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Gas-Phase Chemistry of Methyl(trimethylsilyl)germylene

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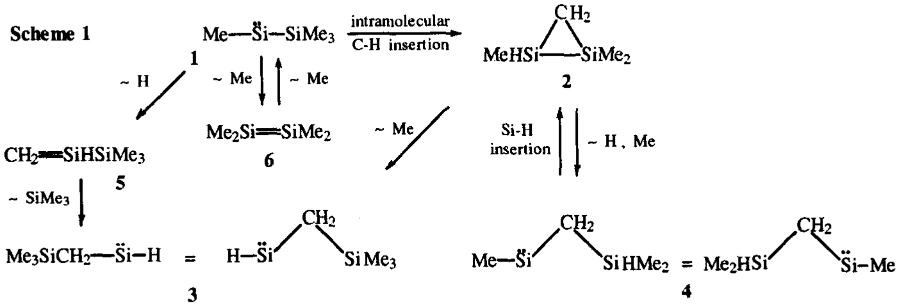
Abstract: The products obtained from the vacuum flow pyrolysis of $(Me_3Si)_2GeHMe$ in the presence of excess 2,3-dimethylbutadiene point to the generation of the alpha-silylgermylene $Me_3Si\text{-}Ge\text{-}Me$, and to its rearrangement via intramolecular C-H insertion to form a silagermirane whose ring-opening leads to isomeric beta-silylgermylenes. Dimerization of $Me_3Si\text{-}Ge\text{-}Me$ to a digermene followed by a sequence of rearrangements is also indicated. Fragmentation of silagermirane intermediates to a heteroene and a divalent species is an important process under these conditions. No products were found that demand the rearrangement of $Me_3Si\text{-}Ge\text{-}Me$ to $Me_2Si{=}GeMe_2$ via a methyl shift. © 1997 Elsevier Science Ltd.

The present work was motivated by the question: do germylenes, molecules containing divalent germanium atoms, undergo rearrangements in the gas-phase?[1]

The pioneering studies by Wulff, Goure and Barton of the chemistry of methyl(trimethylsilyl)silylene $Me\text{-}Si\text{-}SiMe_3$ **1** revealed the richness of the intramolecular reactions of substitut-ed silylenes.[2] Among the new processes discovered by these workers was the intramolecular C-H insertion to give a disilirane **2** that could undergo ring-opening to isomeric beta-silylsilyl-enes **3** and **4**. These steps constitute part of the reaction sequence shown in Scheme 1 below:

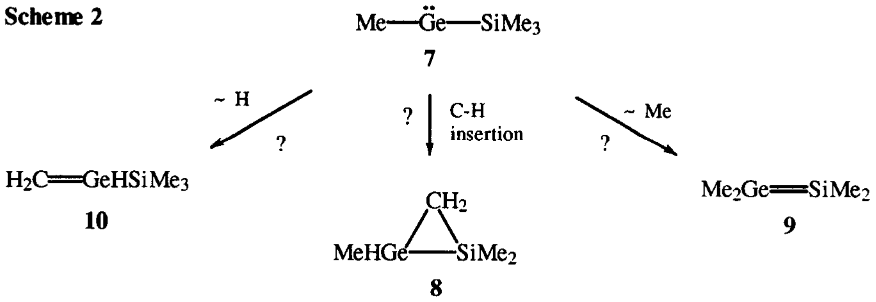
Scheme 1



Germylene reactions analogous to those depicted in Scheme 1 have not heretofore been reported. In considering rearrangements of germylenes analogous to those depicted in Scheme I, it is helpful to keep in mind several questions concerning this reaction sequence that remained unanswered until recently: 1. Is ring-opening of disilirane **2**, with a concomitant methyl-shift, the major pathway leading to H-Si-CH_2SiMe_3 **3**, as proposed by Barton?[1] The alternative silene route to **3** via CH_2=$SiHSiMe_3$ **5** shown in Scheme 1 and considered by Davidson[3] and ourselves,[4] was shown by use of a labelled methyl group to contribute less than 5% to the formation of H-Si-CH_2SiMe_3 **3**.[5] 2. Is the methyl-shift that converts disilene Me_2Si=$SiMe_2$ **6** to Me-Si-$SiMe_3$ **1** reversible? This reaction, that we suggest be named the Barton Rearrangement to recognize its singular importance in the development of organosilicon chemistry, was shown to be indeed reversible, again by the use of a labelled methyl group.[5]

It seemed of interest to inquire whether Me-Ge-$SiMe_3$ **7** differs in its propensity for intramolecular rearrangements from Me-Si-$SiMe_3$ **1**. Possible primary rearrangement steps for the germylene Me-Ge-$SiMe_3$ **7**, shown in Scheme 2, include intramolecular C-H insertion forming a silagermirane **8** and a methyl shift giving a silagermene **9**,[6] both of these processes analogous to those that were detected among the rearrangements of Me-Si-$SiMe_3$ **1**.[2,5] A hydrogen shift affording a germene **10** was another possibility, despite its unimportance in the corresponding silylene reaction.[5]

Scheme 2



Me-Ge-$SiMe_3$ **7** was generated by thermally induced elimination of $HSiMe_3$ from $MeHGe(SiMe_3)_2$ **11**. Precursor **11** was synthesized by the sequence of reactions shown in Scheme 3:

Scheme 3

$$Me_2GeCl_2 + 2\ ClSiMe_3 \xrightarrow[THF]{Li} Me_2Ge(SiMe_3)_2 \quad 28\ \%$$

$$Me_2Ge(SiMe_3)_2 + SnCl_4 \xrightarrow[MeNO_2]{} MeClGe(SiMe_3)_2 \quad 60\ \%$$

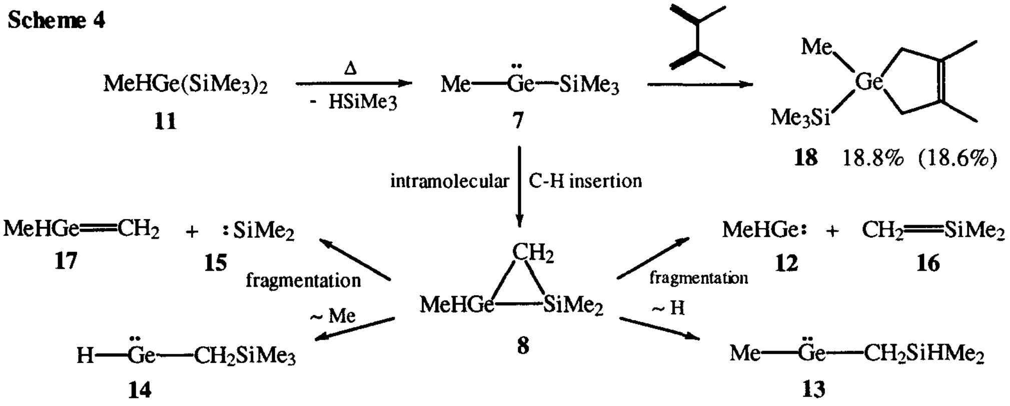
$$MeClGe(SiMe_3)_2 + LiAlH_4 \xrightarrow[Et_2O]{} \underset{\mathbf{11}}{MeHGe(SiMe_3)_2} \quad 86\ \%$$

Flow pyrolysis of $MeHGe(SiMe_3)_2$ **11** was carried out at 330°C and 410°C, at a pressure of 2 torr and residence time of ca. 10^{-3} s, in the presence of an excess of 2,3-dimethylbutadiene, a versatile and efficient gas-phase trapping agent for germylenes,[7] silylenes,[8] and silenes.[9] In addition to trimethylsilane, the expected coproduct of germylene formation, ten products were isolated and characterized, accounting for just over 30% of the starting material consumed. The remainder of the product was polymeric.

