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Laser Ablation of Hexamesitylcyclotrigermane and Hexamesitylcyclosiladigermane in a Molecular Beam

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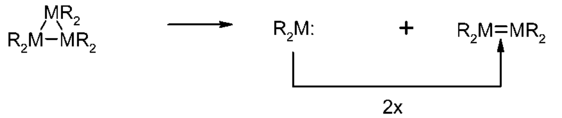
The highly strained group 14 compounds hexamesitylcyclotrigermane, $(Mes_2Ge)_3$ (Mes = mesityl = 2,4,6-trimethylphenyl), and hexamesitylcyclosiladigermane, $[(Mes_2Ge)_2(Mes_2Si)]$, were laser ablated under argon and introduced into a molecular beam. The neutral fragmentation products were photoionized downstream following ablation/gas expansion and characterized by time-of-flight mass spectrometry. The primary products arose from the expected fragmentation of the three-membered ring. For $(Mes_2Ge)_3$, the major products were Mes_2Ge: and $Mes_2Ge{=}GeMes_2$. For the case of $[(Mes_2Ge)_2(Mes_2Si)]$, fragmentation occurred, giving along with Mes_2Ge: and $Mes_2Ge{=}GeMes_2$, three additional products: Mes_2Si:, $Mes_2Ge{=}SiMes_2$, and $Mes_2Si{=}SiMes_2$. The formation of $Mes_2Si{=}SiMes_2$ indicates that significant bimolecular chemistry occurs in the ablation plume. Laser ablation of $(Mes_2Ge)_3$ in argon streams seeded with oxygen bases such as nitrous oxide, ethylene oxide, and diethyl ether resulted in the preferential loss of Mes_2Ge relative to $Mes_2Ge{=}GeMes_2$. For the case of N_2O, an additional digermene to germylgermylene rearrangement is suggested.

Introduction

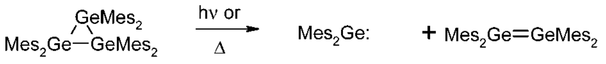
Molecular beam techniques offer a potentially powerful approach to the study of highly reactive main group intermediates in the gas phase. For example, we have found that highly reactive dimethylsilylene (Me_2Si:) and dimethylgermylene (Me_2Ge:) can be generated efficiently in molecular beams from the laser photolysis of $(Me_2Si)_6$ and $(Me_2Ge)_6$, respectively.[1]

Cyclotrimetallanes of the heavier group 14 elements are of great interest due to their high ring strain and their potential 2+1 fragmentation to give highly reactive group 14 carbene analogues (R_2M:) and dimetallenes ($R_2M{=}MR_2$).[2−4] In solution, the divalent carbene analogue usually dimerizes to a dimetallene unless intercepted by a chemical trapping agent (eq 1).



(1)

The kinetically stabilized hexamesitylcyclotrigermane (**1**; mesityl = Mes = 2,4,6-trimethylphenyl) has been extensively studied and found to undergo ring fragmentation both thermally[5] and photochemically.[6] Laser flash photolysis of **1** in solution provided direct and unambiguous evidence for the initial formation of dimesitylgermylene and tetramesityldigermene under photochemical conditions (eq 2).[7] The related cyclosiladigermane, $[(Mes_2Ge)_2(Mes_2Si)]$ (**2**), undergoes a similar regiospecific ring fragmentation both photochemically[8] and thermally[9] to yield dimesitylgermylene (Mes_2Ge:) and tetramesitylgermasilene ($Mes_2Ge{=}SiMes_2$) (eq 3).



(2)

(3)

We report herein the detection of ring fragmentation products from the laser ablation of $(Mes_2Ge)_3$ (**1**) and

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[1] Borthwick, I.; Baldwin, L.; Sulkes, M.; Fink, M. J. *Organometallics* **2000**, *19*, 139.

[2] For a general review on the chemistry of cyclotrimetallanes see: Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.

