 2021, 1411, 1302, 1254, 841, 804; calc. for C₇H₁₆₇₀GeSi 198.02643, measured 198.02657.

Synthesis of 1,2-diethynyl-1,1,2,2-tetramethyldisilane, 116.

To a stirring solution of 15.5 g (0.0829 mol) 115 in 100 ml dry THF cooled to -78°C under an argon atmosphere was added 700 ml 0.5M (0.350 mol) ethynylmagnesium chloride over 1 hour. After slowly warming to room temperature, the reaction was quenched with 1M HCl and the organic portion extracted with pentane. Partial removal of the solvent resulted in a 0.4M solution of product in THF. No further purification was attempted. $^1$H(C₆D₆): s 0.269 (12H), s 2.141 (2H); $^{13}$C(C₆D₆): -3.644, 87.134, 96.160; $^{29}$Si(C₆D₆): -36.526; MS: 166(M⁺, 6.8),
165(5.2), 152(18), 151(100), 111(12), 93(12), 83(84), 73(66), 67(13), 55(22), 53(21); IR(cm\(^{-1}\)) : 3303, 2966, 2904, 2027, 1407, 1321, 1256, 838, 803.

Synthesis of 1,1,2,2-tetramethyl-1,2-diphenyldigermane, \textbf{118}.

A 0.69 g (0.1 mol) suspension of pentane-washed, 1 mm dia. lithium chunks in 100 ml THF was prepared. To this was added 11.5 g (0.044 mol) \(\text{64}\) over a 30 min. period. After stirring at room temperature for 36 hours, the reaction was quenched with 1M HCl and the organic portion extracted with pentane. After drying over Na\(_2\)SO\(_4\), purification by distillation (b.p.=105°C, 0.8 mm Hg) yielded 6.0 g (0.017 mol) of product, a clear colorless liquid, 75% yield. \(^1\)H(CDCl\(_3\)): s -0.316 (12H), m7.27-7.31 (6H), m7.39-7.43 (4H); \(^13\)C(CDCl\(_3\)):
-0.985, 127.881, 128.180, 132.896, 143.089; MS: 362(M\(^+\), 5.4), 360(7.1), 358(6.8), 347(5.9), 345(8.2), 243(28), 241(20), 239(15), 183(21), 181(100), 180(26), 179(72), 177(55),151(30), 149(22), 147(16); IR(cm\(^{-1}\)) : 3061, 3014, 2979, 2912, 2816, 1950, 1879, 1807, 1634, 1574, 1486, 1429, 1370, 1301, 1245, 1091, 1048, 1001, 802; calc. for C\(_{16}\)H\(_{22}\)Ge\(_2\) 354.02075, measured 354.02077.

Synthesis of 1,2-dichloro-1,1,2,2-tetramethylldigermane, \textbf{119}.

Anhydrous hydrogen chloride was bubbled through a solution containing 6.0 g (0.017 mol) \textbf{118} in 100 ml chloroform
at a rate of 60 ml/min. for 5 minutes. Approximately 0.1 g (3 mmol) aluminum trichloride was then added to the reaction mixture. The reaction was complete after 1 hour.

Purification by distillation (b.p. = 50°C, 1 mm Hg) afforded 2.5 g (9.1 mmol) of a clear colorless liquid, 54% yield.

\[^{1}H(C_6D_6): \text{s} 0.599 (12H); \text{^13}C(C_6D_6): 3.793; \text{MS:} 278 (M^+, 11), 276(12), 274(9.0), 243(11), 241(14), 239(11), 141(36), 139(88), 138(17), 137(65), 135(39), 121(21), 119(100), 118(24), 117(74), 115(56), 109(23), 107(18), 106(18), 105(13), 104(85), 103(23), 102(67), 100(50), 91(14), 89(67), 88(20), 87(53), 85(38); \text{IR(cm}^{-1}): 2990, 2916, 2807, 1823, 1410, 1245, 842, 801.\]

Synthesis of 3,3,4,4,7,7,8,8-octamethyl-3,4-digerma-7,8-disila-cycloocta-1,5-diyn, 120.

