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Gas Phase Thermochemistry of Organogermanium Compounds

by

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Gas phase thermochemistry of
organogermanium compounds

John Paul Engel

Under the direction of Thomas J. Barton
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Iowa State University

A variety of silyl- and alkyl- germylene precursors have been synthesized and subsequently pyrolyzed in the gas phase. Arrhenius parameters were obtained employing a pulsed-stirred flow reactor for these unimolecular decompositions. These precursors are divided into two major categories by mechanism of germylene extrusion: α -elimination precursors and germylacetylenes.

The extrusion of germylenes from germylacetylene precursors is of primary interest. A mechanism is proposed employing a germacyclopropene intermediate. Evidence supporting this mechanism is presented.

In the process of exploring germylacetylenes as germylene precursors, an apparent dyatropic rearrangement between germanium and silicon was observed. This rearrangement was subsequently explored.

Gas phase thermochemistry of
organogermanium compounds

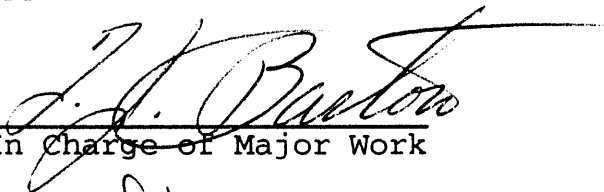
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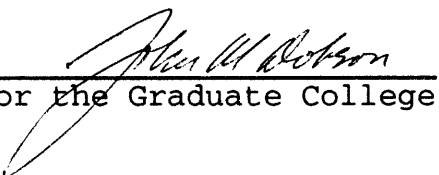
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Ames, Iowa

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.¹ This apparent neglect is due in part to the prohibitive cost of organogermanium compounds and their limited industrial applications. It is little wonder then that the chemistry of divalent germanium compounds (germylenes) has been only briefly explored as compared to that of its counterparts carbenes² and silylenes.³

Even more limited are examples of free germylene formation in the gas phase.^{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 germacyclopropene 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

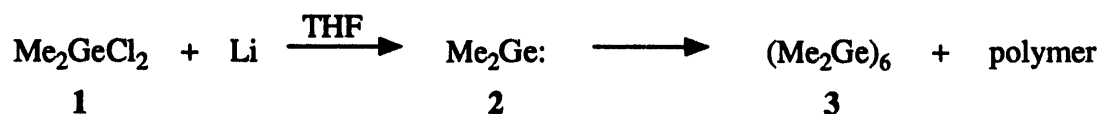
To fully understand the magnitude of the research presented in this dissertation, one must first take a look at the history of divalent germanium chemistry. Early germylene chemistry centered on the dihalogermylenes.⁴ Since these compounds can be isolated and therefore easily characterized, a great deal of attention was directed toward their formation and subsequent reactions. Early studies reporting germylene formation are, however questionable; often limited by the characterization techniques available at the time. This review focusses on alkyl- and aryl-germylene chemistry reported over the past decade with special attention paid to the limited examples of germylenes formed thermally, while in the gas phase.

Methods of Germylene Generation

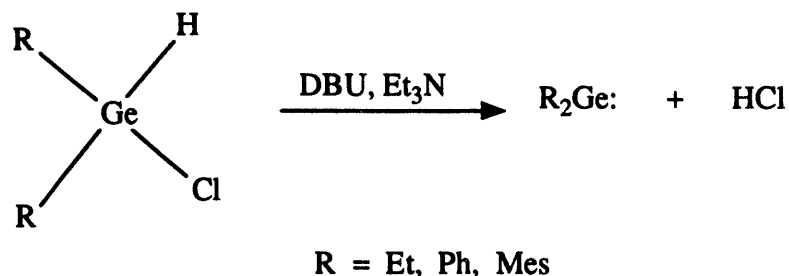
Reduction of Organogermanes

The earliest examples of germylene formation are reductions of organogermanes. The reduction of dihalodiorganogermanes with metals was one method used to produce diorganogermylenes.⁵⁻¹⁴ For example the reduction of dimethyldichlorogermane with lithium in THF gave dodecamethylcyclohexagermane, **3**, and poly(dimethylgermane).

Dimethylgermylene is believed to be an intermediate in this reaction.

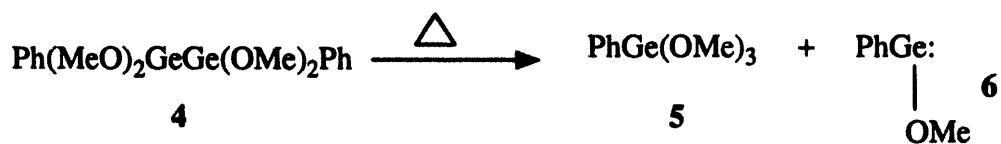


Diethyl-,⁷ dibutyl-,⁸ and diphenyl-⁹⁻¹³ germylene were also reported to be produced in this manner. Lei and Gaspar¹⁵ modified this procedure to sonochemically produce germacyclopent-3-enes. Riviere et al. reported using a strong base such as DBU to dehydrohalogenate organogermanes thus producing germylenes.¹⁶ This procedure was further extended for a number of nucleophilic bases such as triethylamine and pyridine.^{17,18}

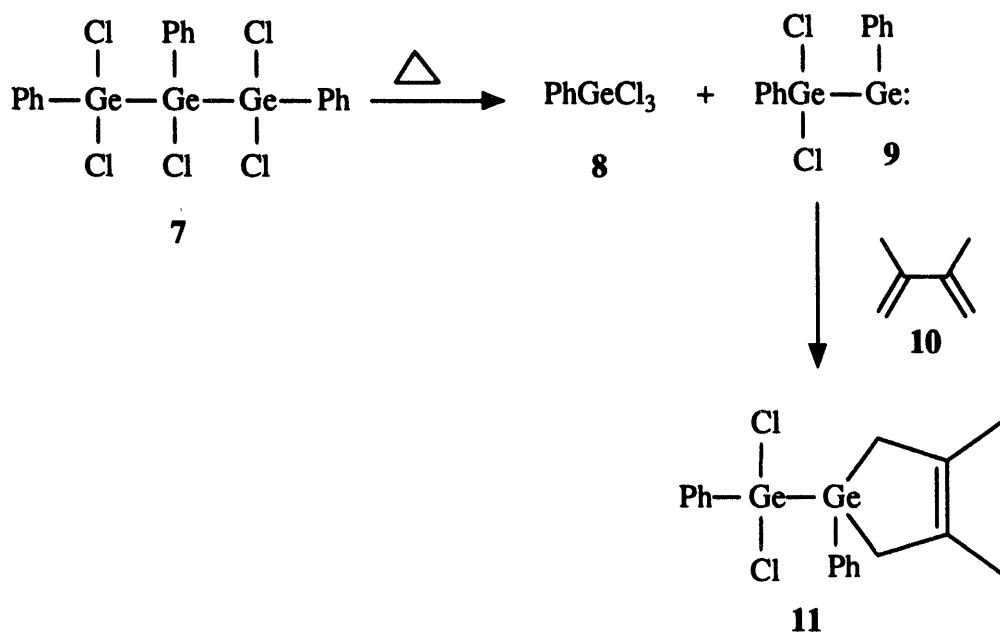


Germylene Formation via Alpha-eliminations

Following the lead of silicon chemistry,³ alpha-elimination of alcohols from hydrido-alkoxygermanes is another early method used to produce germylenes.^{16,19-23} Riviere and Satge²⁰ reported several examples of this type of elimination.

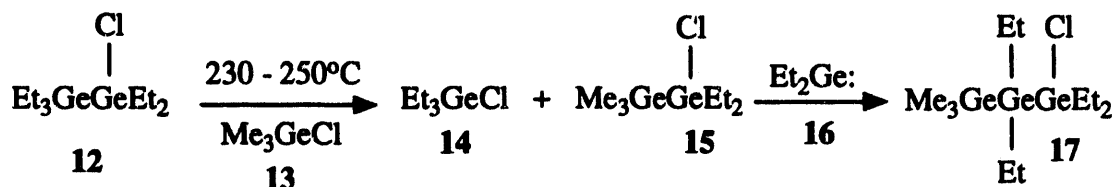


Again paralleling silicon chemistry,³ the alpha-elimination of halogermanes (silanes) is another effective means of producing germylenes.^{4,16,24-27} Satge et al.¹⁶ reported the thermal formation of germyl-germylene **9** and its subsequent reaction with a trapping agent, 2,3-dimethyl-1,3-butadiene, **10**, to form germacyclopent-3-ene **11**.

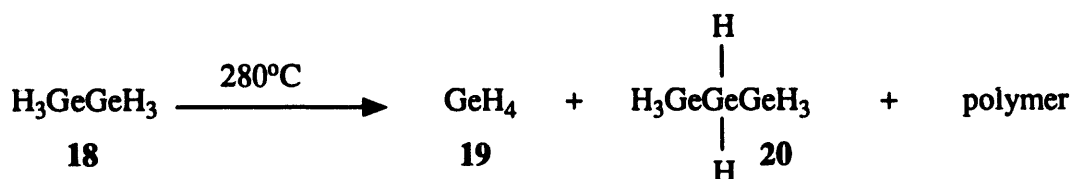


In a more detailed study, Bulten and Noltes²⁶ studied the thermal decomposition of chloropentaethyldigermene, **12**, at 230-250°C. Their kinetic study showed this decomposition to be unimolecular. This conclusion was supported by the formation of mixed methyl- and ethyl- germanes when the

pyrolysis was conducted in the presence of trimethylchlorogermane.

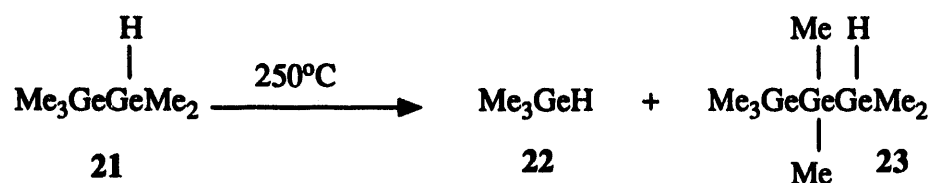


The thermal alpha-elimination of hydridodigermanes has also been shown to be an effective germylene generator.^{16,28,29} After observing the thermal formation of germylene upon pyrolysis of digermane and the subsequent formation of trigermane,¹⁶ Sefcik and Ring studied the relative rates of germylene and silylene insertion into various hydrido-germanes and silanes.³⁰ Surprisingly they were not able to trap the germylene formed with 1,3-butadiene.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.

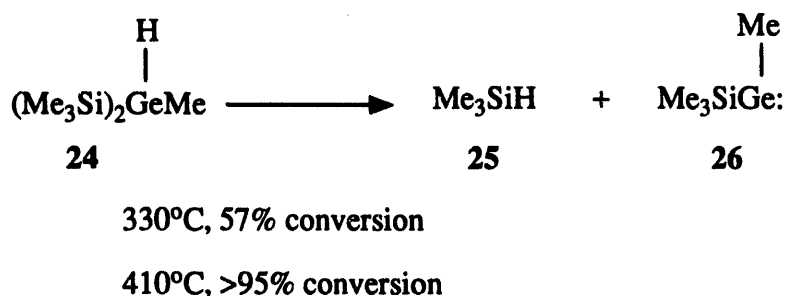


Gaspar et al. thermally prepared dimethylgermylene using this same route.³¹ Upon pyrolyzing pentamethyldigermane at

250°C they found the exclusive products to be trimethylgermane, **22**, and heptamethyltrigermane, **23**.



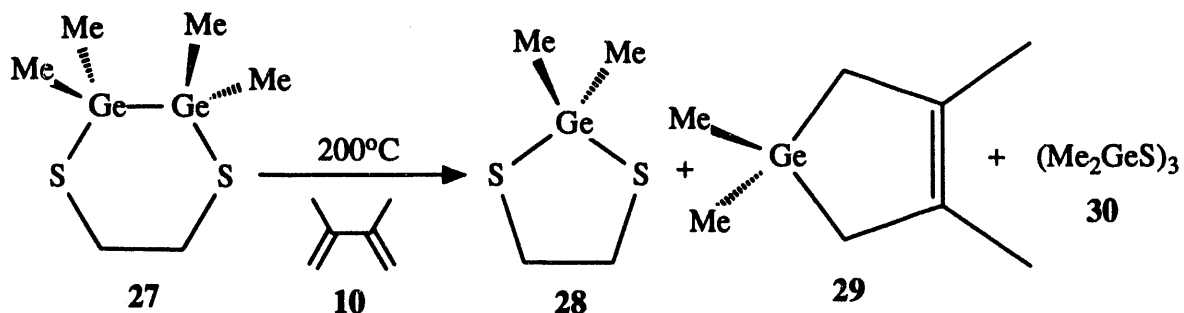
In a later study,³² Gaspar found the dimethylgermylene formed to add stereospecifically to substituted butadienes thus demonstrating the singlet nature of free germylene. Taking this study one step further, Gaspar et al.³³ prepared the first example of a thermally generated silylgermylene with the flow pyrolysis of bis(trimethylsilyl)methylgermane, **24**.



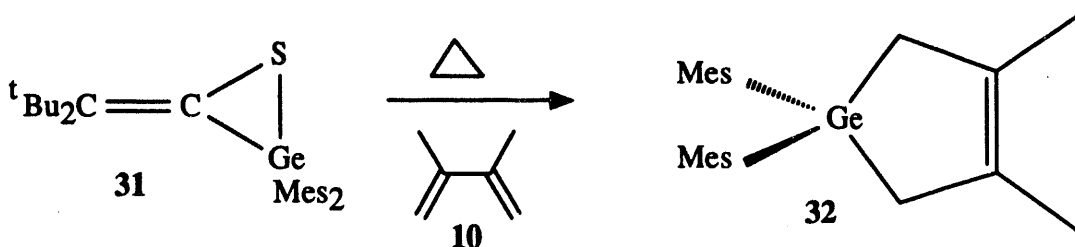
In addition to these alpha-eliminations, Ring et al. proposed that a germylene intermediate is involved in the CVD process of depositing germanium metal on surfaces from germane (GeH_4)³⁴ and methylgermane (CH_3GeH_3).³⁵

Cyclic Germanes as Germylene Precursors

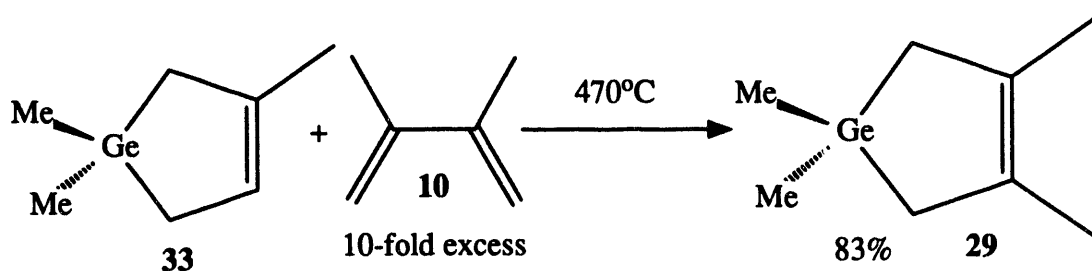
In a related alpha-elimination to form germylenes, Barrau et al. demonstrated that cyclic thiogermanes can be thermally and photolytically treated to form germylenes.³⁶ For instance, 2,2,3,3-tetramethyl-2,3-digerma-1,4-dithiane, **27**, when heated to 200°C in the presence of 2,3-dimethyl-1,3-butadiene 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%).



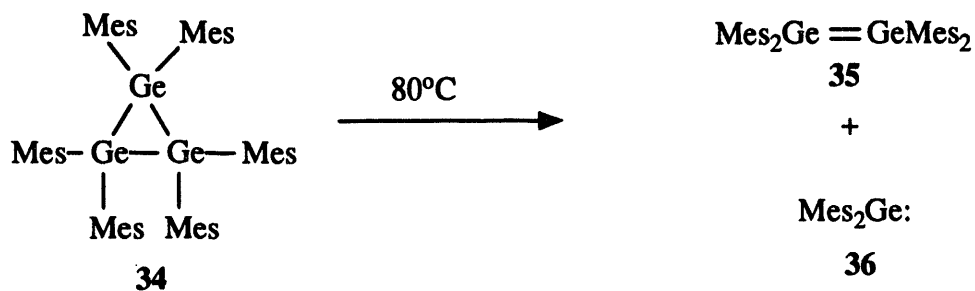
Ando et al. demonstrated how 3-alkylidenethiagermirane, **31**, can be thermally decomposed to extrude dimesitylgermylene and subsequently trapped with 2,3-dimethyl-1,3-butadiene.³⁷



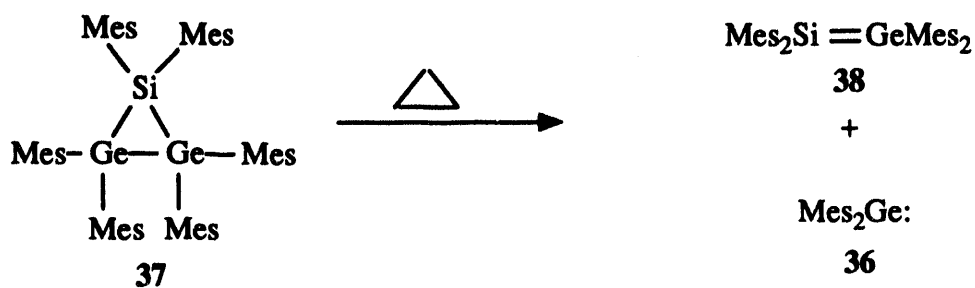
Illustrating the reversible nature of the germylene-1,3-butadiene reaction, Lei and Gaspar¹⁵ used germacyclopent-3-enes to thermally produce dimethylgermylene. For example, the flow pyrolysis of 1,1,3-trimethyl-1-germacyclopent-3-ene, **33**, at 470°C in the presence of a 10-fold excess of 2,3-dimethyl-1,3-butadiene produced **29** in 83% yield.



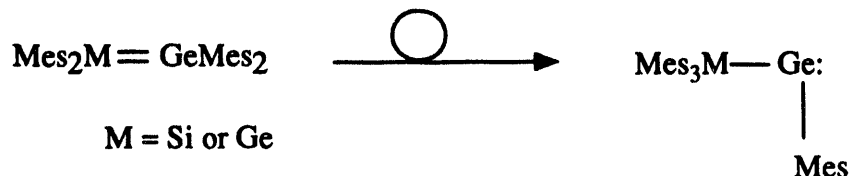
Ando and Tsumuraya demonstrated that cyclotrigermanes (e.g. **34**) can thermally, as well as photolytically extrude germylenes in addition to the corresponding digermenes.³⁸



Baines and Cooke showed that a similar siladigermirane, **37**, when thermolyzed will selectively extrude germylene leaving the resultant germasilene, **38**.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.⁴⁰ A similar rearrangement occurs for the silagermene thus demonstrating the relative stability of germylenes versus silylenes.⁴¹

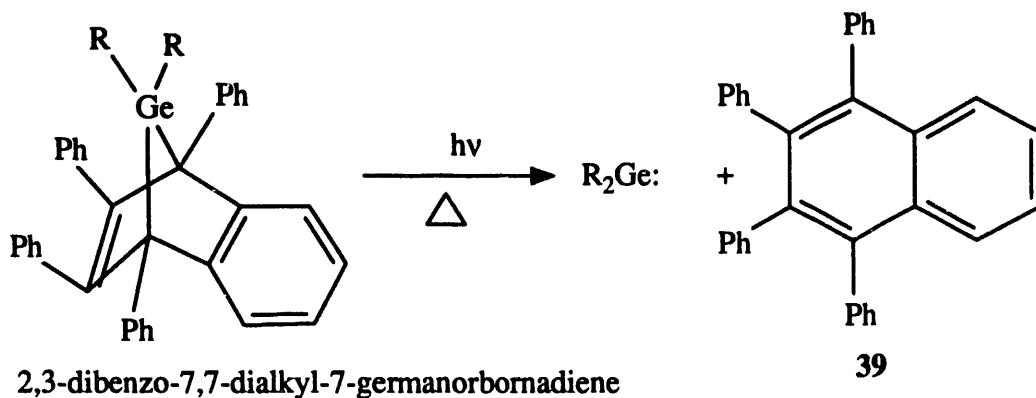


This observation is supported by theoretical studies recently reported by Grev and coworkers.^{42,43} Silylgermylene was calculated to be 6 Kcal/mol lower in energy than germasilene. Germylsilylene was calculated to be 9 Kcal/mol higher in energy than germasilene.

Generation of Germylenes from 7-Germanorbornadienes

The first examples of 7-germanorbornadienes were reported in the 1960's.^{7,44} A number of derivatives were subsequently

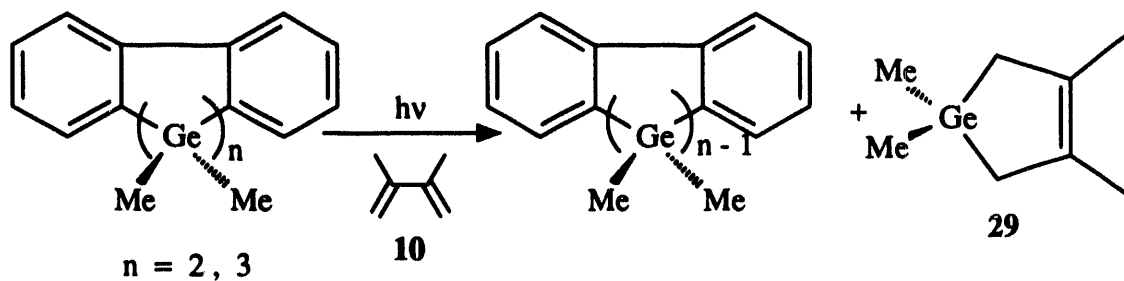
reported.⁴⁵⁻⁵¹ These compounds have the versatility of being both thermal and photochemical precursors to germylenes. However, unlike the thermal precursors in this work, germylene extrusion is believed to go through a diradical intermediate.⁵²



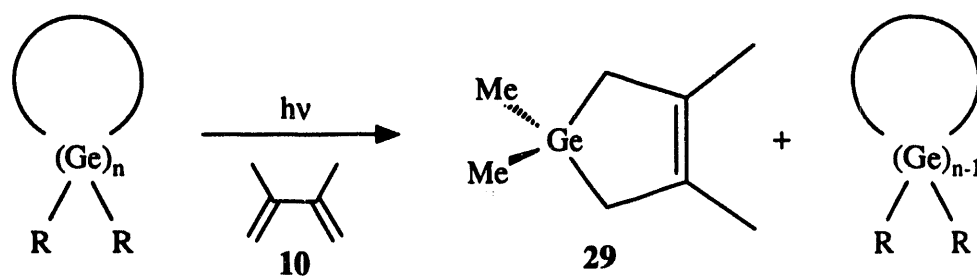
The germylenes evolved from these precursors have received a large amount of attention as attested by the number of papers published in the past decade.⁵²⁻⁷⁵

Photochemically Generated Germylenes

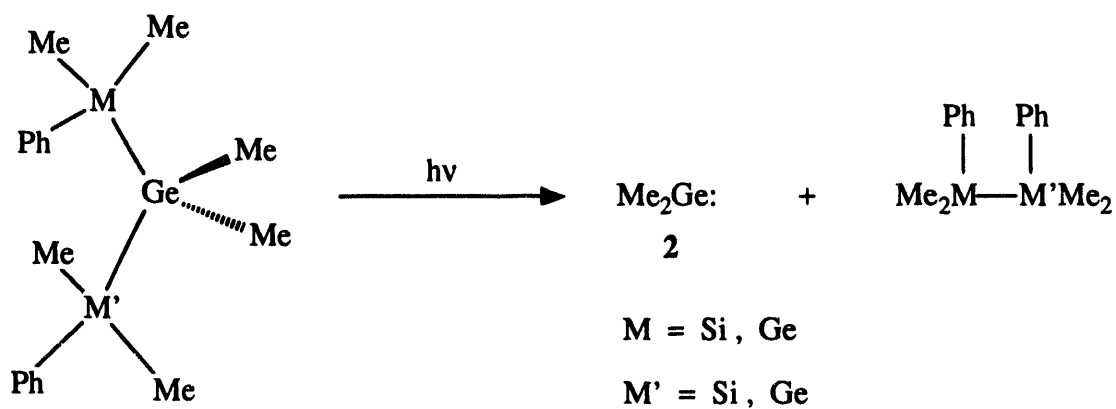
Although many of the germylene precursors previously presented are capable of extruding germylenes upon photolysis, a few additional examples must be mentioned. In 1983, Sakurai and co-workers reported the formation of dimethylgermylene upon photolysis of dibenzo-1,1,2,2-tetramethyl-1,2-germacyclohexa-3,5-diene.⁷⁶ Similarly, dibenzo-1,1,2,2,3,3-hexamethyl-1,2,3-trigermacyclohepta-4,6-diene also extrudes germylene upon irradiation.⁷⁷



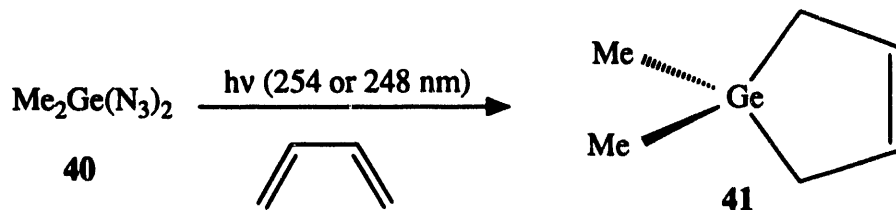
Cyclic germanes have also been shown to be facile germylene precursors.⁷⁸⁻⁸⁴ Cyclics from 3-membered to 6-membered rings have been recently reported to extrude germylene upon photolysis.