[3] For recent references concerning the chemistry of cyclotrigermanes see: (a) Samuel, M. S.; Jennings, M. C.; Baines, K. M. *Organometallics* **2001**, *20*, 590. (b) Ichinohe, M.; Sekiyama, H.; Fukaya, N.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 6781. (c) Valentin, B.; Castel, A.; Rivière, P.; Onyszchuk, M.; Lebuis, A.-M.; Pearson, C. *Main Group Met. Chem.* **1999**, *22*, 599. (d) Valentin, B.; Castel, A.; Rivière, P.; Mauzac, M.; Onyszchuk, M.; Lebuis, A.-M. *Heteroat. Chem.* **1999**, *10*, 125.

[4] For recent references concerning the chemistry of cyclotrisilanes see: (a) von Keyserlingk, N. G.; Martens, J.; Ostendorf, D.; Saak, W.; Weidenbruch, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, *7*, 706. (b) Sasaki, Y.; Fujitsuka, M.; Ito, O.; Maeda, Y.; Wakahara, T.; Akasaka, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y. *Heterocycles* **2001**, *54*, 777. (c) Wiberg, N.; Auer, H.; Wagner, S.; Polborn, K.; Kramer, G. *J. Organomet. Chem.* **2001**, *619*, 110. (d) Belzner, J.; Dehnert, U.; Ihmels, H. *Tetrahedron* **2001**, *57*, 511. (e) Weidenbruch, M.; Meiners, F.; Saak, W. *Can. J. Chem.* **2000**, *78*, 1469. (f) Ostendorf, D.; Saak, W.; Weidenbruch, M.; Marsmann, H. *Organometallics* **2000**, *19*, 4938. (g) Wiberg, N.; Niedermayer, N. *Z. Naturforsch., B: Chem. Sci.* **2000**, *55*, 406. (h) Sasaki, Y.; Konishi, T.; Fujitsuka, M.; Ito, O.; Maeda, Y.; Wakahara, T.; Akasaka, T.; Kako, M.; Nakadaira, Y. *J. Organomet. Chem.* **2000**, *599*, 216. (i) Ostendorf, D.; Kirmaier, L.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, *12*, 2301. (j) Chen, K.-H.; Allinger, N. L.; Mastryukov, V. S. *J. Mol. Struct.* **1999**, *485−486*, 27. (k) Belzner, J.; Ronneberger, V.; Schar, D.; Bronnecke, C.; Herbst-Irmer, R.; Noltemeyer, M. *J. Organomet. Chem.* **1999**, *577*, 330. (l) Weidenbruch, M.; Grybat, A.; Saak, W.; Peters, E.-M.; Peters, K. *Monatsh. Chem.* **1999**, *130*, 157.

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$[(Mes_2Ge)_2(Mes_2Si)]$ (**2**) and some of their properties in a molecular beam.

Experimental Section

All experiments were performed using a reflectron-based molecular beam time-of-flight (TOF) system (mass resolution of ~1000, R. M. Jordan and Company) as previously described.[1] Laser ablation was carried out on samples deposited on $D = 0.25$ in. rotating rods. A 0.5 in. flow extension with a 1.4 mm axial center flow channel was attached to a pulsed solenoid valve (General Valve Series 9). About 0.25 in. down the flow extension, a hole was drilled with its outer circumference open and tangent to the flow channel, such that rotating sample rods would have their surfaces accessible. Perpendicular to the flow channel at this point and facing the rod surface, a ~1 mm hole allowed ablation laser pulses to reach the surface of the rod at the point tangent to the channel flow. The ablation pulses were usually at 355 nm (Nd:YAG third harmonic), on the order of 10 mJ, focused on the rod surface to a spot size of ~1 mm diameter or less. Usually the best results were obtained when timing was set so that the ablation pulses coincided close to the front edge of the gas pulses. Argon carrier gas at a backing pressure of ~100 psig was employed. Typically, a rod length of several inches of deposited sample could sustain an experiment for several hours. Further downstream of the flow channel, the gas expansion was skimmed and introduced into the TOF system. Photoionization of neutral species for TOF mass spectra was carried out using 118 nm pulses obtained by sending 10−20 mJ pulses of a 355 nm Nd:YAG third harmonic into a tripling cell containing 8% Xe in Ar at ~150 Torr. Photoionized product peak signal intensities depended very critically on optimum alignment of the ablation rod; there was a placement tolerance easily of <1 mm, which made the difference between little or no signal from ablation products and a very robust signal. For bracketing of photoionization energy thresholds, other photoionization laser frequencies used were 355 nm (Nd:YAG third harmonic), 308 nm (excimer), 266 nm (Nd:YAG fourth harmonic), and tunable pulses in the range 280−295 nm (typical pulse energy ~1 mJ); two photons at these frequencies could potentially cause photoionization. The tunable pulses were generated by frequency doubling the output of a dye laser (Rhodamine 590 and 610).[10]

