two of which (35e and 36e; $n = 1, 2$) are thermally stable for Ar = C_6H_6, whereas arene permethylation also stabilizes the 37e form, as in the monometallic series. The fourth oxidation state, a 40e anion, is not isolable. It corresponds to an 18e ferrocenyl group attached to a 20e $[Fe(Cp)(Ar)]^-$ species.

In the class I mixed-valence complexes,[14] the electronic structures related to each oxidation state are already known.[13] The most remarkable feature is the cooperative interaction in the Fe^IFe^{II} complexes in which the molecular Fe^I structure is coupled with the lattice. This effect is observed in the variation of the quadrupole splitting with temperature. When no cooperative interaction is observed, i.e. in dilute frozen solutions or even in some solids, a Tanh law of thermal population of the upper Kramers' level is observed with a vibronic reduction factor of 0.2–0.3. On the other hand, many Jahn–Teller active Fe^I compounds show deviation from the regular law, sometimes including breaks indicating phase transitions.[15] Indeed this is the case for **11** and **5**.

Finally, note that these dissymmetric dinuclear sandwich complexes are made of two units. The ferrocene/ferricinium fragment is an electrocatalyst for a number of organometallic reactions working with an oxidative induction.[16,17] The $[Fe(Cp)(Ar)]^{+/0}$ unit is an electrocatalyst for other inorganic and organometallic reactions proceeding by reductive induction.[16,18] Since photoexcited states are at the same time better oxidizing and reducing agents than the ground states, these bifunctional redox and electrocatalysts could find use in energy conversion devices.

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Registry No. **1**, 1287-38-3; **2**, 68499-72-9; **3**, 98162-01-7; **4**, 121072-54-6; **5**, 98162-02-8; **6**, 121072-55-7; **7**, 121072-56-8; **8**, 12176-31-7; **9**, 53702-66-2; C_6Me_6, 87-85-4.

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(14) (a) *Mixed Valence Compounds, Theory and Applications in Chemistry, Physics, Geology and Biology*; Brown, D. B.; Ed.; D. Reidel: Boston, 1980. (b) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357. (c) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (d) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149. (e) Wong, E. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369. (f) Hush, N. S. *Mixed Valence Compounds*; Brown, D. B., Ed.; D. Reidel: Dordrecht, 1980; p 151.

(15) Varret, F.; Mariot, J.-P.; Hamon, J.-R.; Astruc, D. *Hyperfine Interact.* **1988**, *39*, 67.

(16) Astruc, D. *Angew. Chem.* **1988**, *100*, 662; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643.

(17) (a) Desbois, M.-H.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1988**, 472. (b) Amatore, C.; Verpeaux, J.-N.; Madonik, A. M.; Desbois, M.-H.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1988**, 200.

(18) (a) Moinet, C.; Román, E.; Astruc, D. *J. Electroanal. Interfacial Electrochem.* **1981**, *121*, 241. (b) Darchen, A. *J. Chem. Soc., Chem. Commun.* **1983**, 768. (c) Ruiz, J.; Lacoste, M.; Astruc, D., in preparation. (d) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

Kinetic and Labeling Studies of the Formation and Trapping Reactions of Dimethylgermylene

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The kinetics of the thermal decomposition of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabenzonorbornadiene (**1**) have been studied in the presence of excess styrene, 2,3-dimethylbutadiene, and CCl_4. At 78.3 °C the observed rate constant is 1.1×10^{-3} s^{-1} and is independent of the initial concentrations of **1** and the other reagents indicating a first-order, unimolecular decomposition. The same rate constant is also obtained without any added reagents. Activation parameters for the decomposition are $\Delta H^\ddagger = 27.8 \pm 0.6$ kcal/mol and $\Delta S^\ddagger = 6.8 \pm 1.6$ eu. The parameters are consistent with rate-determining cleavage of a single bridgehead germanium–carbon bond to give a diradical intermediate. Generation of dimethylgermylene from **1** in the presence of excess (*E*)-2-deuteriostyrene yields cis and trans isomers of 2,5-dideuterio-1,1-dimethyl-3,4-diphenylgermacyclopentane. The site of the deuterium label is partially scrambled and can be rationalized by postulating acyclic diradical intermediates for the cycloaddition process.