The formation of nine of the ten products can be rationalized by a reaction sequence, shown in Scheme 4, initiated by intramolecular C-H insertion by the divalent germanium atom of Me-Ge-$SiMe_3$ **7** leading to the formation of a silagermirane intermediate **8**. This resembles the chemistry of Me-Si-$SiMe_3$ **1**, but the products from silylgermylene **7** suggest that fragmentation of silagermirane **8** is a more prominent process than fragmentation of the disilirane **2** formed from Me-Si-$SiMe_3$ **1**. No products were detected that demand the intermediacy of $Me_2Ge{=}SiMe_2$ **9**.

Products of addition to 2,3-dimethylbutadiene **18**, **19**, **20**, **21**, and **22**, by the four germylenes **7**, **12**, **13**, **14**, and the silylene **15**, respectively, that are shown as being formed in Scheme 4 were found. Scheme 5 is a continuation of this reaction sequence and includes most of the product-forming steps.

Scheme 4

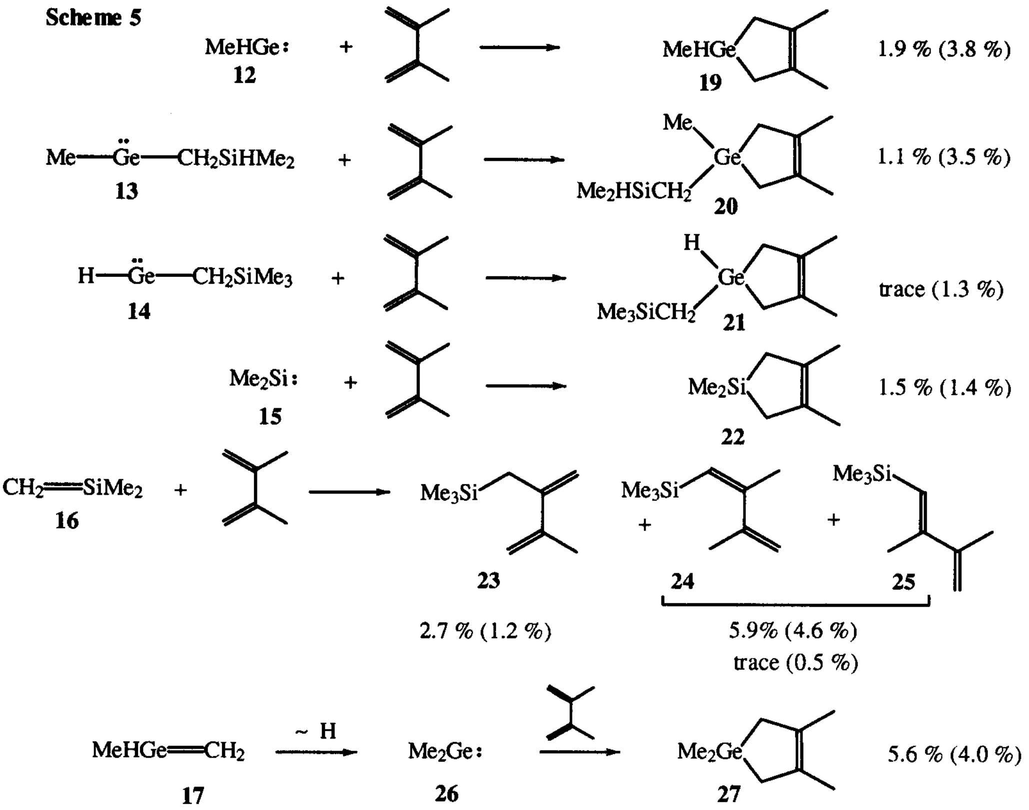


Only ene-reaction products, **23**, **24**, and **25**, were found for the silene $CH_2{=}SiMe_2$ **16** formed in Scheme 4. This ene-reaction has precedent, but (2+4)cycloaddition might also be expected. The trapping of Me_2Ge: **26** suggests the occurrence of a rearrangement of the germene $MeHGe{=}CH_2$ **17** via a hydrogen shift. This is a new reaction, but is surprising only in its apparent facility. The yields of the product-forming reactions obtained at 330°C (and 410°C) are shown in Schemes 4, 5, and 8.

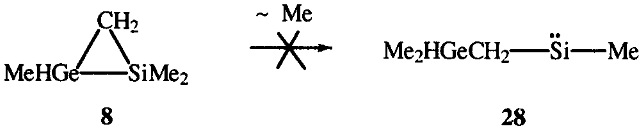
Fragmentation of silagermirane **8** appears to be unselective, since similar yields of products are obtained from the products of the two competing fragmentations: ($MeHGe{=}CH_2$ **17** + :$SiMe_2$ **15**) 7.1%(5.4%) and (MeHGe: **12** + $CH_2{=}SiMe_2$ **16**) 10.5% (10.1%).

If ring-opening of silagermirane **8** shown above in Scheme 4 is the origin of the beta-silylgermylenes **13** and **14** whose adducts **20** and **21**, respectively, were obtained, then ring-opening of **8** is more selective than fragmentation, since no evidence was found for the alternative ring opening of **8** shown below in Scheme 6, in which the shift of a methyl group would lead to the formation of a beta-germylsilylene **28**.

Scheme 5

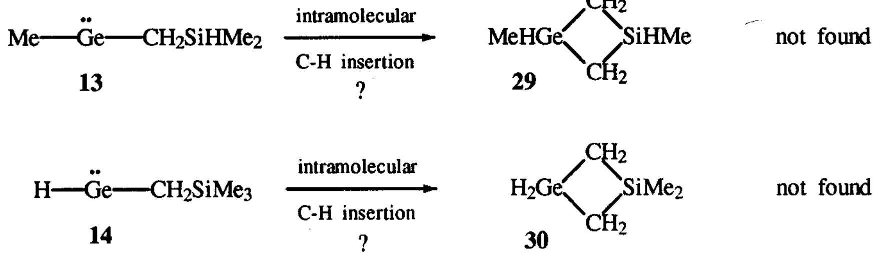


Scheme 6



Intramolecular C-H insertion by beta-silylgermylenes **13** and **14**, depicted in Scheme 7, is apparently slower than the similar process for the corresponding beta-silylsilylenes **3** and **4**,^{2} since the 3-silagermacyclobutanes **29** and **30** that are the resulting products, though presumably stable, were not found.

