of 1 (410 mg, 1 mmol) in 30 mL of methanol was then transferred via cannula to the lithium phenylacetylide. The orange solution progressively turned dark yellow. After being stirred for 1 h at room temperature, 20 mL of ether was added to the reaction mixture. The solution was cooled to −20 °C for 4 h. A total of 309 mg (65% yield) of 11 was isolated as yellow microcrystals.

Method B. Into a Schlenk tube containing a methanol solution (40 mL) of 410 mg of 1 (1 mmol) were successively added at room temperature 0.5 mL of phenylacetylene (5 mmol) and 2 mL of triethylamine (13.8 mmol). After the mixture was stirred for 2 h at room temperature, the solvent was evaporated to dryness. The residue was extracted with 10 mL of dichloromethane. Addition of an excess of ether led to precipitation of a yellow powder of 11 (152 mg, 32% yield). Anal. Calcd for $C_{23}H_{32}ClPRu$: C, 58.05; H, 6.77; P, 6.52. Found: C, 57.95; H, 6.68; P, 6.40. IR (cm^{-1}, Nujol): 2090 ($\nu_{C\equiv C}$). ^1H NMR (CD_2Cl_2, δ): 7.10 (m, 5 H, C_6H_5), 2.09 (s, 18 H, C_6Me_6), 1.50 (d, 9 H, $^2J_{PH}$ = 10.4 Hz, PMe_3). ^{31}P NMR (CD_2Cl_2, δ): 6.90 (s, PMe_3). ^{13}C NMR (CD_2Cl_2, δ): 129.40 (m, C_6H_5), 119.49 (d, $^2J_{PC}$ = 41.1 Hz, Ru–C), 105.44 (s, Ph–*C*) 100.00 (s, C_6Me_6), 16.64 (d, $^1J_{PC}$ = 34.3 Hz, PMe_3), 16.35 (s, $C_6\mathit{Me}_6$).

Generation and NMR Characterization of $[Ru(C_6Me_6)(PMe_3)Cl({=}C{=}CHPh)]CF_3CO_2^-$ (12). A solution of 330 mg (0.7 mmol) of 7 in 4 mL of CD_2Cl_2 in a 10-mm NMR tube was degassed with argon. The addition of a slight excess of CF_3CO_2H led to the immediate formation of a red solution. ^1H and ^{13}C NMR spectra were recorded at −60 °C. ^1H NMR (CD_2Cl_2, δ): 7.30 (m, 5 H, C_6H_5), 5.66 (s, 1 H, $=C\mathit{H}Ph$), 2.20 (s, 18 H, C_6Me_6), 1.64 (d, 9 H, $^2J_{PH}$ = 11.6 Hz, PMe_3). ^{13}C NMR (CD_2Cl_2, δ): 360.34 (d, $^2J_{PC}$ = 20.6 Hz, Ru=C), 130 (m, C_6H_5), 112.30 (d, $^1J_{CH}$ = 198 Hz, $=\mathit{C}HPh$), 100.20 (s, C_6Me_6), 17.48 (q, $^1J_{CH}$ = 130 Hz), $C_6\mathit{Me}_6$), 16.56 (dq, $^1J_{CH}$ = 129 Hz, PMe_3).

Preparation of 4a from 12. To a suspension of 380 mg (1 mmol) of 11 in 50 mL of ether was added by syringe a slight exces of $HBF_4{\cdot}Et_2O$ (0.2 mL). The yellow reaction mixture immediately turned red. Complex 12, which was isolated as a red oil after removal of the solvent, was dissolved in 10 mL of tetrahydrofuran. Then, 1 mL of methanol was added. The red reaction mixture rapidly turned orange. After the mixture was stirred for 1 h, the solvent was removed in vacuo. Adding dichloromethane and then ether and cooling to −20 °C gave 4a ($X^- = BF_4^-$) as orange-red crystals.

New Photochemical Routes to Germylenes and Germenes and Kinetic Evidence Concerning the Germylene–Diene Addition Mechanism[†]

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Upon 254-nm irradiation of phenylbis(trimethylsilyl)germanes, there is competition between two germylene-forming reactions, the unexpected elimination of phenyltrimethylsilane and the elimination of hexamethyldisilane. Irradiation of a phenylmonosilylgermane $PhGeMe_2SiMe_3$ leads to predominant elimination of $PhSiMe_3$, forming dimethylgermylene $Me_2Ge{:}$, accompanied by migration of Me_3Si to the ortho position of the phenyl ring, forming a germene. Laser flash photolysis of $PhGeMe_2SiMe_3$ is a convenient source of $Me_2Ge{:}$, and rate constants are reported for $Me_2Ge{:}$ addition to a series of dienes and other substrates. The kinetic data are in accord with 1,2-addition as the dominant pathway for addition of $Me_2Ge{:}$ to 1,3-dienes.

The mechanistic study of germylenes, carbene analogues containing a divalent germanium atom, is currently an active field,[1] but it has been hampered by a shortage of convenient photochemical precursors. Polygermanes such as $Me_3Ge(GeMe_2)_2GeMe_3$[2] and $(PhGeMe_2)_2GeMe_2$[3] are laborious to synthesize and give clear evidence of radical side reactions. Cyclopolygermanes c-$(GeMe_2)_6$[4] and c-$(GeAr_2)_3$[5] also present synthetic hurdles, as do precursors containing a single germanium atom $(PhSe)_2GeMe_2$[6] and 7-germanorbornadiene derivatives.[7] Diazides such as $Me_2Ge(N_3)_2$ are easy to make but inefficient germylene sources.[8]

Silylgermanes, on the other hand, are readily synthesized, and disilylgermanes $(Me_3Si)_2GeRR'$ have been reported to extrude germylenes under ultraviolet irradiation.[9,10] This process parallels the well-known extrusion of silylenes from chains of three or more silicon atoms.[11]

$$(Me_3Si)_2GeRR' \xrightarrow{h\nu} Me_3SiSiMe_3 + {:}GeRR'$$

In scrutinizing the products from a germylene formed in such a process, $Ph_2Ge{:}$, some of whose reactions we have studied by kinetic spectroscopy,[12] evidence was found for

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[*] To whom correspondence should be addressed.

[†] This work was carried out with financial support from the United States National Science Foundation under Grant No. CHE-88-02677.

(1) No modern review of germylene chemistry has been published in recent years, although some aspects of germylene chemistry were reviewed: Satge, J. *Pure Appl. Chem.* **1984**, *56*, 137. In addition to the references given below, see: Neumann, W. P. *Cycloaddition and Insertion Reactions of Heavy Carbene Analogs*, 31st International Congress of Pure and Applied Chemistry, Sofia, Bulgaria, July–13–18, 1987; Section 6, Organic Chemistry, pp 148–162.