In addition, aryl-digermanes, trigermanes, and mixed silylgermanes have also been shown to act as photochemical precursors to germylenes.⁸⁵⁻⁹²



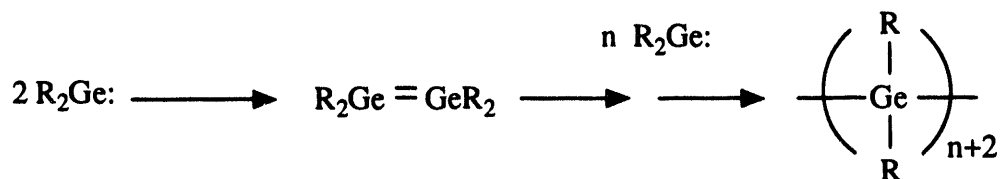
Finally, West et al. reported geminal diazide **40** as a photochemical source of dimethylgermylene.⁹³



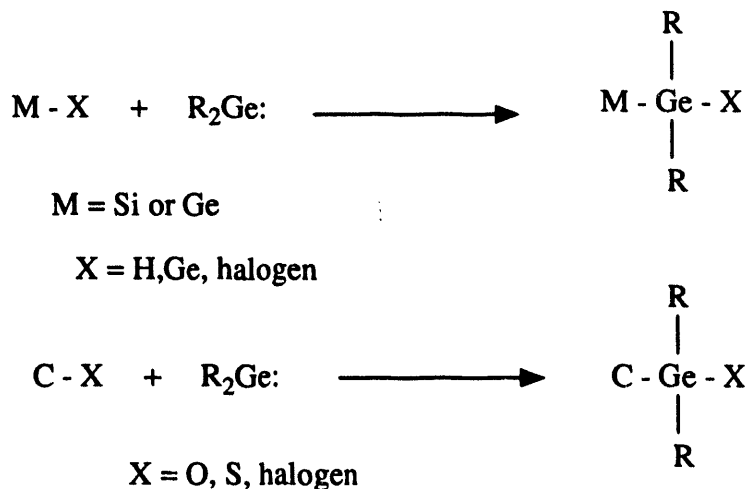
Reactions of Germylenes

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.⁴ It is assumed that a dimerization is the first step in this process, followed by additional germylene insertion.

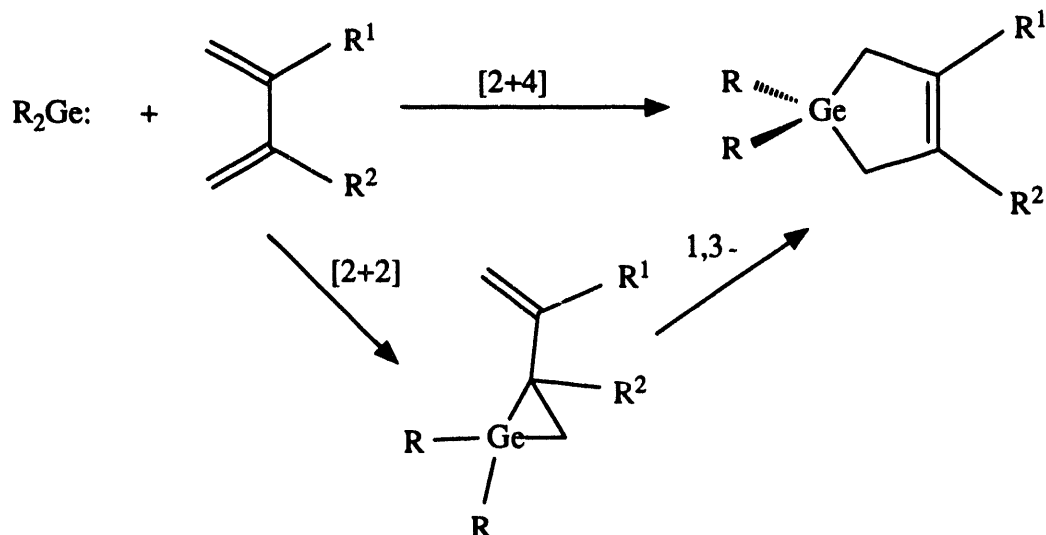


Early examples of thermally produced germylenes were detected by the insertion of germylenes into σ -bonds. As previously demonstrated, Ge-Ge^{16,26,28,29} bonds are efficient germylene traps. In many of these examples, however there is a question as to whether the actual insertion is into a Ge-H, Ge-halogen, or Ge-Ge bond. One study showed insertion of germylenes into Ge-H bonds to be more facile than Si-H bonds.³⁰ However, Mochida reported a detailed study of dimethylgermylene insertion into Si-H bonds⁶⁸ and Baines trapped dimesitylgermylene with triethylsilane.⁴⁰ Several examples of germylene insertion into C-halogen bonds have also been reported.^{55,94,95} Insertion into C-S and C-O bonds is also known.⁹⁴



In general, simple alkenes are inert toward free germylenes.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

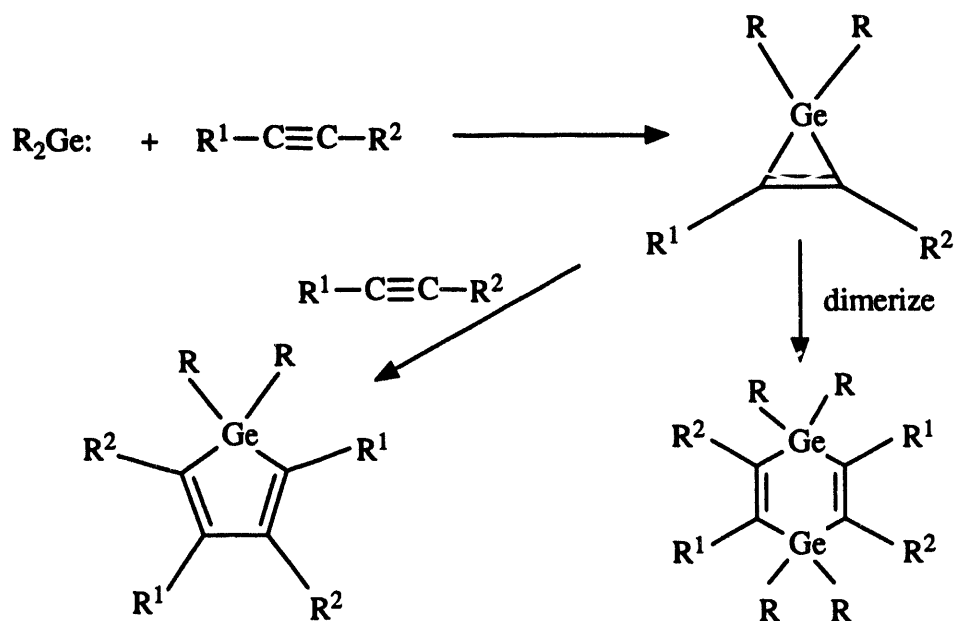
1,3-butadienes.^{15,29,51,91,96-99} A debate has raged over the mechanism for this addition. Neumann contests that germylene addition to conjugated dienes precedes via a [2+4] cycloaddition.^{94,96-99} He cites several examples of stereospecific addition of germylens to dienes to support his view. However, 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 germacyclopropane to form germacyclopent-3-ene.⁹¹



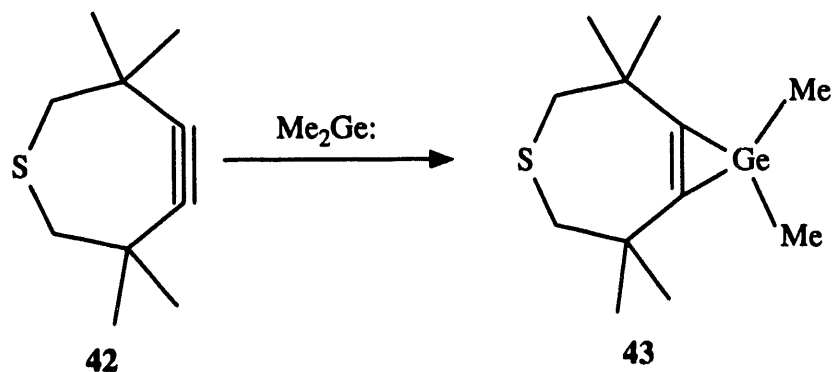
Examples of germylene addition to 1-aza and 1,4-diazabutadienes,⁷¹ vinyl ketones,⁶³ and orthoquinones¹⁰⁰ have also been reported.

Addition of germylens to alkynes occurs at a much slower rate than addition to dienes.⁹¹ Where the reaction does occur,^{73-75,101} it is believed that a germacyclopropene 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.⁷²



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



Calculations by Gordon and coworkers estimate that germacyclopropenes are thermodynamically less stable than silacyclopropenes by approximately 30 Kcal/mol.¹⁰⁴ 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 silylene³ 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 organogermanium compounds is reported.

Germylenes Formed via Alpha-Eliminations

As mentioned earlier, Gaspar and coworkers were the first to thermally prepare a silylgermylene.³³ The major products were the expected butadiene-trapped silyl-germylene (18.8%) and trapped dimethylgermylene (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.

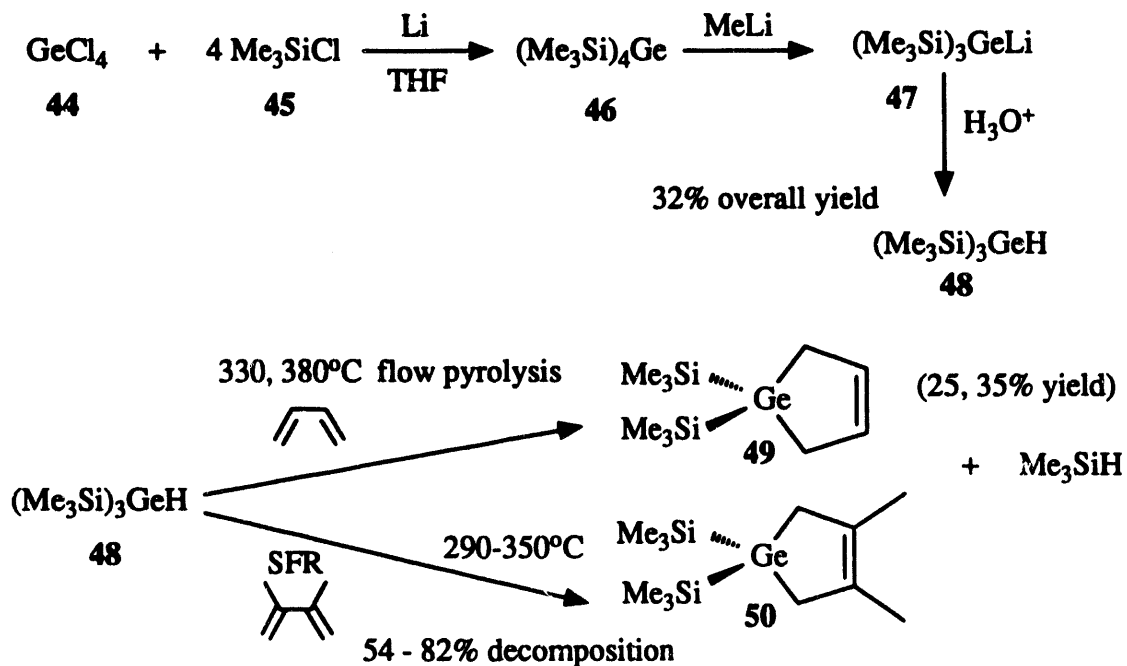
In an attempt to extend Gaspar's work, tris(trimethylsilyl)germane, **48**, was prepared (Scheme 1) in 32% yield from germanium tetrachloride following the procedure of Brook, Abdesaken and Söllradl.¹⁰⁵ When pyrolyzed in a flow pyrolysis apparatus heated to 330°C and 380°C with 1,3-butadiene as the carrier 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 hydrogermylation 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 Gaspar'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.

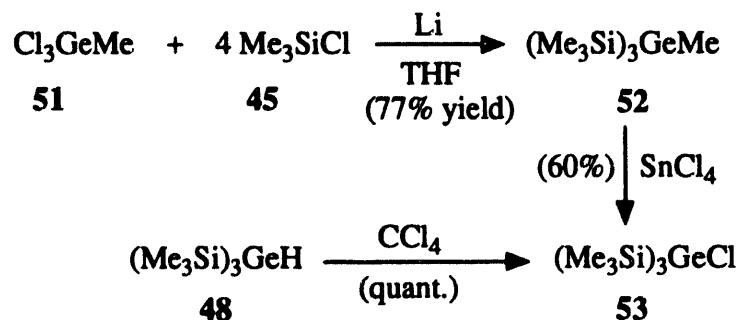
Hydrido-germane **48** can be converted quantitatively to the corresponding chloro-germane, **53** (Scheme 2), by slowly adding it to carbon tetrachloride in the presence of sunlight.¹⁰⁵ Alternatively, treatment of tris(trimethylsilyl)methylgermane, **52**, with tin (IV) chloride afforded **53** in 60% yield.

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

Scheme 1



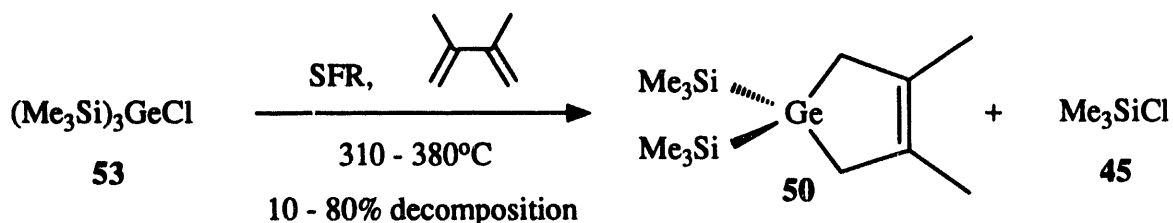
Scheme 2



of 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)¹⁰⁶ gave Arrhenius parameters of $\text{Log}(A/\text{s}^{-1}) = 10.9 \pm 0.2$ and $E_{\text{act}} = 33.4 \pm 0.6$ 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 11.¹⁰⁷ 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



$$\text{Log}(A/s^{-1}) = 10.9 \pm 0.2$$

$$E_{\text{act}} = 33.4 \pm 0.6 \text{ Kcal/mol}$$

Bis(trimethylsilyl)methylchlorogermane, **55**, was prepared as previously reported³³ (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.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%

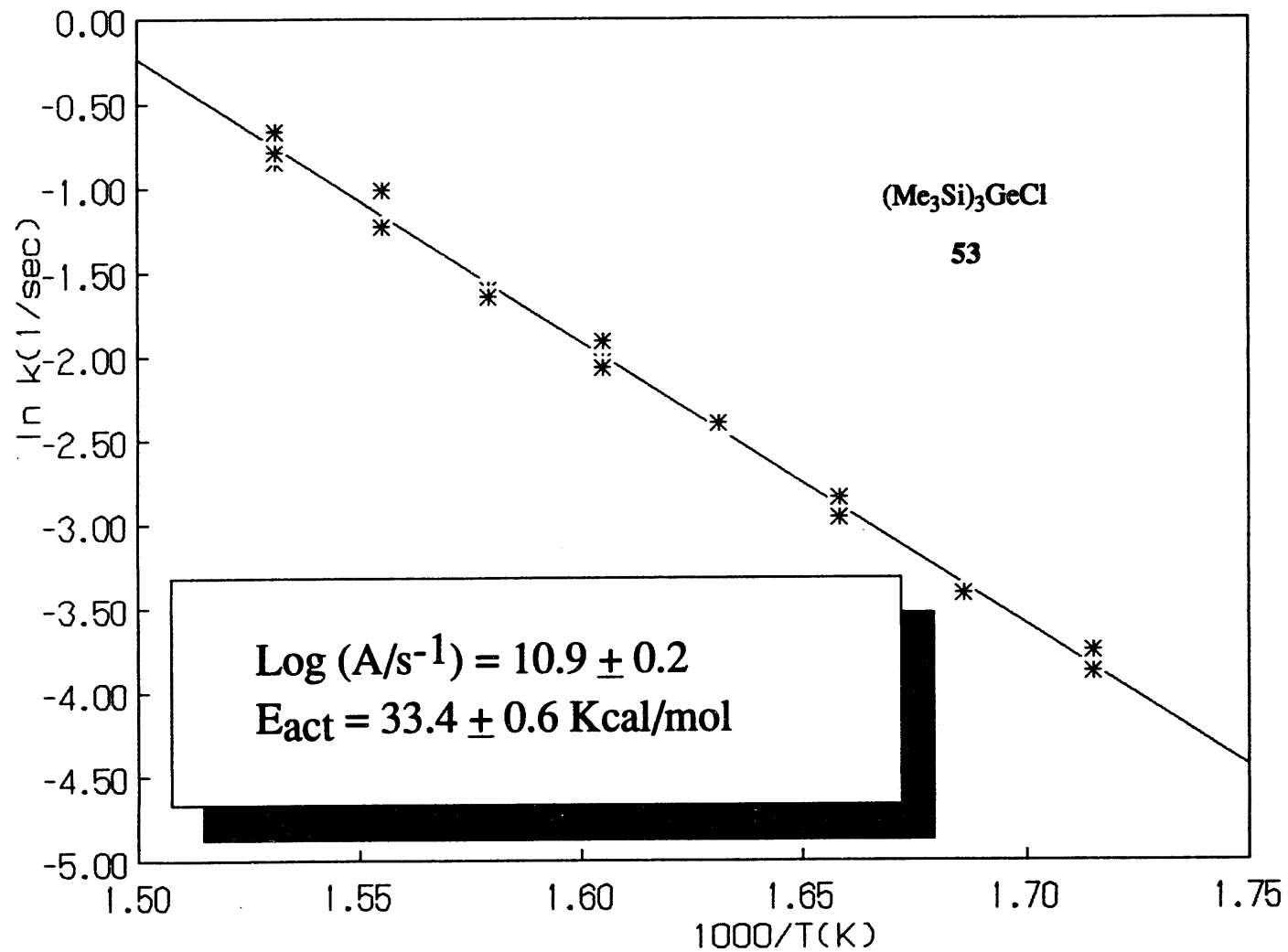
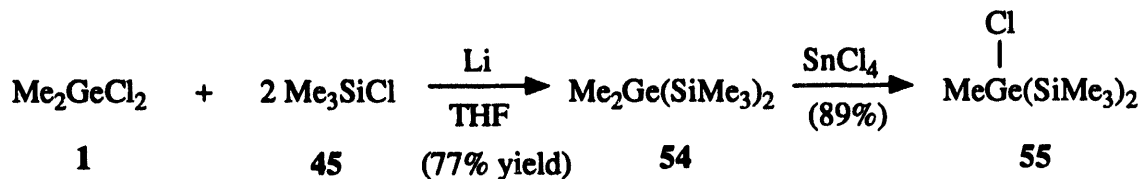
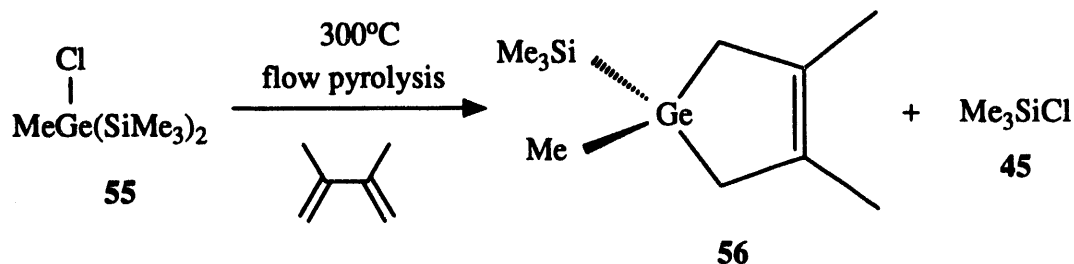


Figure 1, Arrhenius plot for the thermal decomposition of **53** following the formation of **50**.

Scheme 4

starting material remained at this temperature.

Scheme 5

To finish this series, (trimethylsilyl)dimethylchlorogermane, **68**, was prepared (Scheme 6) in a fashion similar to that described by Kumada et al.¹⁰⁴ A germanium-catechol salt, **60**, was prepared in 88% yield following Corriu's procedure.^{110,111} 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%.¹¹⁵ 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: $\text{Log}(A/s^{-1}) = 12.8 \pm 0.1$ and $E_{\text{act}} = 40.1 \pm 0.3$ Kcal/mol. (figure 2) This data is consistent with an α -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: $\text{Log}(A/s^{-1}) = 11.7 \pm 0.3$ 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 bromogermene as a thermal germylene precursor. By treating **67** with bromine, bromo(trimethylsilyl)dimethylgermane, **70**, was prepared.

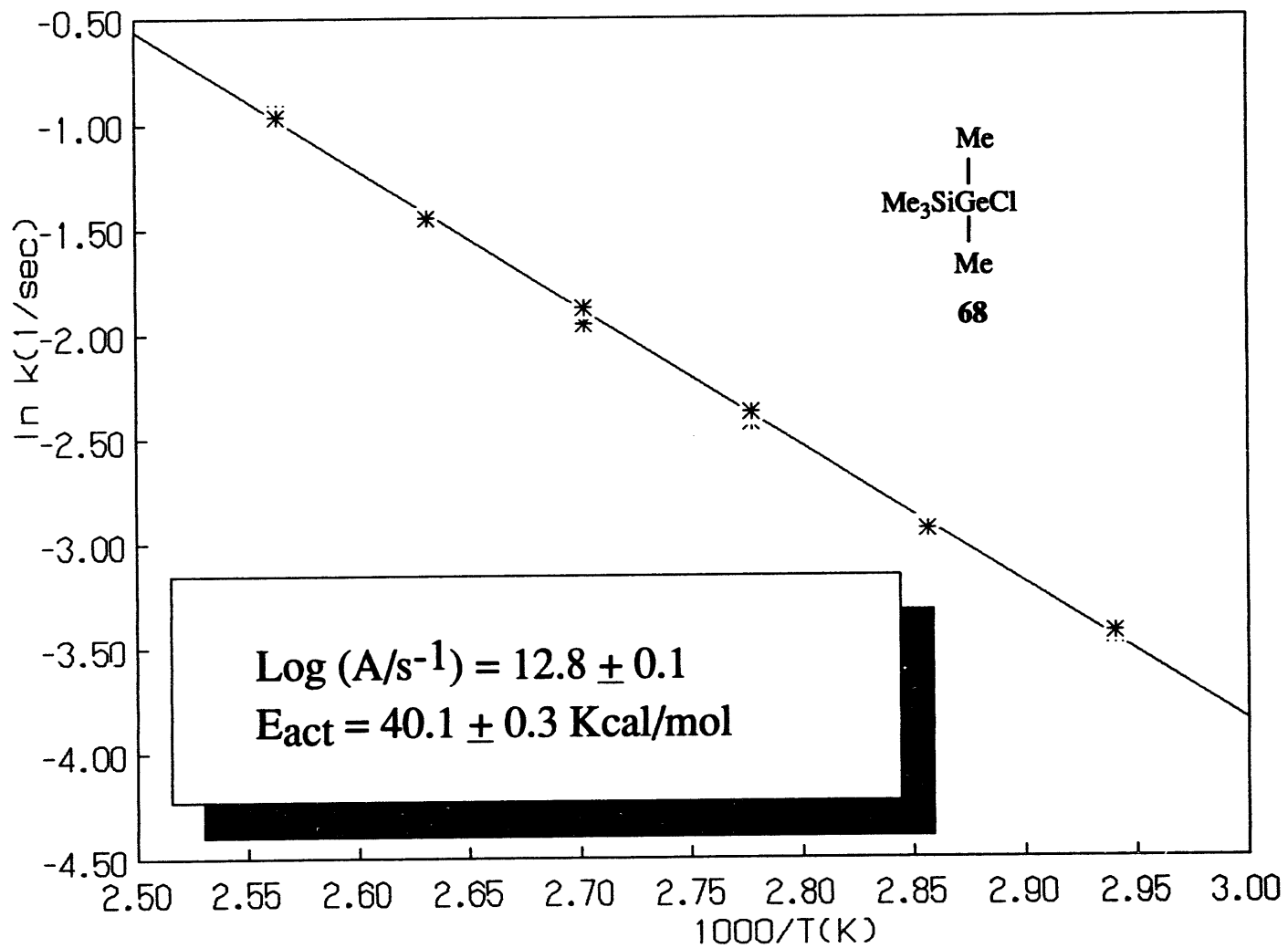
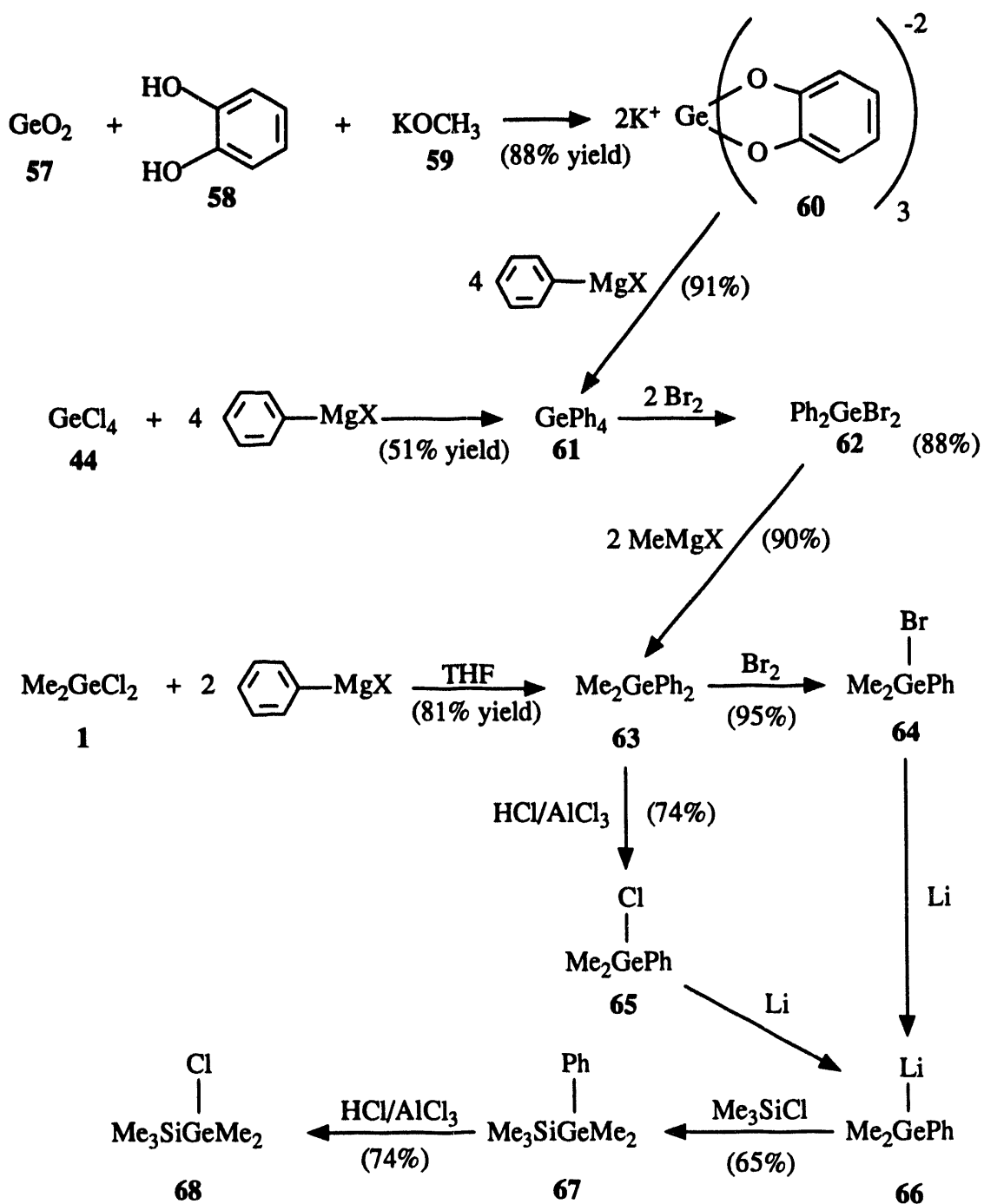
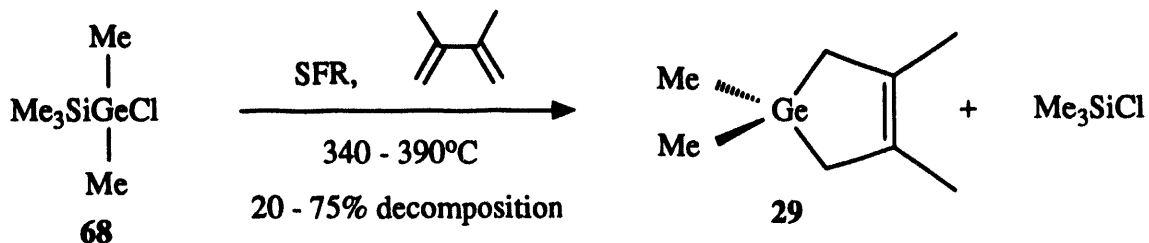


Figure 2, Arrhenius plot for the thermal decomposition of **68** following the formation of **29**.