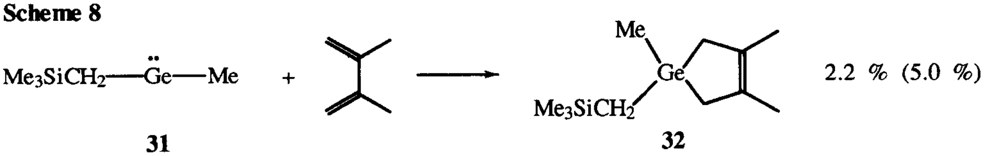
Scheme 7



To this point, the reaction mechanism suggested by the products is relatively simple. Nine of the ten observed products, accounting for over 80% of the total yield of observed products, can be attributed to the initially formed silylgermylene Me-Ge-SiMe$_3$ **7**, and to intermediates formed by fragmentation and ring-opening of a silagermirane **8** arising from intramolecular C-H insertion by **7**, as shown in Schemes 4 and 5.

There is, however, a fly in this mechanistic ointment: the formation of a germacyclopent-3-ene **32**, displayed in Scheme 8, that clearly arises from the addition to 2,3-dimethylbutadiene of a germylene **31** that contains five carbon atoms:

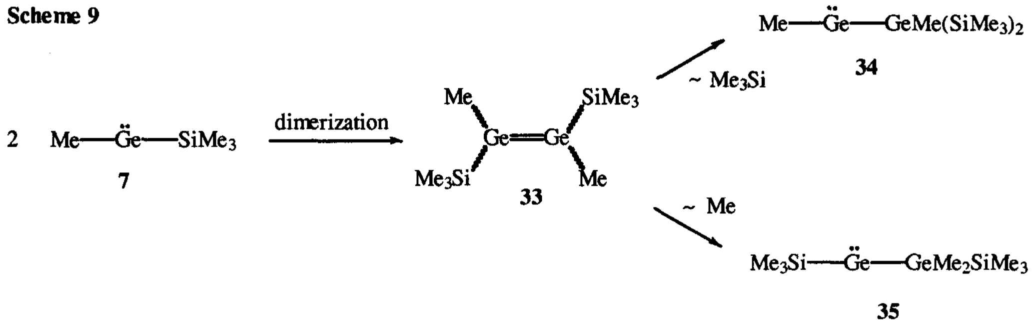
Scheme 8



How can a five-carbon germylene **31** arise from the initially generated four-carbon germylene **7**, or from its precursor **11**? The most likely explanation, if one accepts that both the intramolecular and intermolecular processes that consume initially formed germylene **7** (**7** → **8** and **7** → **18**, Scheme 4) are likely to be slower than their silylene counterparts,[7] is via a reaction sequence beginning with the dimerization of initially formed Me-Ge-SiMe$_3$ **7**, shown in Scheme 9. The resulting mixture of cis- and trans- germylene dimers **33** could rearrange to isomeric alpha-germylgermylenes **34** and **35**:

As indicated by Scheme 10, such an alpha-germylgermylene **34** can give rise to the five-carbon beta-silylgermylene Me$_3$SiCH$_2$-Ge-Me **31**, whose adduct **32** was found (Scheme 8). This transformation is effected by processes similar to those depicted above in Schemes 2 and 4 for the intramolecular rearrangements of Me-Ge-SiMe$_3$ **7**. However, further ambiguity is created when it is realized that such a reaction scheme can also lead to most of the other reactive intermediates trapped by 2,3-dimethylbutadiene upon pyrolysis of MeHGe(SiMe$_3$)$_2$. These are underlined in Schemes 10 to 13, and include MeHGe: **12**, H-Ge-CH$_2$SiMe$_3$ **14**, Me$_2$Si: **15**, CH$_2$=SiMe$_2$ **16**, and Me$_2$Ge: **26**.

Scheme 9

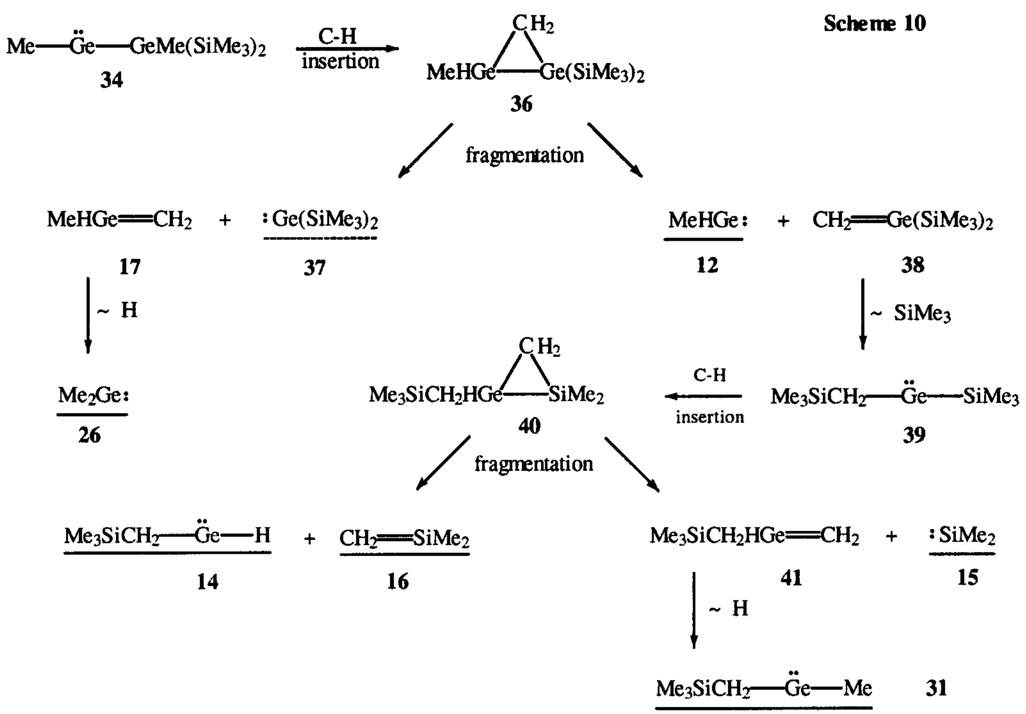


Let us consider in turn the further transformations of the two rearrangement products **34** and **35** shown above in Scheme 9 as arising from the dimerization of Me-Ge-$SiMe_3$ **7**. First, in Scheme 10 and its continuation Scheme 11, rearrangements of the germylgermylene **34** formed by a trimethylsilyl-group shift in the germylene dimer **33** are considered. To construct the sequence shown below in Schemes 10 and 11, all intramolecular C-H insertions by divalent germanium centers that lead to three-membered rings have been assumed to occur. All possible fragmentations of the resulting digermirane **36** and silagermiranes **40**, **42**, and **44**, are also included. Germenes are assumed to rearrange to germylenes readily via H- (**17**, **41**, **46**) and Me_3Si- (**38**, **49**) shifts, but the Me_3Si-shift is expected to predominate if both are available (**10**). Ring-opening of digermiranes and silagermiranes by alpha-elimination are assumed to be slow relative to fragmentation. In the schemes shown below, reactive intermediates whose adducts were observed are underlined with solid lines. Species whose further intramolecular reactions are depicted in subsequent reaction schemes are underlined with broken lines.

The germylgermylene **35** that is shown in Scheme 9 as arising from a methyl-shift in the dimer **33** of Me_3Si-Ge-Me **7** also can be converted, by several pathways, to the five-carbon beta-silylgermylene Me_3SiCH_2-Ge-Me **31** as shown in Scheme 12 and its continuation, Scheme 13. This was constructed using the same assumptions as were employed in the construction of Schemes 10 and 11.