Introduction

Germylenes are logical intermediates for the synthesis of organogermanium compounds. A diverse set of germylenes are known, and they display high reactivity toward a variety of organic compounds.[1] Unfortunately, the mechanistic basis of germylene chemistry is still poorly understood making many germylene reactions unreliable for synthetic planning, including even the reaction of germylenes with alkenes. For example, one of the best studied germylenes, $GeCl_2$, reacts with alkenes by an unknown mechanism to give a variety of organogermanium products, including, in some cases, an alkene–germylene copolymer.[2]

[†] Present address: Department of Chemistry, Reed College, 3203 S.E. Woodstock Blvd., Portland, OR 97202.

(1) (a) Satge, J.; Massol, M.; Riviere, P. *J. Organomet. Chem.* **1973**, *56*, 1. (b) Riviere, P.; Riviere-Baudet, M.; Satge, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 10.

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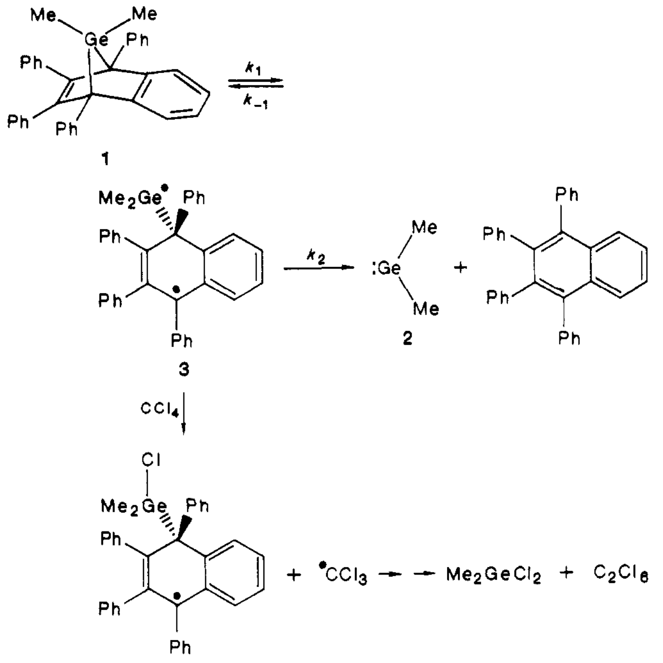
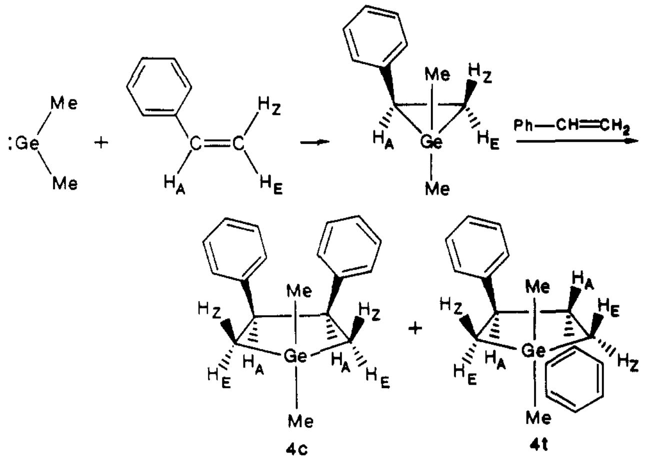
Scheme I



Recently, Neumann and co-workers have reported that dimethylgermylene (**2**), a transient species generated by the thermal decomposition of 7-germanorbornadiene (**1**), can be trapped with a variety of organic reagents such as CCl_4 and 2,3-dimethylbutadiene[3] (DMB) as well as certain alkenes.[4] Neumann has proposed, on the basis of trapping experiments and kinetic measurements, that the reactive intermediate is a free singlet germylene which forms via a concerted fragmentation of precursor **1**.[3,4] An alternative mechanism for germylene formation is shown in Scheme I. This is a stepwise process involving a diradical intermediate, **3**, which can undergo germanium–carbon bond cleavage to yield **2** or abstract halogen from CCl_4. The mechanism of germylene formation, according to this scheme, should be strongly affected by the nature of the trapping reagent. The operation of this latter mechanism could be detected if the reaction rate depended on either the identity or the concentration of the trapping reagent, and so we have determined rate laws for the decomposition of **1** in the presence of several different types of trapping reagents.