Scheme 6

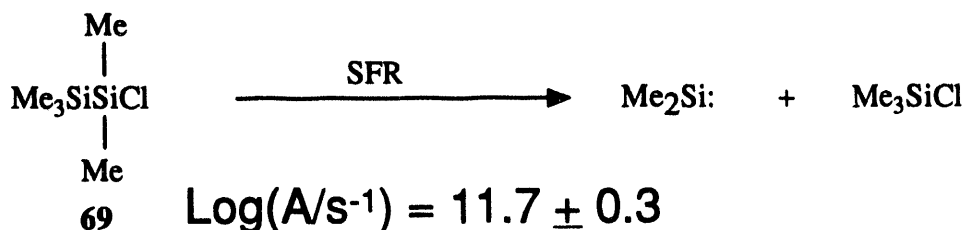


Scheme 7



$$\text{Log}(A/\text{s}^{-1}) = 12.8 \pm 0.1$$

$$E_{\text{act}} = 40.1 \pm 0.3 \text{ Kcal/mol}$$



$$\text{Log}(A/\text{s}^{-1}) = 11.7 \pm 0.3$$

$$E_{\text{act}} = 50.1 \pm 1.1 \text{ Kcal/mol}$$

Pyrolysis of **70** in the presence of DMB gave the expected **29**. Arrhenius parameters (Scheme 8) were also obtained for this compound. $\text{Log}(A/\text{s}^{-1}) = 9.9 \pm 0.6$ 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.

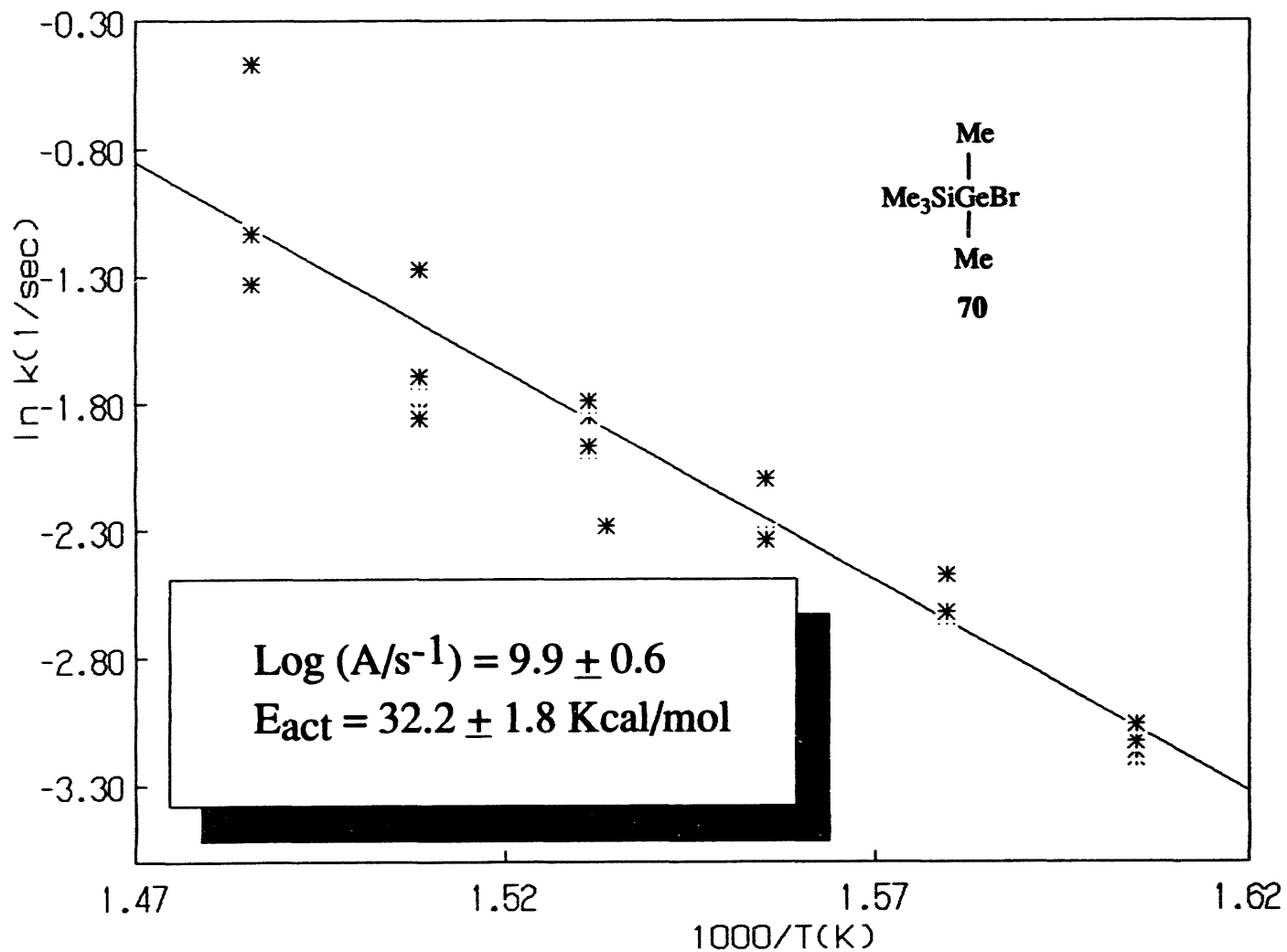
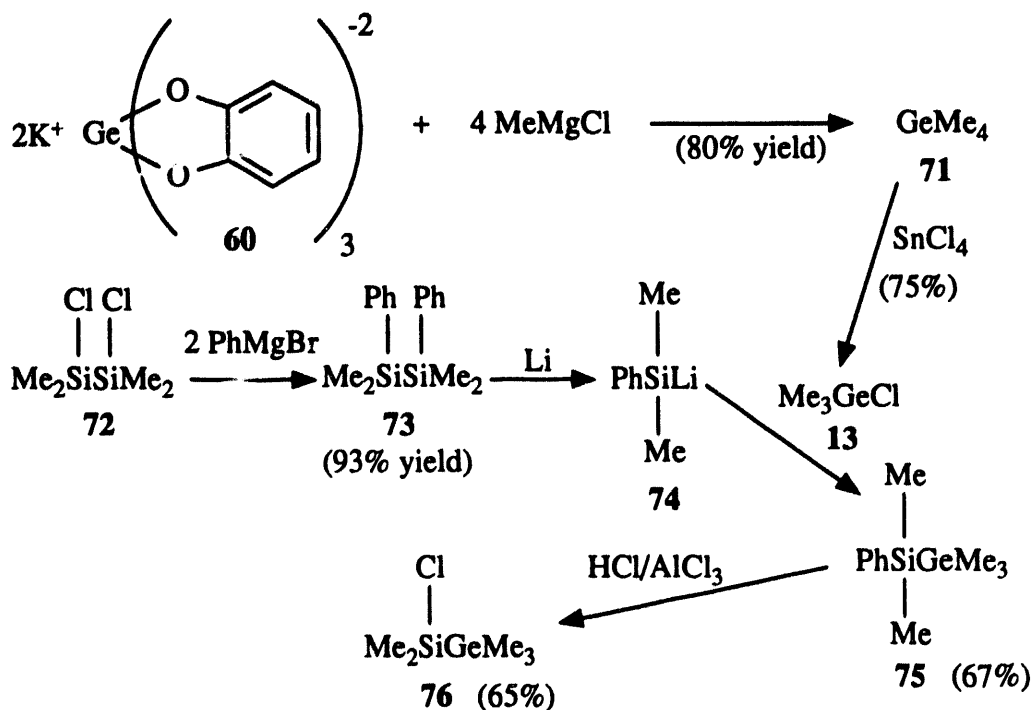


Figure 3, Arrhenius plot for the thermal decomposition of **70** following the formation of **29**.

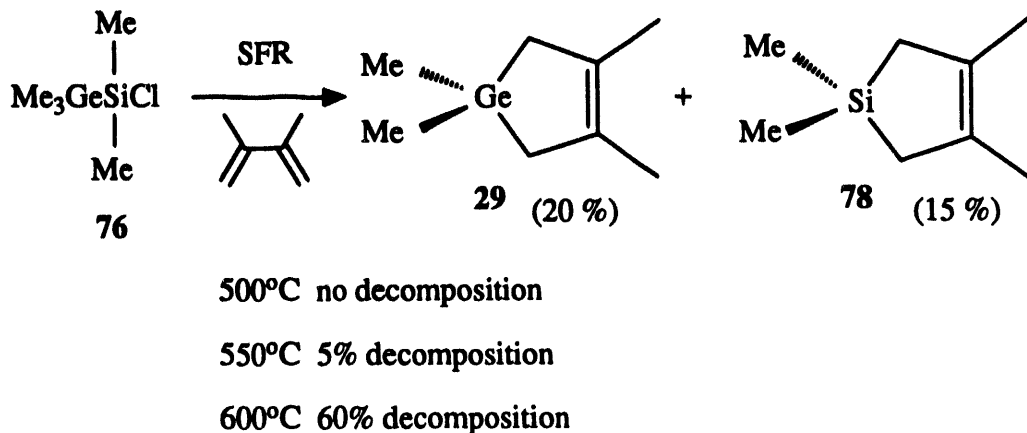
Grignard to **60**. (Note: Compound **71** was also prepared from tris(butane-2,3-diolato)germinate, **77**). Finally, treatment of **75** in chloroform with HCl in the presence of a catalytic amount of AlCl₃ produced **76** in 65% yield.

Scheme 9



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

Scheme 10

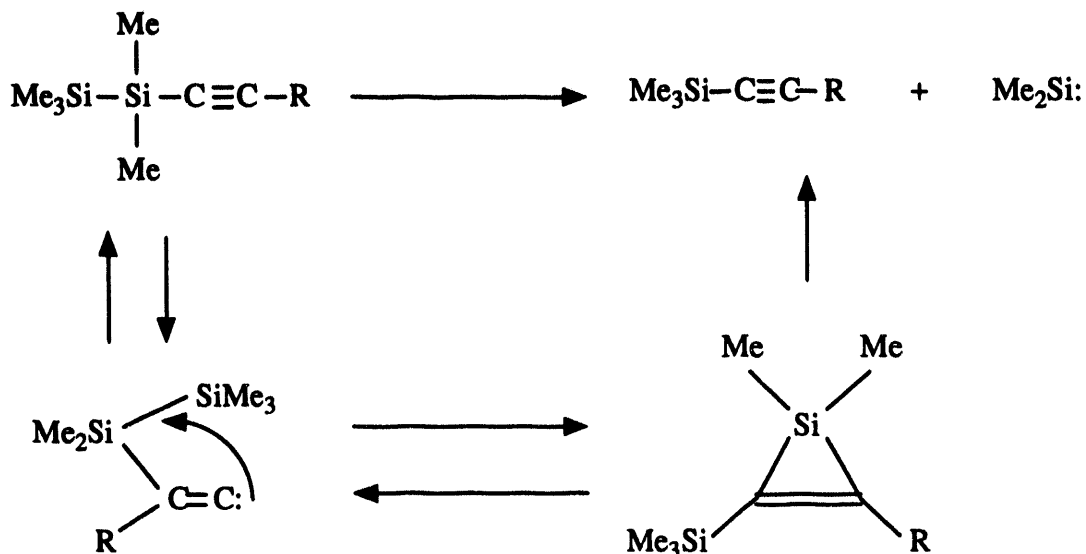
extrusion through some other type of mechanism is competitive with silylene extrusion. A number of examples of germylene extrusion by an alternative mechanism are given in the last section of this discussion. More detail will be given to the possible mechanism there.

Thermochemistry of Germyl-Acetylenes

In studying the thermal rearrangement of ethynyl silanes, Petrich¹¹² found that ethynyl disilanes were convenient thermal precursors to silylenes. A mechanism was developed (Scheme 11) incorporating a vinylidene transition state and a silacyclopropene intermediate.

Given the stability of germylenes relative to silylenes,⁹⁶ it was hypothesized that one could thermally produce germylenes from germyl-acetylenes. The hope was that

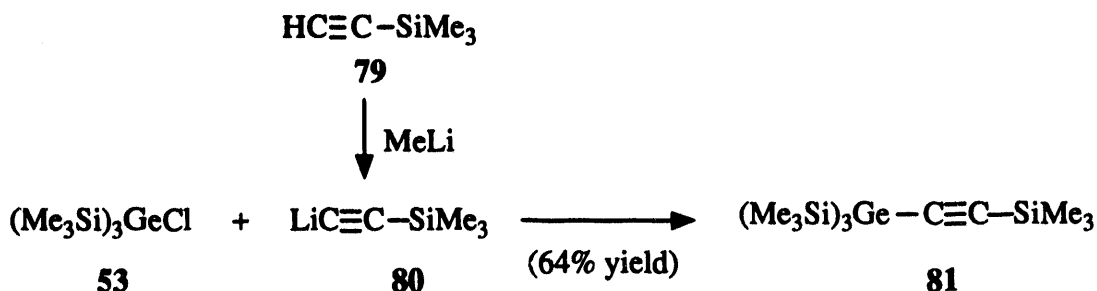
Scheme 11



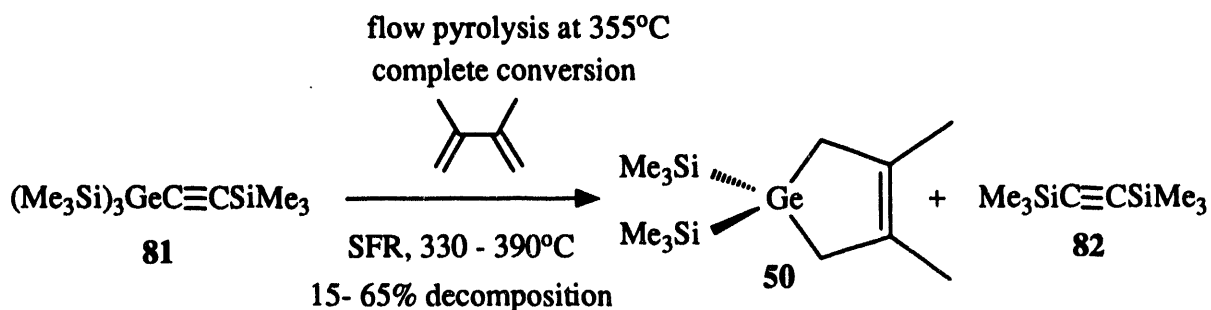
germylenes would be produced at lower temperatures, thus making it possible to isolate germacyclopene intermediates similar to those reported by Krebs and Berndt.^{102,103} Assuming germanium behaved similar to silicon, it was also proposed that the germanium would act as a labeling tool in exploring Petrich's mechanism.

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

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

Scheme 12

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

Scheme 13

$$\begin{array}{l}
 \text{Log}(A/s^{-1}) = 10.5 \pm 0.4 \\
 E_{\text{act}} = 33.8 \pm 1.0 \text{ Kcal/mol}
 \end{array}$$

In a similar fashion, the analogous silicon compound, **83**, was also prepared and pyrolyzed (Scheme 14) in the SFR to give Arrhenius parameters of $\text{Log}(A/s^{-1}) = 11.1 \pm 0.1$ 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

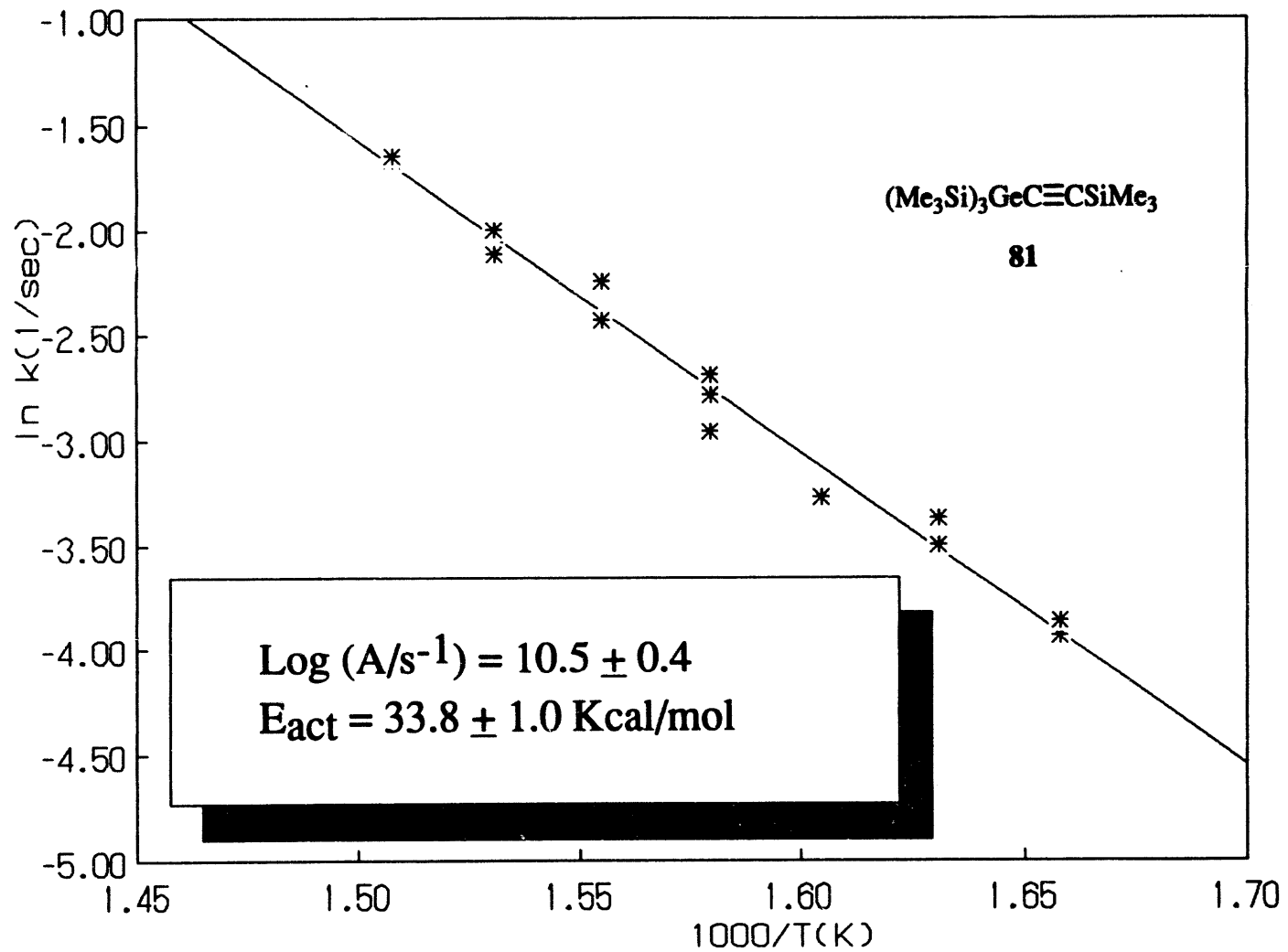


Figure 4, Arrhenius plot for the thermal decomposition of **81** following the formation of **82**.

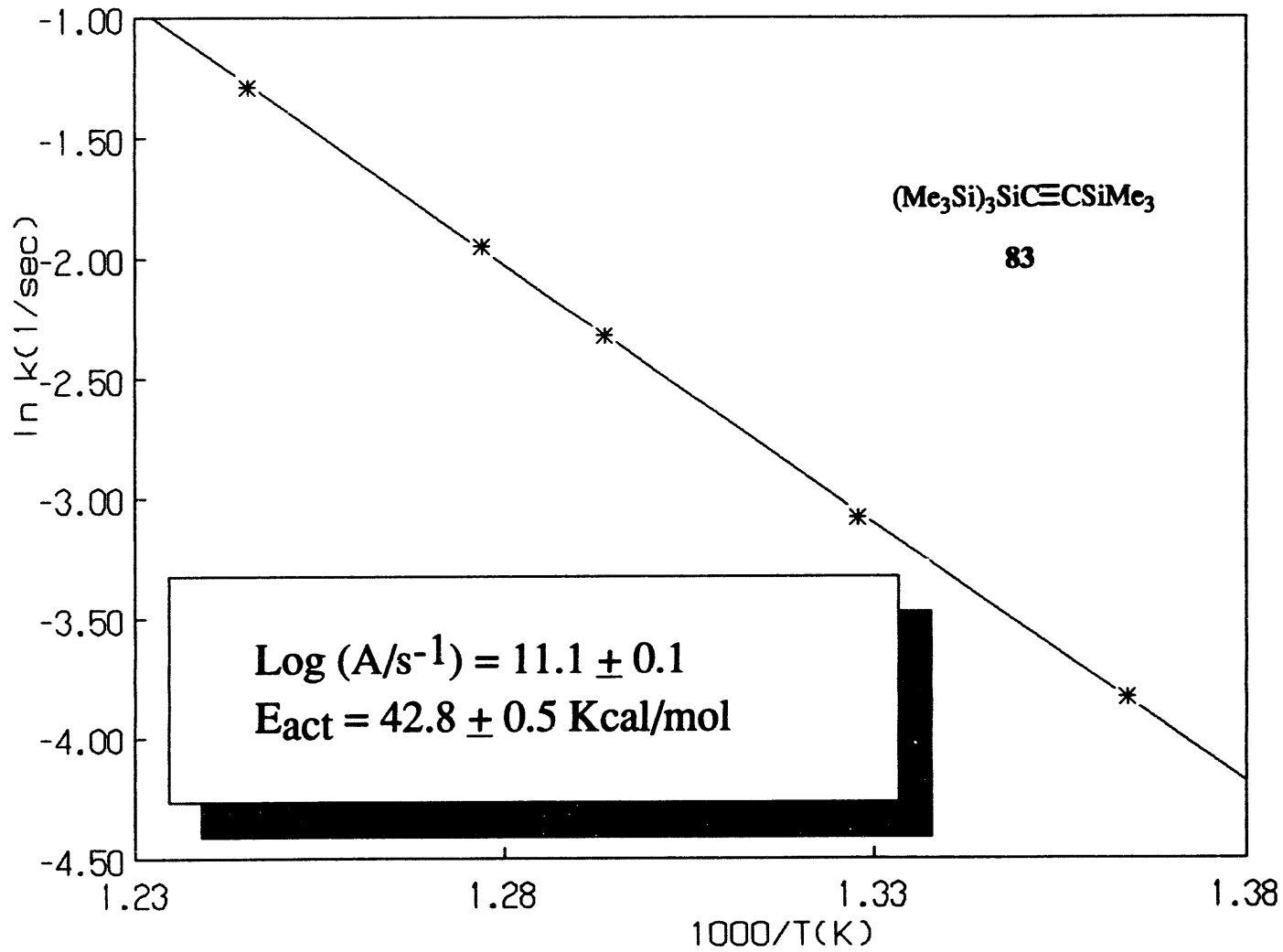
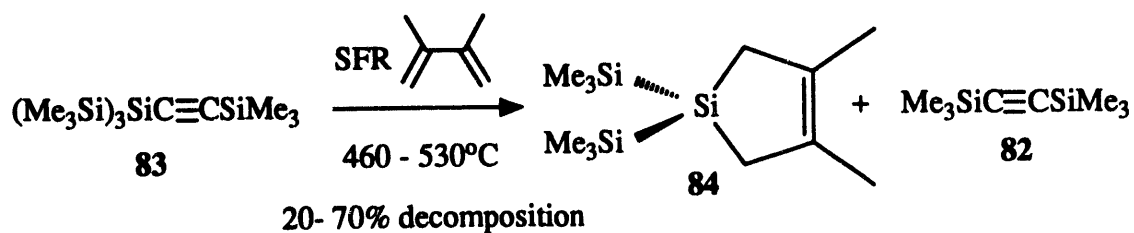


Figure 5, Arrhenius plot for the thermal decomposition of **83** following the formation of **82**.

extruded at a rate 160 times greater than that of the silylene.