At this point our attempts to provide a mechanistic explanation for the products observed upon generation of Me_3Si-Ge-Me **7** in the presence of 2,3-dimethylbutadiene seem to have gone in a circle. Nine of the ten products can be explained by a mechanism, shown in Schemes 4 and 5, in which the silagermirane **8** formed by intramolecular insertion of the divalent germanium center of **7** into a β-methyl group undergoes competing fragmentation and rearrangement. The resulting silylene **15** and three germylenes **12**, **13**, and **14**, undergo addition to 2,3-dimethylbutadiene, as does germylene **7**, yielding silacyclopentene **22**, and

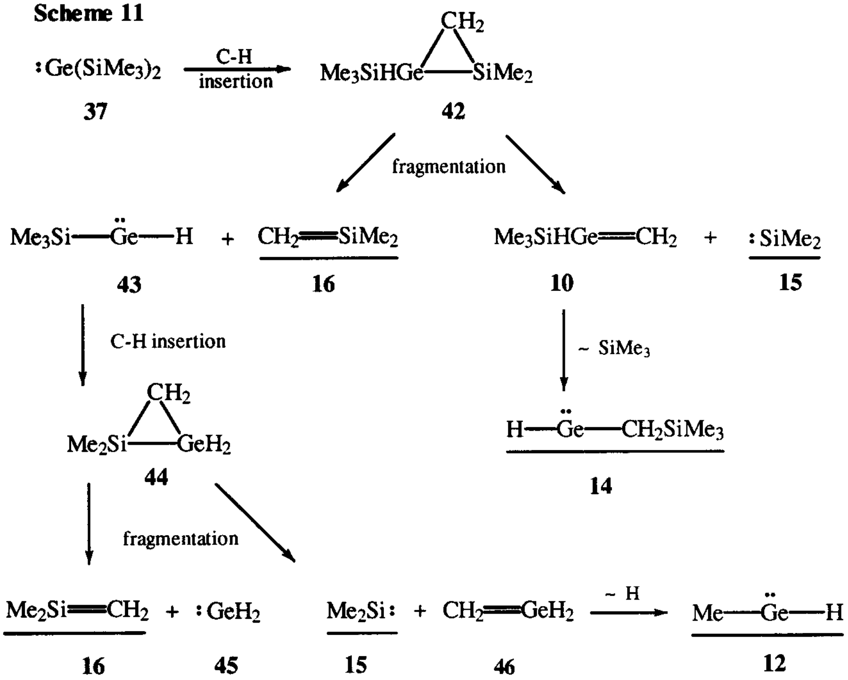
Scheme 10



germacyclopentenes **18**, **19**, **20**, and **21**, respectively. The silene **16** formed by fragmentation of silagermirane **8** seems to react with 2,3-dimethylbutadiene exclusively by an ene-reaction, yielding **23** and its rearrangement products **24** and **25**, while germene **17**, appears to rearrange by a 1,2-hydrogen-shift to germylene **26** that undergoes addition to the diene.

In order to rationalize the formation of the tenth product , the adduct of a β-silylgermylene **31** that contains one more carbon than the initially generated alpha-silylgermylene **7**, a mechanism has been written, displayed in Schemes 9 to 13, that begins with the dimerization of germylene **7**. This mechanism also can explain the generation of reactive intermediates **12**, **14**, **15**, and **16**, whose formation was inferred from the detection of their addition and ene-reaction products. Indeed, Me-Ge-CH_2SiHMe_2 **13** is the only intermediate whose presence can be inferred from its butadiene addition product that can not be rationalized by the dimerization mechanism of Schemes 9 to 13. Thus, dimerization of the initially formed germylene Me-Ge-$SiMe_3$ **7** not only explains the formation of **31**, trapped as product **32**, but also brings into question the origin of eight of the other nine observed products!

Scheme 11

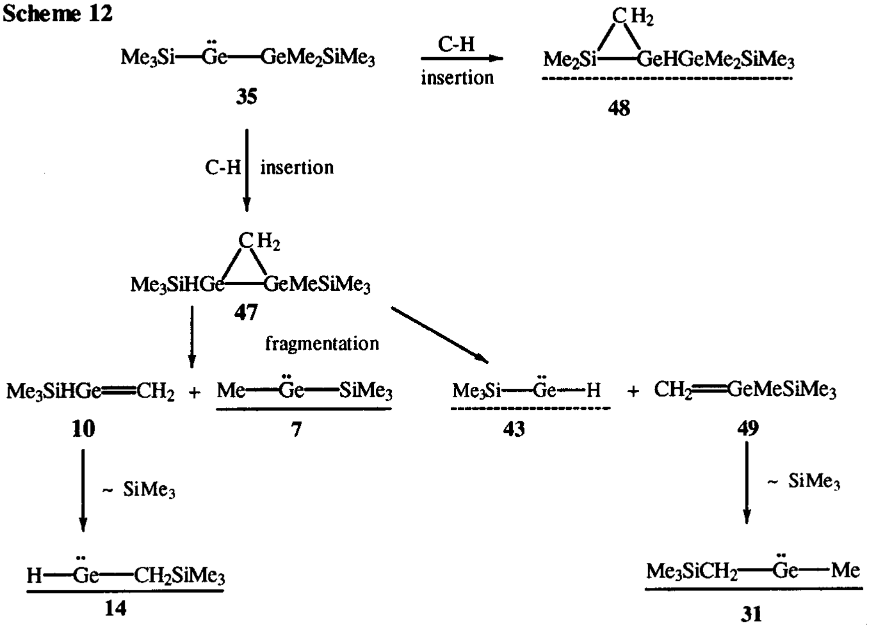


The existence of the alternative mechanistic pathways of Schemes 9 to 13, that rationalize the formation of the observed products by invoking as their primary step the dimerization of the initially formed germylene **7**, rather than an intramolecular C-H insertion reaction as depicted in Scheme 4, would not drastically change the overall mechanistic picture if there were no other differences in the types of elementary processes invoked.

After all, the same intramolecular C-H insertions by divalent germanium centers, leading to three-membered rings, are invoked in both schemes. Similar fragmentations of silagermiranes into a germylene,silene pair and a silylene,germene pair are also invoked in both schemes. The fragmentation of digermiranes into germylenes and germenes is analogous to the silagermirane fragmentations.

There is however a difference worth noting between the mechanisms that begin with dimerization of Me_3Si-Ge-Me **7** shown in Schemes 9 to 13, and the one that is initiated by intramolecular transformations of **7** given in Schemes 4 and 5. Scheme 14 is a reminder that to form Me_3SiCH_2-Ge-H **14** by strictly intramolecular transformations of Me_3Si-Ge-Me **7** requires either ring-opening of silagermirane **8** via α-elimination, or the formation of germene intermediate **10** via hydrogen migration from carbon to germanium (Scheme 2). This latter process appears unlikely in view of the evidence found for a facile rearrangement in the opposite direction, $MeHGe=CH_2$ **17** → Me_2Ge **26**.