(2) Ishikawa, M.; Kumada, M. *Rev. Silicon, Germanium, Tin Lead Compd.* **1979**, *4*, 7.

(3) Wakasa, M.; Yoneda, I.; Mochida, K. *J. Organomet. Chem.* **1989**, *266*, C1.

(4) Carberry, E.; Dombek, B. D.; Cohen, S. C. *J. Organomet. Chem.* **1972**, *36*, 61.

(5) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

(6) Tomoda, S.; Shimoda, M.; Takeuchi, Y.; Kajii, Y.; Obi, K.; Tanaka, I.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1988**, 910.

(7) Neumann, W. P.; Schriewer, M. *Tetrahedron Lett.* **1980**, 3273. Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.

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

(9) Collins, S.; Murakami, S.; Snow, J. T.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 1281.

(10) Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Chem. Lett.* **1987**, *317*.

(11) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

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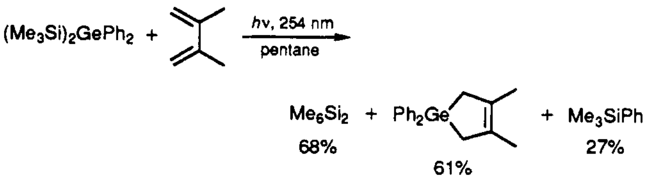
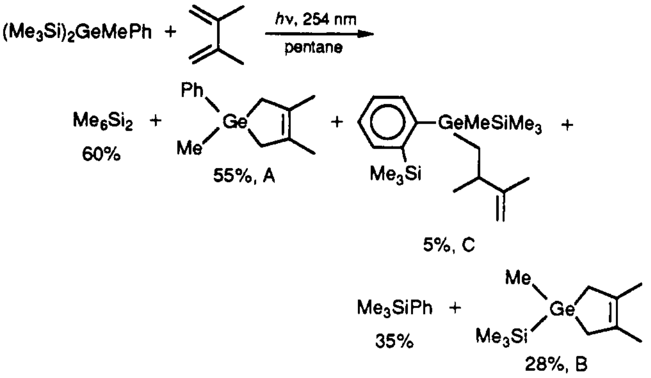
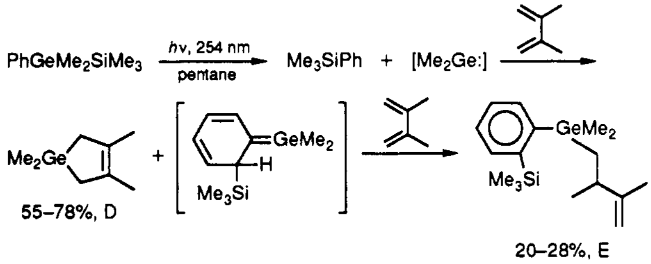
the formation of two different germylenes, although the only adduct obtained was from Ph_2Ge:. Unexpectedly, elimination of phenyltrimethylsilane competed with the well-known elimination of hexamethyldisilane. Two germylenes were also formed from a monophenyl derivative, and both adducts were isolated:[13]





The photolysis of $PhGeMe_2SiMe_3$ was therefore investigated, since the presence of only one silyl group precluded the elimination of a disilane, and the elimination of $PhSiMe_3$ could be anticipated, on the basis of the results reported above. Thus we predicted that a chain of only two higher group XIV atoms could be made, for the first time, to efficiently extrude one of them in the form of a divalent species.

Indeed, the major process is the extrusion of dimethylgermylene, but the occurrence of a formal migration of the silyl group to the aromatic ring, generating a germene, is also evident from the trapping products:[14]



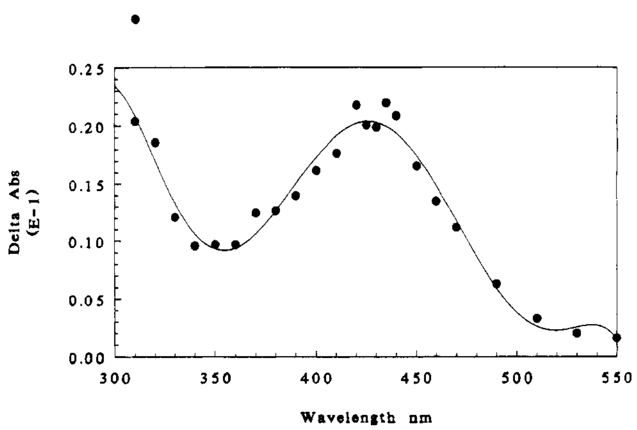


Figure 1. Transient absorption spectrum of a deoxygenated 1.05×10^{-3} M solution of $PhGeMe_2SiMe_3$ in cyclohexane, 0–5 μs after the laser flash.

Table I. Second-Order Rate Constants for the Disappearance of the 425-nm Transient in the 266-nm Photolysis of $PhGeMe_2SiMe_3$ in Cyclohexane

substrate	k_2, $M^{-1}\ s^{-1}$	concn range, M
butadiene	$(1.24 \pm 0.07) \times 10^7$	0.01–0.07
isoprene	$(1.63 \pm 0.13) \times 10^7$	0.01–0.07
2,3-dimethylbutadiene	$(1.71 \pm 0.38) \times 10^{7}$[a,b]	0.0088–0.062
cis-piperylene	$(9.19 \pm 0.41) \times 10^6$	0.0202–0.202
trans-piperylene	$(2.88 \pm 0.24) \times 10^6$	0.0138–0.104
cis,cis-2,4-hexadiene	$(1.22 \pm 0.09) \times 10^6$	0.035–0.210
cis,trans-2,4-hexadiene	$(3.46 \pm 0.48) \times 10^5$	0.07–0.35
trans,trans-2,4-hexadiene	$<5 \times 10^5$	0.07
1-butene	$<10^5$	>0.45
1-hexene	$<10^4$	6.40
1-hexyne	$(3.00 \pm 0.23) \times 10^4$	0.87–5.22
1-propyne	$<10^5$	>0.45
dimethyl disulfide	$<10^7$	0.00555
tetrahydrofuran	$<10^4$	neat
ethanol	$(1.86 \pm 0.12) \times 10^4$	1.71–12
carbon tetrachloride	$(3.15 \pm 0.27) \times 10^{8}$[c]	0.0005–0.005
triethylsilane	$<10^4$	1.51
oxygen	2×10^{9}[d]	0.001

[a] $2.4 \times 10^7\ M^{-1}\ s^{-1}$ (ref 3). [b] $2.2 \times 10^7\ M^{-1}\ s^{-1}$ (Mochida, K.; Kano, N.; Kato, R.; Kotani, M.; Yamaguchi, S.; Wakasa, M.; Hayashi, H. *Organometallics*, in press). [c] $4.9 \times 10^8\ M^{-1}\ s^{-1}$ (*Ibid*). [d] $9.7 \times 10^8\ M^{-1}\ s^{-1}$ (*Ibid*).