Dimethylgermylene differs from other germylenes in its unusual reactivity toward styrene and certain conjugated dienes. Namely, reaction with these alkenes yields germacyclopentanes from the apparent cycloaddition of **2** and two alkenes.[4,5] In the case of styrene cycloaddition it has been proposed that a stepwise process occurs involving first concerted addition of germylene to styrene followed by concerted addition of the germacyclopropane to a second styrene[4] (Scheme II). This mechanism implies that the alkene substituents of each styrene will retain their relative stereochemistry in the product germacyclopentanes **4c** and **4t**. We have tested this prediction by performing the cycloaddition using (*E*)-2-deuteriostyrene.

Scheme II



Experimental Section

Materials. All preparations involving oxygen- or water-sensitive reagents were performed under a nitrogen atmosphere. Benzene, hexane, diethyl ether, and toluene used as solvents were distilled from sodium–benzophenone ketyl solutions. Reagents were obtained commercially (Aldrich). Styrene and phenylacetylene were distilled before use. 7,7-Dimethyl-1,4,5,6-tetraphenyl-7-germabenzonorbornadiene (**1**) was prepared by the method of Neumann and Schriewer.[3a]

Instrumental Methods. ^1H NMR spectra were obtained on a Bruker AF-200 spectrometer using C_6D_6 as a solvent. Nonphase-sensitive 2D NOESY spectra were obtained on a General Electric QE-300 spectrometer using C_6D_6 as a solvent. Chemical shifts are reported as δ values (ppm) downfield from internal Me_4Si. Low-resolution electron-impact mass spectra were obtained on a Hewlett-Packard 5985 GC/MS system using a direct insertion probe. UV/vis spectra were obtained by using a CARY 2300 spectrophotometer.

Kinetic Measurements. Kinetic measurements were obtained by measuring the absorbance at 320 nm of solutions immersed in a thermostated (±0.5 °C) constant temperature bath. All absorbance measurements used to determine rate constants were in the range 0–1.4 where both 1,2,3,4-tetraphenylnaphthalene (ϵ = 4080) and **1** (ϵ = 752) were found to satisfy Beer's law. Absorbance data were fit to the equation

$$A(t) = (A_\infty - A_0)\,(1 - e^{-kt}) + A_0$$

using the nonlinear least-squares method of Levenberg and Marquardt[6] to calculate k, A_0, and A_∞.

Typical Kinetics Procedure. A stock solution of **1** was made by dissolving 40.1 mg (0.0749 mmol) in 25 mL of toluene. A second solution was made by diluting styrene (167.3 mg, 1.61 mmol) to 25 mL with toluene. Equal 1-mL aliquots of each stock solution were combined and diluted to 10 mL with toluene (3.0×10^{-4} M **1**, 6.4×10^{-3} M styrene). This mixture was transferred to a cuvette and flushed with nitrogen and the cuvette placed inside the preheated compartment of the spectrophotometer to begin the reaction.

Preparation of (*E*)-2-Deuteriostyrene. Phenylacetylene (1.98 g, 19.4 mmol) was stirred with zirconocene hydride chloride (5.0 g, 19 mmol) in 125 mL of benzene for 1.5 h. Evaporation of the solvent gave an orange-red glass, which was washed with hexane and then treated with 15 mL of diethyl ether and 5 mL of 20% D_2SO_4/D_2O solution. The mixture was filtered and the ethereal layer separated, washed with water and dried ($MgSO_4$). Evaporation of the solvent, followed by vacuum distillation of the residue gave 0.67 g (33%) of (*E*)-2-deuteriostyrene (bp 61–67 °C, 30 mmHg): ^1H NMR δ 5.59 (d, 1 H, J = 17.6 Hz, H_A), 6.58 (d, 1 H, J = 17.6 Hz, H_Z), 6.85–7.5 (m, 5 H, Ph). A small doublet at δ 5.07 (d, 0.07 H, J = 9.9 Hz, H_E) was assigned to undeuterated styrene.

