J. Am. Chem. Soc. **1998,** *120,* 5005−5016

Transient 1,1-Dimethyl-1-germene, $(CH_3)_2Ge{=}CH_2$. Gas-Phase Pyrolytic Generation and EIMS, Matrix Isolation FTIR, and Theoretical Studies

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Received April 9, 1997

Abstract: Vacuum pyrolyses of 1,1-dimethyl-1-germa-3-thietane **(2)** and 1,1,3,3-tetramethyl-1-germacyclobutane **(3)** most likely proceed with the formation of the same transient species, 1,1-dimethyl-1-germene **(1)**, detected both in the gas phase by electron impact mass spectrometry (EIMS) and in argon solid matrixes at 12 K by Fourier transform infrared (FTIR) spectroscopy. The production of methylgermylene **(6)** in the reactions studied has also been suggested, probably as a result of secondary isomerization of **1** into methylethylgermylene **(8)** and subsequently to 1-methyl-1-germacyclopropane **(9)**, and further dissociation of **9** at higher temperatures, in agreement with the theoretical consideration of the suggested mechanism. Full vibrational assignments for the IR spectra of **1** and **6** have been proposed on the basis of ab initio and density functional theory calculations of the harmonic vibrational frequencies and infrared intensities, and of literature data on related molecules. The assignment of a high-intensity IR band at 847.3 cm^{-1} to a Ge=C stretching vibration coupled with the CH_3 rocking mode in **1** has also been supported by the calculation of potential energy distribution in the internal coordinates and by the observed splitting of this band due to natural isotopic abundance of germanium, being in accord with the B3LYP-calculated $^{70}Ge/^{72}Ge/^{74}Ge/^{76}Ge$ isotopic frequency shifts in **1**. The calculated force constant for the Ge=C bond in **1** confirms a π nature of this bond and yields an estimated bond order to be somewhat lower than the Si=C π-bond order in 1,1-dimethyl-1-silene **(4)**.

Introduction

The group 14 unsaturated organometallic compounds, $R_2M{=}X$, contain double bonds between Si or Ge and carbon or heteroatoms $X = CH_2$, O, N, P, and S, which are considered as new organometallic chemical functions.[2] These functions facilitate much higher reactivity of these compounds in comparison with their carbon analogues; therefore, their application as interesting precursors for new high-performance materials such as polymers and ceramics is being considered. They are also of great fundamental interest since until the mid-1960s these compounds were classified as nonexistent.[3] Some large-size molecules, particularly those with the Ge=C double bond (germenes),[2] have already been stabilized by bulky substituents, isolated, and characterized by standard spectroscopic methods.[2,4] The smaller members of this family exist only as transient species and require application of tricky physicochemical techniques for their studies.

Among the techniques applied to direct studies of these transient species over the last two decades, matrix isolation spectroscopy has proved to be the most successful one since publication in 1976 of the pioneering work of Maltsev, Khabashesku, and Nefedov[5] on infrared spectroscopic observation of 1,1-dimethylsilene in an argon matrix at 10 K, followed by publications of the two U.S. groups on 1,1,2-trimethylsilene.[6] Further matrix isolation studies provided direct spectroscopic data on the monomers of transient organometallic ketones wth the Si=O[7] and Ge=O[8] double bonds as well as of dimethylgermathione, $Me_2Ge{=}S$.[8a,9] UV−vis and IR spectra of matrix-isolated isomeric sila- and germacyclopentadienes, which contain a Si=C or Ge=C bonds in π-conjugation with the C=C bond, have recently been reported.[10,11] However, parent transient molecules with the Ge=C double bond, e.g., $H_2Ge{=}CH_2$ or $Me_2Ge{=}CH_2$, have not yet been characterized by spectroscopic methods although their existence as thermodynamically

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[2] Barrau, J.; Escudie, J.; Satge, J. *Chem. Rev.* **1990**, *90*, 283 and references therein.

[3] (a) Dasent, W. E. *Nonexistent Compounds*; Marcell Dekker: New York, 1965; p 61. (b) Huheey, J. H. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper and Row Publishers: New York, Evanston, San Francisco, London, 1972; p 617. (c) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, *70*, 2140. (d) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 4493.

[4] (a) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798. (b) Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure. Appl. Chem.* **1987**, *59*, 1011. (c) Couret, C.; Escudie, J.; Satge, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411. (d) Lazraq, M.; Escudie, J.; Couret, C.; Satge, J.; Drager, M.; Dammel, R. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828.

[5] Maltsev, A. K.; Khabashesku, V. N.; Nefedov, O. M. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1976**, 1193.

[6] (a) Chapman, O. L.; Chang, C.-C.; Kolc, J.; Young, M. E.; Lowe, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844. (b) Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, R. *J. Am. Chem. Soc.* **1976**, *98*, 7846.

S0002-7863(97)01134-7 CCC: $15.00

stable entities was predicted by calculations[2,12] and also postulated on the basis of chemical trapping[2,13] and kinetic[14] experiments.

In the present work we report the matrix isolation IR spectroscopic characterization of 1,1-dimethylgermene, $Me_2Ge{=}CH_2$ **(1)**, generated by vacuum pyrolysis of 1,1-dimethyl-1-germa-3-thietane **(2)** and 1,1,3,3-tetramethyl-1-germacyclobutane **(3)**. These studies are combined with the EIMS data on vacuum pyrolysis of **2**, and the ab initio and density functional calculations for the isomers and dissociation products from **1**. Some of these results were previously reported at conferences.[10,15a] The choice of **2** as a precursor for transient germene **1** was influenced by thermal decomposition studies of Barrau et al.[13] In view of the recent kinetic studies[14] of the thermal decomposition of 1,1-dimethyl-1-germacyclobutane, suggesting the intermediacy of germene **1**, and in view of the availability of a derivative of germacyclobutane, **3**, the latter compound was used as an independent pyrolytic precursor for **1**.

Experiment and Calculations

General Methods. ^1H and ^{13}C NMR spectra of **2** were recorded on JEOL FX90Q and Bruker AM300 spectrometers. GC−MS analysis was performed on a Varian MAT CH-6 instrument at 70 eV ionization energy.

Materials. 1,1-Dimethyl-1-germa-3-thietane (2). The precursor **2** was synthesized according to a reported multistep procedure.[16] The purity of the isolated sample **2** was about 99%, as established by the GC (5% XE60 on Chromaton NAW paked column), ^1H and ^{13}C NMR, and GC−MS analysis. ^1H NMR ($CDCl_3$, 90 MHz): δ 0.63 s (6H), 2.62 s (4H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 1.93 q (CH_3), 22.49 t (CH_2). HRMS for $C_4H_{10}{}^{70}GeS$: measd 159.974 60, calcd 159.974 62. IR (Ar matrix, 12 K): 2995.3 (m), 2980.0 (m), 2945.1 (m), 2928.2 (s), 1426.0 (m), 1407.3 (w), 1246.2 (m), 1241.2 (s), 1080.7 (vs), 1064.6 (w), 1061.6 (w), 834.3 (vs), 799.8 (m), 791.7 (s), 785.8 (s) 780.7 (m), 776.3 (sh), 728.5 (vw), 687.4 (vw), 626.5 (s), 616.9 (s), 611.0 (s), 580.1 (s), 575.8 (m), 571.4 (m) cm^{-1}. IR (Kr matrix, 12 K): 2986.2 (m), 2972.0 (m), 2938.3 (m), 2923.2 (s), 2918.8 (s), 1422.0 (w), 1407.8 (w), 1243.4 (m), 1238.5 (s), 1080.5 (s), 1063.3 (w), 832.2 (vs), 798.1 (m), 789.7 (m), 784.0 (s), 775.2 (sh), 624.4 (m), 610.3 (ms), 577.1 (m), 571.4 (m), 568.7 (m) cm^{-1}.

1,1,3,3-Tetramethyl-1-germacyclobutane (3). The precursor **3** was received from Professor F. Bickelhaupt,[17a] whose group has developed a convenient one-step synthesis of main group 14 metallacycles.[17b−d] IR (Ar matrix, 12 K): 2984.4 (m), 2961.2 (vs), 2925.2 (s), 2904.6 (m), 2868.6 (m), 1464.2 (m), 1393.9 (w), 1378.7 (w), 1363.5 (m), 1244.2 (w), 1237.1 (s), 1216.0 (m), 1209.0 (w), 1006.5 (m), 831.2 (vs), 788.8 (s), 785.0 (m), 778.0 (m), 761.8 (m), 663.8 (w), 603.9 (m), 592.2 (w), 583.8 (s) cm^{-1}.

Vacuum Pyrolysis−Mass Spectrometry. A vacuum pyrolysis−EIMS study of **2** was carried out at the Central Research Institute for Chemistry in a micropyrolyzer consisting of 2 mm quartz tubing placed into a 40 mm long resistively heated cylindrical furnace. The pyrolyzer was mounted in a vacuum chamber of the mass spectrometer as close as 10 mm to the electron beam. The temperature of the pyrolyzer was varied from 100 to 1100 °C. The pressure in the vacuum chamber during the experiment was kept at about 5×10^{-7} Torr. The measurements were performed with an AEI MS 902 type double focusing mass spectrometer equipped with linked scanning facilities. The appearance energies of some selected ions and ionization energies (IE) of some neutral molecules were obtained from measurements of ionization efficiency curves and application of the semilog plot technique[18] with benzene (IE = 9.41 eV) used as the internal standard.

Matrix Isolation Spectroscopy. Vacuum pyrolysis−matrix isolation IR spectroscopic experiments were done with both germene precursors, **2** and **3**, at temperatures of 500−970 °C and pressures in the pyrolysis zone ranging from 1 to 1×10^{-4} Torr. In these experiments the pyrolyzer dimensions, such as the internal diameter and the length, were varied from 5 to 8 mm and from 50 to 100 mm, respectively. The preliminary experiments on **2** were carried out at the Zelinsky Institute in the pyrolyzer mounted on the shroud of an Air Products helium cryostat.[7−9] During the further work on **2** and **3**, done at Rice University, the pyrolyzer was flanged to a vacuum chamber of the multisurface cryogenic apparatus.[19] The pyrolysis products were co-condensed at 12 K with a large excess of argon (1:1000) on the reflective rhodium-plated copper surfaces, located a distance of 20 mm from the pyrolyzer orifice. The multisurface copper substrate was cooled with the help of a closed-cycle Displex CSW-202 refrigerator from Air Products. The matrixes were analyzed with the IBM 98 FTIR

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(7) (a) Khabashesku, V. N.; Kerzina, Z. A.; Maltsev, A. K.; Nefedov, O. M. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1986**, 1215. (b) Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1986**, *108*, 8118. (c) Maltsev, A. K.; Khabashesku, V. N.; Nefedov, O. M. *Silicon Chemistry*; Ellis Horwood Publishers: Chichester, England, 1988; pp 211−227. (d) Khabashesku, V. N.; Maltsev, A. K.; Nefedov, O. M. 9th IUPAC Conference on Physical Organic Chemistry, August 1988, Regensburg, Germany, Abstract, p 53. (e) Khabashesku, V. N.; Kerzina, Z. A.; Baskir, E. G.; Maltsev, A. K.; Nefedov, O. M. *J. Organomet. Chem.* **1988**, *347*, 277. (f) Khabashesku, V. N.; Kerzina, Z. A.; Nefedov, O. M. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1988**, 2187. (g) Khabashesku, V. N.; Kerzina, Z. A.; Maltsev, A. K.; Nefedov, O. M. *J. Organomet. Chem.* **1989**, *369*, 301. (h) Khabashesku, V. N.; Kerzina, Z. A.; Maltsev, A. K.; Nefedov, O. M. International Conference on Matrix Isolation Spectroscopy, July 1989, Amsterdam, Holland, Abstract, p 72. (i) Maier, G.; Reisenauer, H. P.; Schöttler, K.; Wessolek-Kraus, U. *J. Organomet. Chem.* **1989**, *366*, 25.