Scheme 12

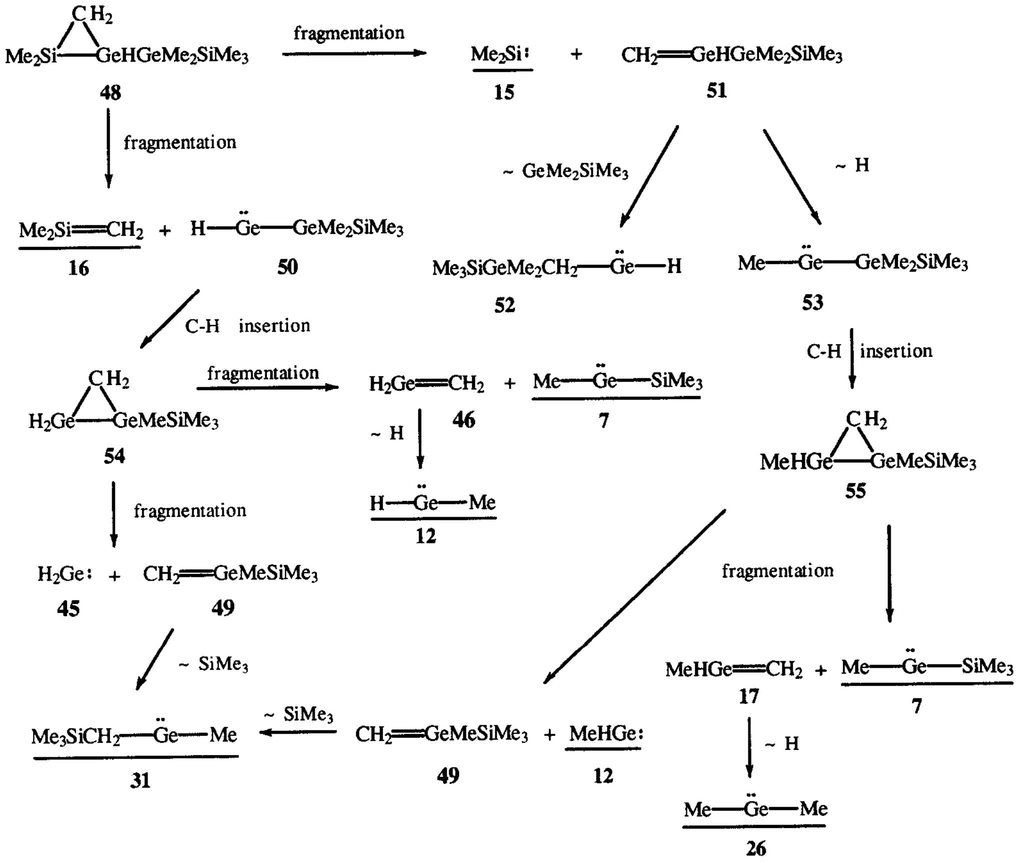


In the germylene-dimerization mechanism of Schemes 9 to 13 Me_3SiCH_2-Ge-H **14** can arise from a sequence of trimethylsilyl migration, intramolecular C-H insertion, and fragmentation steps, without ring-opening via α-elimination, as shown by the **34** → **36** → **38** → **39** → **40** → **14** pathway of Scheme 10, the **34** → **36** → **37** → **42** → **10** → **14** pathway of Schemes 10 and 11, and the **35** → **47** → **10** → **14** pathway of Scheme 12.

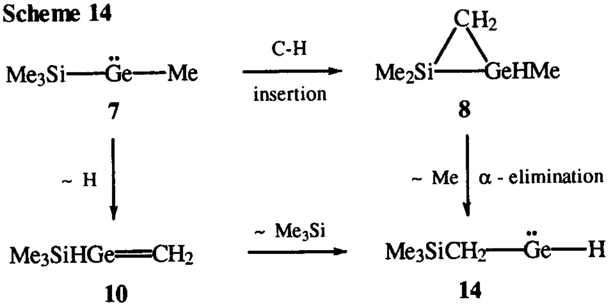
At least some degree of dimerization of the initial germylene Me_3Si-Ge-Me **7** seems demanded by the trapping in at least 2.2% yield of Me_3SiCH_2-Ge-Me **31**, a species that cannot be formed by intramolecular reactions of the initial germylene, but can be formed via a dimerization mechanism.

While it has been indicated above that uncertainty remains about the extent to which dimerization of initially formed Me_3Si-Ge-Me **7** competes with intramolecular rearrangements, the trapping of Me_2HSiCH_2-Ge-Me **13** strongly suggests that intramolecular C-H insertion by Me_3Si-Ge-Me **7** to form 1,2,2-trimethyl-2-silagermirane **8** does occur. It is difficult to explain the formation of Me_2HSiCH_2-Ge-Me **13** without invoking ring-opening of this silagermirane with attendant migration of a hydrogen from germanium to silicon. While intermediate Me_2HSiCH_2-Ge-Me **13** accounts for no more than 3.5 % of the initially formed germylene, its formation is significant as a clear indication that Me_3Si-Ge-Me **7** undergoes intramolecular reactions under the reaction conditions.

Scheme 13

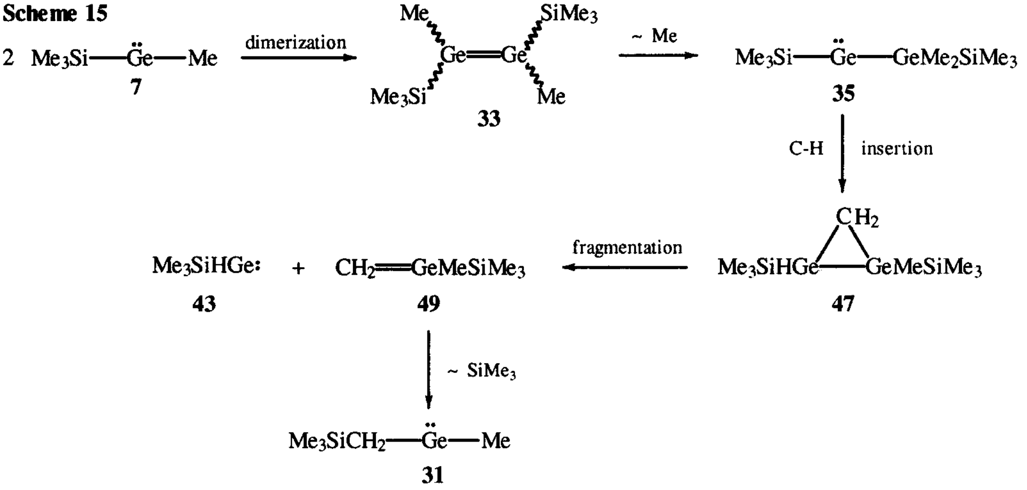


Scheme 14



All the other products could arise via a complex series of reactions initiated by dimerization of Me_3Si-Ge-Me **7**, followed by rearrangement of the resulting digermene **8** via competing Me- and Me_3Si-shifts. Dimerization of Me_3Si-Ge-Me **7** is expected to have a lower barrier than does intramolecular C-H insertion.[10] However the number of steps required to reach most of the intermediates whose trapping products were detected is much greater via the dimerization mechanism than via the intramolecular rearrangements of Me_3Si-Ge-Me **7**. A mechanism with more steps provides greater opportunity for diversion of intermediates. It may be that the five-carbon β-silylgermylene **31** is formed via the dimerization pathway because one of the sequences leading to it requires only the five steps shown in Scheme 15.

