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Supplementary Material Available: Tables of anisotropic

temperature factors, complete bond lengths and angles, and structure factors for (tmed)CuMo(CO)₃(C₅H₅) and [(C₆H₅)₃P]₃CuV(CO)₆ (56 pages). Ordering information is given on any current masthead page.

Silenes and Silenoids. 9. The Synthesis of Polyfunctional Bis(group 14)-Substituted Cyclopentadienes via a Novel Cleavage Reaction of Silicon-Carbon Bonds by Chloride Ion[†]

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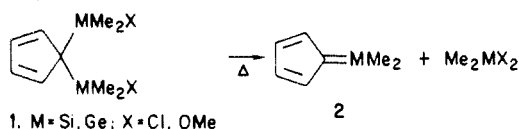
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Group 14 substituted cyclopentadienes of the type C₅H₄(MMe₂X)(M'Me₂Y), 1 (M and/or M' = Si or Ge, X and/or Y = Cl or Me), can be conveniently prepared in good yields by the reaction of *n*-butyllithium with cyclopentadienyltrimethylsilane followed by treatment with Me₂MCl₂ (M = Si or Ge). In hexane the reaction gives 1 (M = Si, M' = Si or Ge, X = Me, Y = Cl). In THF, with excess Me₂MCl₂, an unprecedented lithium chloride catalyzed cleavage of the trimethylsilyl group occurs to give excellent yields of 1 (M and M' = Si or Ge, X and Y = Cl). Methanolysis gives the corresponding methoxy compounds 1 (X and Y = OMe). The chloride ion cleavage reaction occurs only in THF and when the substrate bears a chlorodimethylsilyl or -germyl substituent.

Introduction

We recently reported that 1,1-bis(dimethylmethoxysilyl)cyclopentadiene 1 (M = Si, X = OMe) serves as an efficient precursor to dimethylsilafulvene 2 under unusually mild conditions.¹ Such bis(silyl)- or bis(germyl)-cyclopentadienes 1 with functionality on both metalloidal substituents have not previously been reported. Compounds of this type are of interest because of their potential as precursors to sila- or germafulvenes 2 under relatively mild conditions.¹



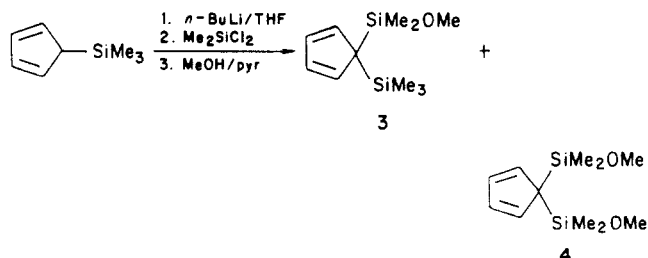
In addition, bis(triorganosilyl)cyclopentadienes are found as mixtures of isomers due to nondegenerate metallotropic rearrangements which occur at room temperature.² However, when one of the alkyl groups on silicon is replaced with a Lewis base substituent, 1,1-bis(silyl)-cyclopentadienes are obtained which are not fluxional at room temperature. For example 1-(dimethylmethoxysilyl)-1-(trimethylsilyl)cyclopentadiene, 3, does not undergo metallotropic rearrangement at room temperature, a fact which has been attributed to an intramolecular interaction between the methoxy oxygen and the trimethylsilyl group.³

In the course of our mechanistic investigation of the silene vs. silenoid problem as related to silafulvenes,¹ we discovered a novel route to bis functional silyl and germyl

cyclopentadienes. The details of this discovery are reported in this paper.

Results and Discussion

The synthesis of 3 by the reaction of [(trimethylsilyl)cyclopentadienyl]lithium with dimethyldichlorosilane followed by methanolysis in the presence of pyridine has been reported by Barton and co-workers.³ When we carried out this reaction using 1.4 equiv of dimethyldichlorosilane and THF as the solvent, in addition to a 30% yield of the expected product 3, we obtained a 15% yield of 1,1-bis(dimethylmethoxysilyl)cyclopentadiene, 4. We subsequently discovered that the use of two or more equivalents of dimethyldichlorosilane and longer reaction times gave yields of 4 in excess of 65%.



The ¹H, ¹³C, and ²⁹Si NMR spectra of 4 indicate that at room temperature it exists essentially exclusively as the 1,1-isomer and is not fluxional. The ¹H NMR spectrum shows an A₂B₂ pattern for the vinyl protons, a single

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

(1) Jones, P. R.; Rozell, J. M., Jr.; Campbell, B. M. *Organometallics* 1985, 4, 1321-1324.