Sample material was deposited on the surfaces of lightly sandblasted brass or glass rods. Both of the cyclic precursors, **1** and **2**, are highly soluble in THF. For a typical rod deposition, ~100 mg of material was dissolved in ~30 mL of THF and then gently sprayed back and forth, using an artist's airbrush, over a ~3 in. length of the rod while rotating. After spraying, the solvent quickly dried, leaving a film of white, finely crystalline material on the rod. In experiments, slow modulations in signal intensity could occur, partly from uneven depositions and partly, probably generally more substantially, from small rod "wobbles". The effect of depositing more material was to produce stronger ablation product signals. There were no obvious differences in observed results using brass or Pyrex rods.

Hexamesitylcyclotrigermane[11] and hexamesitylcyclosiladigermane[9] were prepared according to literature procedures. The cyclotrigermane was purified by recrystallization from THF, and the cyclosiladigermane was purified by trituration with hexanes.

Results

Figure 1 shows TOF mass spectra following ablation of rod-deposited cyclotrigermane (**1**) and cyclosiladigermane (**2**). The mass resolution was somewhat limited employing relatively wide digitizing time windows (typically ~16−116 μs over 1024 digitized channels); mass resolutions under these digitizing conditions were roughly ±1 amu. A number of general features can be seen in these mass spectra. Isotopic structure for germanium-containing product peaks over this digitization range was partially resolved for the lower mass peaks such as Mes_2Ge, which has an isotopic product maximum at 311 amu. However, only unresolved broad line shapes were observed for the higher mass peaks such as Mes_4Ge_2, which has a composite peak that is centered at 622 amu. The unresolved composite peaks have maxima at or close to the unresolved predominant isotopic peak. The germanium-containing products were obvious by their composite line widths (compare with the product peak due to Mes at 119 amu). Comparison between the two mass spectra in Figure 1 facilitates identification of the product peaks corresponding to silicon-containing species.

The top spectrum, which corresponds to the laser ablation of **1**, clearly shows that the two predominant mass peaks belong to Mes_2Ge and Mes_4Ge_2, expected products from the 2+1 fragmentation of the cyclotrigermane. Almost all of the precursor **1** was consumed by the ablation, as evidenced by an extremely small mass peak for Mes_6Ge_3 at 933 amu. The appearance of a significant mesityl peak at 119 amu, along with small peaks corresponding to the products Mes_5Ge_3, Mes_3Ge_2, and MesGe, suggests that Mes−Ge bond cleavage was also occurring but to a much lesser extent than ring cleavage. Most of the other significant peaks (i.e., Mes_2Ge_2 and Mes_3Ge) can be assigned straightforwardly to species containing germanium atoms and Mes units.

The most predominant products from the laser ablation of **2** (bottom spectrum) also appear to have arisen from 2+1 fragmentation of the three-membered ring. In contrast to solution studies, this fragmentation was not regiospecific and gave Mes_4GeSi, Mes_4Ge_2, Mes_2Ge, and Mes_2Si as major products. Similar to the case of the cyclotrigermane, very little of the cyclosiladigermane precursor Mes_6SiGe_2 was observed after the ablation. Minor products due to Mes−(Si,Ge) bond cleavage were also observed, as well as small amounts of Mes_3Ge and Mes_3Si.

Further examination of Figure 1 shows that at least some bimolecular chemistry has occurred. This is necessarily the case for products such as Mes_4Si_2 and Mes_4-

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(5) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770.