Scheme 15



We conclude that Me_3Si-Ge-Me **7** does undergo intramolecular C-H insertion to form 1,2,2-trimethyl-2-silagermirane **8** since, of all reactions considered, ring-opening of this silagermirane is the only process capable of explaining the formation of Me_2HSiCH_2-Ge-Me **13**. Fragmentation of silagermirane **8** seems to be a considerably more important process than ring-opening via α-elimination, the latter being the major pathway, discovered by Wulff, Goure, and Barton, for the consumption of the corresponding disilirane.

Fragmentation of silagermiranes such as **40** or **48**, or digermiranes such as **36**, **47**, **54**, or **55**, formed by rearrangements of the digermene **33** arising from dimerization of Me_3Si-Ge-Me **7** is also necessary to account for the formation of the five-carbon Me_3SiCH_2-Ge-Me **31**.

The tendency for silagermiranes and digermiranes to undergo fragmentation to a germylene and a silene or a germene might have been anticipated from the failure to obtain germiranes from addition of germylenes to olefins, although dienes yield products of addition by germylenes clearly attributable to vinylgermirane intermediates.[7,11] The implication is that germylene extrusion from a germirane is extremely facile, and only an extremely rapid process such as the rearrangement of a vinylgermirane can compete with it.

While more experiments are needed to assess their quantitative importance, the results reported here provide evidence for the occurrence of several new reactions: 1. Intramolecular rearrangement via C-H insertion of an α-silylgermylene forming a silagermirane whose ring-opening leads to the formation of at least one β-silylgermylene. 2. Gas-phase dimerization of a germylene to a digermene (presumably a pair of geometric isomers) that can rearrange to α-germylgermylenes. 3. Fragmentation of silagermiranes to pairs of reactive intermediates, a germylene and a silene, or a germene and a silylene. 4. Germene-to- germylene rearrangements via hydrogen- and methyl-shifts.

No products were found suggesting the occurrence of a process analogous to one known for α-silylsilylenes, the rearrangement of Me_3Si-Ge-Me **7** to $Me_2Si{=}GeMe_2$ **9** via a methyl-shift.

Isotopic labelling experiments of the type that have recently been carried out on Me_3Si-Si-Me **1**[5] will be required to determine the contribution of Me_3Si-Ge-Me **7** dimerization and a hydrogen-shift forming a germene intermediate **7** $\rightarrow$ $Me_3SiHGe{=}CH_2$ **14** to the formation of the observed reactions products. If such labelling experiments can be implemented, the remaining questions about the chemistry of methyl(trimethylsilyl)germylene **7** can be answered. The results already in hand, however, suggest that this is an interesting story that illuminates the subtle differences between germanium and silicon chemistry.

Acknowledgments: We are grateful to the United States National Science Foundation for financial support of this project under Grant No. CHE-88-02677. We thank Tom Barton and Rob Conlin for helpful discussions.

Experimental Section

General Data. All preparative reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Solvents were dried using standard techniques. All air-sensitive liquids including dried solvents were transferred under an atmosphere of dry nitrogen.

^1H and ^{13}C NMR spectra were recorded on Varian XL-300 and Gemini-300 FT spectrometers. GC-mass spectral data were collected at 70 eV on a Finnegan 3200 quadrupole mass spectrometer. High resolution mass spectra were run on a VG-ZAB-SE double-focusing mass spectrometer. Analytical gas chromatography was carried out on a Hewlett-Packard Model 5890 Series II instrument with a flame ionization detector, employing a 15 ft x 1/8 in (id) stainless steel column with 3% OV-17 on Chromosorb W packing. Preparative gas chromatography was performed on an instrument constructed in this laboratory with a thermal conductivity detector employing Gow-Mac code 13-002 dual rhenium-tungsten filaments and a 15 ft x 1/4 in (od) aluminum column with 10% OV-17 or 5% DC-200 silicone oil on 60/80 mesh ABS Anakrom packing.

All yields are moles of product per mole of germylene precursor consumed, as determined by gas chromatography employing separately determined response factors for most of the products isolated. An internal standard, hexadecane, was employed. In a few cases sufficient quantities of products could not be isolated, and it was necessary to assume that response factors for isomeric products of similar structure were equal.

Materials. **2,3-Dimethylbutadiene** Wiley Organics, 99%), **tin tetrachloride** (Aldrich, 99%), and **chlorotrimethylsilane** (Aldrich, 98%) were used as received.

Dichlorodimethylgermane was synthesized by the method of Lee, Bobbitt, Lei, and Gaspar.[12]

Dimethylbis(trimethylsilyl)germane. To a stirred suspension of 17.0 g (159 mmol) $ClSiMe_3$ and 2.0 g (0.286 g atom) freshly cut Li in 150 mL THF was added dropwise a solution of 11.9 g (69 mmol) Cl_2GeMe_2 in 10 mL THF over a 45 min period at 0 °C under a N_2 atmosphere. After addition was complete the reaction mixture was stirred at room temperature for 2 d. The mixture was filtered to remove LiCl, and volatiles were removed on a rotary evaporator. The remaining liquid was treated with 150 ml saturated NH_4Cl solution, the organic layer was separated, and the aqueous layer was twice extracted with 100 mL ether. The combined organic phases were dried over anhydrous Na_2SO_4 and solvent removed in vacuo. Distillation (80-83 °C/20 Torr) gave $Me_2Ge(SiMe_3)_2$ (6.5 g, 33%): ^1H NMR (C_6D_6) δ 0.18 (s, 18 H, SiMe), 0.27 (s, 6 H, GeMe); MS *m/e* (relative intensity) 250 (5, M^+), 235 (11), 162 (24), 161 (11), 160 (18), 158 (12), 145 (15), 131 (19), 73 (100, base).

Chloro(methyl)bis(trimethylsilyl)germane. To a mixture of 6.2 g (24.8 mmoles) of dimethylbis(trimethylsilyl)germane and 40 mL nitromethane was added 7.8 g (30.1 mmoles) tin tetrachloride. The initially inhomogeneous mixture was stirred 2 h at room temperature, then 1 h at 40 °C and became homogeneous. The only products detected by GC analysis of the clear, faintly yellow reaction mixture were $MeClGe(SiMe_3)_2$ and $MeSnCl_3$. After in vacuo removal of the volatile components, pentane was added to the remaining liquid. The pentane solution was separated and dried over anhydrous Na_2SO_4. After evaporation of the pentane 5.9 g (88%) of $ClMeGe(SiMe_3)_2$ was collected: ^1H NMR (C_6D_6) δ 0.18 (s, 18 H, SiMe), 0.67 (s, 3 H, GeMe); $^{13}C\{^1H\}$ NMR (C_6D_6) δ -1.5 (SiMe), -0.1 (GeMe).