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(2) Nefedov, O. M.; Kolesnikov, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 201.

(3) (a) Neumann, W. P.; Schriewer, M. *Tetrahedron Lett.* **1980**, *21*, 3273. (b) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897. (c) Kocher, J.; Lehnig, M.; Neumann, W. P. *Organometallics* **1988**, *7*, 1201.

(4) Kocher, J.; Neumann, W. P. *Organometallics* **1985**, *4*, 400.

(5) (a) Neumann, W. P.; Michels, E.; Kocher, J. *Tetrahedron Lett.* **1987**, *28*, 3783. (b) Preut, H.; Kocher, J.; Neumann, W. P. *Acta Crystallogr., Sect. C* **1985**, *C41*, 912.

(6) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes, The Art of Scientific Computing*; Cambridge: New York, 1986; pp 523–8.

Table I. Pseudo-First-Order Rate Constants for the Thermolysis of 1 in the Presence of Various Reagents

$[1]_0$, 10^{-4} M	trapping reagent	$[\text{trap}]_0$, 10^{-3} M	T, °C	runs	k_{obsd}, 10^{-3} s^{-1}
3.0	styrene	6.4	78.3	3	1.08 ± 0.04
1.5	styrene	6.4	78.3	3	1.06 ± 0.08
0.99	styrene	6.4	78.3	3	1.11 ± 0.03
3.0	styrene	3.2	78.3	3	1.12 ± 0.01
3.0	styrene	2.1	78.3	3	1.10 ± 0.08
3.0	styrene	6.4	83.1	3	1.79 ± 0.01
3.0	styrene	6.4	72.6	3	0.519 ± 0.015
3.0	styrene	6.4	65.9	5	0.236 ± 0.015
3.0	DMB[a]	6.4	78.3	3	1.15 ± 0.02
1.5	DMB[a]	6.4	78.3	3	1.16 ± 0.01
3.0	DMB[a]	3.2	78.3	3	1.13 ± 0.09
3.0	none		78.3	2	1.07 ± 0.02
1.5	none		78.3	3	1.03 ± 0.04
3.0	CCl_4	1000	65.9	3	0.245 ± 0.008
3.0	CCl_4	100	65.9	1	0.212 ± 0.002
3.0	CCl_4	10	65.9	1	0.224 ± 0.002
3.0	CCl_4	6.5	78.3	2	1.05 ± 0.26
3.0	CCl_4	3.3	78.3	2	1.05 ± 0.39

[a] DMB = 2,3-dimethylbutadiene.

Reaction of 1 with (*E*)-2-Deuteriostyrene. A solution of (*E*)-2-deuteriostyrene (0.673 g, 64.0 mmol) and 1 (0.49 g, 0.92 mmol) in 40 mL of toluene was heated at 70 °C for 3 h. After evaporation of the solvent, the residue was extracted with 100% ethanol. Evaporation of the ethanol gave a yellowish oily solid. Preparative TLC (silica gel, hexane, four elutions) afforded 0.057 g (20%) of cis and 0.055 g (19%) of trans isomers of 2,5-dideuterio-1,1-dimethyl-3,4-diphenylgermacyclopentane free of the opposite isomer. ^{1}H NMR spectra of the products show phenyl and methyl resonances identical with those of undeuterated **4c** and **4t**.[4]

Low-resolution MS for **4c**-d_2: m/e (%) 204 (1.9), 205 (17.6), 206 (4.2), 207 (18.5), 208 (10.1), 209 (23.0), 210 (3.8), 211 (5.5), 212 (0.6). For **4t**-d_2 *m/e* (%): 204 (1.9), 205 (19.2), 206 (4.7), 207 (25.2), 208 (12.7), 209 (34.3), 210 (4.4), 211 (7.3), 212 (0.8), 213 (0.2).