A total of 10 ml, 2M (0.020 mol) of ethylmagnesium chloride was added to 1.7 g (0.010 mol) 116 in 20 ml dry THF cooled to -78°C while under an argon atmosphere. The reaction mixture was allowed to warm to room temperature for 15 min. At that time the mixture was cooled back to -78°C at which point 0.5 g (1.81 mmol) 119 was added via syringe. Upon warming to room temperature, the reaction mixture was quenched with 1M HCl and the organic portion extracted with pentane. After drying over Na$_2$SO$_4$/MgSO$_4$, purification by preparative gas chromatography (180°C isothermal, 15' column, flow rate = 29 ml/min., ret. time = 5 min.) gave 250 mg (0.677 mmol) of a
colorless crystalline solid, 37% yield. $^1$H(C$_6$D$_6$): s 0.215 (12H), s 0.331 (12H); $^{13}$C(C$_6$D$_6$): -2.590, -2.219, 117.565, 119.580; $^{29}$Si(C$_6$D$_6$): -35.077; MS: 374(12), 373(12), 372(M$^+$, 36), 371(22), 370(47), 369(20), 368(42), 367(11), 366(20), 355(100), 354(37), 353(91), 352(22), 351(44), 349(15), 255(17), 254(13), 253(61), 252(21), 251(46), 249(31), 245(15), 243(22), 241(21), 239(12), 229(14), 227(11), 179(11), 171(22), 169(24), 167(19), 165(18), 155(23), 141(15), 139(11), 121(11), 119(31), 117(25), 115(24), 113(11), 97(54), 89(16), 87(13), 83(37), 73(93); IR(cm$^{-1}$): 2964, 2911, 2074, 1410, 1251, 812; calc. for C$_{12}$H$_{24}$Si$_2$Ge$_2$Si$_2$ 369.98526, measured 369.98501.

Synthesis of 4,4-dimethyl-3,3-bis(trimethylsilyl)-3,4-disilapentynne, 122.

To a stirring solution of 3 g (10.6 mmol) 121 in 100 ml dry THF, cooled to -78°C while under argon, was added 23.3 ml (11.7 mmol) ethynyl magnesium bromide over a 10 min. period. After 10 minutes the cold bath was removed and the reaction mixture was allowed to warm to room temperature. The reaction was quenched with 1 M HCl and the organic portion was extracted with ether. The product was washed two times with demineralized water and left to dry over MgSO$_4$/Na$_2$SO$_4$. Purification was accomplished by prep GC (180°C isotherm, flow rate = 29, ret time = 7 min., 15' column) yielding 2.19 g (8.05 mmol) of a white crystalline solid, 76% yield. $^1$H(C$_6$D$_6$):
s 0.273 (27H), s 2.107 (1H); $^{13}$C(C$_6$D$_6$): 0.367, 83.459, 96.865;
MS: 272(M$^+$, 2.5), 259(10), 258(17), 257(55), 199(14),
198(15), 183(34), 174(10), 169(12), 159(14), 129(11), 116(18),
73(100); IR(cm$^{-1}$): 3310, 2958, 2904, 1402, 1255, 843.

Synthesis of 2,2,6,6-tetramethyl-5,5-bis(trimethylsilyl)-2-
germa-5,6-disilahept-3-yne, 124.

A total of 1.2 ml of 1.46 M MeLi (1.71 mmol) was added
to a stirring solution of 0.500 g (1.84 mmol) 122 in 30 ml dry
THF while under an argon atmosphere and cooled to -78°C. The
reactant mixture was allowed to stir for 15 minutes at which
time 220 ul (1.85 mmol) Me$_3$GeCl in 10 ml THF was syringed in.
After stirring an additional 15 minutes at -78°C, the cold
bath was removed and the reaction flask and contents were
allowed to slowly warm to room temperature. The reaction was
quenched with 1 M HCl and ether used to extract the product.
Solvent was removed by rotory evaporation and final
purification was accomplished via prep gas chromatography
(200°C isotherm, flow rate = 29, ret. time = 9 min.,
15',10%Carbowax W on Chromosorb W packed column) to give 0.33
g (0.849 mmol) of a clear colorless liquid, 61% yield.

$^1$H(C$_6$D$_6$): s 0.263 (9H), s 0.305 (27H); $^{13}$C(C$_6$D$_6$): -0.039,
0.395, 105.434, 118.141; $^{29}$Si(C$_6$D$_6$): -100.750, -11.984; MS:
390(M$^+$, 5.5), 388(3.8), 375(7), 373(5), 271(5), 229(10),
220(30), 219(10), 218(22), 216(16), 197(12), 155(12), 146(24),
145(14), 144(17), 142(13), 131(19), 73(100); IR(cm$^{-1}$): 2958,
Thermal isomerization of 124 to give 2,2,6,6-tetramethyl-5,5-
bis(trimethylsilyl)-6-germa-2,5-disilahept-3-vne 125.