Methylbis(trimethylsilyl)germane 11. To a stirred solution of 2.5 g (9.5 mmoles) of $MeClGe(SiMe_3)_2$ in 50 mL ether at 0 °C under a nitrogen atmosphere was added slowly 0.18 g (4.7 mmoles) $LiAlH_4$. The reaction mixture was allowed to warm to room temperature and stirring continued for 10 min. GC analysis indicated that reaction was complete, and $MeHGe(SiMe_3)_2$ **11** was the only product, formed in quantitative yield. After filtration under nitrogen, ether was removed by distillation at 20 °C/300 Torr, leaving 2.2 g (95%) of crude product. This was further purified by preparative gas chromatography on a 5 ft x 1/4 inch o.d aluminum column with 10% DC-200 silicone oil on ABS Anakrom 60/80 mesh packing prior to use. The purity of the product **11** thus isolated was 99%: ^{1}H NMR (C_6D_6) δ 0.20 (s, 18 H, SiMe), 0.31 (d, 3 H, J = 4.9 Hz, GeMe), 3.00 (q, 1 H, J = 4.9 Hz, GeH); ^{13}C NMR{^{1}H} (C_6D_6) δ -13.1 (GeMe), 0.5 (SiMe); MS *m/e* (relative intensity) 236 (8, M^+), 221 (17), 219 (13), 164 (21), 162 (85), 161 (25), 160 (61), 158 (43), 147 (24), 146 (11), 145 (26), 143 (15), 131 (23), 129 (10), 117 (10), 115 (14), 89 (18), 87 (12), 74 (17), 73 (100, base), 59 (12).

Pyrolysis Experiments. Flow pyrolysis experiments were carried out in a vertical, unpacked quartz, 10 mm i.d. x 18 cm quartz tube incorporated in a vacuum flow system that has been described previously.[13] The hot zone was treated with hexamethyldisilazane before each pyrolysis. A gaseous mixture of the germylene precursor methylbis(trimethylsilyl)-germane **11** and the trapping agent, 2,3-dimethyl-1,3-butadiene was delivered from a 1L reservoir through a ball-type flow meter, and the pressure was monitored just upstream from the hot-zone by a calibrated thermocouple vacuum gauge. The reaction mixture was collected in a liquid nitrogen cooled U-trap. Preliminary fractionation of the product mixture after a pyrolysis experiment was carried out by trap-to-trap distillation in the vacuum line. Further separation and purification of the products were carried out by gas chromatography, with transfer of products *via* gas-tight syringes and septum-capped ampoules.

In a typical experiment 82 mg (0.35 mmole) methylbis(trimethylsilyl)germane **11** and 285 mg (3.5 mmole) 2,3-dimethylbutadiene was degassed in the reservoir and then volatilized with an infrared heat-gun before being passed during a 2 min. period through the hot-zone at 2 Torr, residence time *ca.* 2 ms. The pyrolysis was repeated three times under the same conditions, and the product mixtures were collected together in a U-trap cooled with liquid N_2. Preliminary separation of the pyrolysates was by trap-to-trap distillation through a CCl_4 slush bath to another bath cooled with liquid N_2. The product mixture collected in the CCl_4 slush bath was separated by gas chromatography on two 15 ft. x 1/4 in. o.d. aluminum columns packed with 60/80 mesh ABS Anakrom, one with 5% DC-200 silicon oil stationary phase and the other with 10% OV-17 silicone oil. The conversion of starting material was found to be 57% at 330 °C and 95% at 410 °C. Yields and spectroscopic data for the individual products are given in Table 1.

Table 1. Yield, NMR and MS data for reaction products from the flow pyrolysis of methylbis(trimethylsilyl)germane in the presence of 2,3-dimethylbutadiene

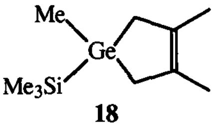
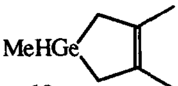
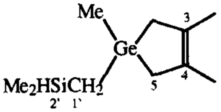
Products	**Yields (%)** **330 °C**	 **410 °C**	**Spectroscopic Data**
 **18**	18.8	18.6	**^{1}H NMR (C_6D_6)** δ 0.14 (s, 9 H, SiMe), 0.33 (s, 3 H, GeMe), 1.62 (bd, 2 H, J_{gem} = 15.6 Hz, C_2, C_5-H), 1.77 (bs, 6 H, CMe), 1.86 (bd, 2 H, J_{gem} = 15.6 Hz, C_2,C_5-H); **$^{13}C\{^1H\}$ NMR (C_6D_6)** δ -4.6 (GeMe), -1.2 (SiMe), 19.7 (CMe), 26.0 (C_2,C_5), 130.8 (C_3,C_4); **MS** *m/e* (relative intensity) 244 (53, M^+), 242 (38), 229 (78), 227 (56), 225 (39), 162 (73), 160 (54), 158 (39), 89 (92), 87 (67), 85 (51), 73 (100, base); **Exact mass determination** for $C_{10}H_{22}GeSi$ calcd. 244.0702, found 244.0701.
 **19**	1.9	3.8	**^{1}H NMR (C_6D_6)** δ 0.24 (d, 3 H, J = 3.2 Hz, GeMe), 1.44 (bd, 2 H, J_{gem} = 16.5 Hz, C_2,C_5-H), 1.68 (bs, 6 H, CMe), 1.81 (bd, 2 H, J_{gem} = 16.5 Hz, C_2,C_5-H), 4.35 (m, 1 H, Ge-H); **$^{13}C\{^1H\}$ NMR (C_6D_6)** δ -5.1 (GeMe), 19.4 (CMe), 24.4 (C_2,C_5), 130.9 (C_3,C_4); MS *m/e* (relative intensity) 172 (38, M^+), 170 (29), 171 (14), 168 (20), 159 (22), 157 (100, base), 156 (29), 155 (75), 153 (57), 129 (14), 127 (11), 117 (18), 115 (68), 114 (19), 113 (54), 111 (40), 101 (12), 99 (13), 91 (18), 89 (75), 88 (27), 87 (53), 85 (40), 74 (19), 72 (13), 67 (29), 55 (20), 53 (10); **Exact mass determination** for $C_7H_{14}Ge$ calcd. 172.0307, found 172.0340.
 **20**	1.1	3.5	**^{1}H NMR (C_6D_6)** δ -0.12 (d, 2 H, $J_{2',1}$ = 4.0 Hz, $C_{1'}$-H), 0.08 (d, 6 H, $J_{2',Me}$ = 3.9 Hz, SiMe), 0.31 (s, 3 H, GeMe), 1.55 (d, 2 H, J_{gem} = 16.2 Hz, C_2,C_5-H), 1.65 (d, 2 H, J_{gem} = 16.2 Hz, C_2, C_5-H), 1.75 (bs, 6 H, C_3,C_4Me), 4.26 (m, 1 H, Si-H); **$^{13}C\{^1H\}$ NMR (C_6D_6)** δ -1.8 ($C_{1'}$), -1.5 (GeMe), -1.4 (SiMe), 19.6 (C_3,C_4Me), 27.6 (C_2,C_5), 133.9 (C_3,C_4); **MS** *m/e* (relative intensity) 244 (2, M^+), 204 (14), 203 (12), 202 (24), 200 (18), 198 (12), 187 (10), 162 (29), 161 (16), 160 (23), 159 (10), 158 (16), 149 (24), 147 (100, base), 146 (29), 145 (74), 143 (54), 121 (13), 119 (59), 118 (16), 117 (49), 115 (43), 113 (10), 91 (11), 89 (59), 88 (15), 87 (46). 85 (33), 74 (14), 73 (43), 59 (33).