These results are rather different from those recently reported by Mochida and co-workers for the irradiation of phenylpentamethyldigermane $PhGeMe_2GeMe_3$ under similar conditions:[15]

$$PhGeMe_2GeMe_3 \xrightarrow[\text{hexane}]{h\nu,\ 254\ \text{nm}} \underset{7\text{-}15\%}{PhGeMe_3} + \underset{8\text{-}12\%}{Me_3GeH} +$$
$$\underset{6\text{-}8\%}{PhGeMe_2H} + \underset{3\text{-}8\%}{Ph_2GeMe_2} + \underset{12\text{-}15\%}{Me_6Ge_2} + \underset{1\%}{(PhGeMe_2)_2} +$$
$$\underset{2\text{-}8\%}{(PhGeMe_2)O} + \underset{3\text{-}4\%}{Me_8Ge_3} + \underset{\text{trace}}{(PhGeMe_2)_2GeMe_2}$$

The large number of products reported by Mochida, some clearly resulting from radical combination and disproportionation, suggest that Ge–Ge bond homolysis is the dominant primary photoprocess. The low yield of $PhGeMe_3$ suggests that photoextrusion of dimethylgermylene is inefficient. When the photolysis of $PhGeMe_2GeMe_3$ was carried out in the presence of 2,3-dimethylbutadiene, only a 3% yield of the Me_2Ge: adduct was reported, along with a 2.5% yield of the $PhGeMe_3$ coproduct of germylene extrusion.[15]

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[12] Konieczny, S.; Jacobs, S. J.; Braddock Wilking, J. K.; Gaspar, P. P. *J. Organomet. Chem.* **1988**, *341*, C17. It should be noted that the rate constants for reactions of diphenylgermylene Ph_2Ge reported in ref 3 are considerably larger than those reported by Konieczny et al.: 7.2×10^5 vs $(2.75 \pm 0.12) \times 10^4\ M^{-1}\ s^{-1}$ for 2,3-dimethylbutadiene and $6.6 \times 10^5\ M^{-1}\ s^{-1}$ for Et_3SiH vs $1.01 \times 10^4\ M^{-1}\ s^{-1}$ for $EtMe_2SiH$. In light of the much smaller rates of reaction for diphenylsilylene Ph_2Si reported by the Gaspar group in the Konieczny paper compared with the rates measured for dimesitylsilylene Mes_2Si by Conlin (Conlin, R. T.; Netto-Ferreirra, J. C.; Zhang, S.; Scaiano, J. C. *Organometallics* **1990**, *9*, 1332), the kinetic results of Konieczny, et al. should be viewed with skepticism until the discrepancies are understood. We have recently repeated the Konieczny experiments, however, and have obtained similar results.

[13] The trace of ene-reaction product was found only by GS-MS analysis and was not fully characterized.

[14] The variation of the germylene-to-germene ratio with the reaction conditions may well be due to different excited-state precursors, with different decay characteristics, being responsible for the two reactive intermediates. This would be in accord with the dual fluorescence observed for $PhGeMe_2SiMe_3$: Sakurai, H.; Shugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837. This point is under serious investigation. See: Bobbitt, K. L. Photochemical Generation of Germylenes and Silylenes: Mechanism of Germylene and Silylene Addition to 1,3-Dienes. Doctoral dissertation, Washington University, St. Louis, MO, Dec 1990.

[15] Mochida, K.; Kikkawa, H.; Nakadaira, Y. *Chem. Lett.* **1988**, 1089.

No evidence was found by Mochida for the formation of a germene by migration of a Me_3Ge group to the phenyl ring upon the ultraviolet irradiation of a series of phenylated digermanes, although this possibility was considered.[16]

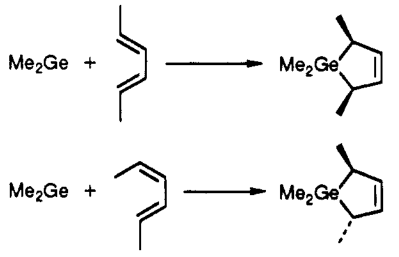
In order to determine whether our new dimethylgermylene precursor would be useful for time-resolved kinetic studies, and if so, to study the addition of Me_2Ge to 1,3-dienes, we investigated the laser flash photolysis of $PhGeMe_2SiMe_3$ in cyclohexane solutions containing various reaction substrates at room temperature.

A transient absorption spectrum, recorded 0-5 μs after the flash, is shown in Figure 1. The second-order rate constants for the disappearance of the λ_{max} = 425 nm transient in the presence of various substrates are given in Table I.

Our confidence that the observed transient is indeed free dimethylgermylene is bolstered by the agreement of its absorption maximum with that reported by various workers, employing various precursors, in both matrix isolation experiments in frozen glasses and via kinetic spectroscopy in fluids.[17]

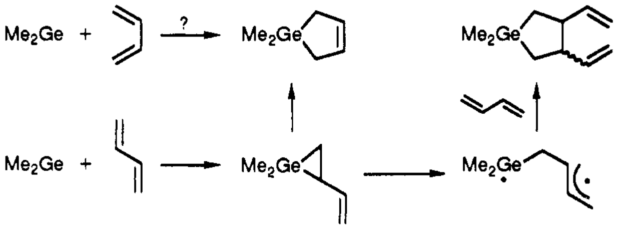
Comparison of the rate constants reported in Table I with the few previous literature values also supports the identification of the 425-nm transient as Me_2Ge:. An apparent disagreement is the rate of reaction with triethylsilane, found by Mochida to occur with $k_2 = 4.2 \times 10^6$ M^{-1} s^{-1}, 10^2 times the upper limit found in our experiments.[20] There is, however, good agreement between the rates of reaction reported here, of the 425-nm transient with oxygen, 2,3-dimethylbutadiene, and carbon tetrachloride, and previous reports of reaction rates for Me_2Ge:.

A comparison of the rate constants for the eight 1,3-dienes reported in Table I permits some interesting conclusions to be drawn concerning the mechanism of addition of dimethylgermylene to these molecules. It has been forcefully argued by Neumann that the stereospecific formation of 1-germacyclopent-3-enes found in his laboratory,[7,21] and in ours,[22] demands the operation of a concerted 1,4-addition.