A 2 ml pentane solution containing 135 mg (0.347 mmol) 124 was pyrolyzed in a packed quartz flow tube maintained at 400°C with argon flowing at the rate of 60 ml/min. The 124 solution was added via syringe over a 15 minute period as the pyrolysate was trapped with a dry ice/IPA bath. GC and GC-MS analyses both were consistent with the near quantitative conversion of 124 to its isomer 125. However, only 30 mg (0.077 mmol) of purified 125, a clear colorless liquid, was recovered from preparative gas chromatography purification (200°C isotherm, flow rate = 29 ml/min., ret. time = 9 min., 15' column) suggesting some decomposition did occur, 22% yield. $^1$H(C$_6$D$_6$): s 0.146 (9H), s 0.284 (18H), s 0.435 (9H); $^{13}$C(C$_6$D$_6$): -0.203, 0.174, 0.238, 108.055, 118.818; $^{29}$Si(C$_6$D$_6$): -89.258, -13.701, -5.300; MS: 390(M$^+$, 7), 388(5), 375(9), 373(6), 271(8), 241(10), 229(14), 227(12), 222(13), 220(46), 219(14), 218(32), 216(24), 213(12), 203(12), 197(14), 183(12), 155(15), 146(32), 145(18), 144(22), 142(17), 131(24), 129(10), 73(100); IR( cm$^{-1}$): 2963, 2904, 2079, 1404, 1253, 845; calc. for C$_{14}$H$_{36}$GeSi$_4$ 386.11372, measured 386.11403.
Synthesis of 2,2,5,6,6-pentamethyl-5-(trimethylsilyl)-2-germa-5,6-disilahept-3-vne, 134.

To a stirring solution of 1.3 g (6.1 mmol) 132 in 30 ml dry THF cooled to -78°C and under argon was added 3.4 ml of a 1.46 M (5 mmol) ethereal solution of MeLi via syringe. Upon addition of MeLi the reaction mixture was allowed to warm to room temperature with the aid of a water bath to assure complete formation of lithioacetylene. Again the reaction mixture was cooled to -78°C at which point 0.94 g (8 mmol) Me₃GeCl was syringed in. Again the dry ice/IPA bath was removed and the reaction pot and contents were allowed to warm to room temperature. Acid workup (1 M HCl) and extraction with ether followed by purification via prep GC (185°C isotherm, ret. time = 5.2 min., flow = 29, 15' column) afforded 1.00 g (3.02 mmol) of a clear, colorless, liquid product, 63 % yield. 

\[ ^1H(C_6D_6): \text{s }0.222 \text{ (18H), s }0.251 \text{ (9H), }0.272 \text{ (3H)}; ^13C(C_6D_6): -7.661, -1.421, -0.104, 108.824, 118.006; ^29Si(C_6D_6): -59.806, -10.532; \text{ MS: } 332 \text{ (M+,4.5), }330(3), 317(8), 315(5), 229(16), 227(12), 213(39), 162(33), 160(24), 158(18), 155(21), 97(9), 73(100); \text{ IR(cm}^{-1}): 2959, 2903, 1411, 1251, 840, 788; \text{ calc. for } C_{12}H_{30}^{74}GeSi_3 \text{ 332.08744, measured 332.08700.} \]

Thermal isomerization of 134 to form 2,2,5,6,6-pentamethyl-5-(trimethylsilyl)-6-germa-2,5-disilahept-3-vne, 135.

A 2 ml pentane solution containing 361 mg (1.09 mmol)
was pyrolyzed in a packed quartz flow tube maintained at 390°C with argon flowing at the rate of 60 ml/min. The solution was added via syringe over a 15 minute period as the pyrolysate was trapped with a dry ice/IPA bath. GC analysis showed the isomerization to be complete and that partial decomposition had occurred by the presence of a small amount of bis(trimethylsilyl)acetylene. Purification by preparative gas chromatography (185°C isotherm, flow rate = 28, ret time = 5 min., 15' column) yielded 130 mg (0.393 mmol) of a clear colorless liquid, for a recovery yield of 36%. \(^1H(C_6D_6):\)

s 0.142 (9H), s 0.210 (9H), s 0.300 (3H), s 0.365 (9H);

\(^{13}C(C_6D_6):\)

-7.284, -2.134, -1.599, 0.067, 110.862, 118.661;

\(^{29}Si(C_6D_6):\)

-53.543, -14.069, -9.697; MS: 332 (M^+, 8), 330 (6), 317 (13), 315 (9), 229 (19), 227 (16), 225 (9), 214 (11), 213 (44), 162 (38), 161 (11), 160 (28), 158 (21), 155 (19), 73 (100);

IR (cm\(^{-1}\)): 2965, 2905, 2087, 1409, 1253, 847, 791, 765; calc. for \(C_{12}H_{30}GeSi_3\) 328.08984, measured 328.08925.

