borons in 1·Cl⁻ are tetrahedral in solution, simultaneously coordinated to the bridging Cl, rather than equilibrating between trigonal and tetrahedral states. Both 1 and PhBCl₂ abstract chloride from triphenylmethyl chloride and p,p′-dimethoxybenzhydryl chloride.[11]

Crystals of 1·Ph₃PNPPh₃Cl suitable for X-ray diffraction were grown from CH₂Cl₂–hexane by vapor diffusion, and the structure was determined.[12] The B₂Cl₅ grouping appears to adopt two similar but distinguishable conformations in the lattice (Figure 1). A common occupancy factor was refined in least-squares cycles for the chlorines in both of these conformations. The major conformer, represented by nonprimed atoms Cl₁–Cl₅, was refined to a value of 0.60 (1); the minor conformer represented by primed atoms Cl₁′–Cl₅′ was refined to a value of 0.40 (1). Pertinent bond lengths and angles are listed in Tables I and II. In both conformations, the geometries at boron are mildly distorted tetrahedral, with C–B bonds <10° out of the naphthalene plane and nonbridging Cl–B bond lengths deviating by <0.2 Å from the 1.75-Å length found in BCl₃.[13] The apparently short Cl₂′–B₁ length may not be meaningful because of the large thermal disorder associated with Cl₂′. The bridging chlorides are unambiguously observed, with the major conformer featuring a bridge nearly in the plane of the naphthalene, while the minor conformer is marked by a more puckered bridge that may result from the strain involved in squeezing a relatively large anion into a restricted space. *This is the first definitive example of Cl⁻ bridging between two otherwise trigonal borons.*

It is interesting to contrast the two structures of 1·Cl⁻ with the structure of the Cl⁻ complex of o-phenylenedimercury dichloride.[3] Because secondary coordination to Hg tends to be orthogonal to the primary bonds and directionally diffuse, the latter complex features Cl⁻ "perched" over the dimercurials. The vacant orbitals on the borons in 1, however, are directional and convergent,[1] so that it is possible for bridging Cl⁻ to "nest" in the electron-deficient region between the B atoms, particularly in the major conformation.

Extensions of our work on anion complexation to rigid, tridentate Lewis acids are under active pursuit.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for (C₆H₅)₆P₂N·C₁₀H₆B₂Cl₅ (15 pages); a listing observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

## Mechanism of Silanone Extrusion from Alkoxyvinylsilanes

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Summary: Flash vacuum pyrolytic studies of several alkoxyvinylsilanes revealed that, if α-hydrogens were present on the alkyl group, decomposition proceeded by extrusion of Me₂Si=O. Deuterium labeling showed that the process was initiated by a novel 1,5-migration of hydrogen.

Several years ago we established[1] that the gas-phase thermolysis of α-silyl methoxysilanes (1) was a convenient route to silenes 2 and have utilized this reaction in the generation of a variety of theoretically interesting silenes.[2] Thus it was a natural extension to exploit this thermal elimination in the synthesis of 1-silaallenes 4[3] for which the only change would involve departure of the trimethylsilyl group in 3 from an sp²-hybridized carbon rather than one of sp³ hybridization.
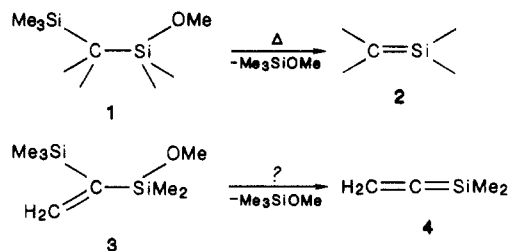
The potential silaallene precursor 3 was synthesized[4] and subjected to flash vacuum pyrolysis (FVP)[6] at temperatures of 750 and 800 °C. Two major products, isopropenylsilane 5 and disiloxane 6, were obtained in respective yields of 34–46% and 35–23% along with lesser amounts (25–12%) of cyclosiloxanes D₃ and D₄.[7] The reaction products reveal no indication of the desired silaallene 4 but strongly suggest the formation of dimethylsilanone, Me₂Si=O. Thus the cyclosiloxanes D₃ and D₄ are cyclic oligomers of dimethylsilanone,[8] 6 can be formed from the well-precedented insertion of silanone into the

(11) The ionization of benzhydryl chlorides by BCl₃ has been exploited in the study of carbocation addition to olefins: Schneider, R.; Grabis, U.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 89–90.

(12) The crystal structure analysis was performed by C. S. Day of Crystalytics Co., Lincoln, NE. A colorless, rectangular parallelepiped crystal of dimensions 0.40 × 0.55 × 0.60 mm was employed. The crystal system was monoclinic, space group P2₁/c, with lattice constants a = 9.974 (3) Å, b = 24.906 (6) Å, c = 17.504 (4) Å, β = 93.93 (2)°, V = 4338 (2) Å³, and Z = 4. The structure was refined to R = 0.055 and Rᵥ = 0.046 by using 2539 independent reflections (≥3 σ(I)) of Mo Kα radiation, 2 θ between 3.0° and 43.0°, and T = 20 °C. The 61 non-hydrogen atoms were located using the SHELXTL Direct Methods programs. All hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp² hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. There were no peaks in the final difference Fourier above the background level (0.24 e/Å³).