The trends revealed by the rate constants in Table I for the effects of methyl substituents on the reactions of Me_2Ge: with 1,3-dienes tell a different story. Nonterminal methyl substituents that greatly increase the equilibrium mole fraction of *S*-cis conformer from 0.01 for unsubstituted butadiene to 0.02 for isoprene and 0.2 for 2,3-dimethylbutadiene[23] lead to only a modest increase of less than 40 ± 38% in k_2. This could be a small electronic effect. Terminal methyl substituents cause a decrease in k_2, but *cis*-piperylene, presumed to have the smaller mole fraction of the *S*-cis conformer[23] necessary for concerted 1,4-addition by Me_2Ge:, reacts more rapidly than does *trans*-piperylene. That this steric effect is due to the substitution pattern of the individual olefin units, rather than the *S*-cis,*S*-trans equilibrium, is dramatically illustrated by the rate constants for addition to the three isomeric 2,4-hexadienes. The cis,cis isomer, presumed to have the smallest *S*-cis content of the three, undergoes addition most rapidly, while the trans,trans isomer, presumed to have the largest *S*-cis content reacts most slowly.

The kinetic results speak for 1,2-addition as the dominant primary reaction of Me_2Ge with 1,3-dienes. The resulting vinylgermirane intermediate is similar to that established for the silylene–diene addition.[25] Reaction of a vinylgermirane with a second molecule of diene would accout for the formation of 3,4-dialkenyl-1-germacyclopentanes, the major products from addition of Me_2Ge: to sterically unencumbered dienes at moderate temperatures.[26] Rapid sigmatropic rearrangement of the vinyl germirane to germacyclopent-3-enes could account for the stereospecificity with which the latter products can be formed. These kinetic results do not, however, rule out a reaction sequence in which concerted 1,4-addition, while slower than 1,2-addition, contributes to the formation of 1-germacyclopent-3-enes.



The much slower rates of reaction of Me_2Ge: with alkynes and monoolefins, compared with 1,3-dienes, speak for a nucleophilic character of Me_2Ge: that has already been revealed by a Hammett $\sigma\rho$ correlation in recent studies by Mochida and Hasegawa of the insertion of Me_2Ge: into Si–H bonds.[27] Koecher and Neumann have deduced that Me_2Ge: reacts with 1,3-dienes as a nucleophile from the effects of substituents at the 1- and 4-positions of the diene on the yields of germacyclopent-3-ene products.[28]

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(16) Mochida, K.; Wakasa, M.; Nakadaira, Y.; Sakaguchi, Y.; Hayashi, H. *Organometallics* 1988, *7*, 1869.

(17) Precursors (absorption maxima, nm): dibenzo-1,1,2,2,3,3-hexamethyl-1,2,3-trigermacyclohepta-4,6-diene (430, matrix, ref 18), benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene (420, matrix, ref 10), $(PhSe)_2GeMe_2$ (420, matrix and solution, ref 6), $(PhGeMe_2)_2GeMe_2$, (422 matrix, 420, solution, ref 3), $Me_2Ge(N_3)_2$ (420–430, matrix, ref 8), c-$(Me_2Ge)_6$ (420 matrix, 450, solution, ref 19), $PhGeMe_2SiMe_3$ (418, matrix, 425, solution, this work).

(18) Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1379.

(19) Mochida, K.; Kano, N.; Kato, R.; Koteni, M.; Yamaguchi, S.; Wakasa, M.; Hayashi, H. *Organometallics*, in press.

(20) We have not detected $HGeMe_2SiEt_3$ as a reaction product when $PhGeMe_2SiMe_3$ is irradiated in pentane solutions containing Et_3SiH. Apparently, insertion of the germylene into the H–Si bond does not compete with polymerization of Me_2Ge:. This implies a sluggish insertion. Triethylsilane was carefully purified, since the commercial material contained several impurities.

(21) Schriewer, M.; Neumann, W. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1019.

(22) Ma, E. C.-l.; Kobayashi, K.; Barzilai, M. W.; Gaspar, P. P. *J. Organomet. Chem.* **1982**, *224*, C13.

(23) These estimates of mole fractions are based on the results of molecular mechanics calculations: Tai, J. C.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *98*, 7928.

(24) There is a discrepancy between the text and Table I of ref 23. The results reported in the table lead to an estimated mole fraction of S-cis conformer for *cis*-piperylene slightly *larger* (0.013 vs 0.010) than that for *trans*-piperylene.

(25) Lei, D.; Hwang, R. J., Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1. Lei, D.; Gaspar, P. P., *J. Chem. Soc., Chem. Commun.* **1985**, 1149; *Res. Chem. Intermed.* **1989**, *12*, 103.

(26) Neumann, W. P.; Michels, E.; Kocher, J. *Tetrahedron Lett.* **1987**, *28*, 3783. For the case of butadiene it was verified that the same products (1,1-dimethyl-1-germacyclopent-3-ene and *cis*- and *trans*-1,1-dimethyl-3,4-divinyl-1-germacyclopent-3-ene) were obtained under our kinetic conditions, as had been reported by Neumann and co-workers.

(27) Mochida, K.; Hasegawa, A. *Chem. Lett.* **1989**, 1087.

(28) Koecher, J.; Neumann, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 3861.

In summary, the elimination of phenyltrimethylsilane from phenyl(trimethylsilyl)germanes is a new photochemical route to germylenes that has allowed the measurement of several new rate constants for dimethylgermylene pertinent to discussions of its reaction mechanisms. The rate constants for reactions of Me_2Ge: with a series of substituted 1,3-dienes are in accord with the view that 1,2-addition is more rapid than 1,4-addition. In the ultraviolet irradiation of $PhGeMe_2SiMe_3$, another new reaction, generation of a germene by migration of the Me_3Si group to the aromatic ring, competes with Me_2Ge: formation. The mechanisms of these new reactions of aryl(silyl)germanes are under investigation.

Experimental Section

General Data. All preparative reactions were carried out in oven-dried glassware, usually under an atmosphere of dry nitrogen or argon. Solvents were dried by using standard techniques. All air-sensitive liquids and the dried solvents were transferred by standard syringe or double-needle techniques.

NMR spectra were recorded on a Varian XL-300 (^1H 300 MHz, ^{13}C 75.4 MHz) or a Varian Gemeni-300 (^1H 300 MHz, ^{13}C 75.4 MHz) instrument. Chemical shifts are reported as δ values measured in ppm downfield from Me_4Si. Combined gas chromatography–mass spectroscopy was performed on a Finnegan 3200 mass spectrometer operating at an ionizing energy of 35 or 70 eV and calibrated against perfluoroalkane. High-resolution mass spectra were recorded on a VG ZAB-SE instrument. The formulas and molecular weights of ions observed in the mass spectra of germanium-containing compounds are based on ^{74}Ge. Ultraviolet spectra were recorded on a Varian Cary 219 spectrometer. Analytical gas chromatography was carried out on a Varian Aerograph 2740-10 FID instrument with a Perkin-Elmer 1000 integrator employing a 10-ft 3% OV-17, on 80/100 mesh Supelcoport, $^1/_8$ in. i.d. packed glass column or a Hewlett-Packard 5890A FID instrument with a Model 3394A integrator employing a 30-m SE-30 capillary column. Preparative gas chromatography was done on an instrument constructed in this laboratory, with a thermal conductivity detector employing Gow-Mac code 13-002 dual tungsten filaments and $^1/_4$ in. o.d. aluminum columns.