**Synthesis of 2,2,5,5,6,6-hexamethyl-2-germa-5,6-disilahept-3-vne, 137.**

To a stirring solution of 0.433 g (2.78 mmol) 95 in 30 ml dry THF cooled to -78°C and under argon was added 1.8 ml of a 1.46 M (5 mmol) ethereal solution of MeLi via syringe. Upon the addition of MeLi the reaction mixture was allowed to warm to room temperature with the aid of a water bath to assure
complete formation of lithio-acetylene. Again the reaction mixture was cooled to -78°C at which point 0.46 g (3 mmol) Me₃GeCl was syringed in. The dry ice/IPA bath was removed and the reactants were allowed to warm to room temperature. After stirring at room temperature for 2 hours the reaction was quenched by adding it to 100 ml 1M HCl. The organic portion was extracted with ether, washed with demineralized water, dried over MgSO₄/Na₂SO₄ and purified by preparative gas chromatography (160°C isotherm, ret. time = 4 min., flow = 28, 15' column). A total of 260 mg (0.954 mmol) of purified product was isolated as a clear colorless liquid, 36% yield.

\[ ^1H(C_6D_6): \text{s 0.171 (9H), s 0.247 (6H), s 0.256 (9H); } ^{13}C(C_6D_6): -2.696, -2.518, -0.232, 111.154, 116.639; ^29Si(C_6D_6): -35.562, -16.845; \text{MS: 274 (M^+,18), 272 (12), 261 (19), 260 (14), 259 (69), 258 (24), 257 (50), 255 (35), 171 (23), 169 (21), 167 (12), 156 (18), 155 (100), 119 (11), 97 (18), 89 (12), 73 (73); IR (cm}^{-1}): 2961, 2907, 1409, 1252, 836, 806; \text{calculated for } C_{10}H_{24}^{70}GeSi_2 270.06596, \text{measured 270.06598.}

**Synthesis of 2,2,5,5,6,6-hexamethyl-6-germa-2,5-disilahept-3-ylene, \textit{138}.**

To a stirring solution of 30 ml (0.5M), (15 mmol) \textit{79} in THF cooled to -78°C and under an argon atmosphere was added 5 ml of 3M MeLi (15 mmol). This solution was allowed to warm to room temperature as CH₄ was evolved. Again the solution was cooled to -78°C at which point 1.5 g (7.1 mmol) \textit{76} in 10 ml
THF was added. The reaction mixture was allowed to warm to room temperature, quenched with 1M HCl, extracted with diethyl ether and left to dry over Na$_2$SO$_4$/MgSO$_4$. Purification by preparative gas chromatography (130°C isotherm, flow rate = 28, ret time = 7 min., 15’ column) afforded 1.257 g, 65% yield. $^1$H(C$_6$D$_6$): s 0.142 (9H), s 0.250 (6H), s 0.301 (9H); $^{13}$C(C$_6$D$_6$): -3.337, -2.411, -0.118, 112.507, 117.116; $^{29}$Si(C$_6$D$_6$): -32.055, -19.012; MS: 274 (M$^+$, 30), 273 (11), 272 (21), 270 (15), 261 (23), 260 (18), 259 (92), 258 (29), 257 (66), 255 (46), 171 (30), 169 (27), 167 (15), 156 (17), 155 (100), 97 (17), 89 (16), 87 (12), 85 (11), 73 (77); IR (cm$^{-1}$): 2968, 2908, 1409, 1255, 844, 808; calc. for C$_{10}$H$_{24}$ GeSi$_2$ 270.06596, measured 270.06549.

Synthesis of ethynyl-undecamethylhexasilacyclohexane, 139.