(8) (a) Khabashesku, V. N.; Boganov, S. E.; Kerzina, Z. A.; Nefedov, O. M. 5th International Conference on Organometallic Chemistry of Germanium, Tin and Lead Compounds, July 1989, Brussels, Belgium, Abstract, p 46. (b) Khabashesku, V. N.; Boganov, S. E.; Nefedov, O. M. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1990**, 1199. (c) Khabashesku, V. N.; Kerzina, Z. A.; Boganov, S. E.; Nefedov, O. M. 9th International Symposium on Organosilicon Chemistry, July 1990, Edinburg, Great Britain, Abstract, p 57.

(9) (a) Barrau, J.; Balaji, V.; Michl, J. *Organometallics* **1989**, *8*, 2034. (b) Khabashesku, V. N.; Boganov, S. E.; Zuev, P. S.; Nefedov, O. M.; Tamás, J.; Gomory, A.; Besenyei, I. *J. Organomet. Chem.* **1991**, *402*, 161. (c) Nefedov, O. M. *Pure Appl. Chem.* **1991**, *63*, 231.

(10) (a) Khabashesku, V. N.; Boganov, S. E.; Antic, D.; Nefedov, O. M.; Michl, J. *Organometallics* **1996**, *15*, 4714. (b) Khabashesku, V. N. 2nd International Conference on Low-Temperature Chemistry, Aug 4−9, 1996, Kansas City, MO.; Durig, J., Klabunde, K., Eds.; University of Missouri−Kansas City; BkMk Press: Kansas City, MO, 1996; Proceedings, pp 137−140. (c) Khabashesku, V. N. Fargo Conference on Main Group Chemistry, May 30 to June 1, 1996, Fargo, ND; North Dakota State University: Fargo, ND, 1996, Abstracts, O-22. (d) Khabashesku, V. N.; Boganov, S. E.; Antic, D.; Michl, J.; Nefedov, O. M. The Fifth Conference on Carbene Chemistry (with International Participation), Sept 16−18, 1992, Moscow, Russia; Russian Academy of Science at Book Palace, Inc.: Moscow, Russia, 1992; Abstracts, pp 157−158.

(11) (a) Khabashesku, V. N.; Balaji, V.; Boganov, S. E.; Matveichev, P. M.; Chernyshev, E. A.; Nefedov, O. M.; Michl, J. *Mendeleev Commun.* **1992**, 38. (b) Khabashesku, V. N.; Balaji, V.; Antic, D.; Boganov, S. E.; Nefedov, O. M.; Michl, J. XXVIth Silicon Symposium, Indianapolis, IN, March 26−27, 1993; Indiana University-Purdue University: Indianapolis, IN, 1993; Abstracts, p D-11. (c) Khabashesku, V. N.; Balaji, V.; Boganov, S. E.; Nefedov, O. M.; Michl, J. *J. Am. Chem. Soc.* **1994**, *116*, 320. (d) Khabashesku, V. N.; Boganov, S. E.; Faustov, V. I.; Gömöry, A.; Besenyei, I.; Tamás, J.; Nefedov, O. M. *High Temp. Mater. Sci.* **1995**, 33, 125.

(12) (a) Grev, R. S.; Schaefer, H. F. *Organometallics* **1992**, *11*, 3489. (b) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 9559.

(13) Barrau, J.; Rima, G.; El-Amine, M.; Satge, J. *J. Organomet. Chem.* **1988**, *345*, 39.

(14) Namavari, M.; Conlin, R. T. *Organometallics* **1992**, *11*, 3307.

(15) (a) Kudin, K. N.; Margrave, J. L.; Khabashesku, V. N. Ninth Summer Research Colloquium: Rice Quantum Institute, Aug 18, 1995; Rice University: Houston, TX, 1995; Abstracts, p 26. (b) Kudin, K. N.; Margrave, J. L.; Khabashesku, V. N. *J. Phys. Chem. A* **1998**, *102*, 744. (c) Khabashesku, V. N.; Kudin, K. N.; Margrave, J. L. *J. Mol. Struct.* **1998**, *443*, 175.

(16) Barrau, J.; Rima, G.; Satge, J. *J. Organomet. Chem.* **1983**, *252*, C73.

(17) (a) Scheikundig Laboratorium, Vrije Universiteit, Amsterdam, The Netherlands. (b) Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 990. (c) Seetz, J. W. F. L.; Van De Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1984**, *277*, 319. (d) Bruin, J. W.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1985**, *288*, 13.

(18) Lossing, F. P.; Tickner, A. W.; Bryce, W. A. *J. Chem. Phys.* **1951**, *19*, 1254.

(19) Hauge, R. H.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L. *Appl. Spectrosc.* **1986**, *40*, 588.

Table 1. Observed Peaks and Their Tentative Assignment in the Vacuum Pyrolysis-Mass Spectra[a] of 1,1-Dimethyl-1-germa-3-thietane **(2)** at Various Temperatures of the Pyrolyzer

m/*z*	ion	100 °C	500 °C	700 °C	900 °C	1100 °C
160	$M^{\bullet+}$	100	100	100	100	100
145	$[M - CH_3]^+$	11	13	14	13	14
132^b	$(CH_3)_2Ge{=}S^{\bullet+}$	115	119	135	130	130
114^b	$(CH_3)_2Ge{=}CH_2^{\bullet+}$ $(A^{\bullet+})$	68	77	92	88	80
102^b	$GeS^{\bullet+}$	19	19	120	125	155
99	$[A - CH_3]^+$	52	59	77	80	76
86	$CH_3GeH^{\bullet+}$ $(B^{\bullet+})$	53	57	89	96	107
85^b	CH_3Ge^+ $[B - H]^+$	110	120	185	200	210
84	$CH_2Ge^{\bullet+}$ $[A - 2CH_3]^{\bullet+}$	23	26	32	35	34
71	GeH+ $[B - CH_3]^+$	23	26	45	47	45
70	Ge^+	16	16	35	40	40
46^b	$CH_2S^{\bullet+}$	17	26	320	230	130
28	$C_2H_4^{\bullet+}$	5	17	630	580	420
15	CH_3^+	9	10	28	210	140

[a] All isotopomers of germanium are taken into account. Peak intensities are given in arbitrary units relative to those of the *m*/*z* 160 ions. [b] Exact mass measurements (*m*/*z*, elemental composition): 132, measd 131.9430, calcd 131.9433, $C_2H_6{}^{70}GeS$; 114, measd 113.9853, calcd 113.9869, $C_3H_8{}^{70}Ge$; 102, measd 101.8960, calcd 101.8963, ^{70}GeS; 85, measd 84.9478, calcd 84.9477 25, $^{70}GeCH_2$; 46, measd 45.9871, calcd 45.9877, CH_2S.

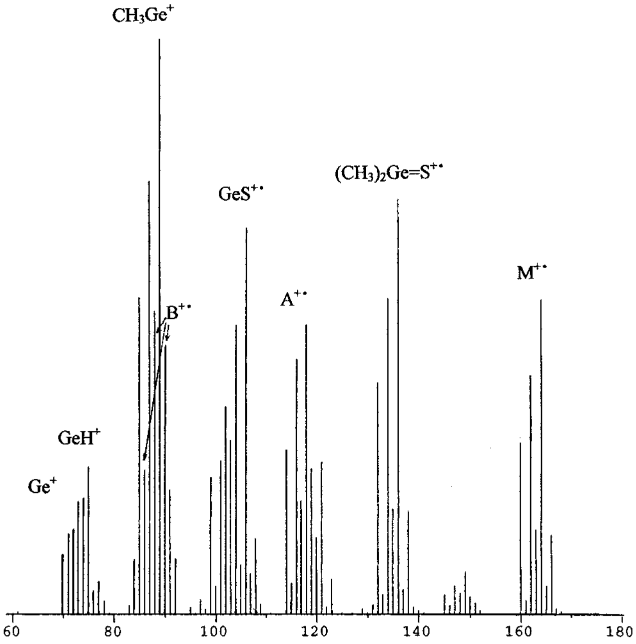


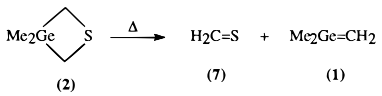
Figure 1. Mass spectrum (70 eV) of vacuum pyrolysis (700 °C) products of **2** showing the isotopic peaks of Ge-containing molecules. Molecular ions are labeled as follows: $M^{\bullet+}$, **2**; $A^{\bullet+}$, **1**; $B^{\bullet+}$, **6**.

spectrometer equipped with a HgCdTe detector. The spectra were collected in the range of 500−4000 cm^{-1} with 0.5 cm^{-1} resolution using the reflection of the infrared beam from the cold substrate surfaces.

Calculations. The ab initio and density functional[20] calculations of the ground-state geometries of the germene **1** and its silicon analogue, $Me_2Si{=}CH_2$ **(4)**, as well as harmonic vibrational frequencies and infrared intensities for **1** and its cyclodimer, 1,1,3,3-tetramethyl-1,3-digermacyclobutane **(5)**, transient methylgermylene, CH_3GeH **(6)**, thioformaldehyde, $H_2C{=}S$ **(7)**, methylethylgermylene, $CH_3GeC_2H_5$ **(8)**, and 1-methyl-1-germacyclopropane **(9)** were done at the restricted Hartree−Fock DZ+d and 6-311G(d, p) levels, and with the MP2/DZ+d and density functional theory B3LYP/6-311G(d, p) methods. The single-point energies for the transition states of isomerization of germene **1** and silene **4**, found at the second-order Moeller−Plesset perturbation theory level (MP2) with the 6-31G* basis set for carbon, hydrogen, and silicon, and DZ+d for germanium, were calculated with the MP2/6-311G** method. All calculations were carried out using the GAUSSIAN 94 program[21] running on an NEC SX-3 supercomputer.