(2) Ustynyuk, Yu. A.; Kisin, A. V.; Pribytkova, I. M.; Zenkin, A. A.; Antonova, N. D. *J. Organomet. Chem.* 1972, 42, 47-63.

(3) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* 1981, 22, 7-10.

Table I. Trimethylsilyl Cleavage Reactions Promoted by Lithium Chloride in THF at Room Temperature

| expt no. | reactant | trap | equiv of LiCl | time, h | % reaction | product, yield (%) | % yield of Me ₃ SiCl |
|----------------|----------|-----------------------------------|---------------|---------|------------|---------------------|---------------------------------|
| 1 | 5 | Me ₂ SiCl ₂ | 0.00 | 42 | 0 | | |
| 2 | 5 | Me ₂ SiCl ₂ | 0.30 | 13 | 82 | 7, 65 | 73 |
| 3 | 5 | Me ₂ SiCl ₂ | 0.30 | 61 | 96 | 7, 73 | 79 |
| 4 | 5 | none | 0.25 | 72 | 46 | 10, 37 ^a | 81 |
| 5 | 5 | Ph ₂ C=O | 0.36 | 96 | 70 | 10, 45 | 64 |
| 6 ^b | 5 | Me ₃ SiOMe | 0.32 | 20 | 84 | 3, 77 | c |
| 7 | 5 | Me ₃ GeCl | 0.87 | 19 | 94 | 9, 79 | 81 |
| 8 | 8 | Me ₂ SiCl ₂ | 0.72 | 46 | 0 | | |
| 9 | 11 | Me ₂ GeCl ₂ | 0.00 | 48 | 0 | | |
| 10 | 11 | Me ₂ GeCl ₂ | 0.74 | 120 | 100 | 12, 84 | 82 |

^aIn addition a small amount of a material tentatively identified as the coupling product between the silenoid, 6, and 5 was obtained. ^bThis reaction was conducted at 60–65 °C rather than at room temperature. ^cBecause of the similarity in retention times for Me₃SiOMe and Me₃SiCl, the yield of Me₃SiCl could not be quantitated.

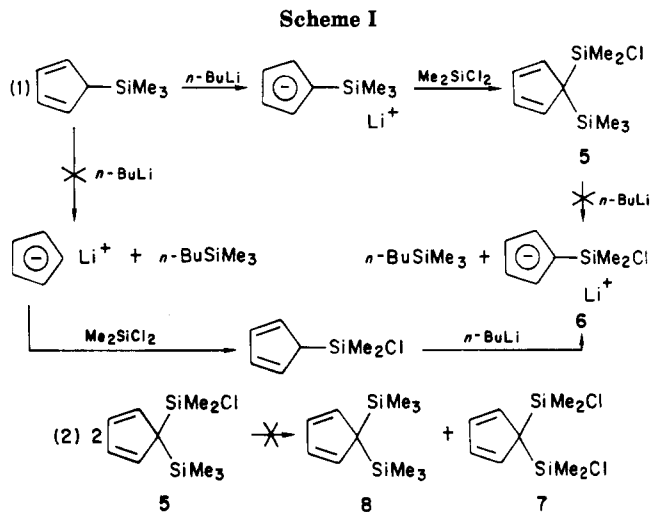
resonance for the silicon methyl protons, and no peaks in the allylic region of the spectrum. The ¹³C spectrum shows a single peak for the methyl and methoxy carbons on silicon and three distinct peaks for the cyclopentadienyl carbons. While compound 3 has two ²⁹Si resonances at 9.3 and -1.7 ppm, compound 4 shows a single resonance at 9.3 ppm. All of these observations are consistent with a significant intramolecular interaction between the methoxy groups on the geminal silyl groups in 4 which may account for the facile elimination of dimethyldimethoxysilane which this compound undergoes to give dimethylsilafulvene.¹

The unprecedented formation of 4 prompted us to investigate the mechanism of its formation in greater detail. The most reasonable precursor is the silenoid, lithium (chlorodimethylsilyl)cyclopentadienide, 6, which could give the bis(chlorodimethylsilyl) compound 7 by coupling with dimethyldichlorosilane. Possible routes for the formation of 6 are illustrated in Scheme I.