The crude chlorosilane 147 (2.6 mmol) was dissolved in 50 ml THF freshly distilled from LiAlH$_4$ and cooled to -78°C. To this was added 19 ml of a 0.5 M (9.5 mmol) THF solution of ethynylmagnesium bromide. The reaction mixture was allowed to slowly warm to room temperature. The reaction was quenched with 1M HCl, washed five times with demineralized water and the organic portion extracted with diethyl ether. A total of 0.82 g (2.29 mmol) crude product was recovered after solvent removal, 95% yield from cyclic-6. $^1$H(C$_6$D$_6$): s 0.187 (6H), s 0.190 (3H), s 0.234 (3H), s 0.238 (6H), s 0.305 (6H), s 0.363
(3H), s 0.400 (6H), s 2.229 (1H); $^{13}$C(C$_6$D$_6$, quantitative): -7.205 (1C), -6.087 (2C), -6.030 (4C), -5.880 (2C), -5.680 (2C), 86.892 (1C), 97.919 (1C); $^{29}$Si(C$_6$D$_6$): -58.339, -41.709, -41.316, -40.972; MS: 360(9), 359(14), 358(M$^+$, 31), 345(19), 344(19), 343(71), 300(15), 299(39), 287(14), 286(22), 285(61), 283(19), 271(13), 270(18), 269(55), 267(16), 241(25), 227(27), 157(12), 129(12), 73(100), 59(18); IR(cm$^{-1}$): 3306, 2956, 2897, 2018, 1406, 1297, 1251, 802.

**Synthesis of chloro-undecamethylhexasilacyclohexane, 147.**

A stirring solution of 0.92 g (2.6 mmol) cyclic-6, 146, in 100 ml CHCl$_3$ was cooled to 0°C while under an argon atmosphere. To this was added 5.2 ml 1M (5.2 mmol) SbCl$_5$ in CH$_2$Cl$_2$. The reaction mixture was allowed to stir for 3 hrs. as it slowly warmed to room temperature. The solvent was removed via vacuum line leaving behind a colored solid. The resultant solid was extracted with pentane leaving behind a dark brown solid. The pentane solution was stripped of solvent leaving behind a white solid. No further purification was attempted. MS: 371(13), 370(36), 369(25), 368(M$^+$, 60), 295(15), 262(12), 261(20), 260(58), 215(26), 202(19), 201(45), 199(17), 187(22), 186(30), 185(13), 171(12), 157(22), 143(11), 125(10), 113(10), 99(11), 73(100), 59(19); IR(cm$^{-1}$): 2957, 2897, 1406, 1252, 804.
Synthesis of [(trimethylgermyl)ethylvinyl]undecamethylhexasilacyclohexane, 149.

Compound 139, 0.3 g (0.84 mmol), was dissolved in 40 ml THF freshly distilled from LiAlH₄ and cooled to -78°C. To this was added 2 ml of 3M (6 mmol) methylmagnesium bromide over a 20 min. period. After stirring at room temperature for 8 hours, 0.6 g (2.4 mmol) Me₃GeBr was added to the reaction mixture upon being cooled to -78°C. After warming to room temperature, the reaction was quenched with 1M HCl and the organic portion extracted with pentane. The crude product was successfully purified using LC employing silica gel and hexanes. A total of 230 mg (0.48 mmol) of product was obtained, 58% yield. $^1$H(C₆D₆): s 0.209 (3H), s 0.220 (6H), s 0.231 (6H), s 0.272 (3H), s 0.284 (9H), s 0.376 (6H), s 0.391 (3H), s 0.441 (6H); $^{13}$C(C₆D₆): -7.255, -6.174, -5.781, -5.688, -5.617, -5.280, -0.182, 30.434, 109.373, 125.806; $^{29}$Si(C₆D₆): -60.475, -41.709, -41.340, -41.046; MS: 476(M⁺, 7.6), 359(19), 358(28), 357(68), 306(10), 301(10), 300(14), 299(42), 283(12), 241(23), 227(11), 73(100); IR(cm⁻¹): 2955, 2897, 1865, 1407, 1250, 836, 803.

Flow pyrolysis of 149 to give 3-(trimethylgermyl)undecamethylhexasilacyclooctyne, 150.