(6) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, *7*, 2015.

(7) Toltl, N. P.; Leigh, W. J.; Kollegger, G. M.; Stibbs, W. G.; Baines, K. M. *Organometallics* **1996**, *15*, 3732.

(8) (a) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487. (b) Kollegger, G. M.; Stibbs, W. G.; Vittal, J. J.; Baines, K. M. *Main Group Metal Chem.* **1996**, *19*, 317.

(9) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419.

(10) Due to the limited amounts of material available and limited dye laser fluences, it was not possible to determine precise values at this time. However, it was possible to bracket the values within ranges by noting the reddest photoionization wavelengths that yielded discernible product peaks via two-photon ionization, as well as the bluest two-photon photoionization wavelength where there was clearly no discernible product peak. The latter limit where no product was seen was always with 308 nm pulses (two-photon energy of 8.05 eV). The values determined were as follows: Mes_2Ge at 8.05−8.41 eV; Mes_3Ge at 8.05−8.41 eV; $Mes_2Ge{=}GeMes_2$ at 8.05−8.41 eV; Mes_2Si at 8.05−8.65 eV; Mes_3Si_2 at 8.05−8.78 eV; and $Mes_2Si{=}SiMes_2$ at 8.05−9.32 eV. More detailed spectroscopy will be reported in the future.

(11) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514.

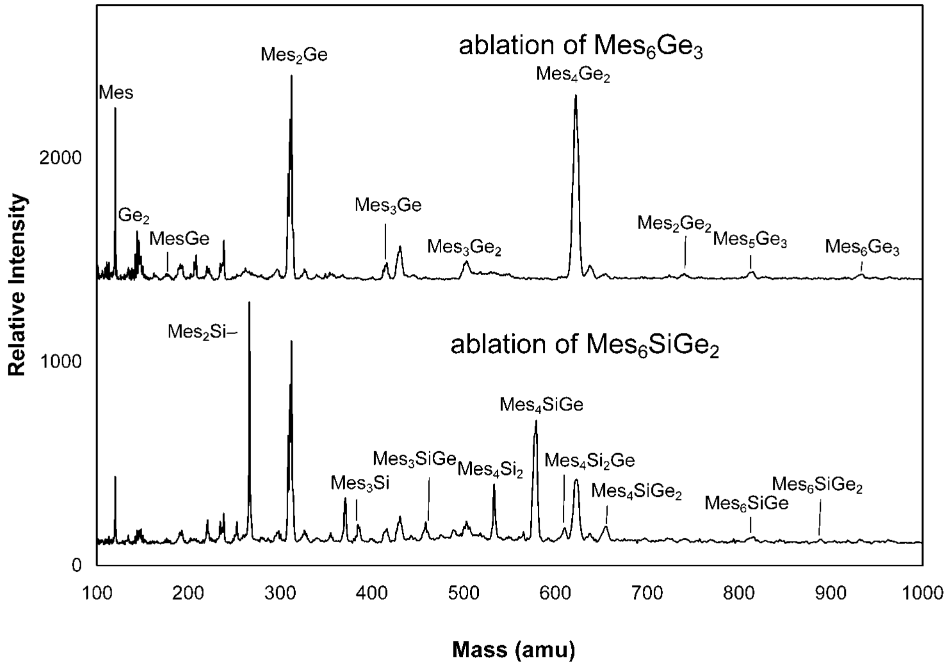


Figure 1. TOF mass spectra from the 355 nm laser ablation of Mes_6Ge_3 (top) and Mes_6SiGe_2 (bottom) in argon. Photoionization is at 118 nm.