Reported yields are based on unrecovered germylene precursor and were determined by gas chromatography with the aid of an inert internal standard. Response factors were determined in most cases.

Materials. Tetraphenylgermane was synthesized by the method of Glockling and Hooten, 77% yield, mp 227–230 °C (lit. 227–230 °C).[28]

Dibromodiphenylgermane was synthesized by the method of King and Eisch, 70% yield, bp 145 °C (0.5 Torr).[29]

Diphenylbis(trimethylsilyl)germane. Into an argon-flushed 100-mL three-necked flask equipped with a reflex condenser, pressure-equalized addition funnel, and mechanical stirrer was placed 2.4 g (22 mmol) of $ClSiMe_3$, 25 mL of dry THF, and 0.4 g (57 mmol) of Li. The solution was cooled to −78 °C, and a solution of 2.8 g (7.3 mmol) of dibromodiphenylgermane in 10 mL of THF was added dropwise. The reaction mixture quickly turned yellow and was stirred an additional $1^1/_2$ h, and the cooling bath was then removed. As the temperature rose to ambient, the mixture turned black. After stirring for an additional 24 h, the Li was nearly consumed. Workup consisted of filtration, dilution with 100 mL of ether, extraction of the organic layer with 10% aqueous HCl and twice with deionized H_2O, drying of the organic layer over $MgSO_4$, and evaporation of solvent. The resulting yellow oil was purified by flash column chromatography on silica gel (hexane, R_f 0.34), total yield 2.2 g (60%). Spectroscopic data are given in Table II. The ^1H NMR and MS data are in accord with reported values.[30]

Dichlorodimethylgermane was synthesized by the method of Lee, Bobbitt, Lei, and Gaspar.[32]

Dimethylbis(trimethylsilyl)germane. Into a 500-mL three-necked flask equipped with a pressure-equalized addition funnel, reflux condenser, and mechanical stirrer was placed, under argon, 4 g (571 mmol) of Li and 37 g (341 mmol) of $ClSiMe_3$ in 105 mL of THF. During addition of 20 g (115 mmol) of Cl_2GeMe_2 in 50 mL of THF, the stirred reaction mixture turned black. The reaction mixture was stirred an additional 4 days and then filtered. After evaporation of the volatiles, distillation yielded the product, 8.0 g (28%), as a fraction with bp 190–195 °C. Spectroscopic data are given in Table II. Anal. Calcd for $C_8H_{24}Si_2Ge$: C, 38.56; H, 9.72. Found: C, 38.09; H, 9.35.

Chloro(methyl)bis(trimethylsilyl)germane. To a 250-mL three-necked flask charged with 6.5 g (26 mmol) of dimethylbis(trimethylsilyl)germane, 64 mL of nitromethane, and a magnetic stirring bar was added via syringe 8.7 g (33 mmol) of $SnCl_4$. The stirred, colorless, two-phase mixture slowly changed to a homogenous milky suspension. After 10 h of stirring, 100 mL of deionized water was added and the organic layer collected in a separatory funnel. Pentane (50 mL) was added and the organic layer extracted twice with deionized water. The organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated yielding 4.0 g (60%) of chloro(methyl)bis(trimethylsilyl)germane, which was used without further purification. Spectroscopic data are given in Table II.

Methyl(phenyl)bis(trimethylsilyl)germane. A phenylmagnesium bromide solution was prepared by addition of 7.0 g (45 mmol) of bromobenzene in 5 mL of THF to 1.2 g (50 mmol) of Mg in 13 mL of THF in a 100-mL three-necked flask equipped with a reflux condenser, pressure-equalized addition funnel, and mechanical stirrer under an argon atmosphere. To the rapidly stirred solution of Grignard reagent was added, dropwise, 4.0 g (14 mmol) of chloro(methyl)bis(trimethylsilyl)germane in 25 mL of THF. Ca. 10 min, after addition was complete, precipitation of magnesium salts turned the reaction mixture milky white. After an additional 12 h of stirring, a saturated aqueous NH_4Cl solution was slowly added (considerable heat was evolved), the reaction mixture was transferred to a separatory funnel, and the organic layer was washed three times with deionized water. The organic layer was dried over $MgSO_4$ and filtered, and volatiles were removed, yielding 3.7 g (80%) crude product. Further purification was by preparative gas chromatography (5-ft 3% DC-200 column on 80/100 mesh Supelcoport, 130 °C, 150 mL of He/min, retention time 8 min). Spectroscopic data re given in Table II. Exact mass determination: calcd for $C_{13}H_{26}GeSi_2$ 312.0767; measured 312.0776. Anal. Calcd for $C_{13}H_{25}GeSi_2$: C, 50.17; H, 8.43. Found: C, 49.63; H, 8.31.

Dimethyldiphenylgermane. A phenylmagnesium bromide solution under argon was prepared by dropwise addition of 54 g (340 mmol) of bromobenzene in 76 mL of THF to 10 g (410 mmol) of Mg and 200 mL of THF in a 1-L three-necked flask equipped with a pressure-equalized addition funnel, reflux condenser, and mechanical stirrer. An ice bath was used to moderate the extremely exothermic reaction, which was stirred an additional 30 min after the 2-h addition period. To the Grignard reagent was added dropwise 20 g (115 mmol) of Cl_2GeMe_2 in 75 mL of THF. The reddish brown reaction mixture was stirred and refluxed for 12 h with the aid of a heating mantle. Then excess Grignard reagent was destroyed by the slow addition of saturated aqueous NH_4Cl, the reaction mixture was filtered, the filtrate was transferred to a separatory funnel and the aqueous phase was removed. After the organic layer was diluted with 100 mL of ether, then washed three times with deionized water, and dried over $MgSO_4$, the volatiles were removed in vacuo. The residue was distilled under vacuum, yielding the product, 22.7 g (77%), as a fraction with bp 95–100 °C (0.01 Torr). Spectral data are given in Table II. Anal. Calcd for $C_{14}H_{16}Ge$: C, 65.44; H, 6.28. Found: C, 66.83; H, 6.46.