Table 1 (continued)

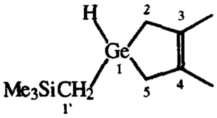
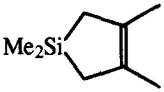
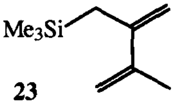
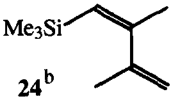
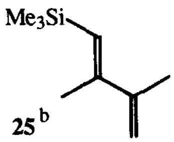
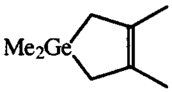
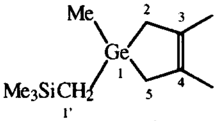
Products **Spectroscopic Data**	**Yields (%)**		**Spectroscopic Data**
	330 °C	**410 °C**	
 **21**	trace	1.3	**^{1}H NMR (C_6D_6)** δ -0.12 (d, 2 H, $J_{1,1'}$ = 3.0 Hz, $C_{1'}$-H), 0.05 (s, 9 H, SiMe), 1.52 (bd, 2 H, J_{gem} = 16.2 Hz, C_2,C_5-H), 1.71 (bs, 6 H, C_3,C_4Me), 1.85 (bd, 2 H, J_{gem} = 16.2 Hz, C_2,C_5-H), 4.43 (septet, 1 H, *J* = 3.0 Hz, GeH); **MS** *m/e* (relative intensity) 244 (8, M^+), 229 (15), 227 (12), 204 (11), 202 (31), 200 (24), 198 (16), 162 (25), 161 (15), 160 (20), 158 (14), 149 (18), 147 (24), 146 (22), 145 (54), 143 (40), 119 (26), 117 (24), 115 (24), 113 (10), 91 (10), 89 (42), 87 (31), 85 (24), 74 (12), 73 (100, base), 67 (17), 59 (35); **Exact mass determination** for $C_{10}H_{22}GeSi$ calcd. 244.0702, found 244.0701.
 **22**	1.5	1.4	identical with those of an authentic sample[a]
 **23**	2.7	1.2	**^{1}H NMR (C_6D_6)** δ 0.01 (s, 9 H, SiMe), 1.76 (bs, 2 H, -CH_2-), 1.84 (bs, 3 H, CMe), 4.78 (bs, 1 H, =CHH'), 4.93 (bs, 1 H, =CHH'), 5.02 (bs, 2 H, =CH_2); MS *m/e* (relative intensity) 154 (10, M^+), 139 (8), 112 (4), 111 (5), 97 (5), 79 (4), 75 (4), 74 (9), 73 (100, base), 59 (8), 53 (5).
 **24**[b]	trace[b]	0.5[b]	**(minor) ^{1}H NMR (C_6D_6)** δ 0.17 (s, 9 H, SiMe), 1.69 (bs, 3 H, CMe), 1.83 (bs, 3 H, CMe), 4.71 (bs, 1 H, =CHH'), 4.88 (bs, 1 H, =CHH'), 5.79 (bs, 1 H, -CH=); **MS** *m/e* (relative intensity) 154 (9, M^+), 140 (14), 139 (100, base), 123 (10), 111 (17, 99 (22), 97 (20), 85 (13), 83 (11), 73 (83), 59 (42), 58 (10).
 **25**[b]	5.9[b]	4.6[b]	**(major) ^{1}H NMR (C_6D_6)** δ 0.17 (bs, 9 H, SiMe), 1.88 (bs, 3 H, CMe), 1.95 (bs, 3 H, CMe), 4.97 (bs, 1 H, =CHH'), 5.11 (bs, 1 H, =CHH'), 5.79 (bs, 1 H, -CH=); **MS** *m/e* (relative intensity 154 (13, M^+), 140 (15), 139 (100, base), 123 (13), 111 (19), 99 (32), 97 (30), 85 (17), 83 (16), 73 (58), 69 (11), 59 (84).

Table 1 (continued)

Products	**Yields (%)**		**Spectroscopic Data**
	330 °C	**410 °C**	
 **27**	5.6	4.0	identical with those of authentic sample[c]
 **32**	2.2	5.0	**^{1}H NMR (C_6D_6)** δ -0.13 (s, 2 H, $C_{1'}$-H), 0.05 (s, 9 H, SiMe), 0.30 (s, 3 H, GeMe), 1.55 (d, 2 H, J_{gem} = 16.5 Hz, C_2,C_5-H), 1.63 (d, 2 H, J_{gem} = 16.5 Hz, C_2,C_5-H), 1.76 (bs, 6 H, C_3,C_4Me); **^{13}C NMR (C_6D_6)** δ 0.9 ($C_{1'}$), 1.1 (SiMe), 1.6 (GeMe), 19.7 (C_3,C_4Me), 28.1 (C_2,C_5), 130.8 (C_3,C_4); **MS** *m/e* (relative intensity) 258 (11, M^+), 243 (23), 241 (17), 239 (12), 176 (25), 174 (19), 172 (13), 163 (15), 162 (13), 161 (61), 160 (22), 159 (44), 157 (33), 147 (23), 145 (21), 143 (15), 115 (10), 89 (19), 87 (15), 85 (11), 74 (10), 73 (100, base), 67 (17), 59 (16); **Exact mass determination** for $C_{11}H_{24}GeSi$ calcd. 258.0859, found 258.0875.

a. Weyenberg, D.R.; Toporcer, L.H.; Neilson, L.E. *J. Org. Chem.* **1968**, *33*, 1975.

b. Geometrical isomers Z-**24** and E-**25** can be separated, but which structure belongs to the major product and which belongs to the minor product cannot be decided on the basis of the available spectroscopic data

c. Ma, E.C.L. doctoral dissertation, Washington University in St. Louis, 1982.

References

1. For a recent review of germylene chemistry, see: Neumann, W.; *Chem. Revs.*, **1991**, *91*, 311.
2. Wulff, W.D.; Goure, W.F.; Barton, T.J.; *J. Am. Chem. Soc.*, **1978**, *100*, 6236.
3. Davidson, I.M.T.; Scampton, R.J. *J. Organometal. Chem.* **1984**, *271*, 249.
4. Boo, B.H.; Gaspar, P.P. *Organometallics*, **1986**, *5*, 698.
5. Lee, M.E.; North, M.A.; Gaspar, P.P. *Phosphorus, Sulfur, and Silicon*, **1991**, *56*, 203.
6. A silagermene $Mes_2Ge{=}SiMes_2$ has been generated in solution, and found to rearrange to a germylene $Mes\text{-}Ge\text{-}SiMes_3$: Baines, K.M.; Cooke, J.A.; *Organometallics*, **1992**, *11*, 3487.
7. Bobbitt, K.L.; Maloney, V.M.; Gaspar, P.P. *Organometallics*, **1991**, *10*, 2772.
8. Atwell, W.H.; Weyenberg, D.R.; *J. Am. Chem. Soc.*, **1968**, *90*, 3438.
9. Wiberg, N.; Preiner, G.; Schiede, O.; Fischer, G. *Chem. Ber.*,**1981**, *114*, 3505.
10. For the analogous silylsilylene **1** strain energy would have to be added to the *ca.* 15 kcal/mol. barrier associated with insertion into a C-H bond to give an estimated barrier for formation of the disilirane ring **2** of >20 kcal/mol.
11. Neumann, W.P.; Michels, E.; Kocher, T. *Tetrahedron Lett.*, **1987**, *28*, 3783.
12. Lee, M. E.; Bobbitt, K. L.; Lei, D.; Gaspar, P. P. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 77.
13. Boo, B. H.; Gaspar, P. P. *Organometallics*, **1986**, *5*, 698.

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