Si_2Ge, which were observed in the laser ablation of **2**. Although not highlighted in the figures, there is considerable variation in peak ratios for the 622 amu centered digermene peak compared to the 311 amu germylene peak depending on differences in individual rod coatings and on the experimental alignment of the ablation laser relative to the rotating rod. The variations in peak ratios result from differences in the relative proportion of digermene molecules formed by unimolecular versus bimolecular pathways, with greater bimolecular chemistry (dimerization) giving higher digermene/germylene product ratios. The sensitivity of this ratio to surface conditions indicates that most of the bimolecular chemistry must have taken place in the vicinity of the initial ablation plume. This phenomenon was confirmed by experiments that were conducted with an additional 0.5 in., 1.4 mm diameter flow extension. There was no obvious difference in the observed digermene/germylene peak ratios with or without the extension for the same given ablation rod placement. In the future, it may be the case that the implementation of more versatile rod positioning on a micrometer scale will allow for tipping an ablation product distribution selectively toward more or less bimolecular chemistry.

Laser Ablation of $(Mes_2Ge)_3$ in the Presence of Oxygen Donors. The oxygen-containing compounds N_2O, ethylene oxide, and diethyl ether were seeded into the argon flows in concentrations of 5−10 mol %. The resulting spectra were significantly different from that for a pure argon stream. In addition, the spectra for each of the co-reactants were very similar to each other. Figure 2 gives the typical result for the case of N_2O; each mass spectrum is normalized to the Mes_4Ge_2 peak. The bottom spectrum corresponds to pure argon gas, the four middle spectra show the effect of increasing dopant, and the top spectrum shows a return to the original spectrum when the dopant was exhausted from the system.

In general, the *absolute* intensities of all observed mass peaks decreased with increasing amounts of dopant. The most striking difference in seeded versus unseeded spectra is the relative disappearance of the Mes_2Ge peak at 312 amu. This seems reasonable in view of the extremely high reactivity of this species. Although the digermene peak was still relatively strong, there was also a pronounced increase in both Mes_3Ge (431 amu) and MesGe (193 amu) peaks relative to this peak. It may be possible that the latter peaks arose from the fragmentation of the isomeric germylgermylene, $Mes_3Ge-Ge-Mes$ via Ge−Ge bond cleavage (see Discussion).

Figure 3 shows the effect of ethylene oxide and diethyl ether as dopants. The effect of increasing dopant in both cases was very similar to that of N_2O in that it resulted in a dramatic diminution of the Mes_2Ge peak relative to the digermene. However, the relative increase in Mes_3Ge and MesGe was not observed in these systems.

Discussion

The laser ablation of **1** and **2** efficiently yielded ring fragments resulting from the breaking of Ge−Ge and Ge−Si bonds; the major products were Mes_2M: and $Mes_2M{=}MMes_2$, where M may be germanium or silicon. Additional products also arose from (Ge,Si)−mesityl bond cleavage, but these were comparatively much less abundant. (Here we assume that each product had roughly comparable photoionization (PI) cross sections at 118 nm, so that peak sizes would then give a rough indication of actual relative product species populations.) Under all ablation conditions, ranging from 5 to 40 mJ pulse energies, the same products were observed, albeit in slightly varying ratios. The most important observation is the propensity for basic ring cleavage. Thus, laser ablation of strained ring precursors appears to be a very promising method of producing reactive group 14 intermediates in good yield. The key role of ring strain can be seen by contrasting with the analo-