Scheme 14



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

$$E_{\text{act}} = 42.8 \pm 0.5 \text{ Kcal/mol}$$

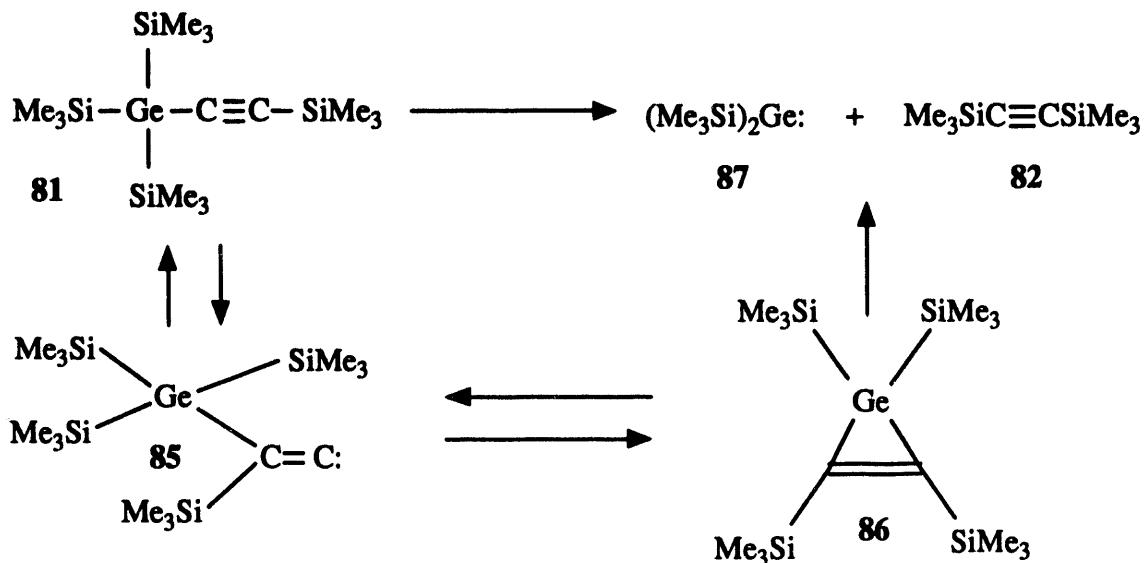
$$\text{For } \mathbf{81}: k_{430} = 0.90 \text{ s}^{-1}$$

$$\text{For } \mathbf{83}: k_{430} = 0.0056 \text{ s}^{-1}$$

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

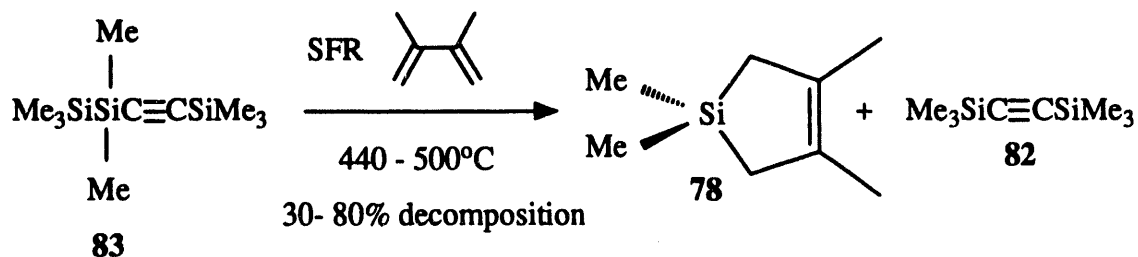
Petrich had obtained the Arrhenius parameters for the thermal decomposition of [(trimethylsilyl)dimethylsilyl]-trimethylsilylacetylene, **83**:¹¹² $\text{Log}(A/\text{s}^{-1}) = 11.5 \pm 0.3$, $E_{\text{act}} = 40.8 \pm 1.1 \text{ Kcal/mol}$. (Scheme 16) These kinetic parameters match those obtained for **83** closely. This suggests that there is little or no substituent effect in silylene formation. This begged the question for germynes. 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



Scheme 16

(ref. 112)

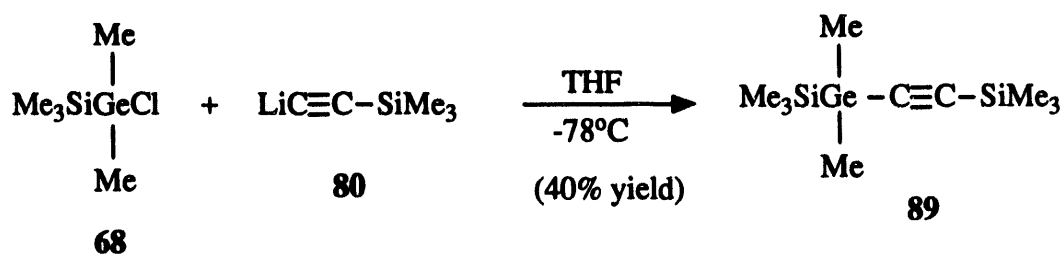


$$\text{Log}(A/s^{-1}) = 11.5 \pm 0.3$$

$$E_{\text{act}} = 40.8 \pm 1.1 \text{ Kcal/mol}$$

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

Scheme 17

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: $\text{Log}(A/\text{s}^{-1}) = 11.5 \pm 0.4$ and $E_{\text{act}} = 40.9 \pm 1.2 \text{ Kcal/mol}$. (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,

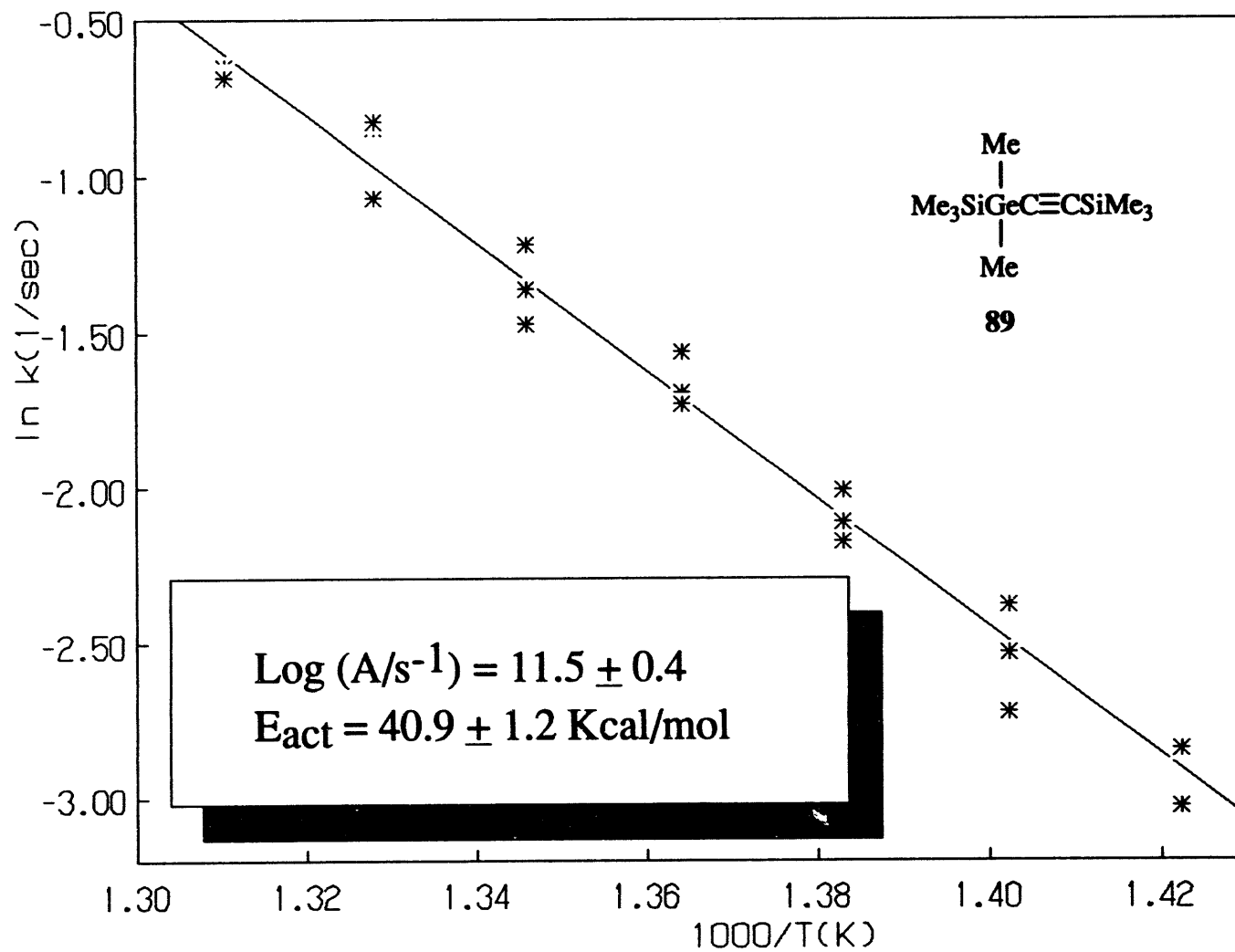
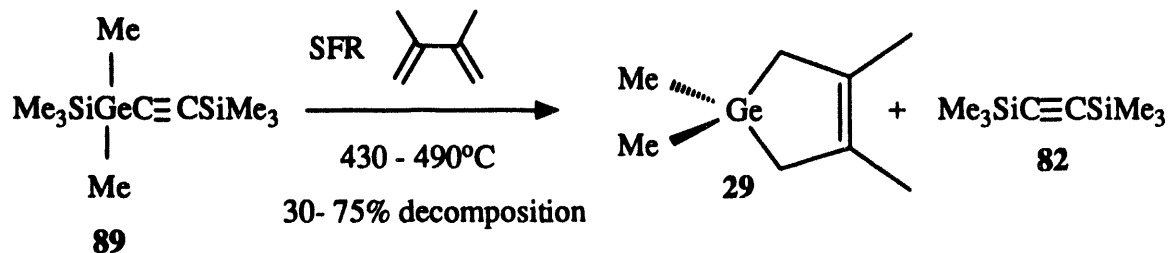


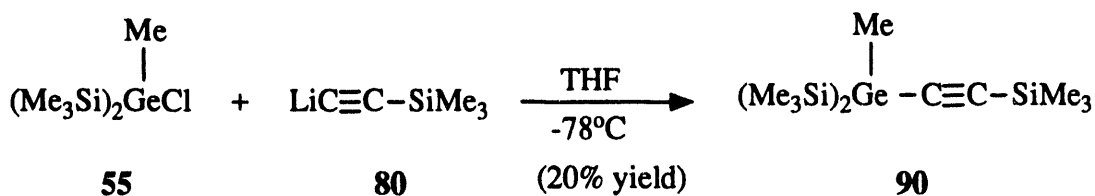
Figure 6, Arrhenius plot for the thermal decomposition of **89** following the formation of **82**.

Scheme 18

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

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

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

Scheme 19

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

To conclude this comparison, [bis(trimethylsilyl)methylsilyl]trimethylsilylacetylene, **92**, was prepared. SFR pyrolysis of this compound (Scheme 21) gave Arrhenius

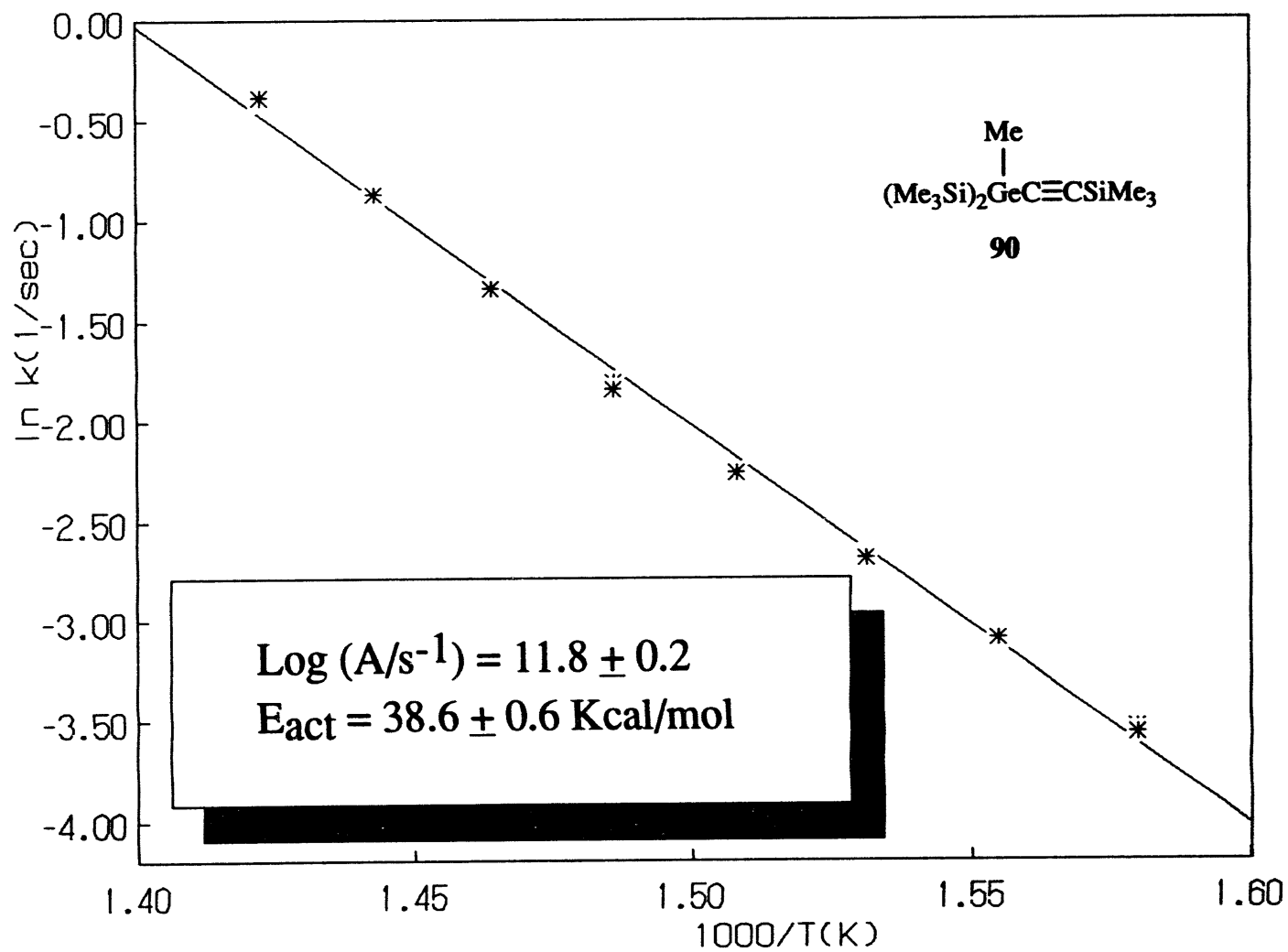
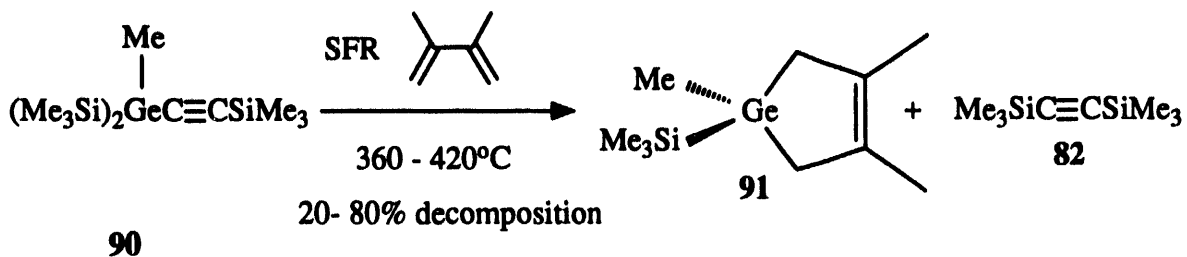


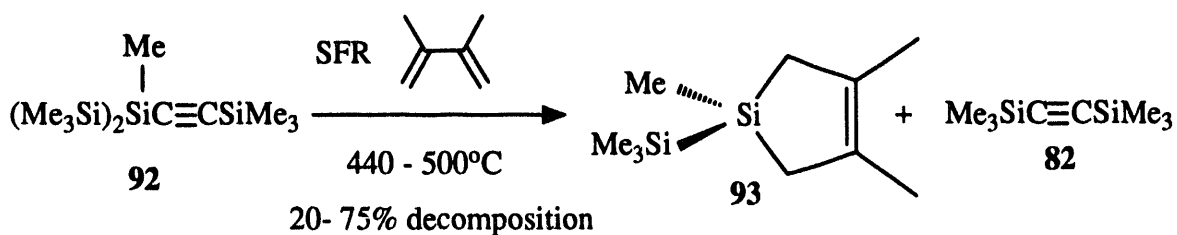
Figure 7, Arrhenius plot for the thermal decomposition of **90** following the formation of **82**.

Scheme 20

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

$$E_{\text{act}} = 38.6 \pm 0.6 \text{ Kcal/mol}$$

parameters of $\text{Log}(A/s^{-1}) = 11.6 \pm 0.2$ and $E_{\text{act}} = 42.2 \pm 0.5$ 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.

Scheme 21

$$\text{Log}(A/s^{-1}) = 11.6 \pm 0.2$$

$$E_{\text{act}} = 42.2 \pm 0.5 \text{ Kcal/mol}$$

$$\text{For } \mathbf{92}: k_{400} = 1.1 \times 10^{-2} \text{ s}^{-1} \quad k_{420} = 2.6 \times 10^{-2} \text{ s}^{-1}$$

$$\text{For } \mathbf{90}: k_{400} = 1.8 \times 10^{-1} \text{ s}^{-1} \quad k_{420} = 4.2 \times 10^{-1} \text{ s}^{-1}$$

Scheme 22 summarizes the Arrhenius parameters just discussed. Clearly as trimethylsilyl groups are replaced with

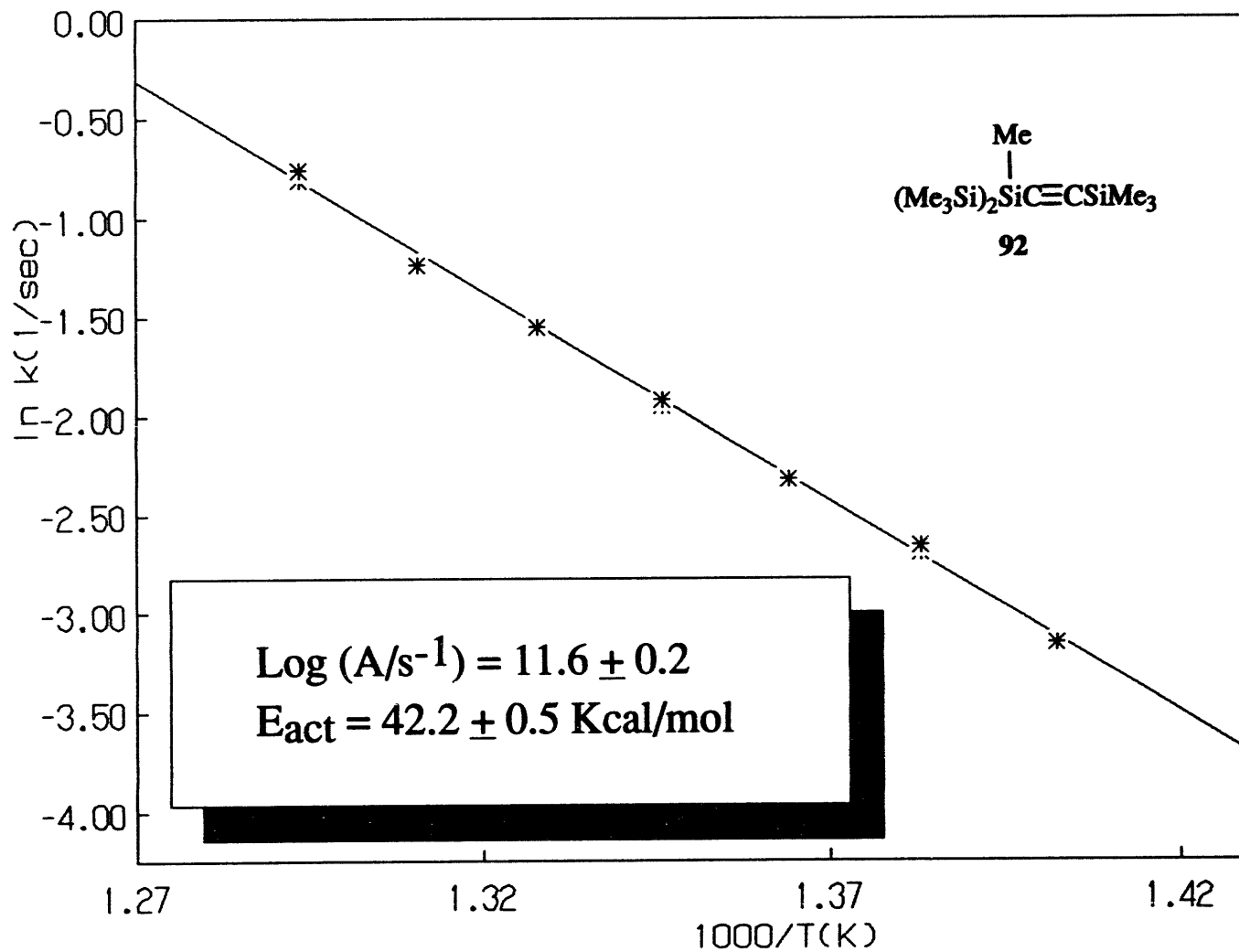
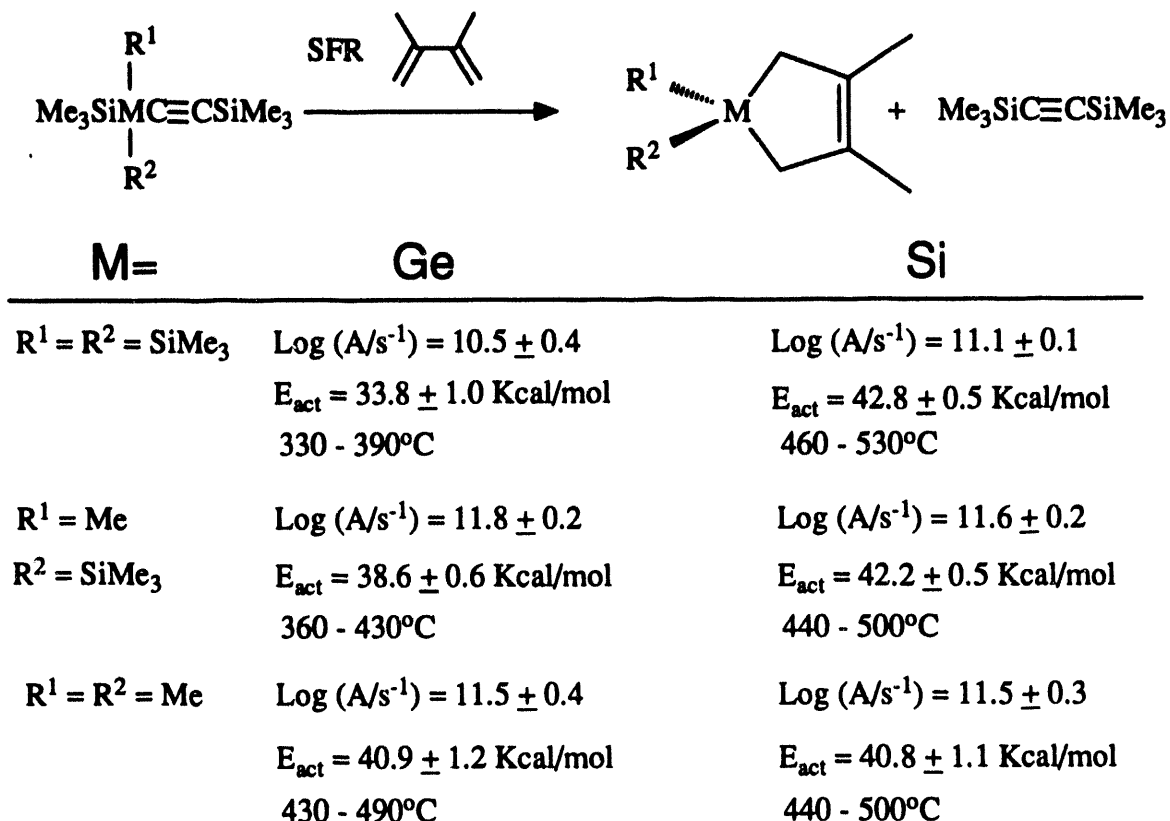


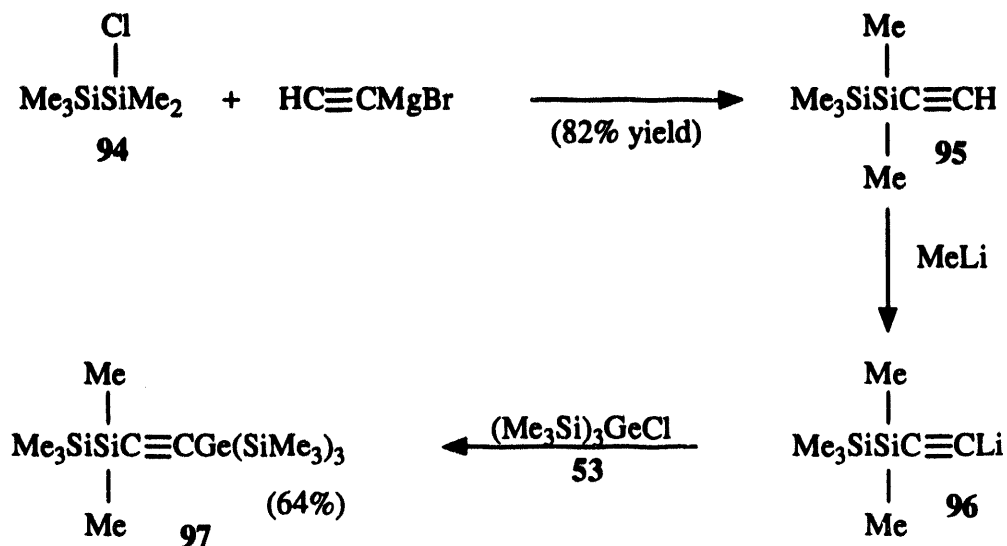
Figure 8, Arrhenius plot for the thermal decomposition of **92** following the formation of **82**.

methyl groups there is an increase in the energy required to extrude the corresponding germylenes.