A solution containing 100 mg (0.211 mmol) 149 in 2 ml toluene was pyrolyzed in a flow pyrolysis apparatus heated to
360°C with a 45 ml/min. flow rate of argon. GC analysis showed a 57% conversion to the desired endocyclic acetylene along with 12% starting material. In addition, there was 22% pentasilacycloheptyne. The product was purified by preparative gas chromatography. $^1$H(C$_6$D$_6$): s 0.212 (6H), s 0.217 (3H), s 0.220 (3H), s 0.250 (3H), s 0.300 (3H), s 0.304 (3H), s 0.325 (6H), s 0.337 (3H), s 0.347 (3H), s 0.360 (9H); $^{13}$C(C$_6$D$_6$): -6.490, -5.823, -5.078, -4.698, -4.585, -4.431, -4.241, -3.873, -2.752, -2.683, -1.793, 1.367, 116.020, 119.779; $^{29}$Si(C$_6$D$_6$): -53.799, -35.695, -35.081, -35.032, -31.716, -30.439; MS: 476 (M$^+$, 18), 474(13), 359(28), 358(40), 357(100), 306(22), 304(14), 302(15), 301(14), 300(21), 299(60), 297(11), 242(11), 241(33), 232(13), 231(13), 230(12), 229(15), 228(12), 227(16), 217(12), 197(11), 183(12), 171(12), 157(10), 155(11), 141(11), 129(12), 73(93); IR(cm$^{-1}$): 2957, 2901, 1407, 1251, 799.

Synthesis of butoxy(trimethylgermyl)dimethylsilane, 151, and 1,3-(trimethylgermyl)-1,1,3,3-tetramethyldisiloxane, 152.

To a stirring solution of 0.5 g (0.02 mmol) 76 in carbon tetrachloride was added 0.8 ml of a 1:1 molar mixture of n-butanol and pyridine (5.1 mmol of each). After stirring under an argon atmosphere for 30 min. The resultant solution was filtered to remove the salt formed. Purification by preparative gas chromatography (120°C isothermal, 9' column, 27 ml/min. flow rate, ret. time = 6 min.) yielded 350 mg (1.41
mmol) of a clear colorless liquid. GC showed an 85-90% conversion. \(^1\)H(C\(_6\)D\(_6\)): \(s\) 0.269 (6H), \(s\) 0.282 (9H), hextet 1.28, 1.31, 1.33, 1.35, 1.37, 1.40, \(J = 7.2\) Hz (2H), pentet 1.44, 1.46, 1.48, 1.51, 1.53, \(J = 7\) Hz (2H), \(t\) 3.504, 3.526, 3.546, \(J = 6.3\) Hz (2H), \(t\) 4.817, 4.763, 4.730, \(J = 7.2\) Hz (3H); \(^1\)\(^3\)C(C\(_6\)D\(_6\)): -2.582, -0.004, 14.015, 19.357, 35.242, 63.564; \(^2^9\)Si(C\(_6\)D\(_6\)): 18.177; MS: 250 (M\(^+\), 1.1), 248 (0.8), 235 (7.0), 193 (8.0), 179 (7.0), 131 (60), 89 (22), 75 (100), 73 (21), 59 (9.0); IR(cm\(^{-1}\)): 2966, 2908, 1386, 1252, 1095, 1043, 979, 886, 808; calc. for C\(_9\)H\(_{24}\)O\(_7\)GeSi 246.08394, measured 246.08366.

In addition to the desired product, there was an appreciable amount of the disiloxane 152 present in the starting material. This material was undoubtedly formed due to partial hydrolysis of chlorosilane 76. This product was purified at the same time as 133. \(^1\)H(C\(_6\)D\(_6\)): \(s\) 0.252 (12H), \(s\) 0.259 (18H); \(^1\)\(^3\)C(C\(_6\)D\(_6\)): -3.102, 2.788; \(^2^9\)Si(C\(_6\)D\(_6\)): 9.997; MS: 370 (M\(^+\), 0.8), 368 (1.1), 366 (1.0), 355 (2.8), 353 (3.6), 351 (3.3), 251 (18), 249 (13), 247 (9.0), 148 (16), 147 (100), 73 (34); IR(cm\(^{-1}\)): 2964, 2906, 1582, 1405, 1255, 1047, 818, 787; calc. for C\(_{10}\)H\(_{30}\)O\(_{7}\)Ge\(_2\)Si\(_2\) 368.02712, measured 368.02800.