Results

Vacuum Pyrolysis−EIMS of 1,1-Dimethyl-1-germa-3-thietane (2). These experiments have been carried out in an attempt to directly detect the germene **1** in the gas phase by mass spectrometry and to optimize the conditions of vacuum pyrolysis of **2** toward production of the highest yield of **1**. The similar approach has proved to be successful in our previous MS studies of transient molecules such as $Me_2Ge{=}S$[4b] and 1*H*-silole.[11d] The mass spectra (Table 1) taken at different temperatures of the pyrolyzer clearly show a sharp increase in the peak intensity of the *m*/*z* 46 ions in comparison with that of the *m*/*z* 160 ions of **2** chosen as a base peak in our measurements. The elemental composition of these ions, established by exact mass measurements, makes their assignment to the thioformaldehyde, $H_2C{=}S$ **(7)**, most likely. According to the earlier suggested[13] 4 → [2 + 2] pathway for the monomolecular thermal decomposition of **2**, this product has to be accompanied by the germene **1** (*m*/*z* 114), as shown by the following equation:



(2) (7) (1)

Indeed, at temperatures of 500 °C and above we have observed a distinct growth of this peak, although it was not directly proportional to the peak of the product **7**. This is likely to be caused by secondary thermal transformations of germene **1**, such as partial isomerization and dissociation under studied conditions. The observation of the growth of peak intensities of the lighter ions with *m*/*z* 86, 85, 71, 70, 28 (C_2H_4), and 15 (CH_3) with the temperature increase supports this assumption. In addition to that the ions with *m*/*z* 132 and 102 have also been observed to gain their peak intensities, indicating formation of dimethylgermathione, $Me_2Ge{=}S$ **(10)**, and germanium sulfide, GeS.

The tentative identitification of the germanium-containing products has been drawn from the exact mass measurements (Table 1) and the observed germanium isotopic patterns of the MS peaks (Figure 1). For instance, the high-resolution mass spectral measurements for the *m*/*z* 114 ions yielded a brutto-formula $C_3H_8{}^{70}Ge$, exactly reproducing the elemental composition of the molecular ion of germene **1** ($\mathbf{A}^{\bullet+}$). The similar measurements on the abundant ions with *m*/*z* 85 (Table 1) allow their tentative assignment to the $[\mathbf{B} - H]^+$ fragment ions of the ^{70}Ge isotopomer of methylgermylene, CH_3GeH, that show a peak of its molecular ion ($\mathbf{B}^{\bullet+}$) at *m*/*z* 86 and are accompanied by the heavier germanium isotopomers observed at *m*/*z* 88, 90, and 92 (Figure 1).

The energetic measurements of the appearance energies (AE) for some selected ions, carried out at temperatures of 100 and 950 °C, have particularly shown a 0.26 eV decrease in the AE of the $Me_2Ge{=}CH_2^{\bullet+}$ ions at the higher temperature. This

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(20) (a) *Modern Density Functional Theory: A Tool for Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995. (b) Wong, N. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(21) *Gaussian 94*: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

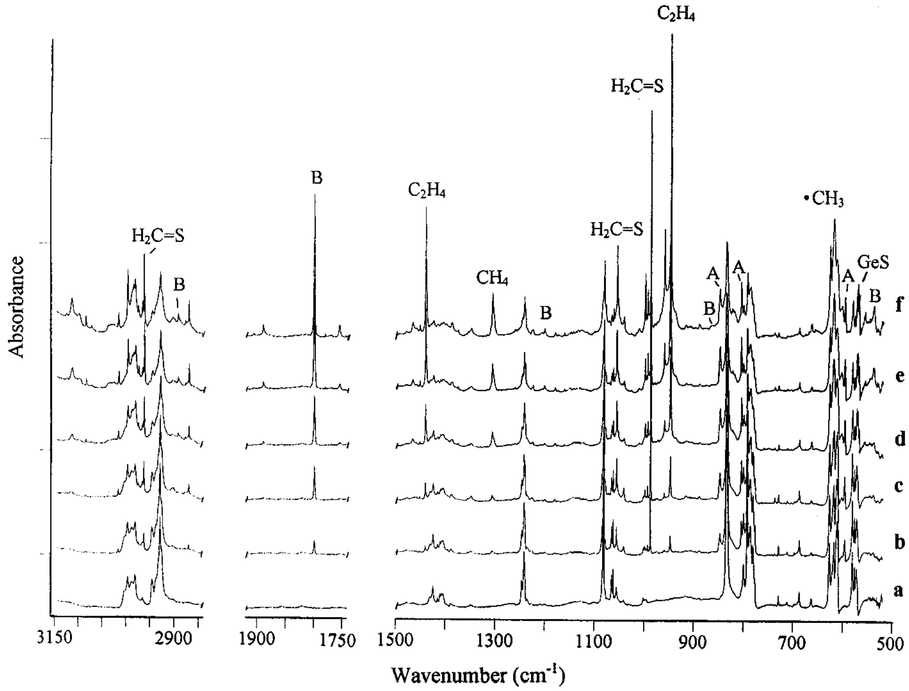

Figure 2. IR spectra (Ar, 12 K) of **2** (a) and pyrolysis (10^{-4} Torr) products of **2** at temperatures of (b) 520 °C, (c) 600 °C, (d) 730 °C, (e) 800 °C, and (f) 900 °C. Labeled peaks: A, germene **1**; B, germylene **6**.

means that some fraction of these ions may indeed originate from the ionization of the germene **1**, produced by pyrolysis. However, the steady concentration of **1** in the gas phase was not sufficient for the separation of its molecular ions from the fragment ions of **2**, and for the determination of the ionization energy (IE) of **1**, whereas the IEs of more stable species, such as $H_2C{=}S$ and GeS, could have been determined, and they are in good agreement with the literature data.[22,23] Our calculations yielded the IE values for the germene **1** as 7.79−7.84 eV, slightly depending on the method used. We expect the experimental IE of **1** to be very close to these calculated values just on the basis of comparison of our B3LYP/6-311G(d,p) calculated IE (7.94 eV) for the silicon analogue of **1**, $Me_2Si{=}CH_2$ **(4)**, with the best known value for the vertical ionization potential (7.98 eV)[24] of this molecule. Although we were not successful in the experimental determination of the IE of **1**, a tentative conclusion on the presence of germene **1** in the gas-phase beam of the pyrolysis products of **2** can be drawn from the MS data. This led us to believe that under conditions of cryogenic matrix isolation it could be possible to accumulate the transient germene **1** in a concentration sufficient for the FTIR spectroscopic characterization.

FTIR Spectra of Matrix-Isolated Pyrolysis Products from 2. The IR spectra of argon matrix-isolated pyrolysis products of **2**, produced at varied temperatures from 520 to 900 °C and a constant pressure of $\sim 10^{-4}$ Torr in the pyrolysis zone, are shown in Figure 2. Besides the bands of an unchanged starting compound **2** (Figure 2a), we have observed in the spectra of matrix-isolated pyrolysis products the bands of monomer thioformaldehyde, $H_2C{=}S$,[25] ethylene, and methane as well as a series of new bands denoted in Figure 2 by A and B labels. The proportional growth of the intensities of these new bands versus increasing pyrolysis temperature has been noted up to the temperature 730 °C (Figure 2b−d). On the basis of these observations and the EIMS studies, and also the expected [2 + 2] stoichiometry of the decomposition of **2**, all these new (both A and B) IR bands could have at this point been attributed to the same single product, germene **1**. However, in the matrix IR spectra of the pyrolysis products of **2** at more elevated temperatures of 800−900 °C (Figure 2e,f) a sharp increase in the intensity of the B-labeled band at 1798.6 cm^{-1}, the appearance of weaker bands at 535.6, 868.8, 1201.2, and 2891.6 cm^{-1}, and a growth of the ethylene bands with respect to those of the thioformaldehyde have been observed. On the contrary, the A-labeled bands at 576.0, 580.1, 596.0, 804.4, 818.8, 847.3, 1241.7, 1348.3, 1416.8, 2874.0, 2927.9, 2973.3, and 3008.0 cm^{-1} are significantly weakened in these spectra. The differences in the behavior of the A- and B-labeled bands are even more notable in the FTIR spectra (Figure 3) plotted after subtraction of the bands of precursor **2** from the spectra of the pyrolysis products of **2** at temperatures of 600 and 900 °C. These observations have ultimately confirmed the presence of two new species in the matrix.

We suggest that the IR bands, labeled by A, belong to the germene **1**, a product of the expected 4 → [2 + 2] unimolecular thermal decomposition of germathietane **2**. The IR spectra, the data for which are listed in Table 2, are in good agreement with the calculated spectra for **1**, one of those, B3LYP/6-311G(d,p), is shown in Figure 3a. This same product, along with the other one, characterized by B peaks in the IR spectra, has been obtained by vacuum pyrolysis of another precursor, germacyclobutane **3**. Additional reasons for the assignment of the A bands to germene **1** have been provided by the matrix warm-up experiments, and also, by the pyrolysis studies of **2** at increased pressures in the reaction zone. The spectra, observed in these experiments, are compared in Figure 4. After warm-

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[22] Wu, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1976**, *98*, 7578.

[23] Bock, H.; Solouki, B.; Mohmand, S.; Block, E.; Revelle, L. K. *J. Chem. Soc., Chem. Commun.* **1977**, 287.

[24] Dyke, J. M.; Josland, G. D.; Lewis, R. A.; Morris, A. *J. Phys. Chem.* **1982**, *86*, 2913.

[25] (a) Johns, J. W. C.; Olson, W. B. *J. Mol. Spectrosc.* **1971**, *39*, 479. (b) Jacox, M.; Milligan, D. E. *J. Mol. Spectrosc.* **1975**, *58*, 142. (c) Watanabe, O.; Suzuki, E.; Watari, F. *Bull. Chem. Soc. Jpn.* **1991**, 64, 1389. (d) Torres, M.; Safarik, I.; Clement, A.; Strausz, O. P. *Can. J. Chem.* **1982**, *60*, 1187.