These routes, involving the cleavage of a trimethylsilyl group from either the starting material or (chlorodimethylsilyl)(trimethylsilyl)cyclopentadiene, 5, by *n*-butyllithium, can be ruled out on the basis of stoichiometry. The formation of 6 by these pathways requires 2 equiv of *n*-butyllithium while we obtain excellent yields of 7 using only 1 equiv of the lithium reagent. In addition, these pathways require the formation of *n*-butyltrimethylsilane which is not produced in the reaction.⁴ The formation of the bis(chlorodimethylsilyl) compound 7 by a disproportionation reaction of 5 (eq 2) can also be discounted on the basis of stoichiometry and the fact that bis(trimethylsilyl)cyclopentadiene, 8, is not observed in the reaction mixtures.

We have obtained evidence that the initial reaction that occurs is the metalation of cyclopentadienyltrimethylsilane. The ¹H NMR spectrum of the mixture produced by the reaction of cyclopentadienyltrimethylsilane with *n*-butyllithium was completely in agreement with that reported for lithium trimethylsilylcyclopentadienide.⁵ The metalation is rapid and, based on the NMR spectrum, essentially quantitative.

When the reaction was monitored by ¹H NMR after dimethyldichlorosilane addition, it was found that the initial product formed was, as expected, 1-(chlorodimethylsilyl)-1-(trimethylsilyl)cyclopentadiene, 5. As the subsequent, substantially slower, reaction occurred, the



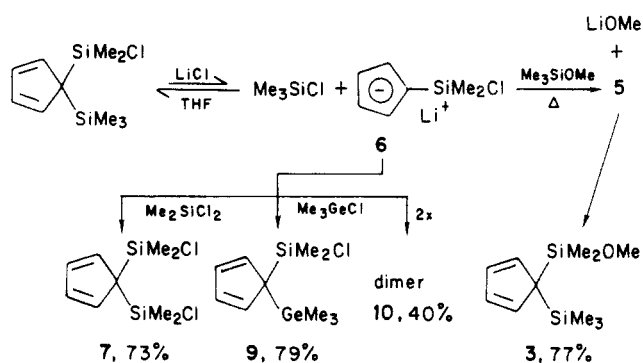
peaks due to 5 and Me₂SiCl₂ diminished and resonances attributable to 1,1-bis(chlorodimethylsilyl)cyclopentadiene, 7, appeared. Significantly, the other product of the reaction was found to be trimethylchlorosilane. Integration of the spectrum when all of 5 had been consumed indicated a 90% yield of Me₃SiCl. After distillation the recovered yield of 7 was 69%. These results indicate clearly that 5 is the precursor of 7 by a process involving the concomitant formation of trimethylchlorosilane.

The reaction apparently only occurs in THF. When hexane was used as the solvent, no 7 is formed and 5 is the major product in 74% isolated yield. Because a major difference between THF and hexane is the solubility of lithium chloride in the former solvent, a series of experiments probing the effects of LiCl on the cleavage of trimethylsilyl-substituted cyclopentadienes were carried out. The results of these experiments are summarized in Table I.

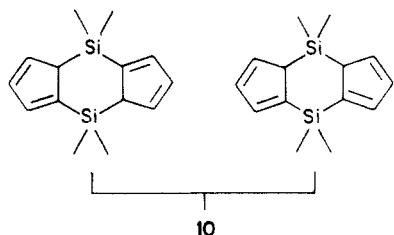
It can be seen that no reaction occurs between 5 and dimethyldichlorosilane (experiment 1) or between (chlorodimethylgermyl)(trimethylsilyl)cyclopentadiene, 11, and dimethyldichlorogermane (experiment 9) in the absence of lithium chloride. The other experiments indicate that cleavage of the trimethylsilyl group from either 5 or 11 occurs to give trimethylchlorosilane in good yields in the presence of less than a stoichiometric amount of LiCl. Because all of the trapping reactions investigated result in the regeneration of LiCl, it functions as a catalyst in these systems. There is no apparent reason that the use of a stoichiometric or excess amount of LiCl could not be used to generate the silenoid 6 or its germanium analogue from 11 under extremely mild and essentially neutral conditions.

(4) An authentic sample of *n*-butyltrimethylsilane was prepared. Whitmore, F. C.; Sommer, L. H.; Digorgio, P. A.; Strong, W. A.; Van Strien, R. E.; Bailey, D. L.; Hall, H. K.; Pietrusza, E. W.; Kerr, G. T. *J. Am. Chem. Soc.* 1946, 68, 475–480. No detectable amounts of the compound were observed in any of the reactions discussed in this paper.
 (5) Kopf, H.; Klouras, N. *Chemica Scripta* 1983, 22, 64–65.

Scheme II



In the absence of a trap (experiment 4), as we have shown previously,¹ **6** undergoes intermolecular coupling with loss of lithium chloride⁶ to give the apparent silafulvene dimers **10**.