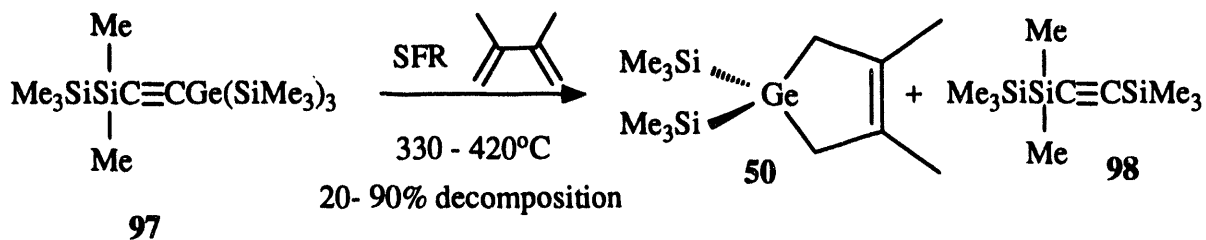
Scheme 22



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.

Scheme 23

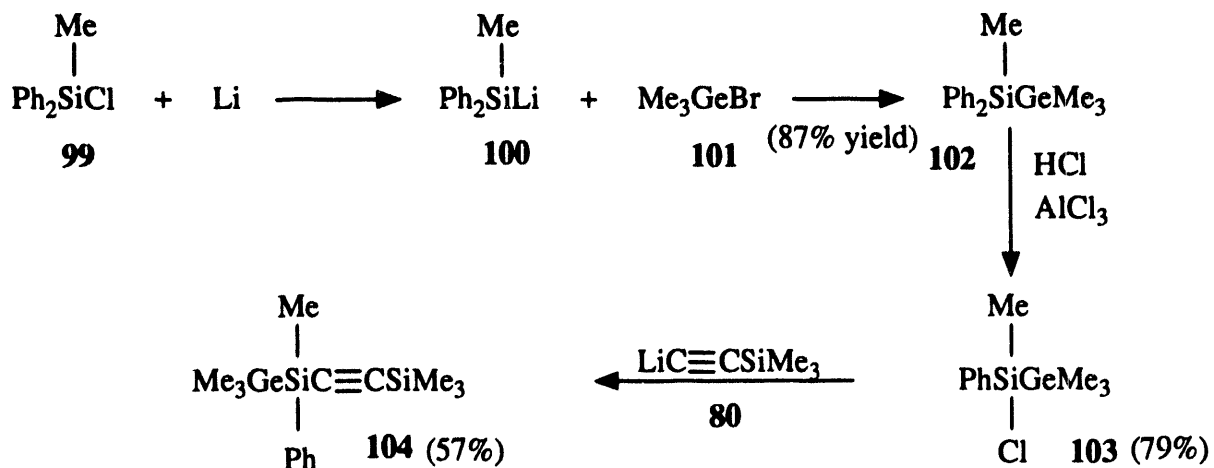
As expected, SFR pyrolysis of **97** (Scheme 24) in the 330-420°C temperature range (20-90% decomposition) with a 20-fold excess of DMB gave trapped bis(trimethylsilyl)-germylene, **50**, and the corresponding trisilylacetylene, **98**, as the exclusive products.

Scheme 24

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.,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 AlCl₃ as catalyst produced **103** in 79% yield. Finally, addition of **80** leads to our target molecule, **104**, in 57% yield.

Scheme 25

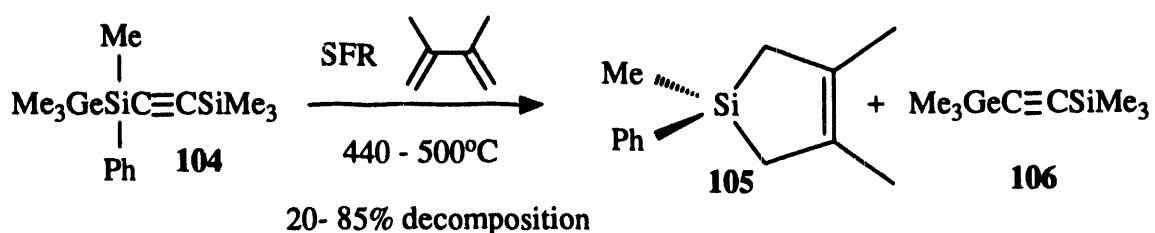


Flow pyrolysis of **104** at 530°C with a 20-fold excess of DMB gave (trimethylgermyl)trimethylsilylacetylene, **106**, and the corresponding trapped silylene, **105**, as the major products.

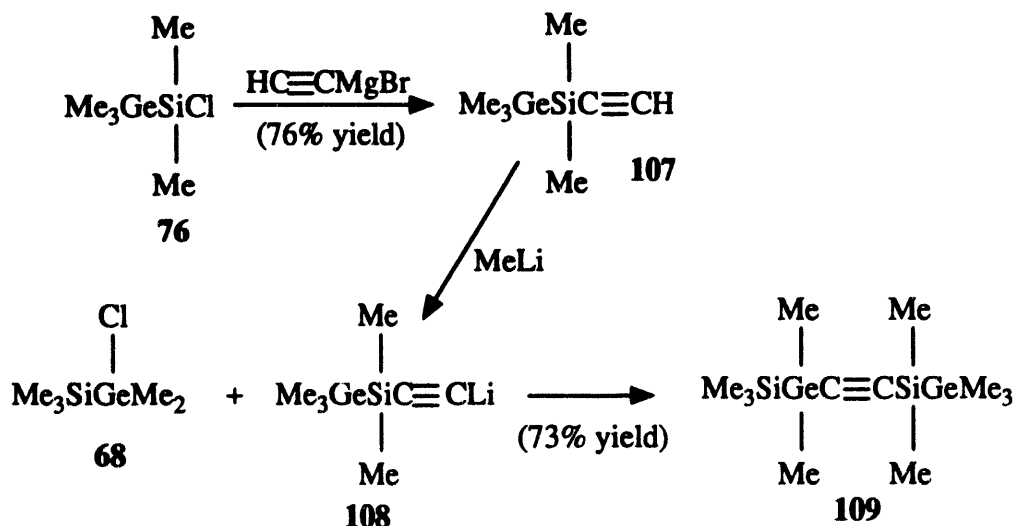
SFR pyrolysis of this mixture from 440-500°C led to

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**.

Scheme 26



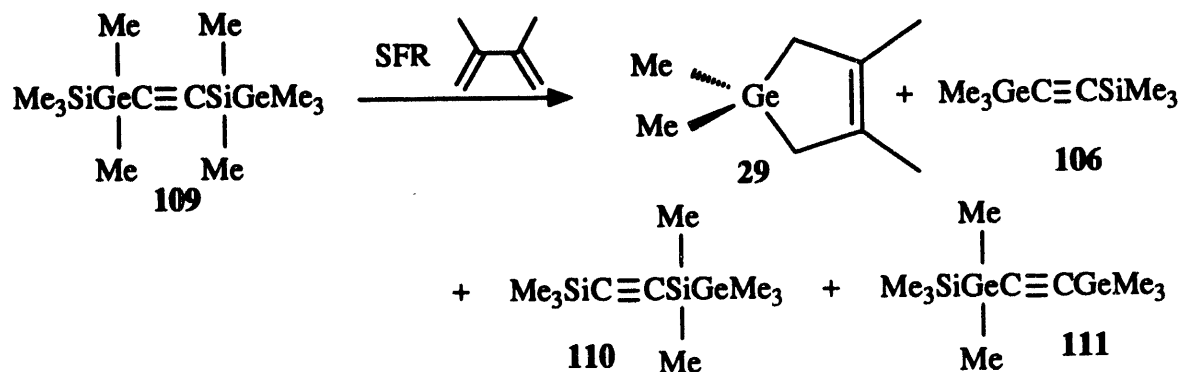
With germlyl-acetylene elimination demonstrated to be a viable route toward silylene formation, a molecule capable of an internal competition reaction between dimethylsilylene and dimethylgermylene extrusion was designed. The kinetic data for the pyrolysis of **88** and **89** were almost identical, therefore compound **109** was chosen as an appropriate model. This molecule was prepared (Scheme 27) from the appropriate lithio-acetylene, **108**, and chlorogermene **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

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. Petrich¹¹² had demonstrated that in the case of disilanes, there was a competition between

Scheme 28



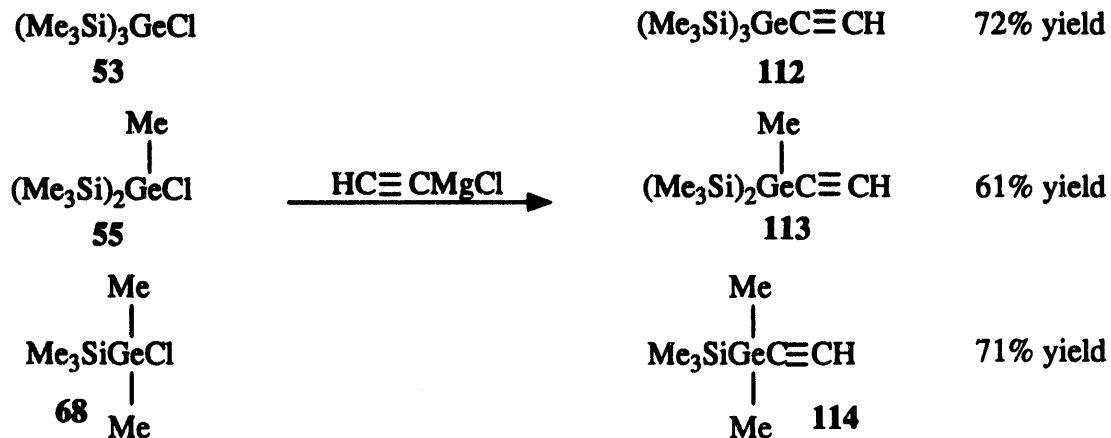
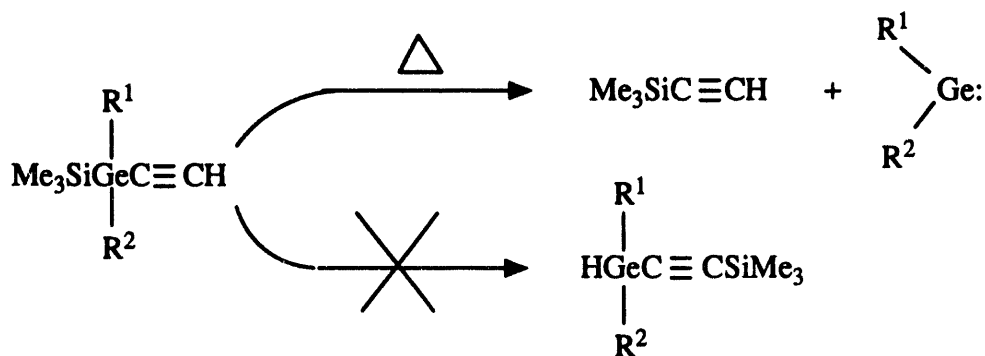
(% as determined by G.C. integration)

Oven Temp.	109	29	110	111	106
430°C	56	14	25	5	-
450°C	42	18	33	7	-
470°C	28	21	38	10	3
490°C	17	21	39	14	9
510°C	15	20	31	14	20
530°C	10	23	27	11	29

an apparent silicon-proton dyatropic 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 germylenes, however the dyatropic 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

Scheme 29Scheme 30

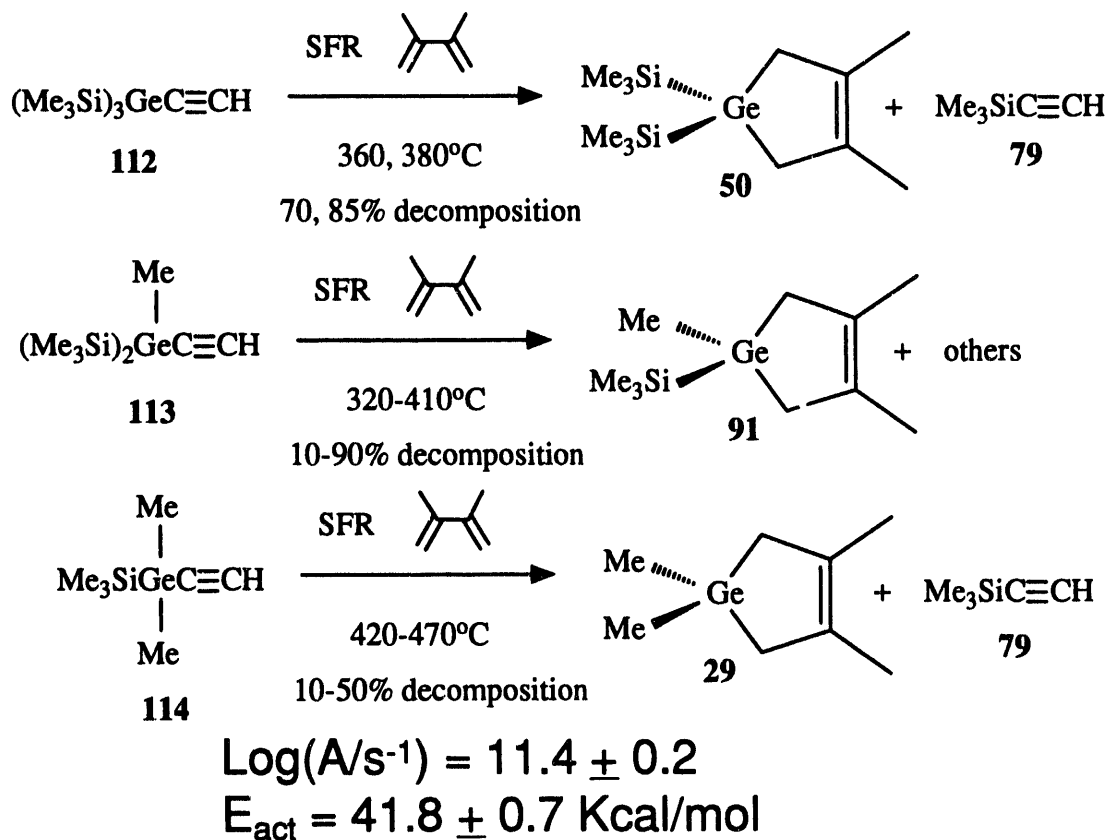
product was the trapped germylene, **50**. This fits the temperature range for decomposition established earlier with **81**. Trimethylsilylacetylene was not detected due to its similarity in GC retention with DMB.

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 trimethylsilyl-acetylene. Pyrolysis from 420-470°C (10-50% decomposition) afforded the following parameters: $\text{Log}(A/\text{s}^{-1}) = 11.4 \pm 0.2$ and $E_{\text{act}} = 41.8 \pm 0.7$ Kcal/mol. (figure 9) This is very close to the kinetic parameters obtained for **89**.

Scheme 31



Our research group has recently developed a strong interest in strained cyclic acetylenes.¹¹³ One approach toward reaching strained rings is to start with larger rings

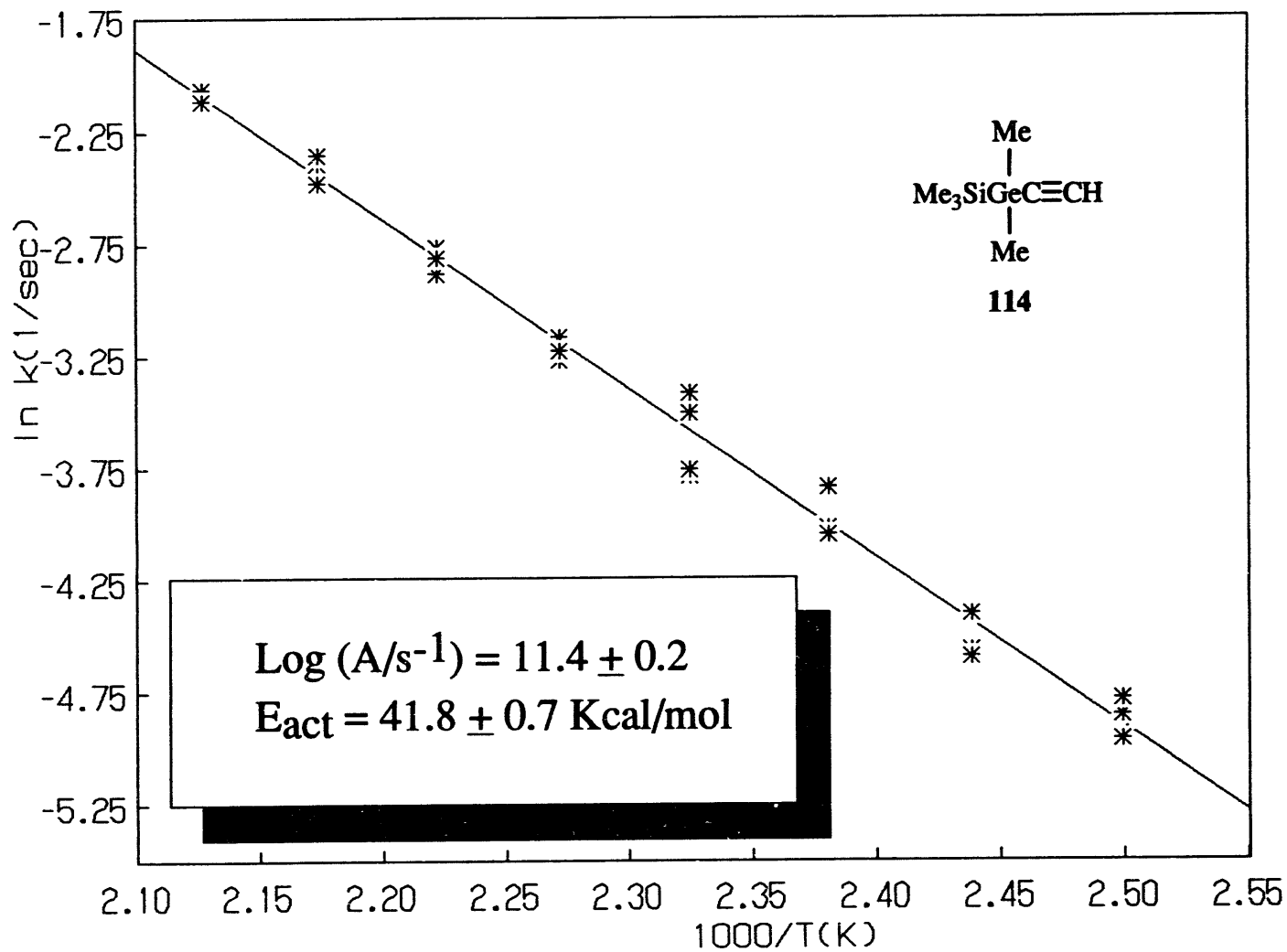


Figure 9, Arrhenius plot for the thermal decomposition of **114** following the formation of **79**.

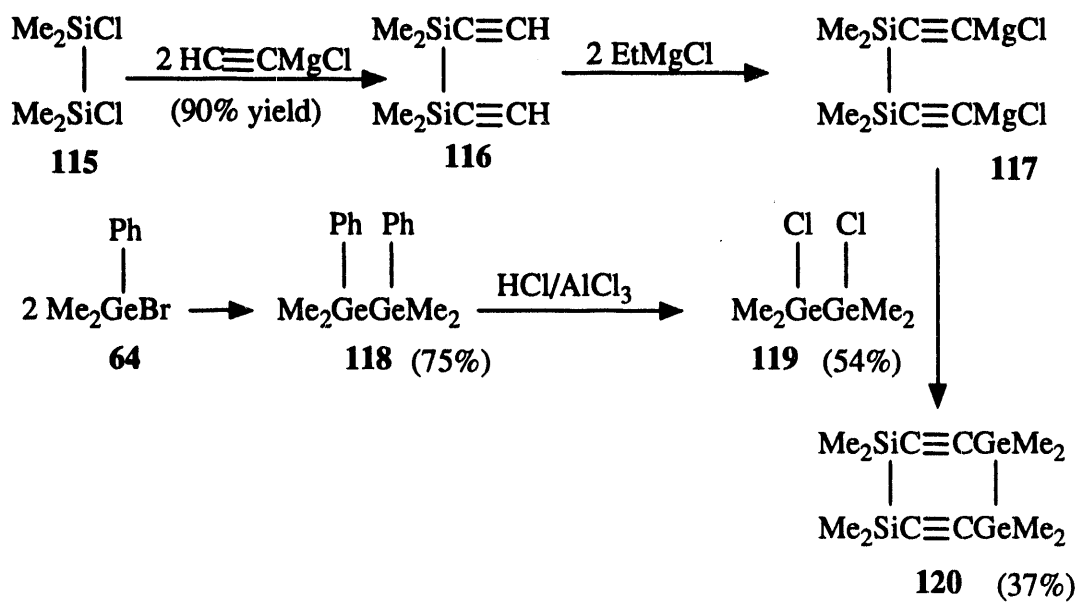
and simply extrude members of the ring. With this in mind, we attempted to use the germyl-acetylene chemistry just described to form a highly strained cyclic-diacetylene. Compound **120** was prepared by the addition of dichlorodigermane **119** to the di-Grignard **117** for an isolated yield of 37%. 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.¹¹³ None of the expected trapped silylene or germylene, nor the resultant strained ring were observed.

Apparent Dyatropic Rearrangement of Silicon and Germanium

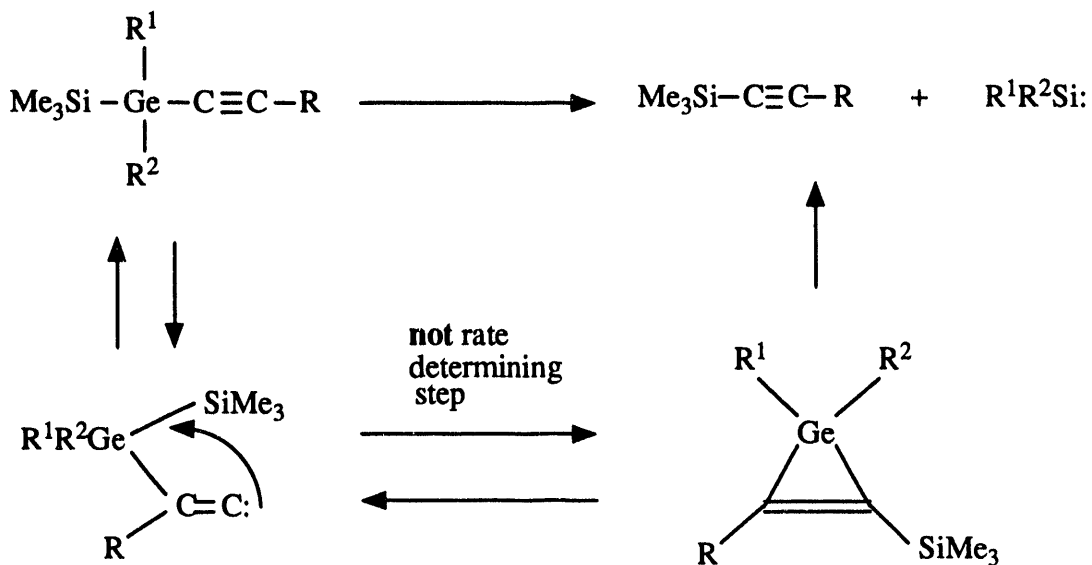
Looking back at our mechanism for germylene extrusion from germylacetylenes (Scheme 33), there are three possible rate-determining steps. In the last section it was shown that vinylidene insertion showed no preference for a Si-Ge bond over a Si-Si bond. This leaves vinylidene formation via a germyl shift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

To test whether vinylidene (or germacyclopropene)

Scheme 32

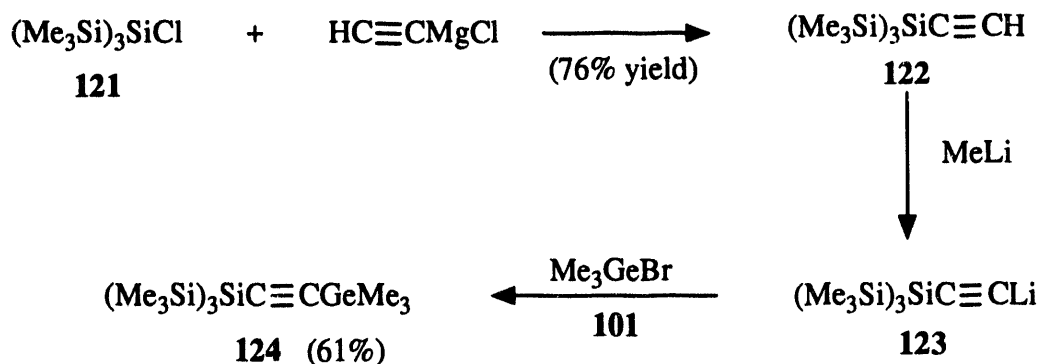


Scheme 33



formation was rate-determining, a compound designed to extrude silylene with a trimethylgermyl group at the terminal acetylene position was desired. If vinylidene (or germacyclopropene) 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.