**Synthesis of allyltrimethylgermane, 156.**

To a stirring solution of 1.31 g (8.56 mmol) trimethylchlorogermande in 200 ml anhydrous diethyl ether
cooled to -78°C was added 4.8 ml 2M (9.42 mmol) allyl magnesium chloride in THF. Upon warming to room temperature the reaction mixture was quenched with 10% HCl and the organic portion extracted with diethyl ether. Purification by preparative gas chromatography (60°C isotherm, flow=30 ml/min., 15' column) yielded 0.839 g of pure product, 62% yield. \(^1\)H(CDCl\(_3\)): s 0.102 (9H), d 1.592, 1.620 J=8.4 Hz (2H), trip. 4.730, 4.763, 4.817 (2H), mult. 5.711, 5.739, 5.746, 5.768, 5.774, 5.796, 5.801, 5.824, 5.830, 5.857 J= 8.7, 1.8 Hz, \(^13\)C(CDCl\(_3\)): -2.737, 23.989, 111.747, 136.087; MS: 160(M\(^+\), 2.2), 158(1.6), 145(12), 143(9), 121(20), 119(100), 118(23), 117(75), 115(56), 105(17), 104(11), 103(16), 101(13), 91(18), 89(49), 88(13), 87(38), 85(23), 75(10); IR(cm\(^{-1}\)): 3083, 2979, 2911, 1801, 1629, 1408, 1303, 1244, 1191, 1147, 1039, 989, 898, 813.

Flow pyrolysis of 156 in the presence of DMB to give 1,1,3,4-tetramethylgermacyclopent-3-ene, 29.

A 3 ml 2,3-dimethyl-1,3-butadiene solution containing 150 mg allyltrimethylgermane, 156, was pyrolyzed in a packed quartz flow tube maintained at 550°C with argon flowing at the rate of 60 ml/min. The butadiene solution was added via syringe over a 15 minute period as the pyrolysate was trapped with a dry ice/IPA bath. GC-IR-MS analysis showed the major products to be Me\(_3\)GeH and the trapped dimethylgermylene, 1,1,3,4-tetramethylgermacyclopent-3-ene, 29. The trapped
germylene was purified by preparative gas chromatography (90°C isotherm, flow rate = 29, ret. time = 4.5 min., 9′ column) yielding 57 mg of pure product. $^1$H(CDCl$_3$): s 0.255 (6H), s 1.478 (4H), s 1.669 (6H); $^{13}$C(CDCl$_3$): -2.267, 19.423, 26.895, 130.844; $^{29}$Si(CDCl$_3$): -10.415; MS: 186(M$^+$, 40), 185 (11), 184(31), 182(22), 173(16), 171(79), 170(21), 169(60), 167(44), 143(8), 129(13), 127(11), 106(12), 104(57), 103(20), 102(42), 101(11), 100(34), 91(21), 89(100), 88(26), 87(77), 85(58); IR(cm$^{-1}$): 2980, 2905, 1827, 1692, 1642, 1447, 1387, 1245, 1168, 1112, 974, 831, 796; calc. for C$_5$H$_{14}$Ge 182.04950, measured 182.04947.

Synthesis of bis(dimethylphenylgermyl)dimethyldimethylsilane, 159.

To a stirring suspension of 3.85 g (0.558 mol) 1 mm dia. lithium chunks in 30 ml dry THF was added 20.61 g (0.0794 mol) over a 30 min. period. An immediate exothermic reaction occurred as the solution turned a dark green color. Periodically a small aliquot of the solution was quenched with trimethylchlorosilane to check the progress of the anion formation. After 2 days of stirring, the anion formation was complete. At this time, a solution containing 3.86 g (0.030 mol) dimethyldichlorosilane in 100 mol dry THF was cooled to -78°C under an argon atmosphere. The anion solution was slowly added to the chlorosilane solution over a 30 min. period. Upon warming to room temperature, the reaction was
quenched with 1M HCl and the organic portion was extracted with diethyl ether. After drying over Na₂SO₄/MgSO₄, the solvent was removed by rotary evaporation. The crude product was not further purified. Based on germyl anion used the yield was approximately 86%. ^H(CDCl₃): s 0.286 (6H), s 0.443 (12H), m 7.291-7.353 (6H), m 7.365-7.414 (4H); ^13C(CDCl₃): -5.016, -3.741, 127.746, 127.888, 133.494, 141.921; ^29Si(CDCl₃): -31.417; MS: 420 (M⁺, 1.0), 418 (1.3), 416 (1.2), 405 (2.4), 403 (3.2), 401 (3.0), 301 (6.5), 299 (4.8), 239 (22), 237 (16), 235 (12), 197 (10), 181 (13), 151 (11), 136 (14), 135 (100), 73 (24); IR (cm⁻¹): 3060, 2976, 2908, 2811, 1950, 1879, 1805, 1632, 1580, 1484, 1427, 1302, 1245, 1086, 1026, 999, 832, 786; calc. for C₁₈H₂₈⁷⁷Ge₂Si 412.04463, measured 412.04478.