The facts that this dimerization is unaffected by benzophenone, a known silafulvene trap,^{3,7} and that no diphenylfulvene, hexamethylcyclotrisiloxane, or octamethylcyclotetrasiloxane are produced in the reaction (experiment 5) are in agreement with our report that the silenoid **6** is the precursor of the dimers at room temperature or below.¹

The results are indicative of an unprecedented cleavage of a silicon-carbon bond by chloride ion under "neutral" conditions which is illustrated in Scheme II. While cleavage or redistribution reactions of organosilanes by electrophilic reagents or by halide ions associated with strong Lewis acids are well-known, cleavage by nucleophilic reagents are much more rare. The cleavage of aryl groups from silicon occurs only with strong bases even when the aryl groups have strongly electron-withdrawing substituents.⁸

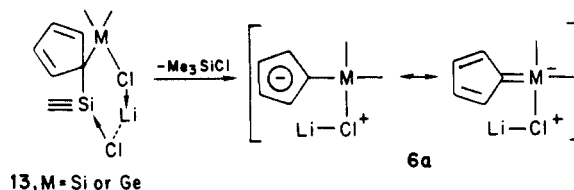
We feel that the lithium chloride reaction must be an equilibrium wherein the back reaction of the silenoid **6** with trimethylchlorosilane to regenerate **5** competes with other reactions. Although **6** has some degree of aromatic stabilization, its concentration must always be low in the reaction systems, consistent with the decreased amount of decomposition and the lower yields of **10** obtained in experiments 4 and 5. The reactions leading to **7** or **9** may also be equilibria which would not be observed under our experimental conditions.

The presence of chloride in the substrate appears to be required. A mixture of bis(trimethylsilyl)cyclopentadiene, **8**, dimethyldichlorosilane, and lithium chloride in THF gave no detectable reaction after 46 h (experiment 8). In addition, no (trimethylgermyl)(trimethylsilyl)cyclopentadiene is produced in the mixed experiment **7**. The formation of this compound would require the cleavage of a dimethylchlorosilyl group from either **5** or **9**. It is pos-

Table II. Solvent-Controlled Syntheses of Group 14 Substituted Cyclopentadienes

| M | solv | isolated yields, % | |
|----|---------|--------------------|----|
| Si | hexanes | 74 | 0 |
| Ge | hexanes | 64 | 0 |
| Si | THF | <1 | 69 |
| Ge | THF | 12 | 40 |

sible that some association between lithium and the chlorosilane or germane, **13**, facilitates the cleavage reaction. However one might anticipate that such an association should be more important in hexane where the reaction does not occur and less significant in THF.



The exact nature of the silenoid intermediate **6** is also not known. It has been suggested that such intermediates have substantial ylide-like character, **6a**.⁶ This suggestion seems inconsistent with the lack of reaction with benzophenone which we observe. Nevertheless it seems clear that solvation of lithium chloride or the silenoid **6** or both by THF is an important factor in the cleavage reaction.

We have observed one reaction in this system which might be interpreted as involving the silafulvene **2** as an intermediate. When a mixture of **5**, lithium chloride, and excess methoxytrimethylsilane, an efficient silene trap,⁹ was heated at 60–70 °C for 20 h, a good yield of **3** was obtained (experiment 6). This result could be interpreted as the loss of LiCl from **6** followed by interception of the silafulvene by methoxytrimethylsilane, a reaction which we have shown occurs to no detectable extent at room temperature.¹ We feel it more likely that **3** arises from a substitution reaction between lithium methoxide and **5**, both of which are formed at the higher temperature by the coupling reaction of the silenoid **6** and methoxytrimethylsilane as is illustrated in Scheme II.¹⁰

The reactions reported herein have substantial synthetic utility. The reaction of **5** with lithium chloride and trimethylchlorogermane in THF provides a convenient, clean route to the mixed chlorosilyl, germyl compound **9**. The intermediate compounds such as **5** or **11** do not have to be isolated. Table II indicates synthetic transformations which can be accomplished directly via the reaction of cyclopentadienyltrimethylsilane and an alkyl lithium reagent. Control of the reaction stoichiometry and/or the solvent provides simple methods for obtaining useful quantities of compounds of the type **3**, **4**, **5**, **7**, **9**, **11**, or **12** in very satisfactory yields. Finally, it should be noted that "one-pot" syntheses of such compounds can easily be designed utilizing the in situ preparation of cyclopentadienyltrimethylsilane by the reaction of cyclopentadienyllithium and trimethylchlorosilane.