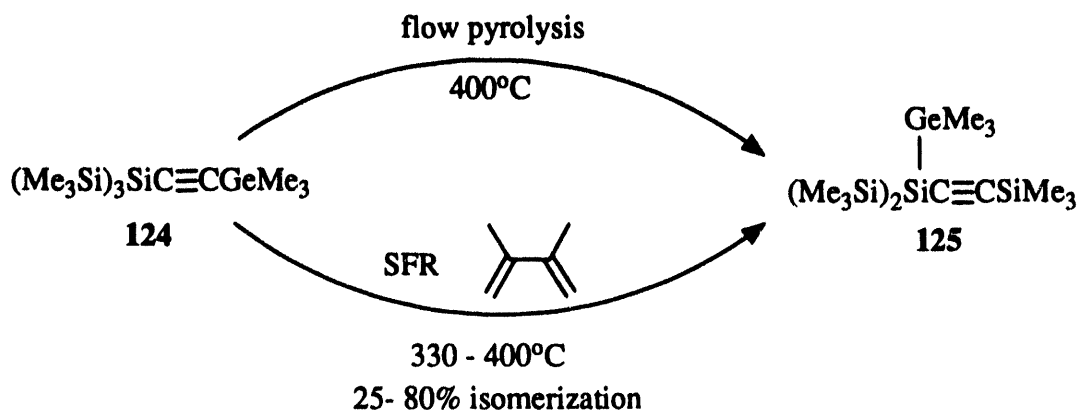
Scheme 34



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



$$\text{Log}(A/\text{s}^{-1}) = 10.2 \pm 0.1$$

$$E_{\text{act}} = 32.7 \pm 0.2 \text{ Kcal/mol}$$

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 undergo 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 germly substituted silylene, **130**.

This data is consistent with Petrich's¹¹² 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.

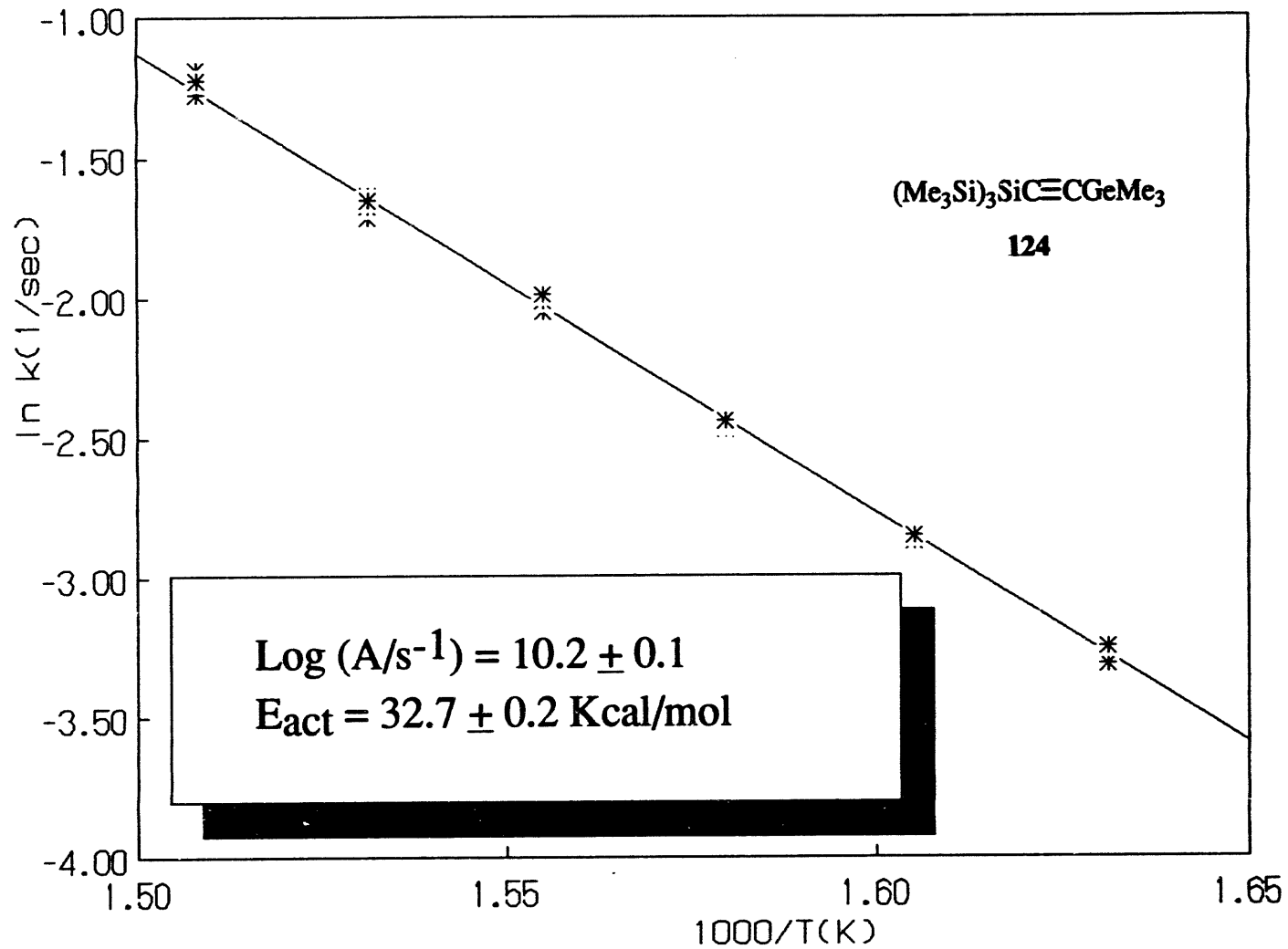
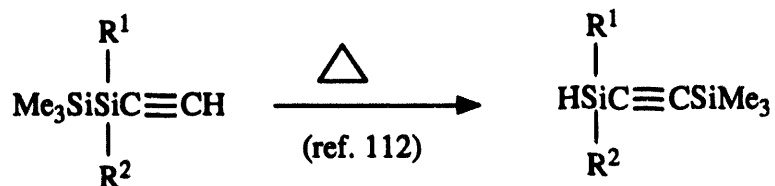


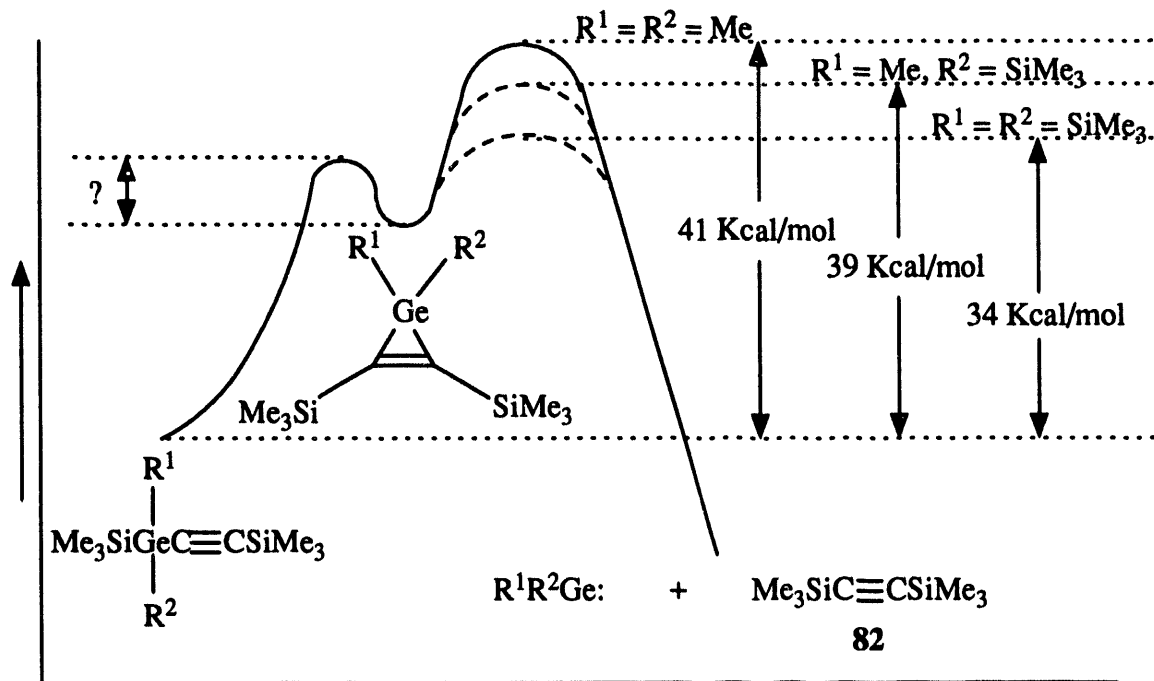
Figure 10, Arrhenius plot for the thermal isomerization of **124** to **125**.

Scheme 37



intermediates. For example, 2,3-silicon substitution on the ring lowers the barrier to germylene extrusion. Whereas with silacyclopropenes there is no substantial substituent effect. These energy differences can be depicted in the form of an energy diagram as shown in Scheme 38.

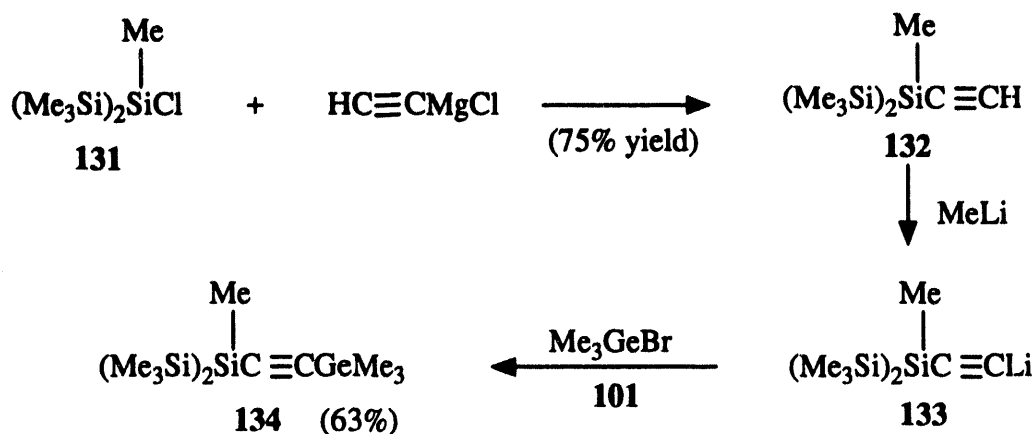
Scheme 38



To further support our conclusions, compound **134** (Scheme 39) was prepared in 63% yield by adding Me_3GeBr 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 [$\text{Log}(A/\text{s}^{-1}) = 11.0 \pm 0.1$, $E_{\text{act}} = 35.7 \pm 0.2$ Kcal/mol] (figure 11) and the extrusion of silylene [$\text{Log}(A/\text{s}^{-1}) = 10.2 \pm 0.4$, $E_{\text{act}} = 37.8 \pm 1.3$ Kcal/mol] (figure 12). Pyrolysis of **135** cleanly led to extrusion of the germylsilylene 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: $^{135}k_{460} = 9.4 \times 10^{-2} \text{ s}^{-1}$, $^{92}k_{460} = 1.0 \times 10^{-1} \text{ s}^{-1}$; $^{135}k_{480} = 1.6 \times 10^{-1} \text{ s}^{-1}$, $^{92}k_{480} =$

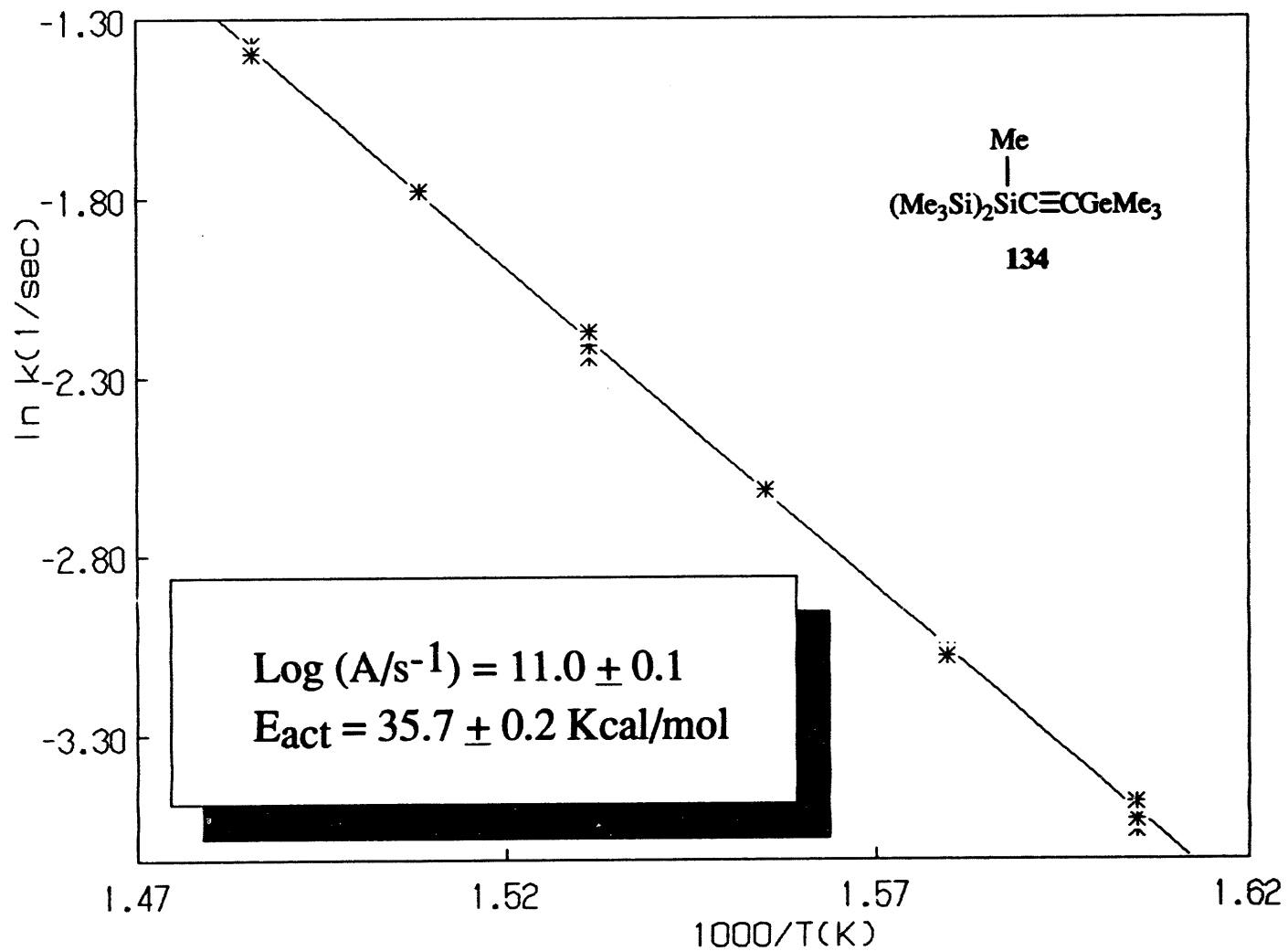


Figure 11, Arrhenius plot for the thermal isomerization of **134** to **135**.

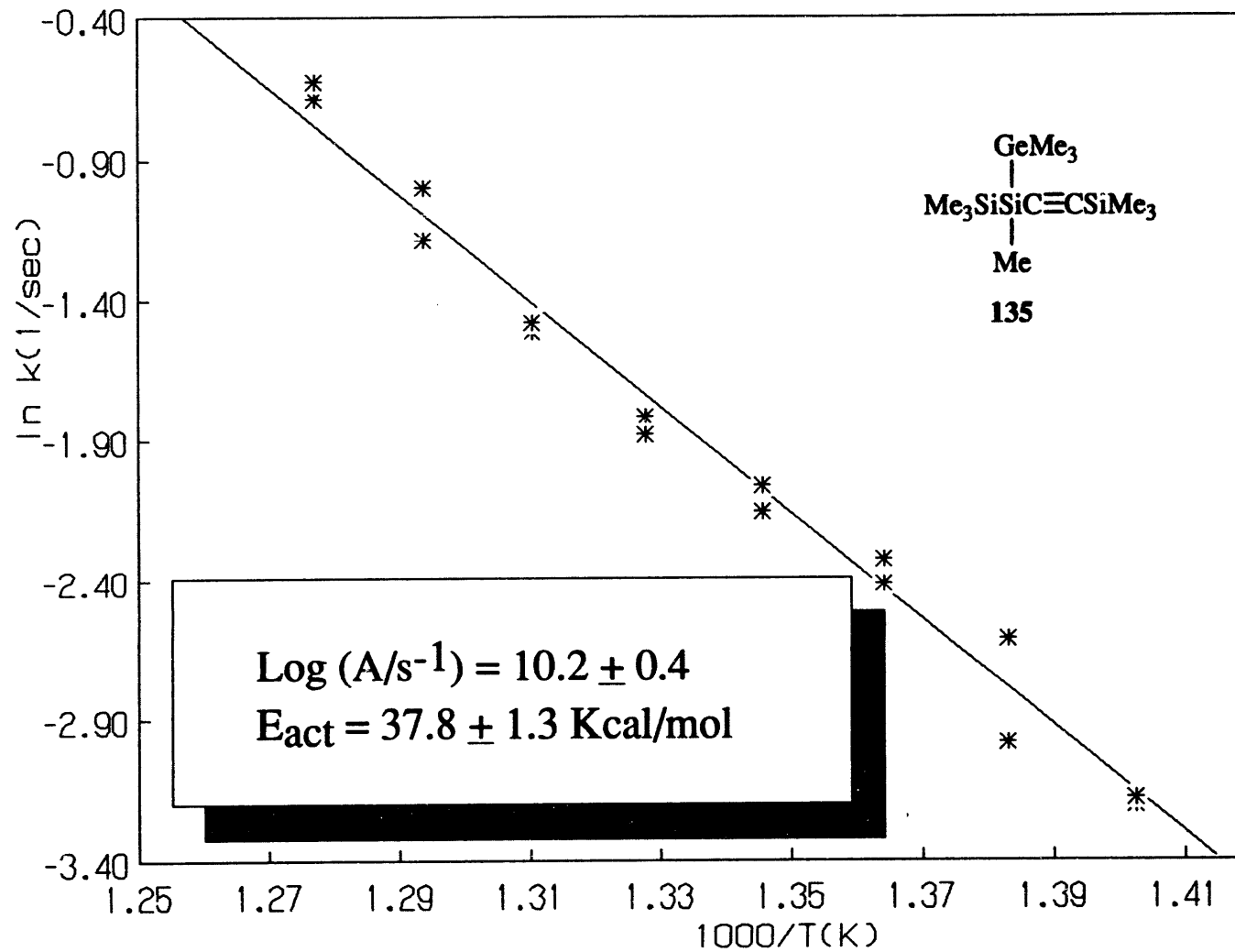
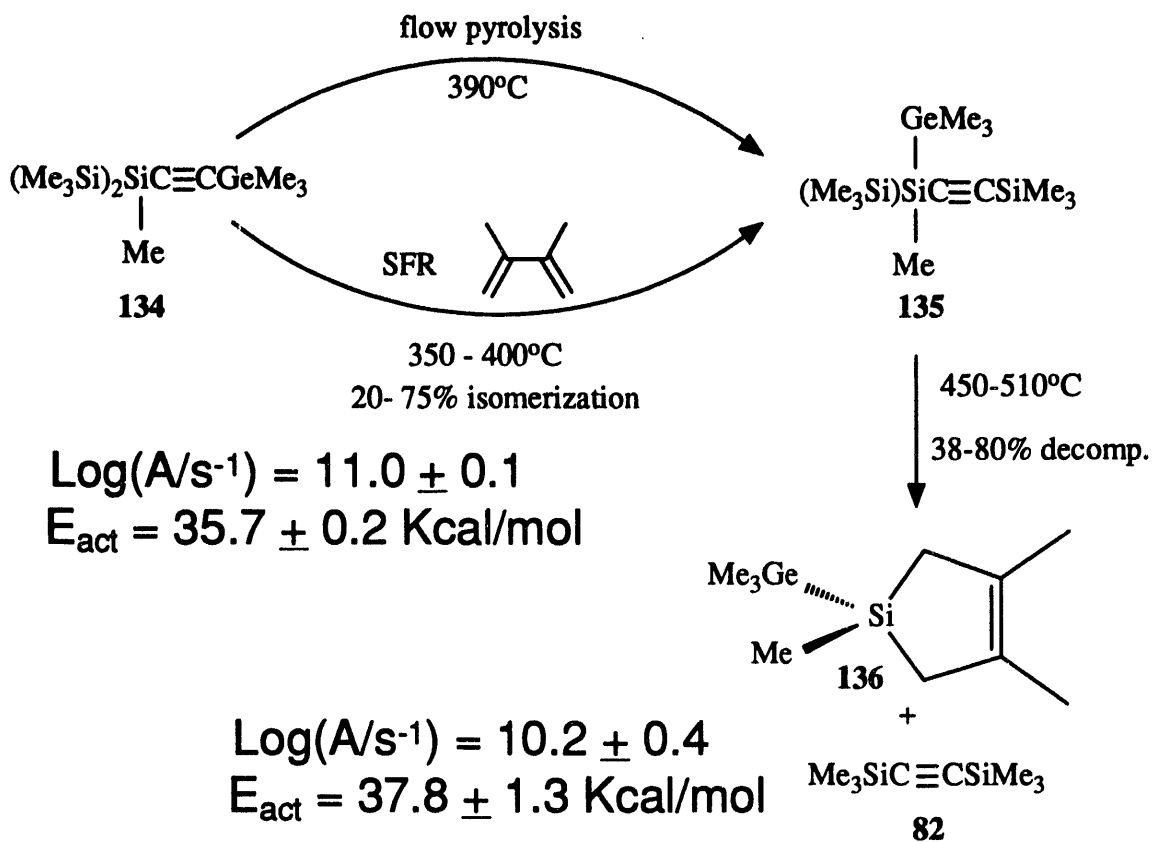


Figure 12, Arrhenius plot for the thermal decomposition of **135** following the formation of **82**.

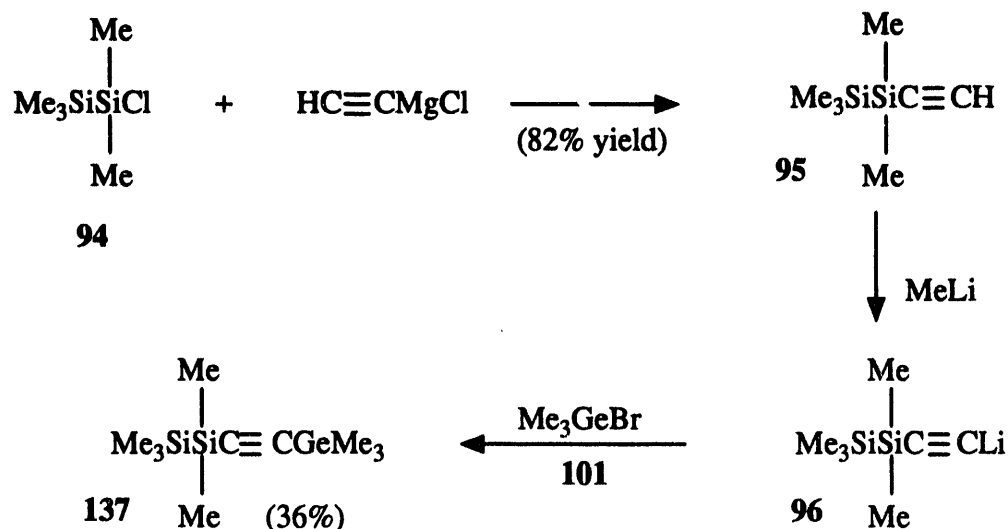
Scheme 40



$2.1 \times 10^{-1} \text{ s}^{-1}$; and $^{135}k_{500} = 3.2 \times 10^{-1} \text{ s}^{-1}$, $^{92}k_{500} = 4.6 \times 10^{-1} \text{ s}^{-1}$.

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

Scheme 41

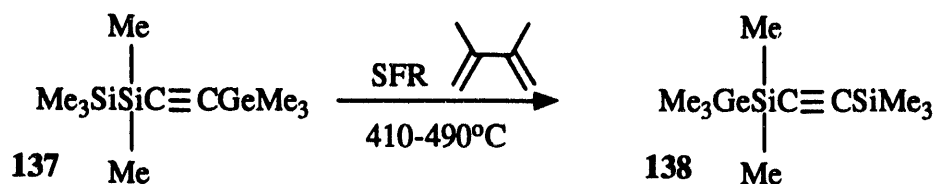
corresponding pyrolysate compositions are reported in Scheme 42.

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.

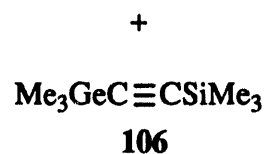
Arrhenius parameters (Scheme 44, figure 13) were obtained for the thermal decomposition of **138**. The higher temperatures required for this decomposition clearly shows that **106** is derived primarily from **137**.