Synthesis of bis(chlorodimethylgermyl)dimethylsilane, 160.

Anhydrous hydrogen chloride was bubbled through a solution containing 8.53 g (20.44 mmol) 159 in 100 ml chloroform at a rate of 30 ml/min. for 5 minutes. Approximately 0.1 g (3 mmol) aluminum trichloride was then added to the reaction mixture. The reaction was complete after 2 hours. Purification by distillation (b.p. = 87°C, 1 mm Hg) afforded 4.5 g (13.5 mmol) of a clear colorless liquid, 66% yield. ^H(CDCl₃): s 0.453 (6H), s 0.778 (12H); ^13C(CDCl₃): -6.007, 4.814; ^29Si(CDCl₃): -19.970; MS: 321 (M⁻15⁺, 0.4), 319 (0.5), 317 (0.4), 197 (17), 119 (13), 117 (10), 93 (10), 89 (18),
Synthesis of 1,3-bis(trimethylsilyl)propyne, 163.

A flask was filled with 4.45 g (0.190 mol) magnesium turnings and 100 ml diethyl ether freshly distilled from lithium aluminum hydride. To this stirring solution was added 0.2 g mercury (II) chloride. After stirring at room temperature for 45 min., the flask and contents were cooled to 0°C as 21.5 g (0.181 mol) of propargyl bromide was added dropwise over 2 hours. The solution was allowed to stir at 0°C for an additional 45 min. at which time the temperature was decreased to -10°C and 72 ml of 2.5M (0.18 mol) n-butyl lithium was added. The mixture was allowed to slowly warm to room temperature where it remained stirring for 2 hours. The mixture was cooled to -10°C again and 46.9 ml (0.37 mol) trimethylchlorosilane was added dropwise. The cold bath was removed and the reaction mixture was allowed to stir overnight. The next morning the reaction was quenched with 1M HCl and the organic portion extracted with diethyl ether. After drying over Na₂SO₄/MgSO₄, purification by distillation (b.p. = 95°C, 50 mm Hg) afforded 31.6 g (0.172 mol) of a clear, slightly pink liquid, 95% yield. ¹H(C₆D₆): s 0.017 (9H), s 0.204 (9H), s 1.397 (2H); ¹³C(C₆D₆): -2.255, 0.523, 8.822, 83.309, 105.954; ²⁹Si(C₆D₆): -19.823, 2.579; MS:
Synthesis of 1,3-bis(trimethylsilyl)-4,4,5,5,6,6-hexamethyl-4,6-digerma-5-silacyclohexa-1,2-diene, 165.

A total of 0.5 g (2.7 mmol) 163 was dissolved with 20 ml dry ether. The mixture was cooled to -78°C at which point 2.47 ml, 2.5M (6.2 mmol) n-butyl lithium was added. The reaction mixture was allowed to warm to room temperature and remain stirring for 3 hours. The mixture was again cooled to -78°C as a 20 ml diethyl ether solution containing 0.902 g (2.7 mmol) 160 was added. The cold bath was removed. Upon warming to room temperature and stirring overnight, the reaction was quenched with 1M HCl and the organic portion extracted with diethyl ether. Purification by preparative gas chromatography (200°C isothermal, 9’ glass column, flow rate = 29 ml/min., ret. time = 15 min.) afforded 180 mg (0.404 mmol) of a clear colorless liquid, 15% yield. $^1$H(C$_6$D$_6$): s 0.198 (18H), s 0.210 (6H), s 0.473 (6H), s 0.493 (6H); $^{13}$C(C$_6$D$_6$): -5.061, -1.122, -0.901, 0.894; $^{29}$Si(C$_6$D$_6$): -35.470, -6.730; MS: 448(M+, 3.6), 447(2.6), 446(4.7), 444(4.1), 331(24), 330(22), 329(79), 328(30), 327(57), 326(11), 325(38), 241(10), 97(10), 73(100); IR(cm$^{-1}$): 2958, 2903, 1842, 1406, 1253, 870, 842; calc. for C$_{15}$H$_{36}^{72.74}$Ge$_2$Si$_3$ 446.05629, measured 446.04058.


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