(9) Davidson, I. M. T.; Wood, I. T. *J. Chem. Soc., Chem. Commun.* **1982**, 550–551. Jones, P. R.; Lee, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 6725–6726. Cheng, A. H.-B.; Jones, P. R.; Lee, M. E.; Roussi, P. *Organometallics* **1985**, *3*, 581–584.

(10) The labeling experiment required to demonstrate this suggestion in our system is nontrivial and has yet to be performed. Whatever the result, it is not relevant to the fundamental content of this report.

(6) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141–177.
 (7) Nakadaira, Y.; Sakaba, H.; Sakurai, H. *Chem. Lett.* **1980**, *9*, 1071–1074.
 (8) Eaborn, C. "Organosilicon Compounds"; Butterworths: London, **1960**; pp 125–159.

Experimental Section

All reactions were carried out under an inert atmosphere of dry nitrogen or argon in glassware that was either oven dried and assembled hot or flame dried. Hexane or THF were purified by refluxing over and distillation from sodium/potassium alloy or lithium aluminum hydride, respectively, immediately prior to use. Solutions of *n*-butyllithium (Aldrich) were standardized by using the method of Kofron.¹¹ Reagents and solvents were transferred using standard syringe techniques. GLC analyses of reaction mixtures were carried out by using a Perkin-Elmer Sigma-3 gas chromatograph equipped with a 25m SE-54 capillary column, flame ionization detector, and a Hewlett-Packard 3390A reporting integrator. Yields were calculated based on response factors using hexadecane or decane as internal standards. Preparative GLC using a Varian 1800 series gas chromatograph with thermal conductivity detection and an 15% OV-17 on 45/60 mesh Supelcoport, 10 ft by 3/8 in. glass column was routinely used to purify samples for characterization. NMR spectra were obtained by using a JEOL FX 90Q, 90 MHz, or a Perkin-Elmer R24B, 60 MHz, spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained by using a Hewlett-Packard 5970a mass sensitive detector and data system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

1,1-Bis(dimethylmethoxysilyl)cyclopentadiene, 4. To a solution of 6.09 g (44.1 mmol) of cyclopentadienyltrimethylsilane in 100 mL of THF cooled in an ice-water bath was added 27.5 mL of a 1.6 M solution of *n*-butyllithium (44 mmol) in hexane. The cooling bath was removed and the solution stirred for 3 h. The solution was cooled with an ice-water bath, and 10 mL (82 mmol) of dimethyldichlorosilane was added. The solution was stirred at room temperature for 4.5 days. One hundred milliliters of hexane was added, the solution was cooled with an ice bath, and 11.6 mL (143 mmol) of pyridine followed by 10 mL (0.25 mol) of methanol was added. The cooling bath was removed and the mixture stirred overnight. GLC analysis of the mixture showed 5% of 3 and 67% of 4. After filtration of the salts, the solution was concentrated under reduced pressure. Vacuum distillation using a 15-cm column packed with glass beads gave 4.92 g of distillate, bp 70–76 °C at 2 torr, amounting to a 43% isolated yield of 4 and a 3% yield of 3.

Previously unreported for (dimethylmethoxysilyl)(trimethylsilyl)cyclopentadiene, 3.¹ ¹³C NMR (neat, D₂O lock solvent): δ (multiplicity of off-resonance proton decoupled spectrum) 134.4 (d) and 131.0 (d), vinyl; 59.6 (s), allylic; 50.0 (q), methoxy; -1.4 and -3.3 (q), silicon methyl. ²⁹Si NMR (neat): δ 9.3 and -1.7. MS [*m/z* (relative intensity), assignment]: 226 (16), P⁺; 211 (24), P⁺ - Me; 181 (17); 123 (15); 122 (100), P⁺ - Me₃SiOMe; 89 Me₂SiOMe⁺; 73 (44); 59 (46); 45 (16). IR (neat) (cm⁻¹, intensity): 3082, m; 2961, s; 2840, m; 1262, s; 1100, s.

Characterization of 4. ¹H NMR (CDCl₃ reference and lock): δ -0.02 (s), 12 H, SiMe; 3.35 (s) 6 H, OMe; 6.3–6.7 (m), 4 H, vinylic. ¹³C NMR (neat, D₂O lock): δ 133.3 and 131.6 (d), vinyl; 62.7 (s), allylic; 50.0 (q) methoxy; -3.6 (q), silicon methyl. ²⁹Si NMR (neat): δ 9.3. MS [*m/z* (relative intensity), assignment]: 242 (15), P⁺; 227 (16), P⁺ - Me; 123 (17); 122 (100), P⁺ - Me₂Si(OMe)₂; 93 (11), 89 (79), Me₂SiOMe⁺; 59 (57). IR (neat) (cm⁻¹, intensity): 3085, m; 2962, s; 2840, s; 1254, s; 1100, s. Anal. Calcd for C₁₁H₂₂O₂Si₂: C, 54.49; H, 9.15. Found: C, 54.57; H, 9.24.