Results and Discussion

Kinetics of Germylene Formation. The 320-nm absorbance of 1,2,3,4-tetraphenylnaphthalene was used to monitor the conversion of 1 to the naphthalene and dimethylgermylene (2). Pseudo-first-order rate constants were obtained by nonlinear least-squares fitting of the absorbance data. Table I shows the average rate constants and their standard deviations for each set of reaction conditions.

The decomposition rate of 1 at 78.3 °C is seen to be unaffected by the identity of the trapping reagent and is also independent of the reagent's concentration. The rate constant is independent of the initial concentration of 1 and remains unchanged when no trapping reagent is used. Solvent (toluene) does not participate in the reaction, even in the absence of other trapping reagents, as judged from the ^{1}H NMR spectrum of the product mixture. Similar results are obtained at 65.9 °C using either styrene or significantly higher concentrations of CCl_4. Again, the rate is independent of the trapping reagent. *These results demonstrate that the decomposition obeys a first-order rate law, and we conclude that the rate-determining step is unimolecular under all of the conditions examined.*

There are two mechanisms that can accommodate our kinetic results. One is rate-determining formation of diradical 3 (Scheme I with rate-determining k_1). This mechanism requires that all subsequent reactions, including formation of germylene 2, be more rapid than the initial germanium–carbon bond cleavage. The other mechanistic alternative is rate-determining formation of 2. In this case formation of 2 occurs by a concerted process involving cleavage of both germanium–carbon bonds in a single step.

The overall temperature dependence of k_{obsd} at four temperatures between 65.9 and 83.1 °C (Table I, entries 1, 6–8) is well fit by the activation parameters $\Delta H^‡ = 27.8 \pm 0.6$ kcal/mol and $\Delta S^‡ = 6.8 \pm 1.6$ eu. If k_{obsd} is identified with k_1, then the activation parameters describe the cleavage of a single bridgehead germanium–carbon bond.

Similar activation parameters have been found for norbornadienes undergoing cleavage of the bridgehead bond. The conversion of 7-*tert*-butoxynorbornadiene to isomeric *tert*-butoxycycloheptatrienes in *n*-decane is characterized by $\Delta H^‡ = 34.5$ kcal/mol and $\Delta S^‡ = 1$ eu.[7] Likewise, the extrusion of dimethoxycarbene from 7,7-dimethoxy-5-phenyl-1,2,3,4-tetrachloronorbornadiene in cyclohexane has $\Delta H^‡ = 34.5$ kcal/mol and $\Delta S^‡ = 8.7$ eu.[8] Both reactions are believed to occur by two-step mechanisms involving rate-determining cleavage of the bridgehead bond.[9] The lower barrier observed for the decomposition of 1 can be rationalized in terms of the relative weakness of germanium–carbon bonds compared to carbon–carbon bonds[10] and the larger degree of resonance stabilization expected for diradical 3.

Concerted fragmentation of 1 to give germylene 2 is also consistent with the temperature dependence of k_{obsd}. The small positive activation entropy could be associated with the partial cleavage of 1 in the transition state. A two-step mechanism with $k_2 < k_1$, as originally suggested,[3a] is unreasonable since this requires the energy of the bridgehead germanium–carbon bonds in 1 to be substantially less than the activation barrier of 27.8 kcal/mol.

Kocher et al. have recently reported an activation barrier of 19 kcal/mol for the decomposition of 1 in CCl_4.[3c] This barrier is substantially less than any germanium–carbon bond energy and is most consistent with concerted fragmentation of 1. It is likely, however, that this value represents a lower bound on the activation barrier; some of the reaction temperatures used to estimate the barrier were far above the solvent's boiling point and may not have been attained.

Stereochemistry of Styrene–Germylene Cycloaddition. We initially attempted to add dimethylgermylene (2) to (*Z*)-2-deuteriostyrene. This styrene was prepared by the reduction of 2-deuteriophenylacetyelene with diisobutylaluminum hydride.[11] Our attempts at cycloaddition failed apparently due to the more rapid reaction of 2 with the 10–20% phenylacetylene contaminating the styrene; the ^{1}H NMR spectrum of the product mixture was similar to the one obtained from the direct reaction of 1 with phenylacetylene.[12]

(*E*)-2-Deuteriostyrene, uncontaminated by phenylacetylene, was prepared fairly easily by a procedure that avoided the difficult separation of styrene and phenylacetylene. Hydrozirconation of styrene with zirconocene hydride chloride in benzene followed by evaporation of the solvent deposited a styrylzirconium complex as an or-

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[7] Lustgarten, R. K.; Richey, H. G., Jr. *Tetrahedron Lett.* **1966**, 4655.