(13) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1972; p 223.

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

(2) Barton, T. J.; Burns, G. T. *J. Organomet. Chem.* **1981**, *216*, C5. Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* **1981**, *103*, 6788. Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 2006.

(3) 1-Silaallenes: Ishikawa, M.; et al. *J. Am. Chem. Soc.* **1982**, *104*, 2872. Ishikawa, M.; Ohshita, J.; Yoshihiko, I. *Organometallics* **1986**, *5*, 1518.

(4) Synthesis of 3 was accomplished in 26% yield by Grignard coupling of 1-bromo-1-(trimethylsilyl)ethene⁵ and dichlorodimethylsilane followed by reaction with LiOMe/THF. Characterization was by ¹H NMR, ¹³C NMR, and mass spectra and combustion analysis.

(5) Boeckman, R. K., Jr.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* **1978**, *58*, 152.

(6) FVP was conducted by slowly distilling the neat material through a 30 cm (1.6-cm o.d.) horizontal quartz tube packed with quartz chips. Pressures typically ca. 10⁻⁴ torr are measured behind a liquid N₂ trap whereas reaction-zone pressures are typically about 10⁻³ torr.

(7) Conversion of 3 was ca. 25% at 750 °C and ca. 50% at 800 °C, and yields are based on reacted 3. At 850 °C conversion was 84% but mass recovery was only 53%. At 800 °C both D₃ and D₄ were observed, but at 750 °C only D₄ was obtained.
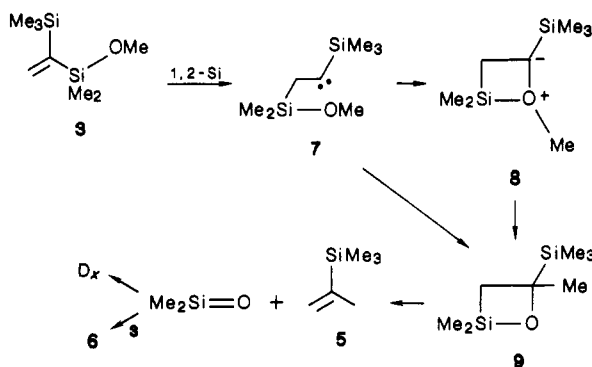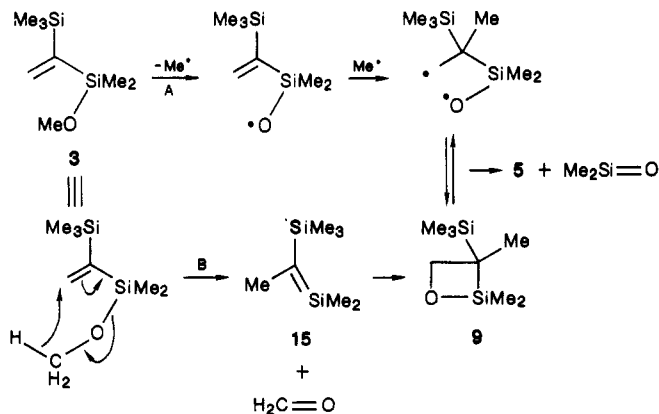
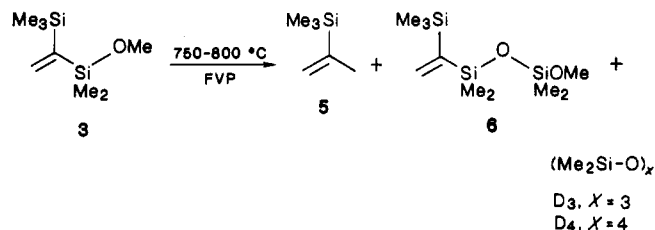(8) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

Scheme I

Scheme II

Si–O bond of **3**, and isopropenylsilane **5** corresponds to the loss of Me$_2$SiO from **3**.


An intriguing possibility for mechanistic rationalization of the surprising extrusion of dimethylsilanone from **3** is that it is initiated by isomerization to carbene **7** via a 1,2-shift of SiMe$_2$OMe (Scheme I). Thus **7** could intramolecularly insert into the C–O bond (either concertedly or via the intermediacy of ylide **8**) to form silaoxetane **9** which would be expected[8] to extrude dimethylsilanone and afford **5**.