A graphic representation of this energy surface is

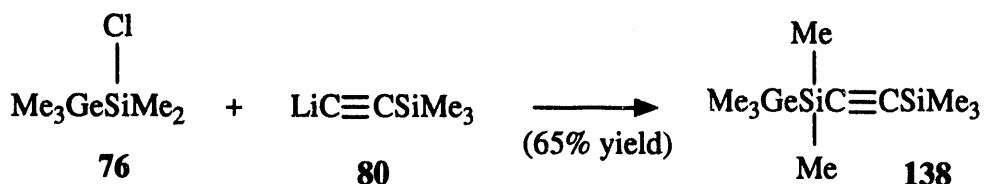
Scheme 42



Oven Temp.	137	138	106
410°C	95%	3.5%	1.5%
430°C	80%	10%	10%
450°C	60%	20%	20%
470°C	40%	25%	35%
490°C	20%	30%	50%



Scheme 43



difficult to present here due to its 3-dimensional nature. In its 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

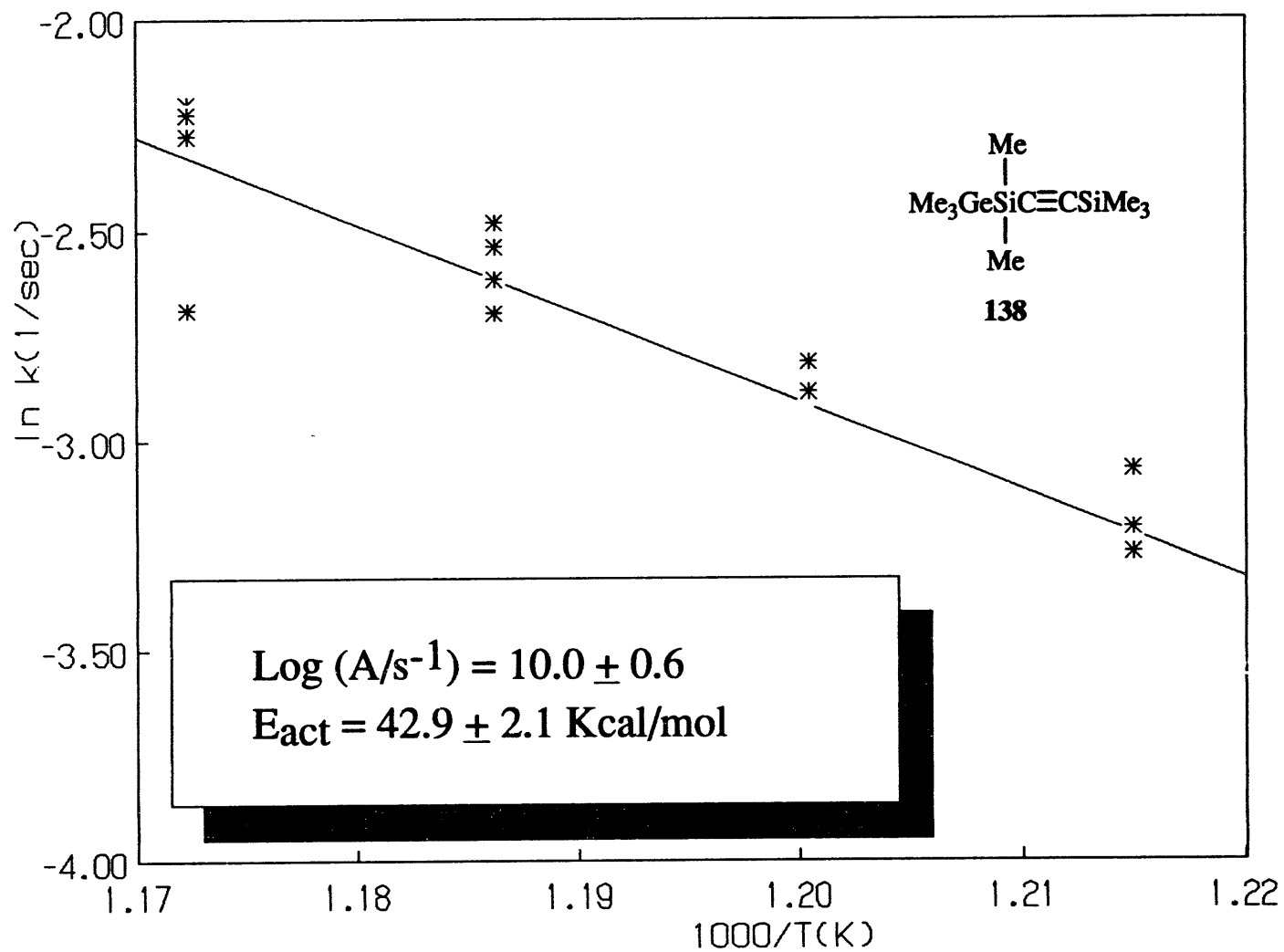
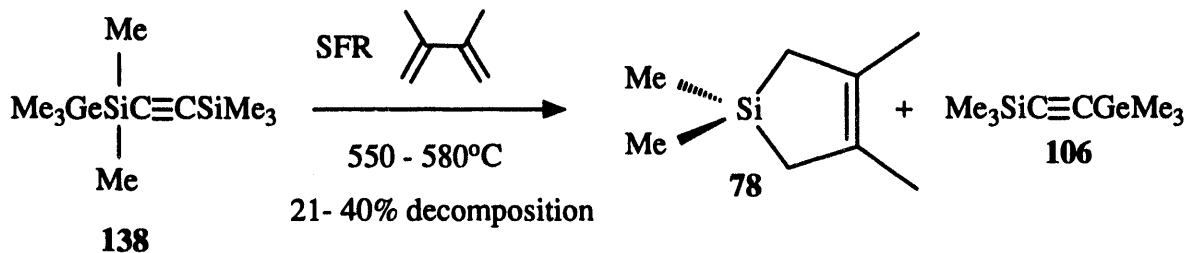


Figure 13, Arrhenius plot for the thermal decomposition of **138** following the formation of **106**.

Scheme 44



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

$$E_{\text{act}} = 42.9 \pm 2.1 \text{ Kcal/mol}$$

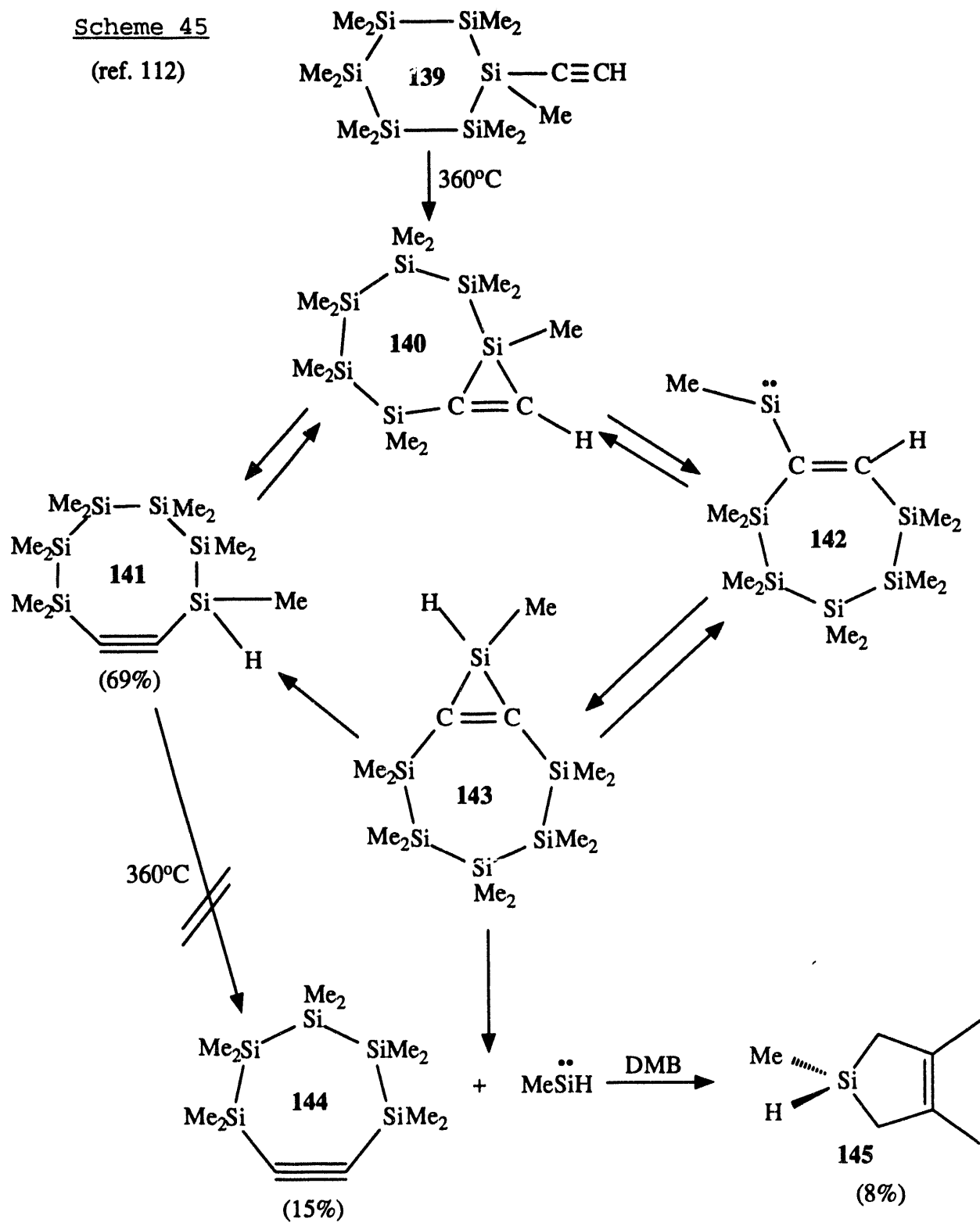
dyatropic rearrangement.

It was desired to test the universality of this thermal rearrangement. Petrich¹¹² 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.

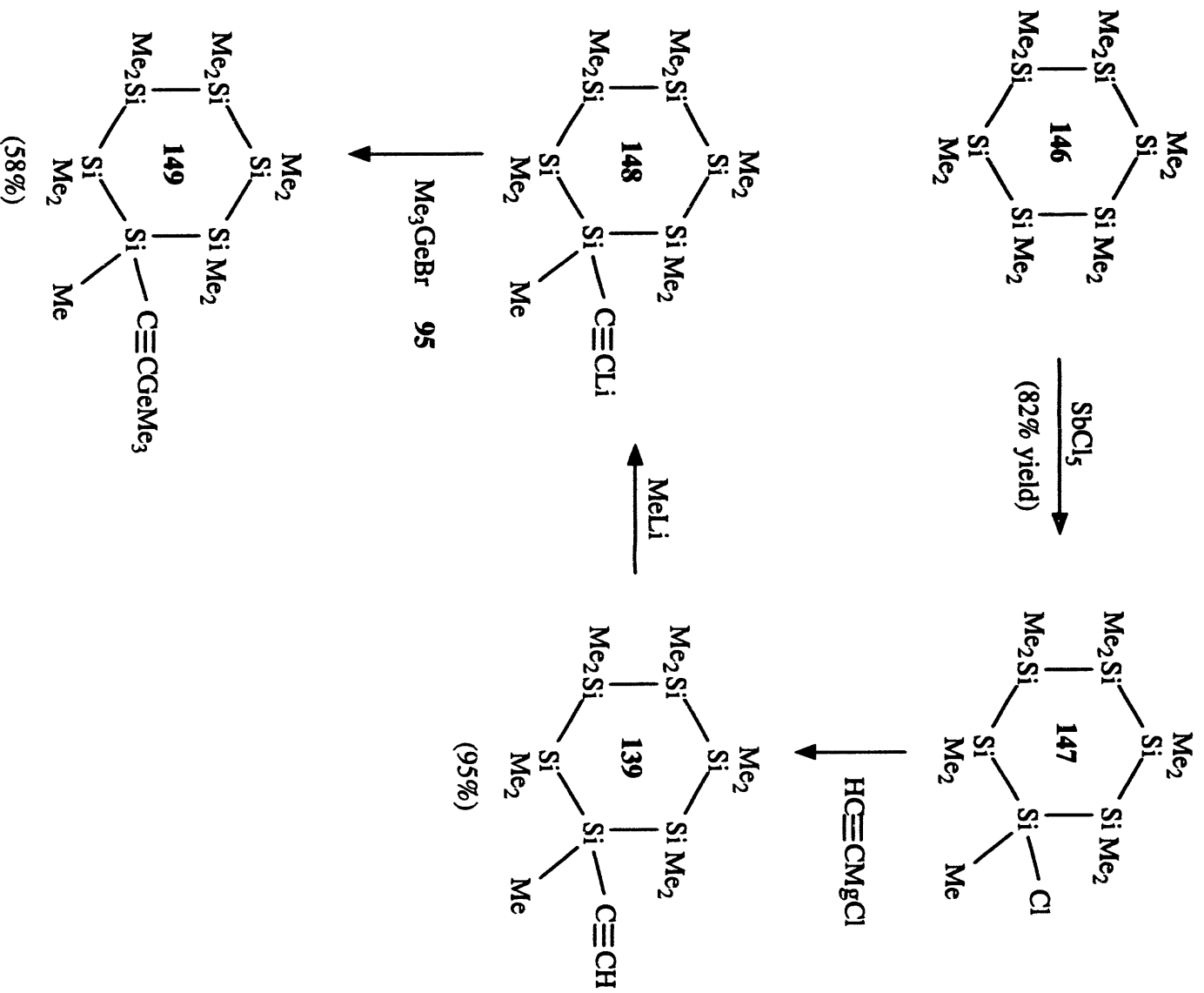
We desired to see if germanium would facilitate this rearrangement. Addition of **101** to lithioacetylene **148** afforded **149** in 58% yield from silylacetylene **139**. Compound **139** was prepared following Petrich's¹¹² procedure by ethynyl Grignard addition to **147** in 95% yield. In turn, **147** was

Scheme 45

(ref. 112)



Scheme 46



prepared in 82% yield by adding SbCl_5 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 germysilylene is observed as evidenced by the formation of **144**. Again it was puzzling that only a trace amount of germysilylene was successfully trapped.

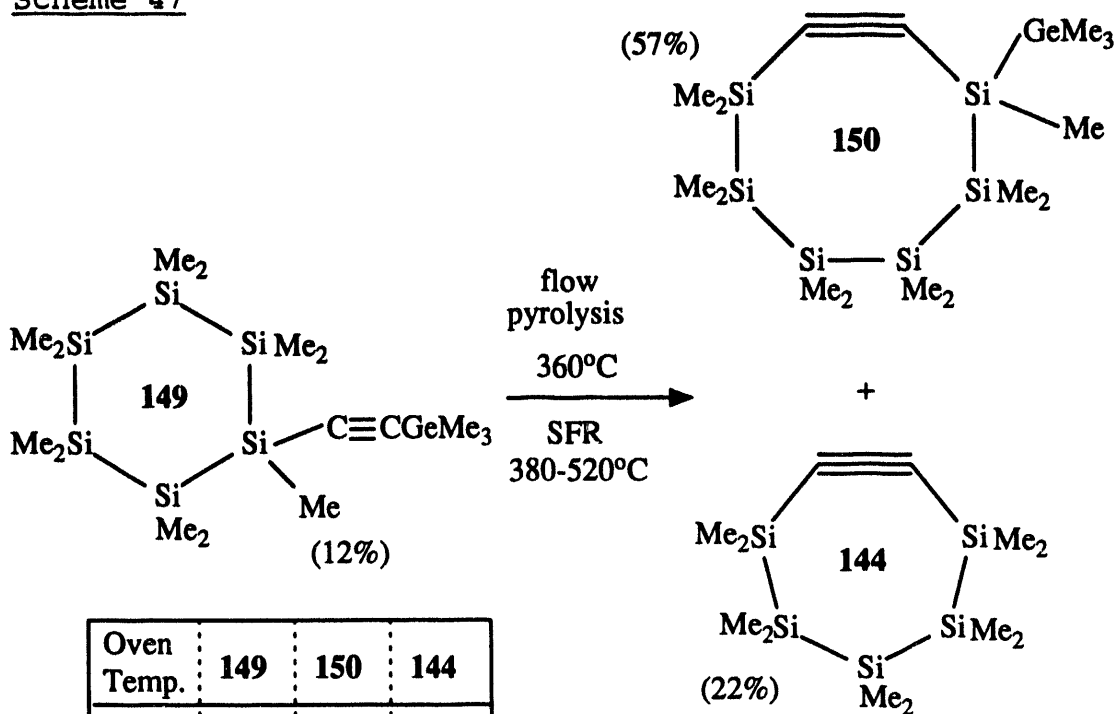
These results are completely consistent with the linear model. However, in order to account for the selective extrusion of germysilylene it becomes necessary to adopt Petrich's vinylsilylene mechanism.

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 organogermanium 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



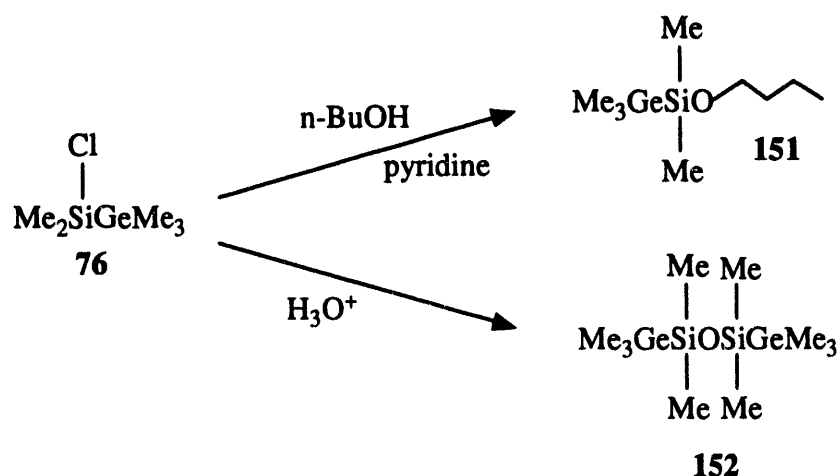
Oven Temp.	149	150	144
380°C	95%	5%	-
400°C	90%	10%	-
420°C	70%	30%	-
440°C	60%	40%	-
460°C	40%	40%	20%
480°C	30%	30%	40%
500°C	30%	20%	50%
520°C	10%	20%	70%

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

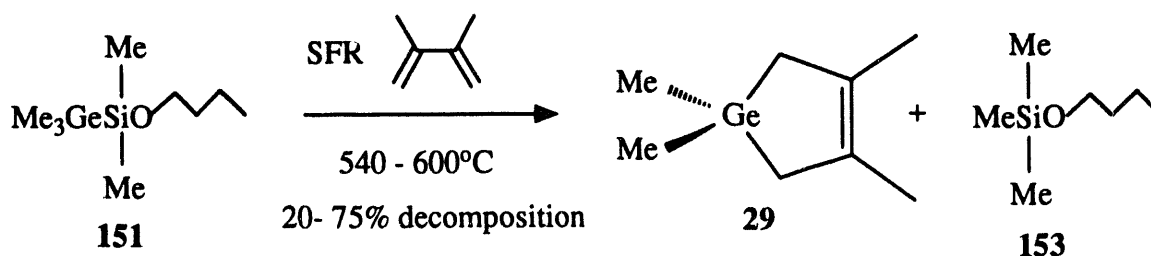
the α -elimination of silylene, compounds **151** and **152** were prepared from **76** as shown in Scheme 48. Compound **151** was prepared by adding a 1:1 molar mixture of n-butanol and pyridine to **76**. Compound **152** was obtained as a by-product from partial hydrolysis of **76**.

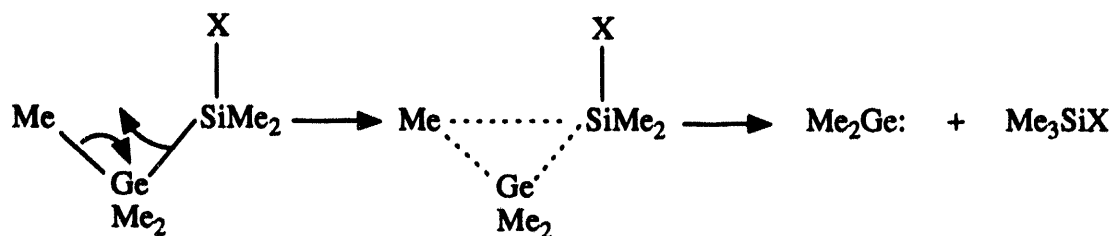
Scheme 48



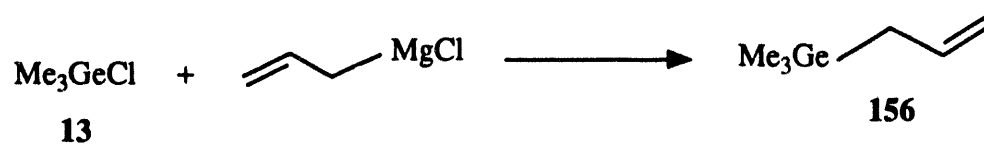
As shown in Scheme 49, SFR pyrolysis of **151** from $540^\circ\text{-}600^\circ\text{C}$ in the presence of a 20-fold excess of DMB lead to the formation of trapped germylene, **29**, and the resultant butoxytrimethylsilane, **153**.

Scheme 49



Scheme 51

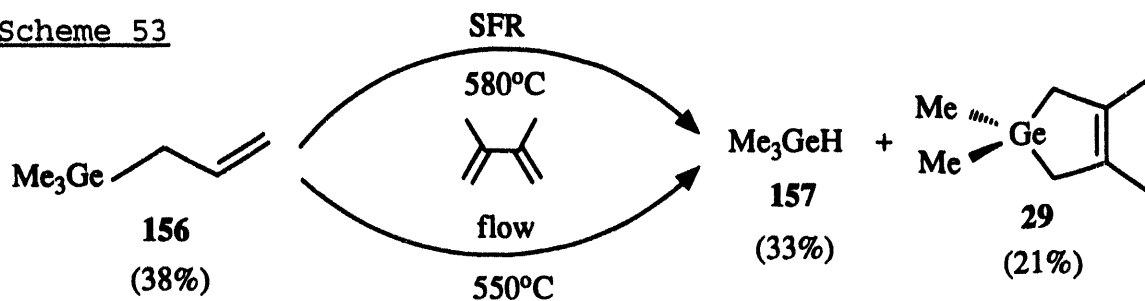
pyrolysis study of allyltrimethylsilane reported by Barton et al.¹¹⁶ compound **156**, prepared as shown in Scheme 52, was pyrolyzed in anticipation of germylene formation.

Scheme 52

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.

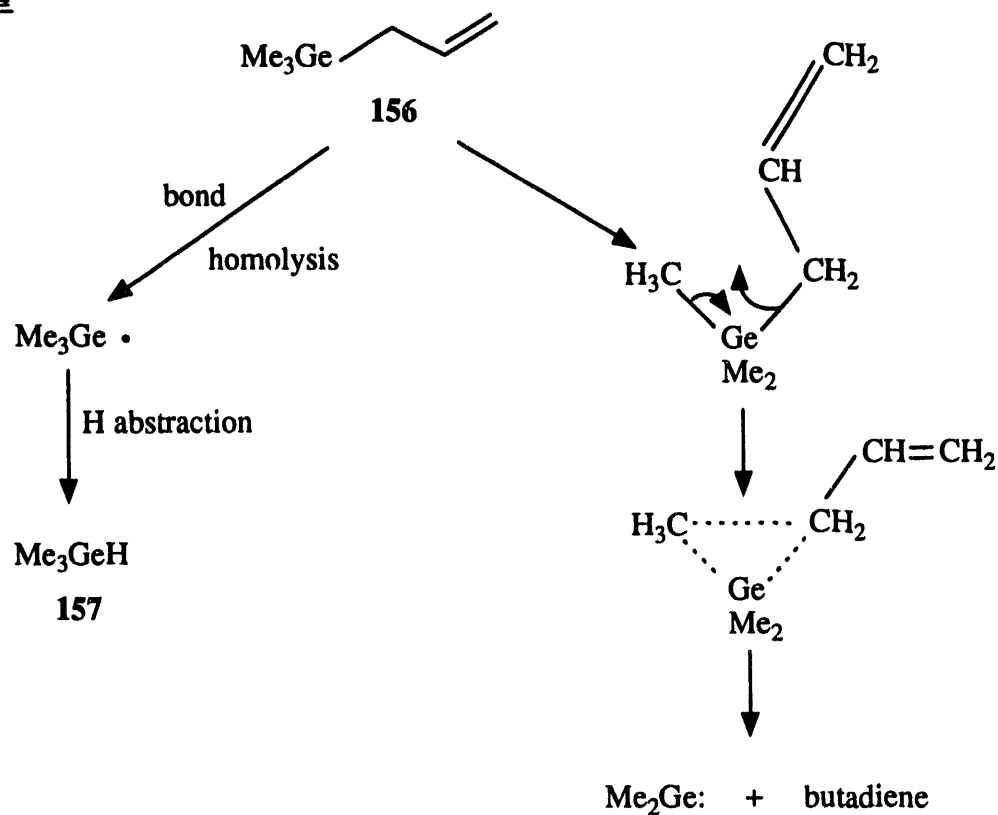
The formation of **157** (Scheme 53) can simply be explained by bond homolysis of the weakest bond in the molecule, the Ge-allyl bond, followed by proton abstraction by the resultant radical. However, the formation of dimethylgermylene is more difficult to explain. It is possible that the trimethylgermyl

Scheme 53



radical has lost a methyl group to form the more stable germylene. Conversely, it is possible a concerted mechanism is involved.