[8] Lemal, D. M.; Gosselink, E. P.; McGregor, S. D. *J. Am. Chem. Soc.* **1966**, *88*, 582.

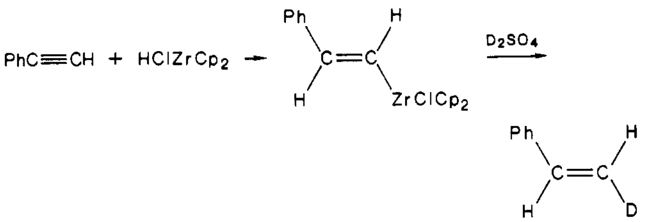
[9] Hoffmann, R. W. *Angew. Chem.* **1971**, *83*, 595.

[10] Standard Ge–C and C–C bond dissociation energies are 76 (ref 10a) and 80 (ref 10b) kcal/mol, respectively. (a) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17. (b) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas-Phase Unimolecular Reactions*; National Standard Data Reference Series NBS 21, U.S. Government Printing Office: Washington, DC, 1970; p 335.

[11] Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

[12] Billeb, G.; Neumann, W. P.; Steinhoff, G. *Tetrahedron Lett.* **1988**, *29*, 5245.

Scheme III



ange-red glass.[13] Unreacted phenylacetylene was removed from this glass by washing it repeatedly with hexane. Hydrolysis of the glass with a mixture of 20% D_2SO_4/D_2O and diethyl ether yielded (*E*)-2-deuteriostyrene (Scheme III).[14]

The ^1H NMR of (*E*)-2-deuteriostyrene shows two doublets for the two alkene hydrogens at δ 6.58 and 5.59 (J = 17.6 Hz). The magnitude of the coupling constant indicates a trans arrangement for the two hydrogens. A small doublet due to residual H_E was observed at δ 5.07 (J = 9.9 Hz) and integrated to 0.07 hydrogen.

We were unable to determine the fraction of d_0 and d_1 material present in the deuterated styrene by mass spectral analysis. Furthermore, mass spectra of the two deuterated germacyclopentanes prepared from the labeled styrene, **4c**-d_2 and **4t**-d_2, showed only weak signals for the molecular ions. These spectra did, however, show an intense set of peaks between m/e 204 and m/e 213, which were assigned to $[Ge(CH_3)_2(CHD{=}CHC_6H_5)]^+$. Least-squares analysis of the ion intensities gives 8.4% d_0, 91.6% d_1 for the ions arising from **4t**-d_2 and 11.7% d_0, 88.3% d_1 for **4c**-d_2. These values compare well with the 7% residual H_E found in the NMR spectrum of the labeled styrene and suggest that the residual NMR signal is due almost entirely to unlabeled material. Accordingly, the stryene-d_1 is almost exclusively the *E* isomer.

Thermolysis of **1** in the presence of excess styrene at 70 °C yields an approximately 1:1 mixture of **4c** and **4t**, which can be separated by repeated TLC.[4] The ^1H NMR spectrum of each isomer shows three separate nonoverlapping multiplets due to the three unique ring hydrogens. The benzylic hydrogen of **4c** is observed at δ 3.38 (H_A) and the methylene hydrogens at δ 1.30 and 1.09, while for **4t** these hydrogens are observed at δ 2.86 (H_A), 1.53, and 1.04.