Dimethyl(phenyl)(trimethylsilyl)germane. 1. For quantities <2 g a modification of the method of Gilman and Gerow was employed.[33] Into a 1-L three-necked flask equipped with a reflux condenser, pressure-equalized dropping funnel, and mechanical stirrer was placed 8.2 g (1.17 mol) of Li, 20 g (77.5

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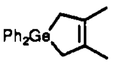
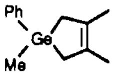
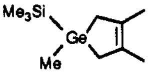
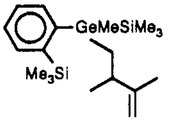
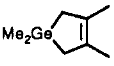
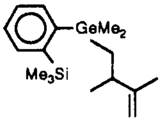
Table II. Spectroscopic Data for Synthetic Intermediates, Germylene Precursors and Their Reaction Products

$(Me_3Si)_2GePh_2$	^1H NMR ($CDCl_3$, 300 MHz): δ 0.20 (s, 18 H, $SiMe_3$), 7.20–7.60 (m, 10 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 0.20 ($SiMe_3$), 127.8, 128.2, 136.0, 139.4 (ipso C) MS (35 eV): *m/e* 374 (M^+, 0.44), 359 (0.44), 224 (27), 151 (27), 147 (18), 135 (base, 100), 73 (98) UV (pentane): λ_{max} 238 nm (ϵ = 15 200)
$(Me_3Si)_2GeMe_2$	^1H NMR ($CDCl_3$, 300 MHz): δ 0.101 (s, 18 H, $SiMe_3$), 0.108 (s, 6 H, $GeMe_2$) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -8.5 ($GeMe_2$), -1.0 ($SiMe_3$) MS (70 eV): *m/e* 250 (M^+, 5), 235 (11), 177 (8), 162 (24), 73 (base, 100) UV (pentane): λ_{max} 221 nm (ϵ = 1953)
$(Me_3Si)_2GeClMe$	^1H NMR ($CDCl_3$, 300 MHz): δ 0.26 (s, 18 H, $SiMe_3$), 0.72 (s, 3 H, GeMe) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -1.8 ($SiMe_3$), 0.03 (GeMe)
$(Me_3Si)_2GeMePh$	^1H NMR ($CDCl_3$, 300 MHz): δ 0.23 (s, 18 H, $SiMe_3$), 0.49 (s, 3 H, GeMe), 7.27–7.44 (m, 5 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -9.4 (GeMe), -0.4 ($SiMe_3$), 126.9 (para CH), 127.7 (ortho or meta CH), 134.4 (ortho or meta CH), 140.7 (ipso C) MS (70 eV): *m/e* 312 (M^+, 19), 295 (8), 193 (6), 162 (42), 135 (61), 73 (base, 100) UV (pentane): λ_{max} 235 (ϵ = 10 200)
Me_2GePh_2	^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (s, 6 H, $GeMe_2$), 7.53–7.59 (m, 6 H, Ar–H), 7.72–7.76 (m, 4 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -3.4 (GeMe), 128.3 (ortho or meta CH), 128.8 (para CH), 133.8 (ortho or meta CH), 140.4 (ipso C)
$Me_3SiGeMe_2Ph$	^1H NMR ($CDCl_3$, 300 MHz): δ 0.15 (s, 9 H, $SiMe_3$), 0.41 (s, 6 H, $GeMe_2$), 7.26–7.32 (m, 3 H, Ar–H), 7.41–7.43 (m, 2 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -4.8 ($GeMe_2$), -1.8 ($SiMe_3$), 126.0 (ortho or meta CH), 127.8 (para CH), 133.8 (ortho or meta CH), 142.6 (ipso C) MS (70 eV): *m/e* 254 (M^+, 2), 239 (6), 181 (6), 135 (base, 100), 73 (51) UV (pentane): λ_{max} 266 nm (ϵ = 10 900)
Me_3SiPh	^1H NMR ($CDCl_3$, 300 MHz): δ 0.39 (s, 9 H, $SiMe_3$), 7.45–7.48 (m, 3 H, Ar–H), 7.63–7.66 (m, 2 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -1.4 ($SiMe_3$), 127.9 (ortho or meta CH), 129.0 (para CH), 133.5 (ortho or meta CH), 140.7 (ipso C) MS (70 eV): *m/e* 150 (M^+, 8), 135 (base, 100), 107 (9), 73 (4)
	^1H NMR ($CDCl_3$, 300 MHz): δ 1.77 (s, 6 H, CH_3), 2.00 (s, 4 H, CH_2), 7.34–7.37 (m, 6 H, Ar–H), 7.50–7.52 (m, 4 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.2 (CH_2), 25.3 (CH_3), 128.3 (ortho or meta CH), 129.0 (para CH), 131.0 (–C=), 134.4 (ortho or meta CH), 138.5 (ipso C) MS (70 eV): *m/e* 310 (M^+, 12), 228 (60), 151 (base, 100), 125 (27)
	^1H NMR ($CDCl_3$, 300 MHz): δ 0.59 (s, 3 H, GeMe), 1.77 (bs, 10 H, CH_2, CMe), 7.26–7.52 (m, 5 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -4.3 (GeMe), 19.5 (CH_2), 26.6 (CMe), 127.9 (ortho or meta CH), 128.3 (para CH), 130.8 (–C=), 133.2 (ortho or meta CH) MS (70 eV): *m/e* 248 (M^+, 3), 229 (13), 166 (38), 151 (base, 100), 89 (10)
 B	^1H NMR ($CDCl_3$, 300 MHz): δ 0.12 (s, 9 H, $SiMe_3$), 0.20 (s, 3 H, GeMe), 1.67 (bs, 10 H, CH_2, CMe) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ -5.0 (GeMe), -1.5 ($SiMe_3$), 19.3 (CH_2), 25.4 (CMe), 131.3 (–C=) MS (70 eV): *m/e* 244 (M^+, 3), 229 (8), 162 (44), 89 (27), 73 (base, 100)
 C	MS (70 eV): *m/e* 394 (M^+, 0.06), 311 (5), 223 (24), 135 (base, 100), 119 (63), 73 (27)
 D	^1H NMR ($CDCl_3$, 300 MHz): δ 0.26 (s, 6 H, GeMe), 1.48 (s, 4 H, CH_2), 1.67 (s, 6 H, CMe) ^{13}C NMR ($CDCl_3$, 75.4 Mz): δ -2.6 (GeMe), 19.2 (CH_2), 26.9 (CMe), 131.1 (–C=) MS (70 eV): *m/e* 186 (M^+, 12), 171 (31), 104 (53), 89 (base, 100)
 E	^1H NMR ($CDCl_3$, 300 MHz): δ 0.33 (s, 9 H, $SiMe_3$), 0.46 (s, 3 H, GeMe), 0.48 (s, 3 H, GeMe), 0.98 (d, 3 H, J_{ab} = 6.8 Hz, CHMe), 1.05 (dd, 1 H, J_{gem} = 13.8 Hz, J_{ab} = 8.1 Hz, GeCHH′), 1.22 (dd, 1 H, J_{gem} = 13.8 Hz, J_{ab} = 6.6 Hz, GeCHH′), 1.64 (s, 3 H, CMe), 2.36 (m, 1 H, $J_{H,Me}$ = 6.8 Hz, J_{ab} = 7.2 Hz, C*H*Me), 4.59 (s, 1 H, CCHH′), 4.66 (s, 1 H, CCHH′), 7.24–7.30 (m, 2 H, Ar–H), 7.52–7.55 (m, 1 H, Ar–H), 7.61–7.64 (m, 1 H, Ar–H) ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 0.3 ($GeMe_2$), 1.35 ($SiMe_3$), 18.7 (CH), 22.5 ($GeCH_2$), 25.0 ($CHCH_3$), 28.1 (CCH_3), 108.6 ($C{=}CH_2$), 127.4 (Ar–CH), 128.0 (Ar–CH), 134.9 (Ar–CH), 135.5 (Ar–CH), 146.1 (Ar–C), 148.2 (Ar–C), 152.3 ($C{=}CH_2$) MS (70 eV): *m/e* 336 (M^+, 0.4), 321 (1), 253 (30), 135 (59), 119 (62), 105 (40), 73 (base, 100)