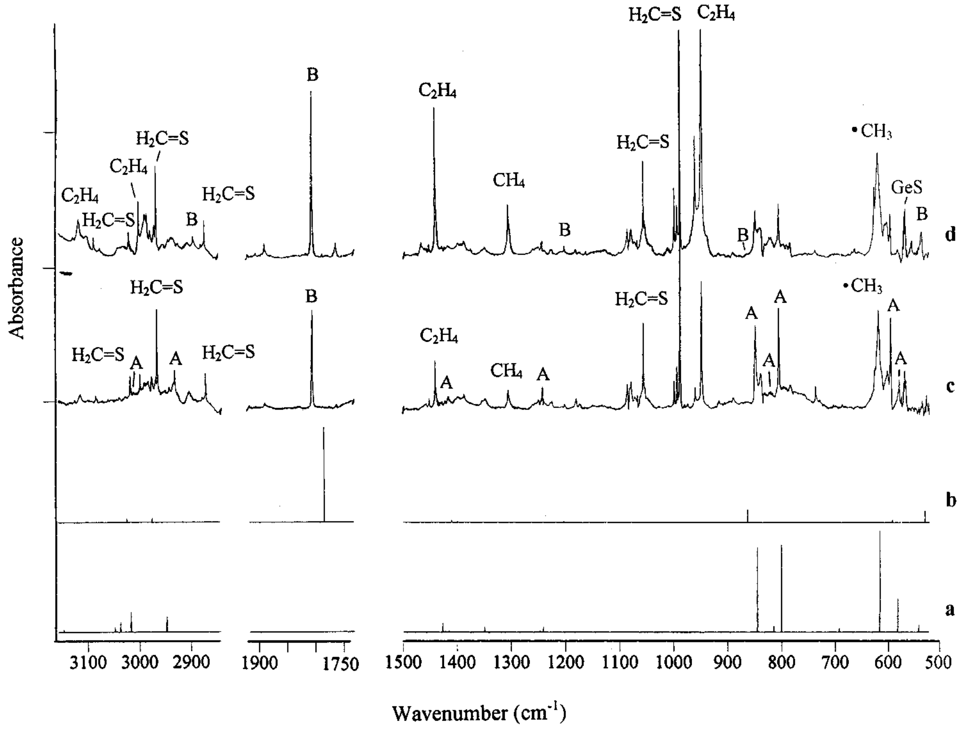

Figure 3. IR spectra (Ar, 12 K): (a) **1**, B3LYP/6-311G(d,p) calculated; (b) **6**, B3LYP/6-311G(d,p) calculated; (c) pyrolysis (10^{-4} Torr) products of **2** at 600 °C after subtraction of the spectrum of **2**; (d) pyrolysis (10^{-4} Torr) products of **2** at 900 °C after subtraction of the spectrum of **2**. Labeled peaks: A, germene **1**; B, germylene **6**.

Table 2. Vibrations of 1,1-Dimethyl-1-germene (**1**)

		frequencies (cm^{-1})					
		calcd (int)[a]					
mode	symmetry	MP2/DZ+d	HF/DZ+d	HF/6-311G(d,p)	B3LYP/6-311G(d,p)	obsd	assignment
1	a_2	107 (0)[b]	101 (0)[c]	107 (0)[c]	104 (0)[d]		CH_3 torsion ip
2	b_1	107 (0)	106 (0)	116 (0)	109 (0)		CH_3 torsion op
3	b_1	125 (1)	146 (3)	145 (1)	122 (1)		$CGeC_2$ deformation
4	a_1	163 (0)	168 (1)	166 (0)	167 (0)		GeC_2 scissor
5	b_2	179 (9)	187 (14)	184 (13)	183 (9)		GeC_2 rock
6	a_2	531 (0)	526 (0)	525 (0)	530 (0)		CH_2 twist
7	a_1	570 (6)	549 (6)	543 (6)	545 (5)	576.0	Ge—C sym stretch
8	b_2	609 (22)	582 (23)	576 (23)	585 (24)	580.1	Ge—C asym stretch
9	b_1	578 (74)	666 (85)	664 (81)	620 (73)	596.0	CH_2 wag
10	b_2	685 (3)	682 (4)	684 (3)	696 (3)		CH_2 rock
11	a_2	786 (0)	775 (0)	777 (0)	791 (0)		CH_3 rock
12	b_2	791 (56)	792 (74)	793 (77)	804 (63)	804.4	CH_3 rock, CH_2 rock
13	b_1	797 (0)	798 (3)	798 (1)	806 (0)		CH_3 rock, CH_2 wag
14	a_1	816 (0.1)	822 (1.3)	816 (4)	819 (4.5)	818.8[e]	Ge═C stretch[e]
15	a_1	843 (54)	844 (74)	840 (70)	849 (61)	847.3	Ge═C stretch, CH_3 rock
16	b_2	1236 (8)	1262 (5)	1259 (6)	1247 (4)	1241.7	CH_3 rock op
17	a_1	1243 (2)	1268 (2)	1264 (2)	1253 (1)		CH_3 rock ip
18	a_1	1332 (3)	1368 (9)	1367 (8)	1356 (4)	1348.3	CH_2 scissor
19	a_2	1393 (0)	1410 (0)	1415 (0)	1422 (0)		CH_3 bend
20	b_2	1401 (3)	1415 (2)	1419 (2)	1429 (2)		CH_3 scissor op op
21	b_1	1404 (19)	1419 (14)	1423 (7)	1433 (13)	1416.8	CH_3 scissor ip
22	a_1	1407 (9)	1420 (7)	1424 (12)	1434 (7)		CH_3 deformation
23	b_2	2880 (10)	2855 (21)	2850 (17)	2962 (11)	2874.0	C—H asym stretch
24	a_1	2880 (6)	2856 (14)	2851 (11)	2963 (7)		C—H sym stretch
25	a_2	2985 (0)	2942 (0)	2912 (0)	3032 (0)		C—H asym stretch
26	b_1	2993 (5)	2942 (19)	2913 (27)	3032 (14)	2927.9	C—H asym stretch
27	b_2	2994 (0)	2960 (6)	2933 (9)	3052 (5)		C—H asym stretch inplane
28	a_1	3007 (2)	2960 (7)	2933 (11)	3052 (7)	2973.3	C—H sym stretch inplane
29	a_1	3008 (2)	2968 (7)	2955 (7)	3063 (3)	3008.0	═CH_2 sym stretch
30	b_2	3089 (0)	3056 (1)	3040 (3)	3163 (2)		═CH_2 asym stretch

[a] Intensity, in km/mol. [b] Scaled by a factor of 0.95. [c] Scaled by a factor of 0.9. [d] Scaled by a factor of 0.975. [e] Tentative assignment; ip, in-phase; op, out-of-phase.

up of the argon matrix, whose IR spectrum is given in Figure 4c, from 12 to 40 K, we viewed the disappearance of the bands tentatively assigned to **1** and appearance of the bands of the 1,3-cyclodimer of **1**, digermacyclobutane **(5)**, at 602.4, 605.9, 791.8, 822.3, 830.6, and 937.3 cm^{-1}, as shown in the spectrum in Figure 4d. The latter bands were even more intense in the

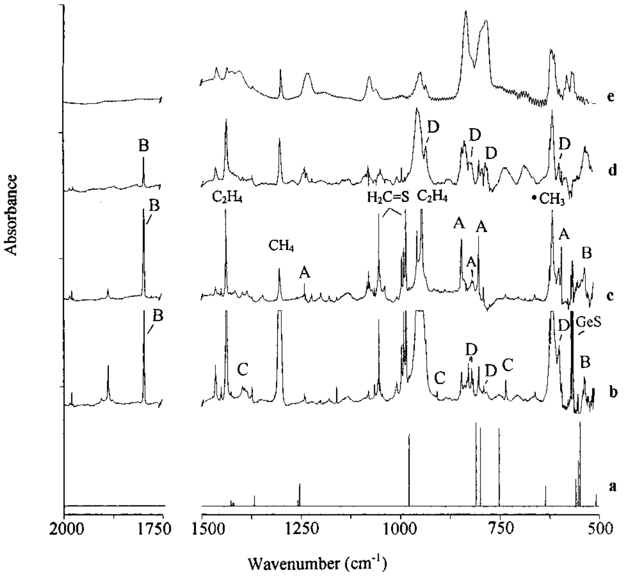

Figure 4. IR spectra: (a) cyclodimer **5**, HF/6-311G(d,p) calculated; (b) pyrolysis (10^{-1} Torr, 800 °C) products of **2** (Ar, 12 K); (c) pyrolysis (10^{-4} Torr, 800 °C) products of **2** (Ar, 12 K); (d) after warm-up of the matrix whose spectrum is shown in (c) from 12 to 40 K; (e) neat condensate at 12 K of the pyrolysis (10^{-4} Torr, 800 °C) products of **2**. The spectrum of **2** is subtracted from the spectra shown in (b)−(e). Labeled peaks: A, germene **1**; B, germylene **6**; C, $(H_2CS)_3$; D, cyclodimer **5**.

spectrum of a neat condensate of the pyrolysis products frozen at 12 K (Figure 4e), while the bands ascribed to **1** were completely absent. The IR bands detected for the cyclodimer **5** in the present work are found to be in good agreement with the calculated spectrum of **5** (Figure 4a) and with the literature data.[26] An increase in pressure in the pyrolysis zone from 10^{-4} to 10^{-1} Torr, which dramatically enhanced the number of intermolecular collisions in the gas phase, also resulted in the depletion of the A peaks and apppearance of the most intense bands of the cyclodimer **5** in the IR spectrum (Figure 4b). The formation of **5** in these experiments could be most reasonably explained by the dimerization of transient germene **1**, proceeding either in the annealed matrixes at cryogenic temperatures or in the gas phase under increased pressure. This is in agreement with our most recent calculations,[15b] predicting virtually zero barrier for the head-to-tail dimerization of **1**. On the basis of these experiments and the calculations, we believe that the new A IR peaks, detected in the spectra (Table 2) of pyrolysis products of **2**, very likely belong to the transient germene **1**.

As for the origin of the B bands, their suggested assignment to methylgermylene **6** is in reasonable agreement with the calculated spectrum of **6** (Figure 3b and Table 3). These bands were shown to grow along with the ethylene absorptions at the expense of the attributed to germene **1** bands in the matrix spectra of the high-temperature (800−900 °C) pyrolysis products. This observation prompted us to consider the possibility of a thermal decomposition path for the germene **1** which proceeds via elimination of ethylene and leads to germylene **6**. The loss of an ethylene molecule as one of the fragmentation routes for **1** has been detected in the daughter ion mass spectra of germathietane **2**. Prior to elimination of C_2H_4 these ions most likely rearrange from the germene structure to methylethylgermylene and then into a germacyclopropane. Therefore, we assume that the loss of ethylene can also take place from the neutrals of germene **1** at high pyrolysis temperatures. It is interesting that a similar high-temperature decomposition route for the silene **4** has not been observed under the same conditions of vacuum pyrolysis.[27] This prompted us to carry out quantum chemical calculations that allow comparison of the relative thermodynamic stabilities for the isomers of germene **1** with those of the silene **4** and also for the products of their thermal dissociation.