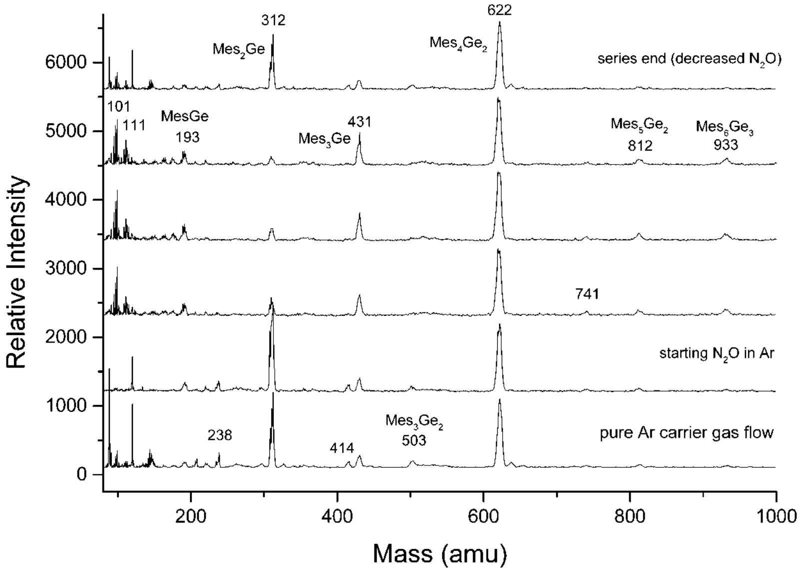


Figure 2. TOF mass spectra from the 355 nm laser ablation of Mes_6Ge_3 in the presence of 10% N_2O in argon. The photoionization is at 118 nm. The 622 amu peak is scaled to the same constant value in all spectra. Bottom spectrum: pure argon. Intermediate spectra: increased time after introduction of 10% N_2O−argon mixture from bottom to top. Top spectrum: reintroduction of pure argon gas.

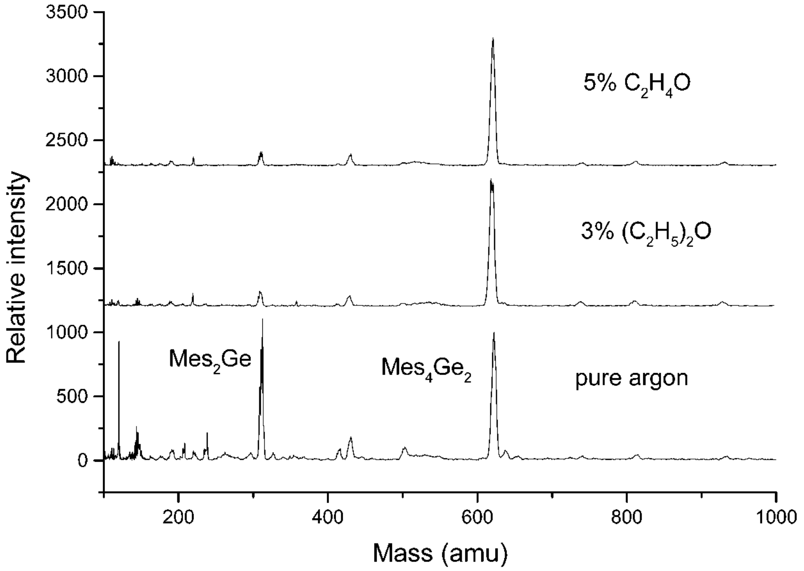


Figure 3. TOF mass spectra from the 355 nm laser ablation of Mes_6Ge_3 in the presence of 3% diethyl ether and 5% ethylene oxide in argon. The photoionization is at 118 nm. The 622 amu peak is scaled to the same constant value in all spectra. Bottom spectrum: pure argon. Middle spectrum: 3% diethyl ether−argon mixture. Top spectrum: 5% ethylene oxide−argon mixture.

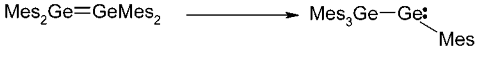
gous laser ablation products using rods coated with $(Ph_2Si)_5$, $(Me_2Si)_6$, and $(Me_2Ge)_6$. In each of these instances, using ablation pulse energies of 5−40 mJ, total product peak intensities were very weak. No peaks related to the fundamental ring units were detected. By far the largest peak in each instance was for either atomic silicon or germanium.

Laser ablation of **1** gave Mes_2Ge: and $Mes_2Ge{=}GeMes_2$ as the most abundant products. This result is consistent with solution phase studies that strongly suggested a 2+1 fragmentation of the cyclotrigermane ring.[5,6] The predominant products produced from laser ablation of **2** also resulted from the ring fragments Mes_2M: and $Mes_2M{=}MMes_2$, with a near statistical distribution of germanium and silicon in the ultimate product distribution. Thus, all of the species Mes_2Ge, Mes_2Si, $Mes_2Ge{=}GeMes_2$, $Mes_2Ge{=}SiMes_2$, and $Mes_2Si{=}SiMes_2$ were observed in the laser ablation of **2**. These observations stand in sharp contrast to the solution thermolysis of the cyclosiladigermane ring to give regiospecific rather than a statistical cleavage of the siladigermane ring.[9] However, the formation of $Mes_2Si{=}SiMes_2$ has been observed in the low-temperature photolysis of the cyclosiladigermane, albeit in lower yield than the germasilene.[8a]