1-(Chlorodimethylsilyl)-1-(trimethylsilyl)cyclopentadiene, 5. In a three-neck 200-mL round-bottom flask equipped with a condenser, gas inlet, stopper, septum, and magnetic stirring bar was placed a solution of 5.48 g (39.7 mmol) of C₅H₅SiMe₃ in 75 mL of hexane. The solution was cooled with an ice-water bath, and 15.9 mL of a 2.5 M solution of *n*-butyllithium (39.8 mmol) was added. After the mixture was stirred for 30 min, 5.5 mL (45 mmol) of Me₂SiCl₂ was added and the mixture was stirred for 4 h. Approximately 4 mL of THF was added, and the reaction was stirred for 44 h at room temperature. The salts were separated by centrifugation and washed with three 15-mL portions of light petroleum ether. The combined organic portions, after concentration, were distilled under vacuum using a 15-cm column packed with glass beads to give 6.74 g (74% isolated yield) of 5, bp 69–72

°C, (2–3 torr).¹ ²⁹Si NMR (neat): δ 19.7 and -0.6. IR (Nujol): 1253 (Si-Me), 496 cm⁻¹ (Si-Cl).

1,1-Bis(chlorodimethylsilyl)cyclopentadiene, 7. A 75-mL Schlenk flask equipped with a gas inlet, magnetic stirring bar, and septum was charged with 40 mL of THF and 3.43 g (24.9 mmol) of C₅H₅SiMe₃. After the mixture was cooled with an ice-water bath, 10 mL of a 2.5 M solution of *n*-butyllithium (25 mmol) in hexane was added dropwise. After being stirred at room temperature for 30 min, the mixture was cooled by using an ice-water bath and 7.5 mL (63 mmol) of Me₂SiCl₂ was added in one portion. The solution was stirred at room temperature for 3 days at which time its ¹H NMR spectrum indicated that all of the initially produced 5 had been consumed. Most of the solvent was removed under reduced pressure, and 25 mL of hexane was added to precipitate the salts, which were removed by centrifugation and washed with two 10-mL portions of hexane. Vacuum distillation using a 15-cm column packed with glass beads afforded 4.33 g (69% isolated yield) of nearly pure 7, a colorless liquid, bp 59–64 °C (0.20–0.25 torr).

¹H NMR (CCl₄ solvent): δ 0.28 (s) 12 H, SiMe; 6.5–7.0 (m) 4 H, vinyl. ¹³C NMR (neat, CDCl₃ external lock): δ 134.6 and 133.4 (d), vinyl; 59.2 (s), allylic; 1.6 (q), silicon methyl. MS [*m/z* (relative intensity) assignment]: 252 (1.8) and 250 (2.6), P⁺; 237 (2.0) and 235 (3.1), P⁺ - Me; 123 (13); 122 (100), P⁺ - Me₂SiCl₂; 95 (16) and 93 (40), Me₂SiCl₂⁺; 65 (21); 63 (21). IR (Nujol) (cm⁻¹, intensity): 1258, s, Si-Me; 499, s, Si-Cl. Methanolysis of this compound in the presence of pyridine gave 4 quantitatively.

1-(Chlorodimethylsilyl)-1-(trimethylgermyl)cyclopentadiene, 9. To a 50-mL Schlenk flask equipped with a magnetic stirring bar, nitrogen inlet, and septum, charged with 20 mL of hexanes and 1.6 g (8.7 mmol) of cyclopentadienyltrimethylgermane,¹² and cooled with an ice-water bath was added 3.4 mL of a 2.6 M solution of *n*-butyllithium (8.8 mmol) and 1 mL of THF. After the solution was stirred 30 min, 1.2 mL (9.9 mmol) of Me₂SiCl₂ was added along with an additional 4 mL of THF. The mixture was stirred at room temperature for 19 h. The salts were removed by centrifugation and washed with three 5-mL portions of hexanes. Vacuum distillation of the combined organic portions gave 1.79 g (74% isolated yield) of 9 as a colorless liquid, bp 46–47 °C (0.10–0.15 torr). This compound was also prepared in 79% yield by the reaction of 5, LiCl, and trimethylchlorogermane in THF at room temperature, Table I (experiment 7).