Isomerization and Dissociation of the Germene 1. The calculated relative energies for the C_3H_8M (M = Ge, Si) isomers are represented by the heats of the isomerization reactions in Table 4. They demonstrate the close stabilities for the germene **1**, methylethylgermylene **(8)**, and 1-methyl-1-germacyclopropane **(9)**. For instance, **1** is 3.1 kcal/mol less stable than **8**, while **8** is only 4.2 kcal/mol more stable than **9**. On the contrary, in the case of silicon analogues the silene **4** is found to be 14.2 kcal/mol more stable than methylethylsilylene **(12)** which in turn is 15.7 kcal/mol less stable than 1-methyl-1-silacyclopropane **(11)**.

Since some examples of the germene-to-germylene isomerization are already known from the direct spectroscopic[10] and theoretical[12,41] studies, the first step of the transformation of germene **1** into germacyclopropane **9** is assumed to be the isomerization of **1** into germylene **8** (Scheme 1) proceeding via a migration of the methyl group in **1** from germanium toward a methylene carbon. This process is predicted to pass on through a transition state (TS_1) with the MP2/6-311G**//MP2/6-31G* calculated barrier of 48.7 kcal/mol. A higher barrier (56.8 kcal/mol) was computed for the similar isomerization of silene **4** into silylene **12**.

The next passage involves the intramolecular insertion of the germylene center in **8** into the terminal C−H bond of the ethyl substituent to yield germacyclopropane **9**. The barrier, separating the carbene analogue structure from metallacyclopropane, was found to be only slightly lower for the pair of silicon molecules **12** and **11** (14.4 kcal/mol) than for their germanium relatives **8** and **9** (18.5 kcal/mol). The dissociation of germacyclopropane **9** into germylene **6** and ethylene was calculated to be endothermic by 25.5 kcal/mol. In comparison, the extrusion of ethylene from silacyclopropane **11**, yielding methylsilylene **13**, was found to be even more endothermic (48.3 kcal/mol).

The calculations also predict that direct dissociation of the germene **1** into a singlet dimethylgermylene and methylene is highly endothermic (Table 4). The calculated energy required for this reaction (106.6 kcal/mol) reflects the total strength of the σ and π Ge═C bond in **1**. For comparison, the energy needed for the similar dissociation of the silene **4**, i.e., the overall strength of the σ and π Si═C bond, is calculated to be significantly higher (124.2 kcal/mol).

Thus, the calculation data suggest that the transformation of the M═C (M = Ge, Si) double-bonded structure into a carbene analogue CH_3MH and ethylene could proceed via an isomerization−dissociation mechanism, involving a thermolabile metallacyclopropane. This route requires lower energy in the case of germene **1** as compared with the silene **4** and is also much more thermodynamically favorable than the direct dissociation path. These data are consistent with the experiment, providing a reasonable explanation for the generation and detection of methylgermylene **6** in the present work and no observation of

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(26) Aleksanyan, V. T.; Mironov, V. F.; Mikhailyants, S. A.; Gar, T. K. *Bull. Acad. Sci. USSR Chem. Div.* **1970**, 2026.

(27) (a) Khabashesku, V. N. Ph.D. Thesis, Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, USSR, 1979. (b) Nefedov, O. M.; Maltsev, A. K.; Khabashesku, V. N.; Korolev, V. A. *J. Organomet. Chem.* **1980**, *201*, 123.

(28) Seidl, E. T.; Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 3643.

Table 3. Vibrations of Methylgermylene (6)

		frequencies (cm^{-1})				
		calcd (int)[a]				
mode	symmetry	MP2/DZ+d	HF/DZ+d	B3LYP/6-311G(d,p)	obsd	assignment
1	a″	146 (0)[b]	154 (0)[c]	100 (0)[d]		CH_3 torsion, GeH twist out-of-phase
2	a″	537 (42)	515 (44)	516 (44)	535.6	Ge−C stretch
3	a″	565 (2)	577 (4)	564 (2)		CH_3 rock, GeH twist
4	a′	598 (10)	589 (17)	597 (12)		GeH rock, CH_3 rock out-of-phase
5	a′	874 (48)	871 (67)	867 (53)	868.8	CH_3 rock, GeH rock in-phase
6	a′	1207 (14)	1234 (9)	1208 (8)	1201.2	CH_3 rock
7	a′	1379 (6)	1397 (4)	1406 (5)		CH_3 deformation
8	a″	1395 (12)	1412 (8)	1417 (10)		CH_3 deformation
9	a′	1810 (334)	1742 (432)	1786 (380)	1798.6	Ge−H stretch
10	a′	2851 (5)	2826 (19)	2930 (6)		C−H sym stretch
11	a″	2953 (9)	2903 (26)	2989 (19)	2891.6	C−H asym stretch
12	a′	3001 (8)	2942 (19)	3038 (17)		C−H stretch

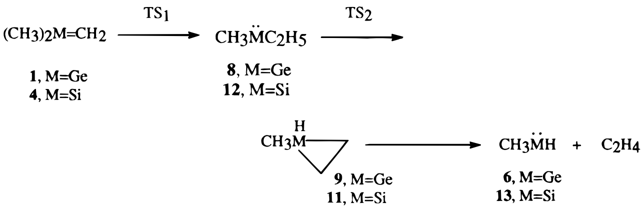
[a] Intensity, in km/mol. [b] Scaled by a factor of 0.95. [c] Scaled by a factor of 0.9. [d] Scaled by a factor of 0.975.

Table 4. MP2/6-311G**//MP2/6-31G* Calculated[a] Barriers ($\Delta H^{\ddagger}$) and Heats of Reaction (ΔH) (kcal/mol) for the Isomerization and Dissociation of C_3H_8M (M = Ge, Si) Isomers

isomerization	$\Delta H^{\ddagger}$	ΔH	dissociation	ΔH
			M=Ge	
$1 \rightarrow 8$	TS_1 48.7	−3.1	$9 \rightarrow 6 + C_2H_4$	25.5
$8 \rightarrow 9$	TS_2 18.5	4.2	$1 \rightarrow Me_2Ge\ (^1A') + CH_2\ (^1A')$	106.6
			M=Si	
$4 \rightarrow 12$	TS_1 56.8	14.2	$11 \rightarrow 13 + C_2H_4$	48.3
$12 \rightarrow 11$	TS_2 14.4	−15.7	$4 \rightarrow Me_2Si\ (^1A') + CH_2\ (^1A')$	124.2

[a] Corrected by HF/3-21G* zero-point vibrational energy.

Scheme 1

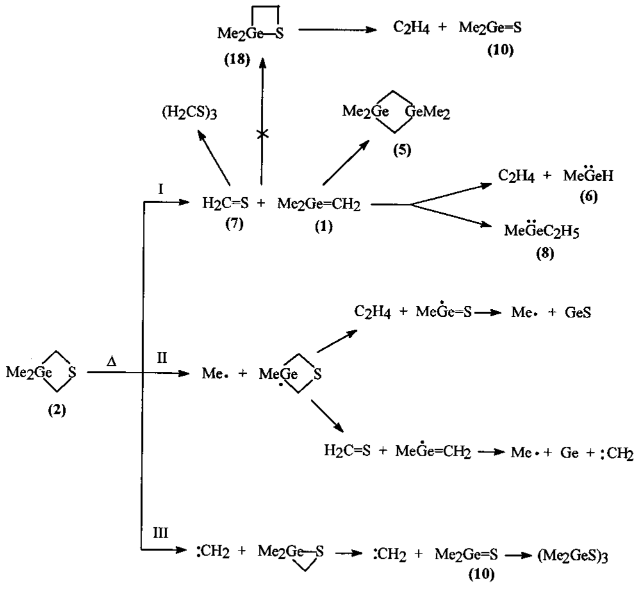


the methylsilylene **13** in the studies on pyrolytically produced silene **4**.[27]

Mechanistic Aspects of Vacuum Pyrolysis of Germathietane 2. Combined EIMS and matrix isolation FTIR spectroscopic data on vacuum pyrolysis of **2** assisted by the theoretical calculations on transformations of germene **1** provide a reasonable foundation for mechanistic interpretation of the thermal decomposition of **2**. Scheme 2 summarizes all reactions and products from **2** that we believe to be observed in the present work. We suggest three parallel routes for the unimolecular decomposition of **2**, which are realized under pressures as low as 10^{-4} Torr in the reaction zone. Route I represents a 2 + 2 cycloreversion, yielding $H_2C{=}S$ **(7)** and germene **1** as primary products, and ethylene, methylgermylene **(6)**, and, probably, methylethylgermylene **(8)** as secondary products. Formation of the CH_3 radical and GeS molecule can be described by route II. Note that both thermal decomposition routes I and II proceed along fragmentation pathways similar to those of the molecular ion of **2** in the mass spectra. The latter were considered earlier by Barrau et al.,[16] and have been confirmed in the present work by studies of daughter ion mass spectra of **2**.

The germathione **10** was detected only in the mass spectra of pyrolysis products, and not in the matrix IR spectra. This can be explained by a much longer residence time for the molecules of **2** in the pyrolyzer used in the vacuum pyrolysis−EIMS experiments, which facilitated the decomposition of **2** along an additional route III. Under the increased pressure in the reaction zone (10^{-1} to 1 Torr) of the pyrolyzer employed in the matrix isolation experiments, we did not observe either a dimer or a trimer of germathione **10**, $(Me_2GeS)_2$ and $(Me_2GeS)_3$,[9] respectively. This very likely indicates that (i) route III is not feasible at a shorter residence time and (ii) the proposed[13] secondary 2 + 2 cycloaddition of $H_2C{=}S$ to germene **1** and a further 2 + 2 cycloreversion of the resulting 1-germa-2-thietane **(18)**, yielding ethylene and germathione **10**, are not taking place because of an extremely fast dimerization of **1**.[15b]

Scheme 2



FTIR Spectra of Matrix-Isolated Pyrolysis Products of 1,1,3,3-Tetramethyl-1-germacyclobutane (3). In the Ar matrix IR spectra (Figure 5b−d) of the pyrolysis products of **3** at temperatures of 670−900 °C and a pressure of $\sim 1 \times 10^{-4}$ Torr in the reaction zone we have detected, besides the bands of 2-methyl-1-propene,[29] a set of bands that matches the IR spectrum of germene **1**, which we believe has been generated by pyrolysis of **2**. These bands, labeled A in Figure 5, also disappeared simultaneously on annealing the matrix from 12 to 40 K, producing the bands of the cyclodimer **5** instead. These results provide additional evidence for the gas-phase generation and subsequent trapping of the transient germene **1** in a cryogenic matrix and allow us to confirm the assignment of the IR bands of **1**.