The contrast in results may arise from the nature of laser ablation. In a composite sense, laser ablation may have both thermal and photolytic components. The ablation pulse initially produces a hot, highly energetic plasma, where both thermal and possibly nonspecific multiphotonic photolytic events can occur. Under these highly energetic laser ablation conditions, it is possible that an effective 1+1+1 cleavage of the three-membered ring may occur via photodissociation of the germasilene,[8b] followed by near statistical dimerization of the resulting fragments. Bimolecular reactions in the laser ablation of **2** must surely occur in order to explain the significant presence of $Mes_2Si{=}SiMes_2$ and Mes_4Si_2Ge.

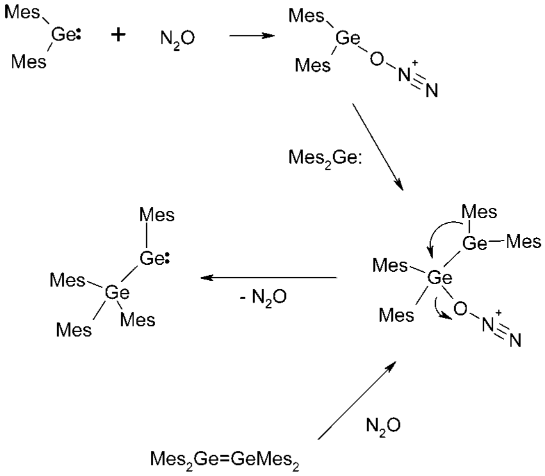
Since the possibility of bimolecular chemistry was indicated, we attempted to explore the reaction of some exogenous reagents with intermediates arising from the laser ablation of **1**. It was anticipated that the reaction of nitrous oxide and ethylene oxide with Mes_2Ge: might produce dimesitylgermanone ($Mes_2Ge{=}O$)[12] or possibly the oxygenation products of the much less reactive tetramesityldigermene.[13,14] In both cases when these gases were used as dopants, the Mes_2Ge peak essentially disappeared, leaving $Mes_2Ge{=}GeMes_2$ as the largest peak in the mass spectrum. The selective disappearance of Mes_2Ge is reasonable due to the high reactivity of this species. Surprisingly, however, no significant *new* product peaks were observed. Similar behavior was observed when diethyl ether was used as a dopant. Diethyl ether is not generally known to react with germylenes other than to form a Lewis acid−base adduct,[15] which suggests that all spectra represent some sort of reaction of the germylene with an oxygen-centered Lewis base. The lack of a product peak in the mass spectrum may possibly relate to the formation of ionic products instead of neutral species in the plume, in which case they would not be detected in our experiments.

Interestingly, laser ablation of **2** in the presence of N_2O also produced significant relative increases in the amounts of Mes_3Ge and MesGe species. These two species seem to be reasonable fragmentation products of the germylgermylene, $Mes_3Ge{-}GeMes$. As seen in Figure 2, even in the absence of N_2O, fragments due to the putative germylgermylene species are produced to some extent. The thermal isomerization of the germylgermylene from the digermene $Mes_2Ge{=}GeMes_2$ has been previously reported in solution (eq 4).[16] Theoretical calculations indicate that the conversion of the parent digermene, $H_2Ge{=}GeH_2$, to germylgermylene, H_3GeGeH, is endothermic by 2 kcal/mol, with an activation barrier of 12 kcal/mol.[17] Presumably on the basis of sterics, the effects of replacing a hydrogen with a bulky aryl group would be to further stabilize the digermene while substantially increasing the barrier to interconversion.



$$Mes_2Ge{=}GeMes_2 \longrightarrow Mes_3Ge{-}\ddot{Ge}{-}Mes \qquad (4)$$

Scheme 1. Possible Mechanisms for the N_2O-Catalyzed Formation of Trimesitylgermylmesitylgermylene