mmol) of dimethyldiphenylgermane, and ten drops of dry DME. After ca. 30 min of rapid stirring, this heterogeneous mixture turned intense green. Stirring was continued 4 h, and then 50 mL of dry DME was added, and the mixture was rapidly stirred for 17 h. An additional 100 mL of dry DME was added and then 28.6 a (264 mmol) of freshly distilled $ClSiMe_3$ in 50 mL of dry DME was rapidly added. After an additional 1 h of stirring, the mixture was filtered and the volatiles were removed in vauco. To the liquid residue was added 100 mL of ether, and the organic phase was washed three times with deionized water in a separatory funnel. The organic layer was dried over $MgSO_4$ and filtered, and the ether was removed. The resulting yellow liquid was subjected to flash column chromatography (silica gel, pentane), and the fractions were analyzed by TLC. The pure product (99% by GC), 5.1 g (40% yield), eluted earlier than the 7.0 g of recovered, unreacted dimethyldiphenylgermane.

2. For the synthesis of larger quantities, the key intermediate, dimethyl(phenyl)germyllithium was prepared from chlorodimethyl(phenyl)germane. In a three-necked 500-mL flask equipped with a reflux condenser, pressure-equalized addition funnel, and a mechanical stirrer, a solution of phenylmagnesium bromide was prepared by addition of 13.5 g (86.4 mmol) of bromobenzene in 50 mL of THF to 3.1 g (127 mmol) of Mg and 100 mL of THF. Addition required 2 h, as considerable heat was evolved, and the resulting mixture was stirred an additional 1 h. The black solution of Grignard reagent was filtered through glass wool during transfer to a 250-mL pressure-equalized addition funnel mounted on a 1-L three-necked flask equipped with a reflux condenser and mechanical stirrer, in which was placed a solution of 15.0 g (86.4 mmol) of dichlorodimethylgermane in 200 mL of THF, cooled to -12 °C with an acetone/ice bath. After dropwise addition over 1.5 h of the Grignard reagent solution to the cooled, stirred

chlorogermane solution, a heating mantle was fitted, and the mixture was refluxed for 12 h. Workup consisted of transfer to a single-neck flask, removal of solvent by distillation, addition of 200 mL of toluene to precipitate salts, filtration, and removal of toluene from the filtrate by simple distillation. Vacuum distillation of the chlorodimethyl(phenyl)germane yielded 13.3 g (83%) of product, bp 90 °C (50 Torr).

Into a 250-mL three-necked flask equipped with a reflux condenser, pressure-equalized addition funnel, and mechanical stirrer was placed 2.0 g (0.28 mol) of finely cut Li and 100 mL of THF. To the stirred mixture was added dropwise, over 30 min, 15.0 g (69 mmol) of chlorodimethyl(phenyl)germane in 50 mL of THF. A slightly exothermic reaction was evident, and the mixture rapidly turned emerald green. The reaction mixture was stirred an additional 3 h, then 30 g (276 mmol) of $ClSiMe_3$ in 50 mL of THF was added, and stirring was continued an additional 1 h. Workup consisted of filtration and removal of the volatiles in vacuo from the filtrate. The resulting yellow liquid was diluted with 200 mL of ether, the resulting solution was washed in a separatory funnel three times with deionized water, the organic layer was dried over $MgSO_4$ and filtered, and the ether was removed. Purification of the product by flash column chromatography (silica gel, pentane) yielded 14.0 g of pure dimethyl(phenyl)(trimethylsilyl)germane (80% yield), identical with that from the smaller scale method. Spectral data are given in Table II. The bp and ^1H NMR spectrum are in accord with reported values.[33] Anal. Calcd for $C_{11}H_{20}GeSi$: C, 52.21; H, 7.97. Found: C, 52.52; H, 7.97.

Photolysis Procedures. All product studies were carried out by irradiation of reaction mixtures in a 2 × 35 cm quartz tube fused via a graded seal to a greaseless Teflon stopcock fitted with Viton O-rings. Reaction mixtures were made with pentane (dried over CaH_2) solvent and were degassed by at least three freeze–pump–thaw cycles on a vacuum line that would pump to 5 mTorr. During long irradiations, reaction mixtures were "redegassed" every 12 h to ensure the exclusion of oxygen. The product studies employed a Rayonet RS preparative photochemical reactor equipped with a series of low-pressure mercury lamps (120 W). Reaction mixtures for quantitative product studies were prepared with an initial total absorbance of ca. 1 at 254 nm and conversions were kept below 50%. Larger scale irradiations were carried out with higher concentrations of precursor molecules.

Larger Scale Irradiations. Irradiation of Diphenylbis(trimethylsilyl)germane in the Presence of 2,3-Dimethylbutadiene. The reaction mixture consisted of 0.1612 g (0.2163 mmol) of $(Me_3Si)_2GePh_2$, 0.354 g (2.16 mmol) of 2,3-dimethylbutadiene, and 0.1576 g of hexadecane (internal standard) dissolved in 50 mL of pentane. After 1-h irradiation (64% conversion), three products were detected by gas chromatography: hexamethyldisilane (68%), Me_3SiPh (27%), and 3,4-dimethyl-1,1-diphenyl-1-germacyclopent-3-ene (61%). The germacyclopentene was purified by preparative gas chromatography (12-ft 10% OV-17 column on 80/100 mesh Supelcoport, 240 °C, 85 cm^3/min He, retention time 15 min) and spectral data are given in Table II. Anal. Calcd for $C_{18}H_{20}Ge$: C, 69.64; H, 6.76. Found: C, 69.98; H, 6.53.