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(29) Barnes, A. J.; Howells, J. D. R. *J. Chem. Soc., Faraday Trans. 2* **1973**, 532.

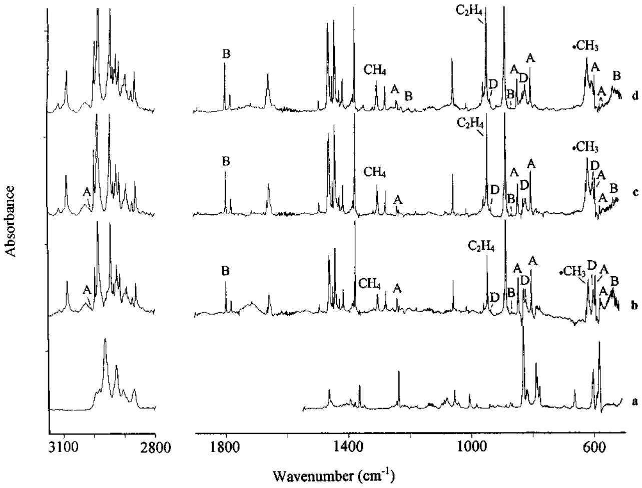
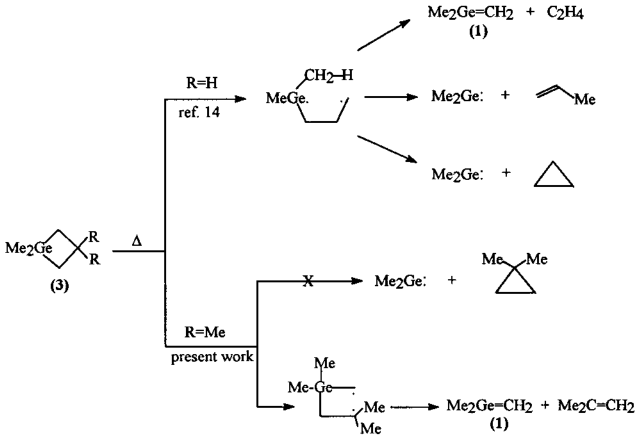


Figure 5. IR spectra (Ar, 12 K) of (a) **3** and of the pyrolysis (10^{-4} Torr) products of **3** at temperatures of (b) 600 °C, (c) 700 °C, and (d) 800 °C. The spectrum of **3** is subtracted from the spectra shown in (b)−(d). Labeled peaks: A, germene **1**; B, germylene **6**; D, cyclodimer **5**.

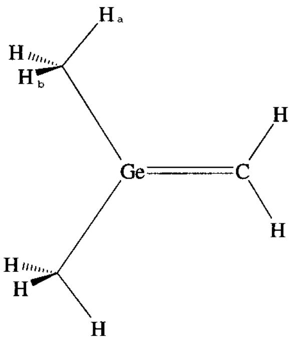
Scheme 3



The other observed set of bands, labeled B, coincide with the bands assigned to the germylene **6** in the spectra of pyrolysis products from **2**. Their intensities have also been noted to grow significantly along with those of ethylene as the pyrolysis temperature increased from 670 to 900 °C, while the bands of germene **1** are reduced at the same time. These observations gave us independent experimental support of the suggested mechanism of formation of methylgermylene **6** via high-temperature fragmentation of germene **1** (Scheme 1).

In an earlier study[14] of the gas-phase decomposition of 1,1-dimethyl-1-germacyclobutane at lower temperatures (410−500 °C) two parallel unimolecular reaction channels, leading to germene **1** and ethylene, as well as dimethylgermylene, cyclopropane, and propene, have been suggested on the basis of final products and kinetic Arrhenius parameters. A proposed reaction mechanism (Scheme 3) involved an initial ring opening at the Ge−C bond site to produce germanium and a carbon-centered biradical. The formation of two transient species, germene **1** and dimethylgermylene, chemically trapped by butadiene, was postulated. In our matrix isolation study of the vacuum pyrolysis of 3,3-dimethyl-substituted germacyclobutane **3** we did not observe either the IR bands of dimethylgermylene[30] or those of 1,1-dimethylcyclopropane[31] or of any hydrocarbon other than 2-methyl-1-propene.[29] This means that the decomposition of **3** most likely follows a single reaction channel, a 2 + 2 cycloreversion. An earlier C−C bond cleavage in the ring is more favorable for 3,3-dimethyl derivative **3** since in the biradical formed the β stabilization of the one carbon radical center by germanium is assisted by the stabilization of the other carbon radical center by the hyperconjugation effect of two methyl groups (Scheme 3). Since dimethylgermylene extrusion from this biradical is not feasible, this implies that 1,1,3,3-tetramethyl-1-germacyclobutane (**3**) is probably a more selective precursor for germene **1** than 1,1-dimethyl-1-germacyclobutane.[14]

Chart 1. Optimized Geometry of 1,1-Dimethyl-1-germene (**1**)



	bond length, Å					angle, deg.			
	Ge=C	Ge-C	C-H	C-H$_a$	C-H$_b$	CGeC	HCGe	H$_a$CGe	H$_b$CGe
HF/DZ+d	1.761	1.947	1.085	1.091	1.093	123.0	122.1	110.3	110.7
HF/6-311G(d,p)	1.765	1.954	1.076	1.083	1.085	123.2	121.9	110.3	110.4
MP2/DZ+d	1.772	1.937	1.100	1.105	1.106	122.8	121.6	110.0	110.6
B3LYP/6-311G(d,p)	1.780	1.962	1.083	1.090	1.092	122.7	121.5	109.8	110.5

Discussion

Germene 1. Molecular Geometry. Calculations done at several levels of theory all yielded planar (C_{2v}) optimized geometry for the singlet ground state of **1** (Chart 1). The Ge=C bond lengths, 1.761 and 1.765 Å, computed at the SCF RHF level of theory with the DZ+d and 6-311G(d,p) basis sets, respectively, 1.772 and 1.780 Å, found in the MP2/DZ+d and B3LYP/6-311G(d,p) approximations, respectively, are very close to the values calculated for parent germene, $H_2Ge{=}CH_2$, by Schaefer[12a] with the DZP basis set at the CISD and SCF levels of theory, and Gordon[12b] using RHF and MP2 methods with the 3-21G(d) basis set. They are also close to the reported X-ray diffraction Ge=C bond lengths, 1.801 Å[4c,d] and 1.827 Å,[4a,b] in the stable germenes, isolated in 1987 through the use of bulky groups for steric and electronic stabilization. The valence angles at the double-bonded germanium and carbon are calculated to be near 120°, to confirm the sp^2 hybridization state of both atoms. In general, the RHF, MP2, and B3LYP geometries agree to within 0.02 Å for bond lengths and 0.6° for bond angles (Chart 1).

IR Spectrum. A full assignment of the experimental bands in the IR spectrum of germene **1** has been suggested by

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[30] (30) Barrau, J.; Bean, D. L.; Welsh, K. M.; West, R.; Michl, J. *Organometallics* **1989**, *8*, 2606.

[31] (31) (a) Durig, J. R.; Neuse, A. B.; Milani-Nejad, F. J. *J. Mol. Struct.* **1981**, *72*, 57. (b) Bush, S. F.; Dixon, P. W. *Spectrochim. Acta, Part A* **1978**, *34A*, 515.

[32] (32) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, 11, 493.

[33] (33) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986,** 5, 2057.

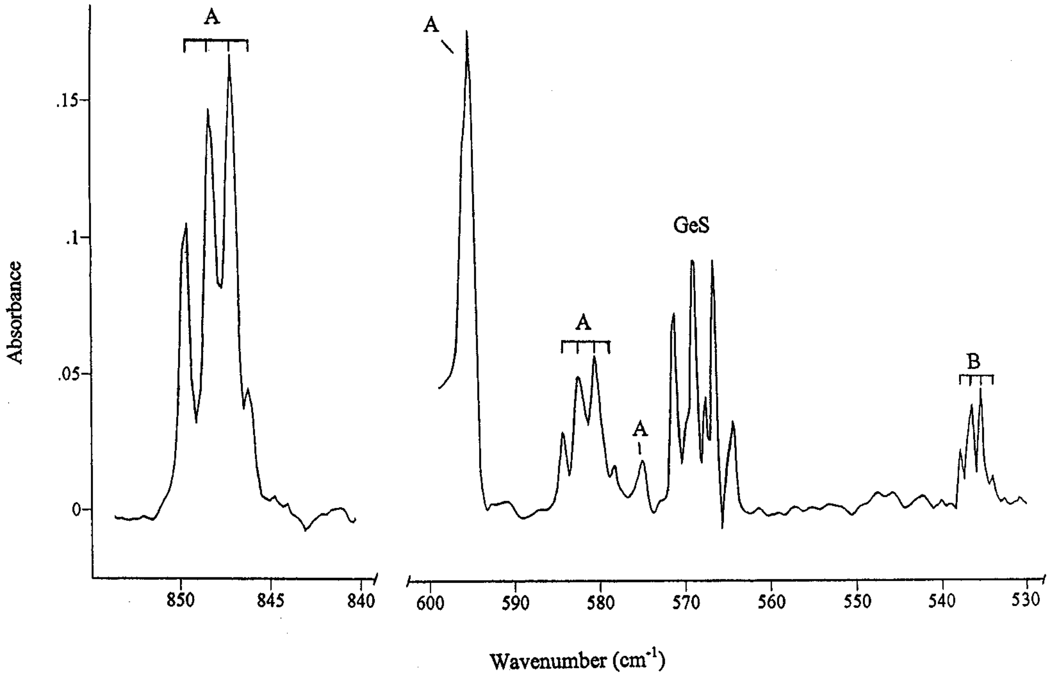

Figure 6. Germanium−carbon stretching mode sections (850−840 and 600−530 cm^{-1}) of the IR spectrum of the pyrolysis products of **2** shown in Figure 3c. Labeled are peaks of Ge isotopomers: A, germene **1**; B, germylene **6**.

comparison with the IR spectra of 2-methyl-1-propene[29,34] and methylgermanes,[35] and with the ab initio and density functional theory (DFT) calculated vibrational spectra of **1** including the IR absorptions for all germanium isotopomers. The molecule has 30 normal vibrational modes; 5 of them have a_2 symmetry and are forbidden in the IR spectrum. Four infrared active vibrations, calculated to lie below 500 cm^{-1}, could not be observed in our experiments. We have experimentally found 13 out of the 21 expected fundamentals in the 500−4000 cm^{-1} spectral region.