Very interestingly, the ratio of Mes_3Ge and MesGe peaks relative to $Mes_2Ge{=}GeMes_2$ is greatly increased in the presence of N_2O, suggesting that N_2O may mediate or catalyze the isomerization reaction. One possible route is through a zwitterionic digermane-N_2O intermediate formed by the direct reaction of tetramesityldigermene with N_2O as shown in Scheme 1. Neighboring group participation in the form of a 1,2 aryl migration[18] would give the germylgermylene with the concerted elimination of N_2O. Another possible route, involving the same digermane-N_2O zwitterionic intermediate, occurs from the reaction of N_2O with dimesitylgermylene to give an initial Lewis acid−base adduct. Stable dimesitylgermylene adducts with THF have been postulated to be precursors to the digermene even in the presence of triethylsilane, an efficient scavenger for the free germylene.[13] Subsequent reaction of the dimesitylgermylene adduct with free germylene, as shown in Scheme 1, affords the zwitterionic digermane-N_2O intermediate which leads to the isomerization. At the present time, we are unable to distinguish whether any particular pathway is predominant.

A similar catalyzed rearrangement of a doubly bonded silicon compound by a Lewis base appears to occur for the peculiar reaction of 2-silapropene ($MeHSi{=}CH_2$) with methanol and other trapping reagents at ~100 K in 3-methylpentane glasses.[19] The only observed trapped products appear to arise from the slightly thermodynamically favored isomeric dimethylsilylene (Me_2Si:), although the activation barrier for a 1,2 hydrogen shift is found to be in excess of 40 kcal/mol in the gas phase.[20,21] While not suggested in the original paper, the interconversion may be explained by a catalyzed process involving the trapping reagent. In this case, the direct interaction of the Lewis base with the polar Si=

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(12) Germanones from the reaction of germylenes with oxygen donors: (a) Wegner, G.; Berger, R. J. F.; Schier, A.; Schmidbaur, H. *Organometallics* **2001**, *20*, 418. (b) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, *12*, 1087. (c) Barrau, J.; Rima, G.; El Amine, J.; Satgé, J. *J. Chem. Res.* **1985**, 30. (d) Pfister-Guillouzo, G.; Guimon, C. *Phosphorus Sulfur* **1985**, *23*, 197. (e) Barrau, J.; Rima, G.; Lavayssierre, H.; Dousse, G.; Satgé, J. *J. Organomet. Chem.* **1983**, *246*, 227. (f) Barrau, J.; Bouchaut, M.; Lavayssierre, H.; Dousse, G.; Satgé, J. *Helv. Chim. Acta* **1979**, *62*, 152.

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(17) Grev, R. S.; Scaeffer, H. F., III. *Organometallics* **1992**, *11*, 3489.

(18) Neighboring group participation by aryl groups via phenonium ions is well-known in solvolysis reactions. Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A., Ed.; Wiley: New York, 1972; Vol. 3, pp 1347−1483.

(19) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1845.

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(21) Conlin, R.; Kwak, T.; Woo, Y. *J. Am. Chem. Soc.* **1986**, *108*, 834.

C bond of the silene would give a zwitterionic intermediate that may be the low-energy precursor to the rearrangement.

Conclusion

Laser ablation of cyclotrigermanes and cyclosiladigermanes provides excellent gas phase sources of heavy group 14 carbene analogues and dimetallenes. The intermediates are produced in sufficient abundances to potentially enable straightforward spectroscopic interrogations such as ionization potential determinations.[10] In contrast to solution studies where 2+1 fragmentation predominates, significant effective 1+1+1 processes must exist for the cyclotrimetallanes in the laser ablation plume. This results in an apparent nonregiospecific fragmentation of the cyclosiladigermanes to give products with near statistical amounts of silicon and germanium.

It is also demonstrated that selective reaction chemistry between dimesitylgermylene and exogenous oxygen bases can be observed. Although no neutral products have been detected for these reactions, further experiments selective for the detection of ionic products may help elucidate the course of these reactions. We are currently examining the extension of this technique to other group 14 cyclotrimetallanes as well as other strained group 14 ring systems.

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