Non-phase-sensitive 2D NOESY spectra of the germacycles allowed complete assignment of the ring hydrogen resonances. NOE is a through-space effect; therefore, the largest enhancements are expected between spins located on the same face of the germacycle. The NOESY spectra of **4c** and **4t** show unequal enhancements between the benzylic hydrogen, H_A, and the two methylene hydrogens. We assign to H_E the signal that shows the larger enhancement with H_A. Unequal enhancements are also observed between the two methylene hydrogens and the phenyl hydrogens, but, as expected, the magnitude of the enhancements is reversed. The signal showing a larger effect from the phenyl hydrogens is assigned to H_Z. Thus, for **4c** we have δ 1.09 (H_E) and 1.30 (H_Z) and for **4t** δ 1.53 (H_E) and 1.04 (H_Z).

Interestingly, H_Z is the more upfield resonance in **4t**, but the more downfield resonance in **4c**. A model of **4c** shows that the cis arrangement of phenyl rings requires them to lie roughly face to face, causing H_Z to lie in the deshielding region of the adjacent phenyl group. The phenyl groups in **4t**, on the other hand, can rotate more freely causing H_Z to spend more time in the shielding region.

Thermolysis of **1** with an excess of (*E*)-2-deuteriostyrene at 70 °C for 3 h gave **4c**–d_2 and **4t**–d_2 in an approximately 1:1 ratio. The NMR spectrum of each isomer now shows the resonances of the three ring hydrogens as broadened multiplets of unequal area; for **4c**-d_2 H_Z/H_E equals 3.23, and $(H_Z + H_E)/H_A$ equals 1.21, while for **4t**-d_2 H_Z/H_E equals 3.10 and $(H_Z + H_E)/H_A$ equals 0.905. Since the labelled styrene contains 7% unlabelled material, a completely stereospecific cycloaddition would have made H_Z/H_E 1/0.07 or 14.3.

The NMR spectrum of the excess unreacted styrene, recovered by evaporation of the reaction mixture, is unchanged from that of the starting material. Control experiments show that the two germacycle isomers do not interconvert upon heating to 70 °C, exposure to room lighting, or repeated TLC. Finally, mass spectral analysis of the labeled germacycles (see above) suggests that approximately one deuterium is associated with each styrene group in the germacycle. We conclude, therefore, that the *cycloaddition process is responsible for scrambling of the deuterium label and cannot be stereospecific.*

The cycloaddition is moderately stereoselective, however, since most of the label remains in H_E. Assuming the starting styrene is 9% d_0, 91% d_1 material (the values obtained by averaging the different MS and NMR estimates of deuterium content in the labeled styrene), a stereospecific cycloaddition would have placed 0.09 hydrogen in H_E and 1.00 hydrogen in H_Z, while complete randomization of the label would have placed 0.545 H, or half of the available hydrogen, in each site. If two processes, one stereospecific and the other stereorandom, operate, then the amounts of hydrogen expected for H_E and H_Z are given by

$$H_Z = 1.00f_S + 0.545f_R \qquad (1)$$

$$H_E = 0.09f_S + 0.545f_R \qquad (2)$$

where f_S and f_R describe the fraction of material reacting by a stereospecific or stereorandom mechanism, respectively. Replacing f_S with $(1 - f_R)$ allows solution for f_R in terms of the H_Z/H_E ratio and shows that 36–39% of the germacycles must be formed by a stereorandom process. Alternatively, f_R can be interpreted as the fraction of scrambling produced by a single, partially stereoselective cycloaddition mechanism.

An alternative cycloaddition mechanism that allows for randomization of the deuterium label is given in Scheme IV. Cleavage of the germacyclopropane to give diradical **5** followed by addition of a second styrene, would yield diradical **6**. The direction of ring cleavage and subsequent styrene addition are governed by the stabilizing effect of the phenyl groups on the radical centers. Scrambling of the deuterium label could occur in either **5** or **6** due to rotation about a carbon–carbon bond. Incomplete scrambling could result from ring closure of **6** at a rate that is competitive with bond rotation. This mechanism accounts for three observations: high regioselectivity, formation of **4c** and **4t** in equal amounts, and loss of stereochemistry within each styrene group.