Irradiation of Methyl(phenyl)bis(trimethylsilyl)germane in the Presence of 2,3-Dimethylbutadiene. The reaction mixture consisted of 0.2139 g (0.657 mmol) of $(Me_3Si)_2GeMePh$, 0.539 g (6.57 mmol) of 2,3-dimethylbutadiene, and 0.1739 g of hexadecane (internal standard) dissolved in 50 mL of pentane. After 1.5-h irradiation (48% conversion), five products were detected: hexamethyldisilane (60%), Me_3SiPh (35%), 1,3,4-trimethyl-1-phenyl-1-germacyclopent-3-ene (A, 55%) 1,3,4-trimethyl-1-(trimethylsilyl)-1-germacyclopent-3-ene (B, 28%), and (2,3-dimethyl-3-butenyl)methyl(trimethylsilyl) [o-(trimethylsilyl)phenyl]germane (C, 5%). The products were separable on 10% OV-17 or 7.5% SE-30 columns, 12 ft, 110–220 °C, but product A could not be separated from the starting germane on SE-30 columns. Spectroscopic data for products A, B, and C are given in Table II. Exact mass determination: calcd for A, $C_{13}H_{18}Ge$: 248.06085; measured 248.06145.

Irradiation of Dimethyl(phenyl)(trimethylsilyl)germane in the Presence of 2,3-Dimethylbutadiene. Reaction mixtures typically consisted of 0.20–0.40 g (0.8–1.6 mmol) of $PhGeMe_2SiMe_3$, 0.7–1.4 g (8–16 mmol) of 2,3-dimethylbutadiene, and 0.2–0.3 g of dodecane (internal standard) in 50 mL of pentane. After 6–10-h irradiation (60–90% conversion), three products were detected: Me_3SiPh (61–85%), 1,1,3,4-tetramethyl-1-germacyclopent-3-ene (D, 55–78%), and dimethyl-(2,3-dimethyl-3-butenyl)[o-(trimethylsilyl)phenyl]germane (E, 20–28%). The products were separated by preparative gas chromatography on either the OV-17 or the SE-30 column described above. Spectral data for products D and E are given in Table II. Anal. Calcd for E, $C_{17}H_{30}GeSi$: C, 60.93; H, 9.02. Found: C, 60.53; H, 9.23.

Small-Scale Photolysis. Irradiation of Dimethyl(phenyl)(trimethylsilyl)germane. A solution of 11.9 mg (0.0471 mmol) of $PhGeMe_2SiMe_3$, 38.6 mg (0.47 mmol) of 2,3-dimethylbutadiene, and 10 mg of dodecane (internal standard) in 25 mL of pentane was irradiated 1 h (47% conversion). Three products were detected by capillary column gas chromatography: Me_3SiPh (72%), 1,1,3,4-tetramethyl-1-germacyclopent-3-ene (D, 71%), and dimethyl(2,3-dimethyl-3-butenyl)[o-(trimethylsilyl)phenyl]germane (E, 27%).

Laser Flash Photolysis. The techniques employed to obtain the transient absorption spectrum shown in Figure 1 and the bimolecular rate constants for disappearance of the transient upon laser flash photolysis of $PhGeMe_2SiMe_3$ have been described previously.[12,34]

Either an excimer laser (Lambda Physik LPX 1101, KrF, λ = 248 nm, 20-ns pulse width, attenuated to 20–35 mJ/pulse) or a Q-switched Nd-YAG laser (Datachrom 5000 YAG, frequency quadrupled to 266 nm, 10-ns pulse width, 20–28 mJ/pulse) was employed to irradiate solutions of $Me_3SiGeMe_2Ph$ in dry cyclohexane (1.1×10^{-3} M for 248-nm irradiation 5.5×10^{-3} for 266-nm irradiations). The monitoring system consisted of a 300-W Xe arc lamp, a Jarrel-Ash monochromator, and a Hamamatsu IP28 photomultiplier tube. Signals from the photomultiplier tube were fed to either a TEKs468 storage oscilloscope or a 7912 AD digitizer. Kinetic traces from at least eight decays were averaged. Digital data were transferred to a Hewlett-Packard VectraCS computer for processing. The pseudo-first-order rate constants from first-order decays of the transient absorption at 425 nm were plotted against substrate concentrations to obtain second-order rate constants. With this apparatus, transient absorption spectra at a particular time after the laser flash, such as that shown in Figure 1, are constructed from the kinetic traces at many wavelengths.

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Registry No. Br_2Ph_2Ge, 1080-42-8; $(Me_3Si)_2GePh_2$, 111655-78-8; $(Me_3Si)_2GeMe_2$, 134847-63-5; $(Me_3Si)_2GeClMe$, 134847-64-6; $(Me_3Si)_2GeMePh$, 134847-65-7; Me_2GePh_2, 7301-42-0; $Me_3SiGeMe_2Ph$, 37899-63-1; Me_3SiPh, 768-32-1; Cl_2GeMe_2, 1529-48-2; 3,4-dimethyl-1,1-diphenyl-1-germacyclopent-3-ene, 5764-69-2; 1,3,4-trimethyl-1-phenyl-1-germacyclopent-3-ene, 51533-82-5; 1,3,4-trimethyl-1-(trimethylsilyl)-1-germacyclopent-3-ene, 134847-66-8; (2,3-dimethyl-3-butenyl)methyl(trimethylsilyl)[o-(trimethylsilyl)phenyl]germane, 134847-67-9; 1,1,3,4-tetramethyl-1-germacyclopent-3-ene, 5764-66-9; dimethyl(2,3-dimethyl-3-butenyl)[o-(trimethylsilyl)phenyl]germane, 134847-68-0; hexamethyldisilane, 1450-14-2; 2,3-dimethylbutadiene, 513-81-5; butadiene, 106-99-0; isoprene, 78-79-5; *cis*-piperylene, 1574-41-0; *trans*-piperylene, 2004-70-8; *cis,cis*-2,4-hexadiene, 6108-61-8; *cis,trans*-2,4-hexadiene, 5194-50-3; *trans,trans*-2,4-hexadiene, 5194-51-4; 1-butene, 106-98-9; 1-hexene, 592-41-6; 1-hexyne, 693-02-7; 1-propyne, 74-99-7; dimethyl disulfide, 624-92-0; tetrahydrofuran, 109-99-9; ethanol, 64-17-5; carbon tetrachloride, 56-23-5; triethylsilane, 617-86-7; oxygen, 7782-44-7; dimethylgermylene, 74963-95-4.

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