¹H NMR (CDCl₃): δ 0.14 (s) 9 H, GeMe₃; 0.27 (s) 6 H, SiMe₂; 6.1–6.6 (m) 4 H, vinylic protons. ¹³C NMR (CDCl₃, -10 °C¹³): -0.9 (q) GeMe₃; 1.5 (q) SiMe₂; 56.8 (s) allylic; 131.4 (d) and 134.6 (d) vinylic. MS: *m/z* (relative intensity) 278 (3.2), 277 (1.7), 276 (6.7), 275 (1.9), 274 (5.6), 272 (2.8), 263 (9), 261 (20), 259 (16), 123 (14), 122 (92), 121 (28), 119 (100), 118 (26), 117 (76), 115 (58), 107 (11), 93 (16), 89 (20), 87 (15), 79 (13), 73 (12), 65 (14), 63 (17), 43 (10).

1-(Chlorodimethylgermyl)-1-(trimethylsilyl)cyclopentadiene, 11. In a 100-mL three-neck flask fitted with a septum, magnetic stirring bar, and argon inlet was placed a solution of 1.05 g (7.58 mmol) of C₅H₅SiMe₃ in 15 mL of hexane. To the solution, cooled with an ice-water bath, was added 3.0 mL of a 2.5 M solution of *n*-butyllithium (7.5 mmol) in hexane, after which the solution was stirred at room temperature for 2 h. The mixture was cooled with an ice-water bath, and 1.68 g (9.71 mmol) of dimethyldichlorogermane was added. After the mixture was stirred at 0 °C for 1 h, 0.5 mL of THF was added and the mixture was stirred at room temperature for 24 h. The precipitated salts were removed by centrifugation and washed with three 5-mL portions of hexane. Vacuum distillation using a 15-cm column packed with glass beads gave 1.35 g (64% isolated yield) of 11, a colorless oil, bp 71–72 °C (0.25 torr).

¹H NMR (CDCl₃): δ 0.05 (s) 9 H, SiMe₃; 0.47 (s) 6 H, GeMe₂; 6.4–6.9 (m) 4 H, vinyl protons. ¹³C NMR (CDCl₃, -10 °C¹³): δ -1.31 (q), SiMe₃; 3.49 (q), GeMe₂; 58.6 (s) allylic; 132.3 (d) and 134.1 (d), vinyl. MS: *m/z* (relative intensity) 278 (1.4), 276 (2.8), 274 (2.1), 272 (1.3), 261 (11), 170 (20), 169 (9), 168 (96), 167 (28), 166 (74), 164 (53), 153 (11), 151 (10), 141 (11), 139 (25), 137 (25),

(12) Davison, A.; Rakita, P. E. *Inorg. Chem.* 1970, 9, 289–294.

(13) The ¹³C NMR spectra of these germanium compounds gave broadened peaks at room temperature. Sharp, well-resolved spectra could be obtained at -10 °C.

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135 (15), 122 (26), 121 (12), 119 (14), 117 (10), 109 (18), 107 (28), 105 (16), 95 (11), 93 (16), 89 (13), 87 (10), 81 (11), 79 (12), 77 (10), 74 (12), 73 (100), 67 (11), 59 (21), 55 (13), 53 (19), 45 (44), 44 (14), 43 (45). Anal. Calcd for $C_{10}H_{19}ClGeSi$: C, 43.61; H, 6.95. Found: C, 43.88; H, 7.08.

1,1-Bis(chlorodimethylgermyl)cyclopentadiene, 12. A solution of 1.47 g (8.47 mmol) of Me_2GeCl_2 in 5 mL of THF was placed in a 50-mL flask equipped with a magnetic stirring bar, argon inlet, septum, and a reflux condenser. The solution was cooled by using an ice-water bath, and 10 mL of an 0.4 M solution of lithium (trimethylsilyl)cyclopentadienide in THF was added by using a syringe. The mixture was stirred at room temperature for 42 h and refluxed for 3 h. After removal of most of the solvent under reduced pressure, the salts were precipitated by adding 15 mL of hexane, separated by centrifugation, and washed with three 5-mL portions of hexane. The combined organic portions were distilled by using a 15-cm column packed with glass beads. The major fraction, bp 60–70 °C at 0.05–0.06 torr, contained 0.13 g (12% isolated yield) of 11 and 0.55 g (40% isolated yield) of 12.