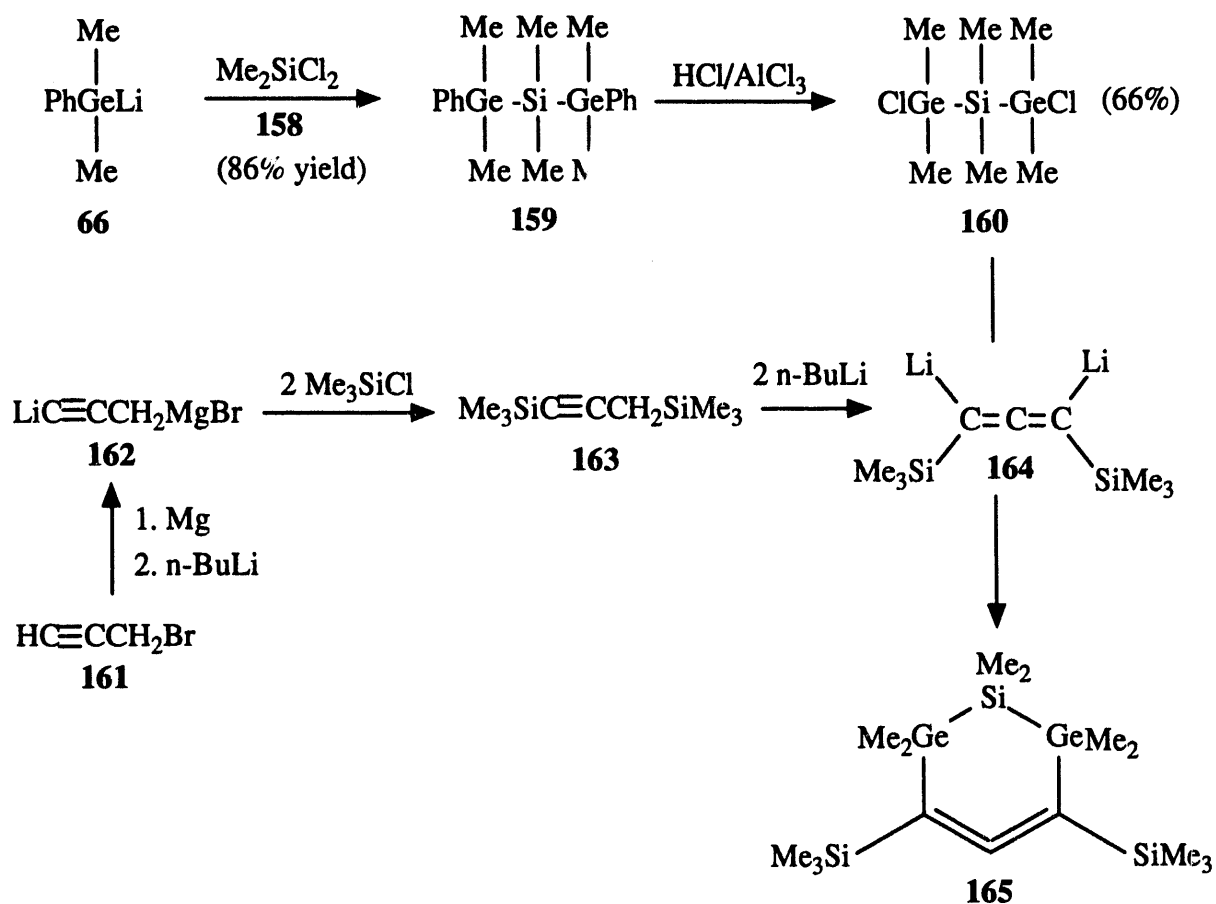
Scheme 54



Our interest in strained cyclic compounds¹¹⁷ led us to one final example of organogermanium thermochemistry.

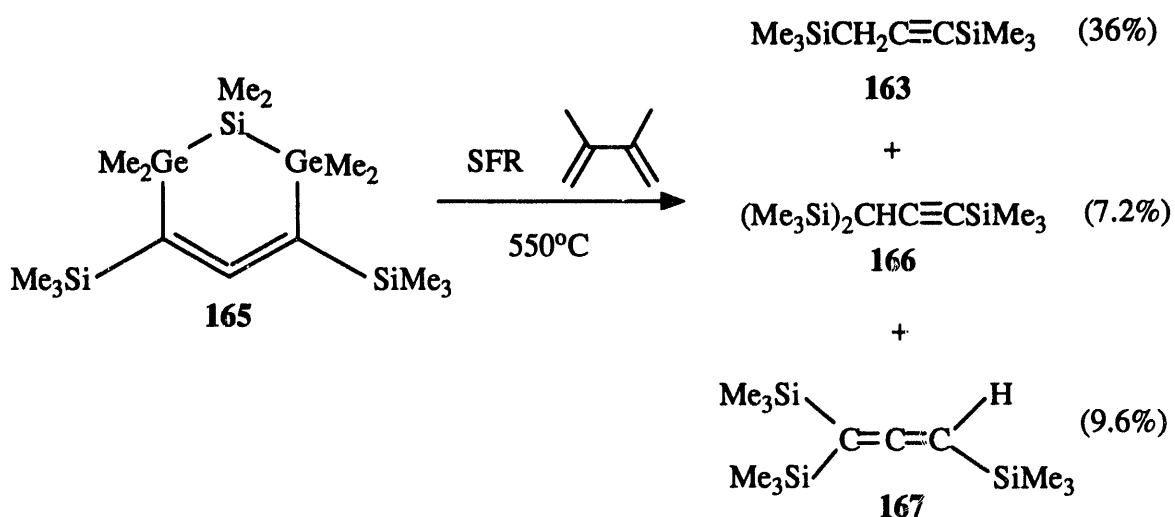
Compound **165** was prepared as shown in Scheme 55 by the addition of **160** to dilithioallene **164**. Compound **160** was prepared in 66% yield by replacing the phenyl groups of **159** with chlorines using HCl/AlCl₃. Addition of two equivalents of germyl anion **66** to dimethyldichlorosilane, **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 ^1H (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 ^1H and ^{13}C NMR are reported as parts per million using the stated solvent as standard (ie. 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 μm 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.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 cm³ and a τ 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 ResultsSynthesis of 2,2,4,4-tetramethyl-3,3-bis(trimethylsilyl)-2,4-disila-3-germapentane, 46.

Following the procedure of Brook et al.,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 $\text{Na}_2\text{SO}_4/\text{MgSO}_4$. The resultant solid was recrystallized from acetonitrile yielding 53.5 g (0.147 mol) of a white crystalline compound, 40.5% yield. $^1\text{H}(\text{C}_6\text{D}_6)$: δ 0.365; $^{13}\text{C}(\text{C}_6\text{D}_6)$: 3.494; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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,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). $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.281 (27H), s 2.159 (1H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: 2.710; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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.³³ 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) dimethyldichlorogermane and 9.2 g (0.047 mol) methyltrichlorogermane 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 8.7g (0.028 mol) tris(trimethylsilyl)methylgermane, 60% yield, as a clear colorless liquid.

For **52**: $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.225 (27H), s 0.261 (3H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -13.791, 1.213; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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**: $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.160 (18H), s 0.255 (6H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -7.861, -0.574; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -9.211; MS: 250(M^+ , 3), 235(6),

177(4), 162(13), 145(11), 131(14), 73(100); IR(cm^{-1}): 2958, 2903, 1406, 1253, 840, 788.

Synthesis of 3-chloro-2,2,4,4-tetramethyl-3-trimethylsilyl-2,4-disila-3-germapentane, 53.

Following the procedure of Brook et al.,¹⁰⁵ 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.³³, 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_4 . GC analysis showed complete conversion to the desired product. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.327 (27H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: 0.082; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -2.456; MS: 328(M^+ , 1), 313(6), 220(32), 146(37), 131(39), 73(100); IR(cm^{-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°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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.198 (18H), s 1.757 (6H), s 1.891 (4H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -0.139, 19.642, 22.413, 131.904; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{12}\text{H}_{28}^{70}\text{GeSi}_2$ 298.09726, measured 298.09751.

Synthesis of bis(trimethylsilyl)chloromethylgermane, 55.

Following the procedure of Gaspar et al,³³ a solution of 2.6 g (10.5 mmol) **54** in 30 ml CH_3NO_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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. Removal of the pentane left 2.5 g (9.34 mmol) (89 %) of crude product which was not further purified. $^1\text{H}(\text{CDCl}_3)$: s 0.235 (18H), s 0.671 (3H); $^{13}\text{C}(\text{CDCl}_3)$: -1.526, 0.116; $^{29}\text{Si}(\text{CDCl}_3)$: -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 form 1-trimethylsilyl-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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.135 (9H), s 0.332 (3H), s 1.770 (6H), q 1.59, 1.65, 1.83, 1.89 (4H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -4.620, -1.179, 19.685, 25.939, 131.270; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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.,¹¹⁰ 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 rotary 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. $^1\text{H}(\text{CD}_3\text{OD})$: mult. 6.374-6.418 (6H), mult. 6.538-6.583 (6H); $^{13}\text{C}(\text{CD}_3\text{OD})$: 112.646, 118.061, 151.061.

Synthesis of tetraphenylgermane, 61.

Following the procedure of Corriu et al,¹¹¹ a stirring suspension of 12.34 g (26.0 mmol) **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) **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. $^1\text{H}(\text{CDCl}_3)$: m 7.305-7.380 (6H), m 7.480-7.520 (4H); $^{13}\text{C}(\text{CDCl}_3)$:

128.244, 129.085, 135.382, 136.094; MS: 382 (M^+ , 0.4),
307(20), 306(18), 305(99), 304(34), 303(70), 302(11), 301(51),
230(20), 229(20), 228(100), 227(59), 226(83), 225(33),
224(57), 223(18), 154(17), 153(22), 152(20), 151(75), 150(23),
149(59), 147(43), 125(13), 123(13), 99(17), 97(12), 77(27),
74(10), 51(70).

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 dimethyldiphenylgermane, 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.

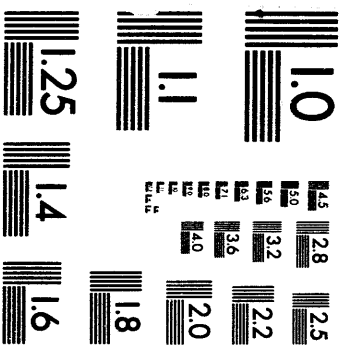
Synthesis of bromodimethylphenylgermane, **64**.

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. $^1\text{H}(\text{CDCl}_3)$: s 1.060 (6H), m 7.39 - 7.44 (3H), m 7.57 - 7.62 (2H); $^{13}\text{C}(\text{CDCl}_3)$: 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 $\text{C}_8\text{H}_{11}^{79}\text{Br}^{70}\text{Ge}$ 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. $^1\text{H}(\text{CDCl}_3)$: s 0.909 (6 H), m 7.38 - 7.42 (3H), m 7.54 - 7.58 (2H); $^{13}\text{C}(\text{CDCl}_3)$: 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.



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Synthesis of dimethyl(trimethylsilyl)phenylgermane, 67.

Following the procedure of Kumada et al.,¹⁰⁹ 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.,¹⁰⁹ 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 as 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. $^1\text{H}(\text{CDCl}_3)$: s 0.224 (9H), s 0.665 (6H); $^{13}\text{C}(\text{CDCl}_3)$: -2.224, 3.636; $^{29}\text{Si}(\text{CDCl}_3)$: -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 $\text{C}_5\text{H}_{15}^{35}\text{Cl}^{74}\text{GeSi}$ 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.159 (9H), s 0.744 (6H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -2.340, 3.244; $^{29}\text{Si}(\text{C}_6\text{D}_6)$:

-6.018; MS: 258(1.2), 256(M⁺, 1.6), 254(1.2), 241(0.8), 239(0.5), 177(1.0), 155(1.1), 153(1.7), 151(1.2), 104(6.9), 102(5.7), 100(4.0), 89(3.5), 87(2.8), 85(2.1), 75(3.6), 74(8.5), 73(100), 59(2.1); IR(cm⁻¹): 2961, 2906, 1406, 1255, 841, 798; calc. for C₅H₁₅⁷⁹Br⁷⁰GeSi 251.93694, measured 251.93709.

Synthesis of tetramethylgermane, 71.

Following the procedure of Corriu et al.,¹¹¹ 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. ¹H(CDCl₃): s 0.090; ¹³C(CDCl₃): -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 $\text{Na}_2\text{SO}_4/\text{MgSO}_4$, 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. $^1\text{H}(\text{CDCl}_3)$: s 0.343 (12H), m 7.31-7.33 (6H), m 7.40-7.44 (4H); $^{13}\text{C}(\text{CDCl}_3)$: -3.920, 127.682, 128.394, 133.836, 138.972; $^{29}\text{Si}(\text{CDCl}_3)$: -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) Me_3GeCl 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 $\text{Na}_2\text{SO}_4/\text{MgSO}_4$. Distillation (b.p. = $38-40^{\circ}\text{C}$, 0.5 mm Hg) afforded 3.86 g

(0.121 mol) of a clear, colorless, liquid product, 67% yield.
 $^1\text{H}(\text{CDCl}_3)$: s 0.11 (9H), s 0.350 (6H), m 7.286 - 7.308 (3H), m
 7.398 - 7.430 (2H); $^{13}\text{C}(\text{CDCl}_3)$: -3.392, -3.069, 127.756,
 128.504, 133.623, 139.226; $^{29}\text{Si}(\text{CDCl}_3)$: -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 $\text{C}_{11}\text{H}_{20}^{74}\text{GeSi}$ 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%. $^1\text{H}(\text{CDCl}_3)$: s 0.221 (9H), s
 0.492 (6H); $^{13}\text{C}(\text{CDCl}_3)$: -3.585, 2.769; $^{29}\text{Si}(\text{CDCl}_3)$: 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
 $\text{C}_5\text{H}_{15}\text{Cl}^{74}\text{GeSi}$ 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. $^1\text{H}(\text{CD}_3\text{OD})$: d 1.054, 1.074 (18H), octet 3.118-3.159 (6H) $J=6.6$ Hz, 2.0 Hz; $^{13}\text{C}(\text{CD}_3\text{OD})$: 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_2O . 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.185 (9H), s 0.310 (27H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: 0.530, 1.058, 109.245, 115.107; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{14}\text{H}_{36}^{70}\text{GeSi}_4$ 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(C₆D₆): s 0.149 (9H), s 0.287 (27H); ¹³C(C₆D₆): 0.224, 0.348, 108.311, 118.320; ²⁹Si(C₆D₆): -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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. Removal to the solvent by vacuum line and subsequent purification by preparative gas chromatography (100 $^{\circ}\text{C}$ isotherm for 6.5 min. ramping at 6 $^{\circ}\text{C}/\text{min.}$ to 230 $^{\circ}\text{C}$, ret. time = 15 min., flow = 28, 15' column) yielded 100 mg (0.048 mmol) purified product (a clear colorless liquid), 50% yield. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.158 (9H), s 0.186 (9H), s 0.371 (6H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -2.949, -1.941, 0.302, 113.803, 113.875; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{10}\text{H}_{24}^{70}\text{GeSi}_2$ 270.06596, measured 270.06584.

Synthesis of 2,2,5,6,6-pentamethyl-5-(trimethylsilyl)-5-germa-2,6-disilahept-3-yne, **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) chlorogermane **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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.185 (9H), s 0.242 (18 H), s 0.423 (3H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -7.640, -0.759, 0.424, 112.065, 114.786; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{12}\text{H}_{30}^{70}\text{GeSi}_3$ 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. $^1\text{H}(\text{C}_6\text{D}_6)$: 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); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -4.620, -1.179, 19.685, 25.939, 131.270; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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-yne, 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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.145 (9H), s 0.218 (18H), s 0.259 (3H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -7.953, -1.471, 0.117, 111.282, 118.092; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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(cm^{-1}): 2961, 2902, 2086, 1405, 1254, 848, 790; calc. for $\text{C}_{12}\text{H}_{30}\text{Si}_4$ 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) chloropentamethyldisilane 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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. The ether was distilled off and only a small amount of 95 was purified for spectral characterization.

$^1\text{H}(\text{C}_6\text{D}_6)$: s 0.124 (9H), s 0.196 (6H), 2.150 (1H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -3.131, -2.704, 88.687, 95.832; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.206 (9H), s 0.251 (6H), s 0.317 (27H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -2.419, -2.369, 1.100, 110.755, 113.177; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{16}\text{H}_{42}^{70}\text{GeSi}_5$ 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) Me₃GeBr 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(CDCl₃): s 0.254 (9H), s 0.668 (3H), m 7.340-7.362 (6H), m 7.478-7.510 (4H); ¹³C(CDCl₃): -4.411, -2.402, 127.867, 128.871, 134.684, 137.020; ²⁹Si(CDCl₃): -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 bubbled 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-disilahept-3-yne, 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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. 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.

$^1\text{H}(\text{C}_6\text{D}_6)$: s 0.163 (9H), s 0.309 (9H), s 0.507 (3H), m 7.143-7.192 (3H), m 7.679-7.711 (2H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -3.501, -3.003, -0.089, 110.399, 119.324, 128.342, 129.460, 134.361, 135.558; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{15}\text{H}_{26}^{70}\text{GeSi}_2$ 332.08161, measured 332.08174.

Flow pyrolysis of **104** to give 1,3,4-trimethyl-1-phenyl-1-silacyclopent-3-ene **105** and (trimethylsilyl)trimethylgermylacetylene, **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. $^1\text{H}(\text{CDCl}_3)$: 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); $^{13}\text{C}(\text{CDCl}_3)$: -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-yne, **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) Me_3GeBr 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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.171 (9H), s 0.251 (9H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -0.346, 0.117, 112.251, 114.217; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{Na}_2\text{SO}_4/\text{MgSO}_4$. 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%. $^1\text{H}(\text{CDCl}_3)$: s 0.190 (9H), s 0.238 (6H), s 2.458 (1H); $^{13}\text{C}(\text{CDCl}_3)$: -3.188, -2.917, -1.956, -1.934, 111.852, 116.859; $^{29}\text{Si}(\text{CDCl}_3)$: -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 $\text{C}_7\text{H}_{16}^{74}\text{GeSi}$ 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_2SO_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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.165 (9H), s 0.293 (6H), s 0.334 (9H), s 0.373 (6H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -3.188, -2.917, -1.956, -1.934, 111.852, 116.859; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{12}\text{H}_{30}^{74}\text{Ge}_2\text{Si}_2$ 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 $40\text{-}50^\circ\text{C}$, 72% yield. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.371 (27H), s 2.140 (1H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: 1.029, 83.701, 94.443; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $-78^{\circ}C$ 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_2SO_4 . Purification by preparative gas chromatography ($140^{\circ}C$ 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. $^1H(C_6D_6)$: s 0.226 (18H), s 0.427 (3H), s 2.125 (1H); $^{13}C(C_6D_6)$: -8.233, -1.324, 86.434, 93.956; $^{29}Si(C_6D_6)$: -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 $C_7H_{22}^{70}GeSi_2$ 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 $-78^{\circ}C$ 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.094 (9H), s 0.316 (6H), s 2.076 (1H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -3.124, -2.048, 89.008, 93.659; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_7\text{H}_{16}^{70}\text{GeSi}$ 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.269 (12H), s 2.141 (2H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -3.644, 87.134, 96.160; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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-dipenyldigermene, 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) **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_2SO_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. $^1\text{H}(\text{CDCl}_3)$: s -0.316 (12H), m 7.27-7.31 (6H), m 7.39-7.43 (4H); $^{13}\text{C}(\text{CDCl}_3)$: -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 $\text{C}_{16}\text{H}_{22}^{70}\text{Ge}_2$ 354.02075, measured 354.02077.

Synthesis of 1,2-dichloro-1,1,2,2-tetramethyldigermene, 119.

Anhydrous hydrogen chloride was bubbled through a solution containing 6.0 g (0.017 mol) **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.

$^1\text{H}(\text{C}_6\text{D}_6)$: δ 0.599 (12H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: 3.793; 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); 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-diyne, 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 $\text{Na}_2\text{SO}_4/\text{MgSO}_4$, 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. $^1\text{H}(\text{C}_6\text{D}_6)$: δ 0.215 (12H), δ 0.331 (12H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -2.590, -2.219, 117.565, 119.580; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{12}\text{H}_{24}^{72,74}\text{Ge}_2\text{Si}_2$ 369.98526, measured 369.98501.

Synthesis of 4,4-dimethyl-3,3-bis(trimethylsilyl)-3,4-disilapentyne, **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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$. 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. $^1\text{H}(\text{C}_6\text{D}_6)$:

s 0.273 (27H), s 2.107 (1H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: 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 μl (1.85 mmol) Me_3GeCl 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 rotary 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.

$^1\text{H}(\text{C}_6\text{D}_6)$: s 0.263 (9H), s 0.305 (27H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -0.039, 0.395, 105.434, 118.141; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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,

2908, 2075, 1406, 1253, 841; calc. for $C_{14}H_{36}^{70}GeSi_4$ 386.11372, measured 386.11390.

Thermal isomerization of **124** to give 2,2,6,6-tetramethyl-5,5-bis(trimethylsilyl)-6-germa-2,5-disilahept-3-yne **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., m 15' column) suggesting some decomposition did occur, 22% yield. $^1H(C_6D_6)$: s 0.146 (9H), s 0.284 (18H), s 0.435 (9H); $^{13}C(C_6D_6)$: -0.203, 0.174, 0.238, 108.055, 118.818; $^{29}Si(C_6D_6)$: -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 $C_{14}H_{36}^{70}GeSi_4$ 386.11372, measured 386.11403.

Synthesis of 2,2,5,6,6-pentamethyl-5-(trimethylsilyl)-2-germa-5,6-disilahept-3-yne, 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) Me_3GeCl 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.222 (18H), s 0.251 (9H), 0.272 (3H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -7.661, -1.421, -0.104, 108.824, 118.006; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -59.806, -10.532; MS: 332 (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); IR(cm^{-1}): 2959, 2903, 1411, 1251, 840, 788; calc. for $\text{C}_{12}\text{H}_{30}^{74}\text{GeSi}_3$ 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-yne, 135.

A 2 ml pentane solution containing 361 mg (1.09 mmol)

134 was pyrolyzed in a packed quartz flow tube maintained at 390°C with argon flowing at the rate of 60 ml/min.. The **134** 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 **135**, a clear colorless liquid, for a recovery yield of 36%. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.142 (9H), s 0.210 (9H), s 0.300 (3H), s 0.365 (9H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -7.284, -2.134, -1.599, 0.067, 110.862, 118.661; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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 $\text{C}_{12}\text{H}_{30}^{70}\text{GeSi}_3$ 328.08984, measured 328.08925.

Synthesis of 2,2,5,5,6,6-hexamethyl-2-germa-5,6-disilahept-3-yne, **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) Me_3GeCl 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 $\text{MgSO}_4/\text{Na}_2\text{SO}_4$ 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.171 (9H), s 0.247 (6H), s 0.256 (9H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -2.696, -2.518, -0.232, 111.154, 116.639; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -35.562, -16.845; 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; calc. for $\text{C}_{10}\text{H}_{24}^{70}\text{GeSi}_2$ 270.06596, measured 270.06598.

Synthesis of 2,2,5,5,6,6-hexamethyl-6-germa-2,5-disilahept-3-yne, 138.

To a stirring solution of 30 ml (0.5M), (15 mmol) **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 CH_4 was evolved. Again the solution was cooled to -78°C at which point 1.5 g (7.1 mmol) **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 Na₂SO₄/MgSO₄. Purification by preparative gas chromatography (130°C isotherm, flow rate = 28, ret time = 7 min., 15' column) afforded 1.257 g, 65 % yield. ¹H(C₆D₆): s 0.142 (9H), s 0.250 (6H), s 0.301 (9H); ¹³C(C₆D₆): -3.337, -2.411, -0.118, 112.507, 117.116; ²⁹Si(C₆D₆): -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 C₁₀H₂₄⁷⁰GeSi₂ 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 LiAlH₄ 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. ¹H(C₆D₆): 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); $^{13}\text{C}(\text{C}_6\text{D}_6)$, quantitative): -7.205 (1C), -6.087 (2C), -6.030 (4C), -5.880 (2C), -5.680 (2C), 86.892 (1C), 97.919 (1C); $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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_2Cl_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)ethynyl]undecamethylhexasila-cyclohexane, 149.

Compound **139**, 0.3 g (0.84 mmol), was dissolved in 40 ml THF freshly distilled from LiAlH_4 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) Me_3GeBr 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. $^1\text{H}(\text{C}_6\text{D}_6)$: 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); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -7.255, -6.174, -5.781, -5.688, -5.617, -5.280, -0.182, 30.434, 109.373, 125.806; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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. $^1\text{H}(\text{C}_6\text{D}_6)$: 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); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -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; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -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), 213(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. $^1\text{H}(\text{C}_6\text{D}_6)$: 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, 3.525, 3.546, $J = 6.3$ Hz (2H), t 4.817, 4.763, 4.730, $J = 7.2$ Hz (3H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -2.582, -0.004, 14.015, 19.357, 35.242, 63.564; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: 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 $\text{C}_9\text{H}_{24}\text{O}^{70}\text{GeSi}$ 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**. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.252 (12H), s 0.259 (18H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -3.102, 2.788; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: 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 $\text{C}_{10}\text{H}_{30}\text{O}^{72,74}\text{Ge}_2\text{Si}_2$ 368.02712, measured 368.02800.

Synthesis of allyltrimethylgermane, **156**.

To a stirring solution of 1.31 g (8.56 mmol) trimethylchlorogermane 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. $^1\text{H}(\text{CDCl}_3)$: 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, $^{13}\text{C}(\text{CDCl}_3)$: -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_3GeH 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. $^1\text{H}(\text{CDCl}_3)$: s 0.255 (6H), s 1.478 (4H), s 1.669 (6H); $^{13}\text{C}(\text{CDCl}_3)$: -2.267, 19.423, 26.895, 130.844; $^{29}\text{Si}(\text{CDCl}_3)$: -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 $\text{C}_8\text{H}_{16}^{70}\text{Ge}$ 182.04950, measured 182.04947.

Synthesis of bis(dimethylphenylgermyl)dimethylsilane, 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) **64** 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 ml 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%. ¹H(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 C₁₈H₂₈⁷⁰Ge₂Si 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. ¹H(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),

87(14), 85(10), 73(100); IR(cm^{-1}): 2978, 2912, 2809, 1811, 1408, 1256, 840, 791.

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 $\text{Na}_2\text{SO}_4/\text{MgSO}_4$, 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. $^1\text{H}(\text{C}_6\text{D}_6)$: s 0.017 (9H), s 0.204 (9H), s 1.397 (2H); $^{13}\text{C}(\text{C}_6\text{D}_6)$: -2.255, 0.523, 8.822, 83.309, 105.954; $^{29}\text{Si}(\text{C}_6\text{D}_6)$: -19.823, 2.579; MS:

184(M⁺, 9.0), 169(22), 96(26), 73(100); IR(cm⁻¹): 2962, 2896, 2154, 1401, 1258, 1151, 1034, 848..

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. ¹H(C₆D₆): s 0.198 (18H), s 0.210 (6H), s 0.473 (6H), s 0.493 (6H); ¹³C(C₆D₆): -5.061, -1.122, -0.901, 0.894; ²⁹Si(C₆D₆): -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 C₁₅H₃₆^{72,74}Ge₂Si₃ 446.05629, measured 446.04058.

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