One band found above 3000 cm^{-1} in the IR spectrum of **1** at 3008.0 cm^{-1} has been assigned to the symmetric $=CH_2$ stretching vibration. This agrees with the calculations (Table 2) and with the literature data that show this type of stretching mode to be located in the 2880−3000 cm^{-1} region in the IR spectra of alkenes with the terminal $=CH_2$ group, e.g., 2-methyl-1-propene.[29,34] The band of the antisymmetric $=CH_2$ stretching vibration was not observed most likely because of its low intensity and also overlap with the bands of ethylene or 2-methyl-1-propene in the 3075−3110 cm^{-1} spectral region.

The three bands at 2874.0, 2927.9, and 2973.3 cm^{-1} belong to the CH stretching vibrations of the methyl groups in reasonable agreement with the calculations and with the literature data on the vibrations of $(CH_3)_2Ge$ fragments in methylgermanes.[35] The CH_3 deformation vibrational frequencies are located in the 1390−1460 cm^{-1} region in the IR spectra of methylgermanes.[35] In this region we observed only one band at 1416.8 cm^{-1}. On the basis of calculations, this band was assigned to the in-phase CH_3 scissoring mode.

The scissoring CH_2 deformation mode in 1,1-dialkylalkenes is found in the 1400−1420 cm^{-1} spectral region. The calculations predict this vibration to show in **1** at lower frequencies, 1332−1368 cm^{-1}, depending on the theory level employed (Table 2). In good agreement with these calculations is the band at 1348.3 cm^{-1}. The band at 1241.7 cm^{-1} was attributed to the out-of phase CH_3 deformation rocking mode in good agreement with the calculations and with the well-established location of this fundamental in the 1200−1250 cm^{-1} region in the IR spectra of di- and tetramethylgermanes.[35]

For the assignment of the IR bands lying below 1000 cm^{-1} the observation of the isotopic structure of these bands due to the natural abundance of germanium at a higher spectral resolution (Figure 6) and comparison with the B3LYP calculated isotopic frequencies (Table 5) was of particular help. The latter calculations predict that four modes, ν_7, ν_8, ν_{14}, and ν_{15} (Table 5), are sensitive to the variation of the isotopic mass of the germanium atom, thus indicating that these modes involve the stretchings of the germanium−carbon bonds. Among these modes the location of the Ge=C stretching mode in the IR spectrum of germene **1** is the most exciting matter in the present spectral interpretation. In the parent germene, $H_2Ge{=}CH_2$, previous theoretical calculations[2,12b] predicted the Ge=C stretch to lie in the spectral range of 785−906 cm^{-1}. Our own calculations on this germene, done with the density functional theory B3LYP/6-311G(d,p) method, yielded (after scaling by a factor of 0.975) the value of 813 cm^{-1} for this vibrational mode.[15b] The frequency of the Ge=C stretching vibration in 1,1-dimethyl-1-germene (**1**) is expected to be somewhat higher, by the analogy with the increase in the frequency of the Si=C stretching mode in 1,1-dimethyl-1-silene (1003 cm^{-1})[5,27] with respect to parent silene, $H_2Si{=}CH_2$ (985 cm^{-1}).[36] And indeed, the calculations with four different theoretical approximations predict the frequencies to be higher for the Ge=C stretch in **1**, and this vibrational mode to contribute to two computed frequencies, at 816−822 and 840−849 cm^{-1} (Table 2). This effect is due to the coupling of the Ge=C stretching vibration with the CH_3 rocking mode of the same (a_1) symmetry, as demonstrated with the help of the XMol vibration visualization program.[37]

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(34) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasseli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: San Diego, CA, 1991.

(35) Maslowsky, E. *Vibrational Spectra of Organometallic Compounds*; John Wiley and Sons: New York, London, Sydney, Toronto, 1977.

(36) (a) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 597. (b) Reisenauer, H. P.; Mihm, G.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 854. (c) Maier, G.; Mihm, G.; Reisenauer, H. P.; Littman, D. *Chem. Ber.* **1984**, *117*, 2369.

Table 5. Infrared Absorptions (cm^{-1}) and Band Isotopic Splittings ($\Delta\nu$) of Germanium Isotopomers of Germene **1** and Germylene **6** in Solid Argon Matrix

	vibrational mode		frequency			$\Delta\nu$	
			calcd[a]	obsd		calcd	obsd
$(CH_3)_2Ge{=}CH_2$ (**1**)	Ge=C str; CH_3 rock	^{70}Ge	851.6	849.6	70/72	1.1	1.2
		^{72}Ge	850.5	848.4			
		^{73}Ge	850.0		72/74	0.9	1.1
		^{74}Ge	849.6	847.3			
		^{76}Ge	848.8	846.3	74/76	0.8	1.0
	Ge=C str	^{70}Ge	821.5				
		^{72}Ge	820.3				
		^{73}Ge	819.7				
		^{74}Ge	819.0	818.8			
		^{76}Ge	817.7				
	Ge−C asym str	^{70}Ge	589.3	583.6	70/72	1.6	1.7
		^{72}Ge	587.5	581.9			
		^{73}Ge	586.6		72/74	1.7	1.8
		^{74}Ge	585.8	580.1			
		^{76}Ge	584.2	578.5	74/76	1.6	1.6
	Ge−C sym str	^{70}Ge	546.7				
		^{72}Ge	546.3				
		^{73}Ge	546.0				
		^{74}Ge	545.8	576.0			
		^{76}Ge	545.4				
CH_3GeH (**6**)	Ge−C str	^{70}Ge	519.2	538.1	70/72	1.3	1.3
		^{72}Ge	517.9	536.8			
		^{73}Ge	517.3		72/74	1.2	1.2
		^{74}Ge	516.7	535.6			
		^{76}Ge	515.6	534.3	74/76	1.2	1.3

[a] B3LYP/6-311G(d,p). Scaled by 0.975.

The frequencies at 816−822 cm^{-1} are predicted to show very low band intensity, as indicated by computed vibrational oscillator strengths within 0.1−4.5 km/mol, depending on the method used for spectral calculations. In contrast, the band intensities for the frequencies at 840−849 cm^{-1} are calculated to be much higher, 54−74 km/mol. On the basis of these predictions and on the known assignment to the Si=C stretch in the IR spectrum of silene **4**[27] of a high-intensity band at 1003.5 cm^{-1}, we in our preliminary reports[10b,c,15a] have also tentatively assigned an intense band at 847.2 cm^{-1} to the Ge=C stretch in **1**.

In the present work we have additionally performed a vibrational analysis and coordinate transformation in **1** with the help of the REDONG program package[38] that allows one to start from a GAUSSIAN 94 calculation of vibrational frequencies and then, through several subsequent operations, to obtain a force field and potential energy distribution (PED) for internal-coordinate modes. The PED for the calculated high-intensity mode at 840−849 cm^{-1} yielded contributions from the Ge=C stretch, which substantially vary with the theory level employed for the spectral calculations, i.e., 30% at MP2/DZ+d, 65% at HF/DZ+d, 27% at HF/6-311G(d,p), and only 10% at B3LYP/6-311G(d,p). Despite of broad variation, these data surely point out the strongly mixed character of this mode in **1**. In addition, the substantial contribution of the Ge=C stretch to this mode is clearly demonstrated by the observed isotopic structure of the band at 845−850 cm^{-1} in a higher resolution spectrum (Figure 6) which is in reasonable agreement with the calculated $^{70}Ge/^{72}Ge/^{74}Ge/^{76}Ge$ isotopic splitting (Table 5). These data finally confirm our previous preliminary assignment of an intense band at 847.2 cm^{-1} to this mode.

On the other hand, the PED for the computed ν_{14} mode at 816−822 cm^{-1} yields even higher (93−99%) contribution from the Ge=C stretch. However, the very low infrared intensity of this fundamental, predicted to be 15−540 times weaker than ν_{15} (Table 2), creates difficulties for its reliable experimental observation. The broad band at 818.8 cm^{-1} in the Ar matrix spectra overlaps with the intense bands of a cyclodimer **5** also absorbing in this region; therefore, it could be observed as a tiny IR peak only when the content of **5** in the matrix is very low, e.g., at pyrolysis temperatures of **2** as low as 600 °C, and not at higher temperatures. The low intensity of this peak precludes the observation of the expected Ge isotopic splitting patterns for this mode; therefore, the assignment of this feature to the Ge=C stretching mode in **1** can be regarded only as very tentative.

The rocking CH_3 modes are normally found as high-intensity bands at 750−875 cm^{-1} in the IR spectra of methylgermanes.[35] Our calculations predict these modes in **1** to be located within the 775−849 cm^{-1} region. In the IR spectrum of **1** we observed two intense bands at 804.4 and 847.3 cm^{-1}. They are in excellent agreement with the calculated frequencies at 791−804 and 840−849 cm^{-1}, which show high computed band intensities. On the basis of the calculations and assistance from the XMol animation of these vibrations, we assigned the observed band at 804.4 cm^{-1} to the b_2 CH_3 rocking mode coupled with the CH_2 rocking mode of the same symmetry. The assignment of the band at 847.3 cm^{-1} to the a_1 CH_3 rocking mode strongly mixed with the Ge=C stretching vibration has already been discussed above.

Our calculations predict the CH_2 wagging mode to show the highest intensity in the IR spectrum of **1** and to be located in the 578−666 cm^{-1} region (Table 2). In agreement with this prediction the most intense band observed in **1** at 596.0 cm^{-1} was assigned to this out-of-plane bending vibration. The frequency of this mode is red-shifted in **1** by about 300 cm^{-1} as compared to the CH_2 wagging mode in alkenes, e.g.,

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(37) *XMol, Version 1.3.1*: Minnesota Supercomputer Center, Inc., Minneapolis, MN, 1993.

(38) Allouche, A. *REDONG, Vibrational Analysis and Coordinate Transformation of a GAUSSIAN 88 calculation*; CNRS URA 773, Marseille, France; QCPE Program No. 628; Department of Chemistry, Indiana University, Indiana.

2-methyl-1-propene, where a very intense band of this fundamental is found at 888 cm^{-1} in an Ar matrix.[29] Such a large frequency shift in **1** is likely to be consistent with the reduced strength of the Ge═C π bond (32−33 kcal/mol in $H_2Ge{=}CH_2$)[12b] with respect to that of the C═C π bond (64−68 kcal/mol in $H_2C{=}CH_2$)[2], which sharply decreases the force constant and the vibrational energy of the out-of-plane bending motion of the ═CH_2 group in **1**.

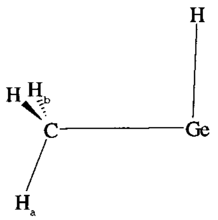
The two other bands, observed at 580.1 and 576.0 cm^{-1}, belong to the antisymmetric ν_8 and symmetric ν_7 Ge−C stretches, respectively, in good agreement with the calculations (Table 2) and literature data on the IR spectra of methylgermanes, where those modes are observed in the 550−620 cm^{-1} region.[35] The assignment to the Ge−C antisymmetric stretch is also well supported by the observation of the band isotopic structure in the 578−584 cm^{-1} spectral range (Figure 6) found to be in accord with the calculated isotopic splitting of the ν_8 fundamental (Table 5).