In their original report, Neumann and Kocher observed that the cycloaddition is not affected by the addition of *tert*-butyl bromide, a known scavenger of germanium-centered radicals.[4] From this result, they inferred that diradical **5** could not function as an intermediate. The negative scavenging result may be due to ineffective scavenging under their experimental conditions. Another alternative would be for styrene to add directly to the

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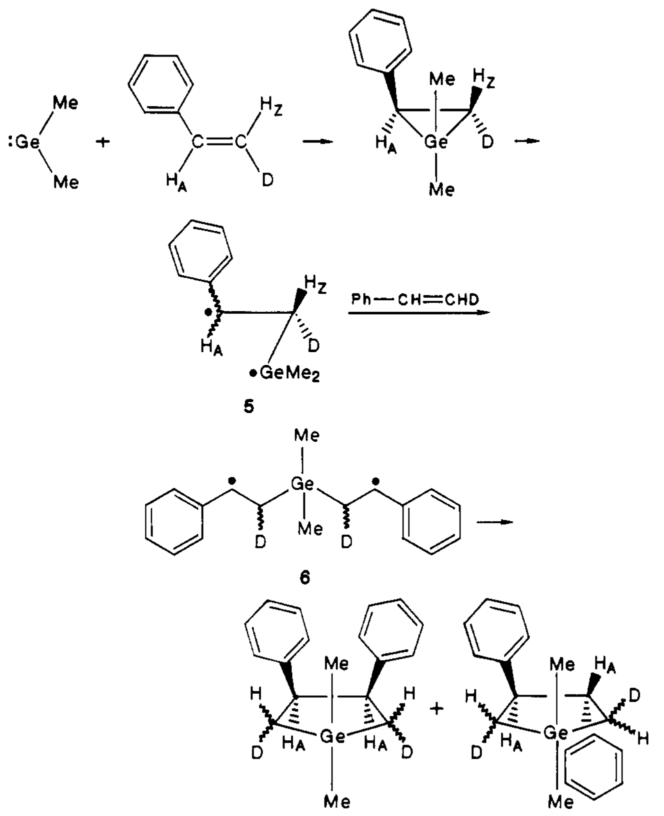
(13) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373.

(14) Labinger, J. A.; Hart, D. W.; Seibert, W. E., III; Schwarz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

Scheme IV



germacyclopropane to give diradical **6** directly.

A similar cycloaddition of styrene and dimethylsilylene has been observed by Seyferth and co-workers.[15] The regiochemistry of this reaction depends on the alkenes employed. Styrene gives products with phenyl groups in both the α- and β-positions, while α-methylstyrene appears to give products analogous to **4c** and **4t**, i.e., with β-phenyl groups only. A related reaction may be the two-atom insertion of styrene and other activated alkenes into hexamethylsilirane.[15] This reaction is regioselective in that the phenyl, or another activating group, always ends up in the β-position. Seyferth has suggested a radical mechanism for the two-atom insertion that is comparable to Scheme IV, i.e., rupture of the silirane to give a silicon-carbon diradical analogous to **5** followed by radical addition to the activated alkene.[15a]

Summary

1 decomposes by a first-order process that is unaffected by the presence of trapping reagents. The activation parameters for this process are consistent with direct conversion of **1** into **2**. They are also consistent with rate-determining formation of diradical **3**, followed by more rapid formation of dimethylgermylene (**2**).

Cycloaddition of **2** with (*E*)-2-deuteriostyrene is not stereospecific. Approximately 36–39% of the cycloaddition occurs via a process that randomizes the position of the deuterium label. This randomization, as well as the high degree of regioselectivity, suggests that diradical species such as **6** may be involved in the reaction. It is interesting to note that 1,1-dimethyl-3,3,4,4-tetraphenylgermacyclopentane readily decomposes to 1,1-diphenylethylene and polygermylene.[5b] This cycloreversion may be facilitated, not only by the crowded C_3–C_4 bond of the germacycle but also by the extra stabilization conferred by four phenyl groups upon diradicals such as **6**.

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Registry No. **1**, 76054-64-3; **2**, 74963-95-4; **4c**, 94070-43-6; **4t**, 94070-44-7; $HClZrCp_2$, 37342-97-5; (*E*)-2-deuteriostyrene, 6911-81-5; phenylacetylene, 536-74-3.

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[15] (a) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. (b) Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics* **1984**, *3*, 574.