1H NMR ($CDCl_3$): δ 0.61 (s) 12 H, $GeMe_2$; 6.5–7.0 (m) 4 H, vinylic protons. ^{13}C NMR ($CDCl_3$, -10 °C): δ 3.53 (q), $GeMe$; 60.1 (s) allylic; 132.6 (d) and 133.8 (d), vinylic. MS: m/z (relative intensity) 342 (1.5), 340 (1.6), 338 (1.2), 170 (22), 169 (11), 168 (100), 167 (29), 166 (74), 164 (56), 153 (18), 151 (16), 149 (13), 141 (12), 139 (29), 137 (25), 135 (16), 111 (12), 109 (22), 107 (17), 105 (11), 89 (16), 87 (12), 77 (15). Anal. Calcd for $C_9H_{16}Cl_2Ge_2$: C, 31.73; H, 4.85. Found: C, 31.76; H, 4.74.

General Procedure for the Lithium Chloride Catalyzed Cleavage Reactions. The reaction of 5 with lithium chloride is given as a typical example. A Pyrex tube was charged with 25.3

mg (0.60 mmol) of LiCl which was dried by heating with a flame under high vacuum, ca. 0.05 torr. After the solution was cooled, a magnetic stirring bar, 4.0 mL of THF, 250 μ L (2.05 mmol) of Me_2SiCl_2 , and 0.463 g (2.01 mmol) of 5 were added under nitrogen. The tube was degassed and sealed. After 13 h the tube was opened (experiment 2) and the contents were analyzed by GLC using an internal standard method. The starting silane 5 was 82% reacted, and the absolute yields of 7 and Me_3SiCl were 65% and 73%, respectively.

The details and results of these experiments are summarized in Table I. In all of the experiments product identities were confirmed by comparison of GLC retention times, GC/MS, and 1H NMR with those authentic samples. No reaction was observed in the absence of LiCl (experiments 1 and 9) or with bis(trimethylsilyl)cyclopentadiene, 8 (experiment 8).

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Registry No. 3, 78133-11-6; 4, 96502-50-0; 5, 96502-49-7; 6, 98991-12-9; 7, 53212-72-9; 9, 98991-13-0; 10, form a, 78921-94-5; 10, form b, 79317-67-2; 11, 98991-14-1; 12, 98991-15-2; $C_5H_5SiMe_3$, 25134-15-0; Me_2SiCl_2 , 75-78-5; $C_5H_5GeMe_3$, 26168-12-7; Me_2GeCl_2 , 1529-48-2; LiCl, 7447-41-8; Me_3GeCl , 1529-47-1; lithium (trimethylsilyl)cyclopentadienide, 76514-39-1.

Kinetics and Mechanism of the Pyrolysis of Diallyldimethylsilane

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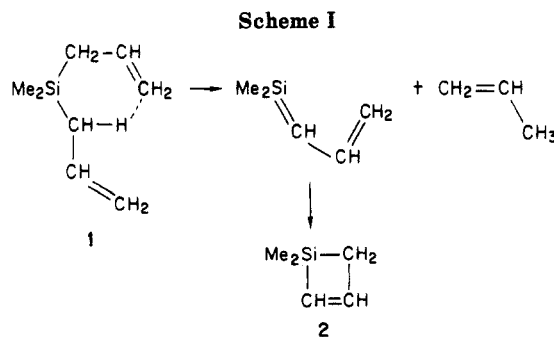
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A gas-kinetic study of the pyrolysis of diallyldimethylsilane is described. The main reaction, for which Arrhenius parameters are reported, is the retroene elimination of propene with formation of a silacyclobutene; there are also extensive secondary reactions which are explained by analogy with the pyrolysis of allyltrimethylsilane. Analogies are also drawn with the pyrolysis of related hydrocarbons.

Introduction

While attempting to study silabutadienes, Block and Revelle found that flash vacuum pyrolysis (FVP) of diallyldimethylsilane (1) at 873 K gave mainly propene and 1,1-dimethyl-1-silacyclobutene (2), with some unspecified minor products.² Very reasonably, they suggested retroene elimination of propene, followed by cyclization of a transient silabutadiene, as shown in Scheme I.

We are actively interested in gas-kinetic studies of the interplay between molecular and radical pathways in the pyrolysis of organosilicon compounds and of the role of silyl radicals, silenes, silenes, and silylenes as intermediates in these pyrolysis mechanisms. By carrying out the first kinetic study of the pyrolysis of allyltrimethylsilane, we were able to show that radical-forming homolysis and a silene-forming retroene reaction were both important primary reactions and that the formation of vinyltrimethylsilane (which



had previously prompted controversial mechanistic speculation) was a secondary reaction resulting from radical addition to allyltrimethylsilane.³ By combining these kinetic studies with deuterium labeling experiments, we have subsequently refined these conclusions to give a

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