Ge═C Force Constant and Bond Order. The matrixes of the force constants in internal coordinates for **1** were calculated with the use of the REDONG program package[38] for all sets of scaled vibrational frequencies computed by a GAUSSIAN 94 program at four different levels of theory (Table 4). The average value of the force constant of the Ge═C double bond is found to be 4.74 mdyn/Å. This value is substantially higher than the force constant of the Ge−C single bond, e.g., in methylgermane, CH_3GeH_3 (2.72 mdyn/Å),[35] and points to the additional π bonding between germanium and carbon in **1**.

The order of this bond can be estimated with the help of Siebert's rule, which establishes the empirical relationship between bond order and force constants of single and multiple bonds.[39] The application of this rule indicated the Ge═C bond order in **1** to be 1.57. This means that the Ge═C bond order in **1** is somewhat lower than the Si═C bond order in the silene **4**, which was estimated earlier as 1.62[27] and a short time ago as 1.66[15c] with the use of the same empirical rule. It should be noted that such estimations are consistent with the relative strengths of the Ge═C and Si═C π bonds in the parent germene, $H_2Ge{=}CH_2$, and in silene, $H_2Si{=}CH_2$, calculated to be 32−33[12b] and 35−36[2] kcal/mol, respectively, and provide an additional indication that the former is somewhat weaker than the latter.

The calculated Ge═C bond order in **1** is found to be close to the order of the same bond in stable 1,1-dimesityl-2-fluorenylidene-1-germene **(19)**,[4c,d] estimated by MNDO to be 1.50.[2] From the closeness in bond orders and bond lengths for the Ge═C bond in transient germene **1** and stable germene **19** one should reasonably expect relatively close values for their Ge═C stretching vibration frequencies. However, a much higher vibrational frequency (988 cm^{-1})[4d] than in **1** has been attributed to this mode in the Raman spectrum of crystalline **19** on the basis of comparison with the MNDO simulated spectrum.[2] Such a large shift (by 140−170 cm^{-1}) of the Ge═C stretch in **19** with respect to **1** does not seem rational. Therefore, taking this into account and also the much lower reliability of the MNDO method in prediction of vibrational frequencies than in the ab initio and density functional theory calculation methods used here, we assume that the proposed assignment[4d] of the 988 cm^{-1} band to the Ge═C stretch in stable germene **19** is probably not correct.

Chart 2. Optimized Geometry of Methylgermylene (**6**)



	bond length, Å				angle, deg.		
	Ge-C	Ge-H	C-H_a	C-H_b	HGeC	H_aCGe	H_bCGe
HF/DZ+d	1.991	1.596	1.092	1.097	94.6	112.4	110.1
MP2/DZ+d	1.980	1.595	1.105	1.111	93.6	112.8	109.6
B3LYP/6-311G(d,p)	2.012	1.604	1.091	1.096	93.2	112.5	109.6

Methylgermylene (6). Molecular Geometry. The calculations, done at three different levels of theory for the singlet ground state of **6**, yield an optimized C_s structure (Chart 2) with a Ge−C bond length of 1.980−2.012 Å, a Ge−H bond length of 1.595−1.604 Å, and an H−Ge−C angle of 93.2−94.6°, close to those calculated by Grev[12a] at the CISD and SCF levels with the DZP basis set, 2.001−2.004 Å, 1.586−1.589 Å, and 93.7−94.8°, respectively. The H−Ge−C angle is found to be close to the calculated H−Si−C angle (95.0−95.9°) in singlet methylsilylene,[40,41] and slightly smaller than the C−Ge−C angle in dimethylgermylene (97.8°).[42]

The C−H_a bond is located in the same plane as the lone pair on the germanium, i.e., in a cis-position to it, and has a length of 1.091−1.105 Å. The other two C−H_b bonds are calculated to be slightly longer (1.096−1.111 Å), showing the same size effect as found earlier[40] for the C−H bonds in methylsilylene. The Ge−H distance of 1.595−1.604 Å in **6** is in close agreement with the value of 1.60 Å estimated for this bond in singlet GeH_2.[43]

IR Spectrum. The HF, MP2, and B3LYP calculated and observed frequencies of **6** are given in Table 3. This molecule has 12 vibrations, 11 of which are located in the 500−4000 cm^{-1} spectral region. The most intense band, observed at 1798.6 cm^{-1}, was assigned to the Ge−H stretching mode on the basis of calculations that predict this fundamental to have a very high intensity in the infrared and to lie at 1742−1810 cm^{-1}. The other observed bands for **6** are found to be much weaker (Figures 2 and 3). This is not at all surprising, since in the IR spectra of matrix-isolated methylsilylene only the strong band of the Si−H stretch and none of the other modes due to their much lower intensities has been detected.[36]

An assignment of the weak bands in **6** was done on the basis of their reasonable agreement with the calculated frequencies (Table 3). A band at 2891.6 cm^{-1} has been assigned to the antisymmetric C−H stretching mode. A low-intensity absorption at 1201.2 cm^{-1} was attributed to the CH_3 rocking deformation mode which in dimethylgermylene has been observed in the 1195−1234 cm^{-1} region.[30] A weak broad band at 868.8 cm^{-1} belongs to the CH_3 rocking mode mixed with the in-phase GeH rocking mode, as demonstrated by the XMol vibration animation. The last observed weak band is located within 534−

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[39] (a) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*; Springer-Verlag: Berlin, 1966. (b) Siebert, H. *Z. Anorg. Allg. Chem.* **1953**, *273*, 170.

[40] Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 7644.

[41] Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125 and references therein.

[42] Barthelat, J.-C.; Saint Roch, B.; Trinquier, G.; Satge, J. *J. Am. Chem. Soc.* **1980**, *102*, 4080.

[43] (a) Smith, R. G.; Guillory, W. A. *J. Chem. Phys.* **1972**, *56*, 1423. (b) Smith, R. G.; Guillory, W. A. *J. Appl. Spectrosc.* **1973**, *27*, 137.

538 cm^{-1} and shows a clear quadruplet due to the natural isotopic content of germanium (Figure 6), in good agreement with the calculated isotopic splitting for the Ge−C stretching vibration (Table 5). This observation makes this band assignment unequivocal and agreeable with the earlier observation of the Ge−C stretches in dimethylgermylene at 527 and 541 cm^{-1}.[30]

Methylethylgermylene (8). We could tentatively assign to **8** only three weak absorptions, appearing in the 500−1000 cm^{-1} region of the IR spectra of the pyrolysis products of **2** at temperatures higher than 800 °C. Their agreement with the calculated most intense fundamentals of **8** in this region has served as a basis for the proposed vibrational assignment. The observed bands at 528.0 and 554.8 cm^{-1} were thus attributed to the Ge−C stretching vibrations of the Ge−CH_2 and Ge−CH_3 groups, respectively. A band at 783.6 cm^{-1} was assigned to the CH_3 rocking mode. The detection of additional bands of **8**, predicted by the calculations to have significant intensities in the 2800−2950 cm^{-1} spectral region, was obscured by their overlapping with more intense peaks from the other pyrolysis products.

1-Methyl-1-germacyclopropane (9). It is known that the simplest of the silacyclopropanes isolated to date, hexamethylsilacyclopropane, thermally decomposes with the extrusion of dimethylsilylene at temperatures as low as 65−75 °C.[44] According to our calculatons (Table 4), the germacyclopropane **9** was expected to be less thermostable than its silicon analogue **11**, and methylgermylene extrusion was expected to proceed even easier. This gives a reasonable explanation of why the transient molecule **9** has not survived and therefore has not been detected under the higher temperature conditions used in our vacuum pyrolysis experiments.

Conclusion

Our EIMS and matrix isolation−vacuum pyrolysis studies of the germathietane **2**, as well as matrix isolation FTIR investigation of the pyrolysis products of germacyclobutane **3**, suggest that the transient germene **1** has been generated in the gas phase from two independent precursors and subsequently trapped as a monomer in a cryogenic inert matrix at 12 K. Another transient species, methylgermylene **6**, is also likely to be produced during vacuum pyrolyses of both precursors, **2** and **3**. It is proposed that the germylene **6** is a product of secondary isomerization and dissociation reactions of the germene **1**, which is hence shown to be less thermostable than it silicon analogue, the silene **4**. The structural assignments of **1** and **6** are supported by the observation of the isotopic splitting of the germanium−carbon stretching modes in the IR spectra due to the natural abundance of germanium. The structural revelation of **6** also rests on mechanistic arguments, an apparent similarity of the fragmentation of **1** to yield **6** under electron impact in the mass spectra through unimolecular thermal decomposition, and on theoretical calculations of the expected products.

The calculations, done at several levels of theory, permitted a reasonable assignment of observed IR peaks in the spectra of germene **1** and germylene **6** to vibrational modes. The spectral interpretation in **1** was assisted by the calculations of potential energy distributions for each vibrational mode in internal coordinates. The assignment of a high-intensity band at 847.3 cm^{-1}, showing a clear germanium isotopic splitting, to a Ge═C stretching vibration strongly coupled with the CH_3 rocking mode in **1** seems certain, while the interpretation of the absorption at 818.8 cm^{-1} as a pure Ge═C stretch should be regarded as tentative in view of very low infrared intensity and as yet unsure experimental detection of this feature.

The calculated average value of the force constant of the Ge═C double bond in **1** (4.74 mdyn/Å) is substantially higher than the force constant of the Ge−C single bond in methylgermane (2.72 mdyn/Å), thus confirming the existence of π-bonding between germanium and carbon in **1**. The estimated Ge═C bond order in **1** (1.57) is slightly lower than the Si═C bond order in the silene **4** (1.62−1.66), which is found to be consistent with the calculated π-bond strengths in these group 14 metallaalkenes.

Acknowledgment. The work at Rice has been supported by Marchem and The Robert A.Welch Foundation of Texas, and by a grant for supercomputer time from the Houston Advanced Research Center. V.N.K. thanks Professor F. Bickelhaupt for the generous gift of the sample of 1,1,3,3-tetramethyl-1-germacyclobutane, and Drs. A. Gömory and N. D. Kagramanov for assistance during a series of vacuum pyrolysis−EIMS experiments in Budapest. The authors also thank the reviewers for valuable comments on the manuscript. This project was initiated by VNK and co-workers at the Zelinsky Institute of Organic Chemistry.

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(44) (a) Delker, G. L.; Wang, Y.; Stucky, G. D.; Lambert, R. L.; Haas, C. K.; Seyferth, D. J. *Am. Chem. Soc.* **1976**, *98*, 1779. (b) Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *201*, 179. (c) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.