Although isomerization of an olefin to an alkylcarbene is certainly anticipated to be quite a high-energy process,[9] there is one apparently documented example involving aryl migration[10] and a very likely example involving silicon migration[11] in the literature. To test the hypothesis of Scheme I the FVP[12] of vinylsilane **10** was conducted and found to produce propene (58%), disiloxane **11** (21%), and minor amounts of D$_3$ and D$_4$, all in accord with this mechanism. Likewise ethoxyvinylsilane **12** afforded butene, disiloxane **13**, D$_3$, and D$_4$,[13] but the butene formed was

Scheme III
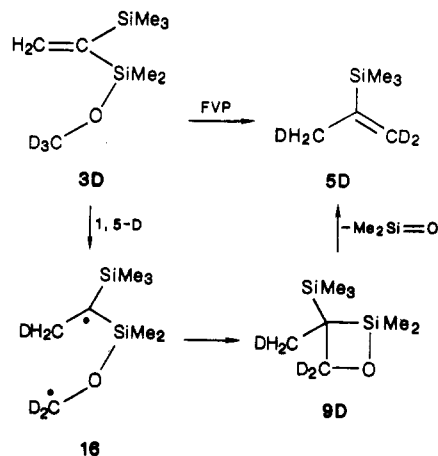
2-butene, and subsequent experiments revealed that the 1-butene required by the carbene mechanism did *not* isomerize to 2-butene under these experimental conditions. Further evidence against the carbene mechanism was found in the FVP of phenoxyvinylsilane **14** which was recovered totally unscathed even at 900 °C.
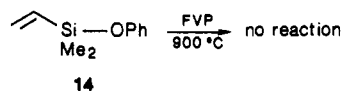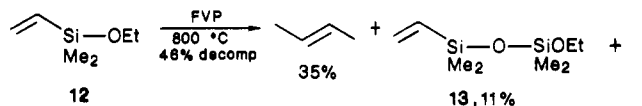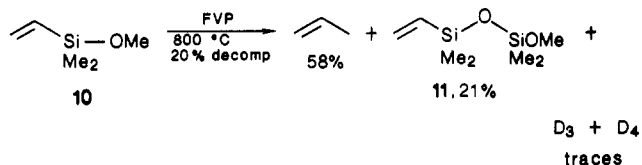
These results are consistent with either a mechanism involving initial C–O homolysis (Scheme II, path A), where it is assumed that the initial 1-butene from **12** is isomerized via hydrogen atom abstractions and that methyl radical addition is regiospecific to produce a radical that is β to two silicons, or by a retro-ene type route (Scheme II, path B) involving concomitant formation of a silene and a carbonyl species which would be expected to cycloadd to the silene to produce silaoxetane **9**. Path B is rendered unlikely by the observations that (1) copyrolysis of **3** and 1,3-butadiene did not intercept silene **15**, (2) no formaldehyde was observed among the products, and (3) copyrolysis of **3** and benzaldehyde did not afford 1-phenylpropene, which would be expected from the reaction of benzaldehyde and **15**.

Both paths A and B of Scheme II (as well as Scheme I) are eliminated from consideration by the results of a single labeling experiment. FVP of the trideuteriomethyl derivative of **3**, **3D**, afforded isopropenylsilane **5D** with the three deuteriums *exclusively* (by ^{1}H and ^{2}H NMR) in the 1,1,3-positions. Futhermore, intramolecularity is strongly supported by the fact that the copyrolysis of equimolar amounts of **3** and **3D** yielded only (from mass spectra) **5** and **5D**. These labeling results force us to the surprising

(9) Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Brinkley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389.

(10) Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936.

(11) Conlin, R. T.; Huffaker, H. B.; Kwak, Y. W. *J. Am. Chem. Soc.* **1985**, *107*, 731.

(12) Yields are corrected for unreacted starting material which at 800 °C for **10** was 80% and for **12** was 54%.

(13) This experiment was complicated by the competing extrusion of ethylene from **12** to produce dimethylvinylsilanol.

conclusion that the decomposition mechanism (Scheme III) is initiated by an intramolecular hydrogen (deuterium) transfer from the methoxyl group to the olefinic terminus to afford the 1,4-diradical **16** which closes to silaoxetane **9D** which in turn proceeds directly to products.[14]

If indeed this mechanism, which fits all the known facts of this decomposition, is correct, one would expect an isotope effect between **3** and **3D**, albeit small at such extreme temperatures. Compounds **3** and **3D** were pyrolyzed in a stirred-flow reactor[15] at 695.4 °C (60 mL/min of He), and from the apparent rate constants for formation of **5** and **5D** k_H/k_D was determined to be 1.34 ± 0.08, consistent with C-H(D) cleavage in the transition state.

Current efforts, which will be reported in a full paper along with complete details of this work, include synthetic modification of **3** so as to promote silaallene formation and/or reduced decomposition temperatures to allow obtainment of reliable Arrhenius parameters for this process. The generality of intramolecular H-atom transfer to produce diradicals is also being probed in carbon systems devoid of silicon.

(14) It is, of course, possible to write the mechanism of Scheme III as an ionic process initiated by hydride transfer. However, in the absence of solvent stabilization, the energetics of charge separation are normally considered to be prohibitive.

(15) Our stirred-flow reactor is modeled after the design of Davidson.[16]

(16) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* 1975, *71*, 972.

Formation of a Trishomocubane Structure Containing Three Rhenium and Eight Arsenic Atom Vertices. The Crystal Structure of {cyclo-[(AsMe)₇(As)Re(CO)₄]Re₂(CO)₆}

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Summary: Pentamethylcyclopentaarsine, cyclo-(AsMe)₅, reacts with Re₂(CO)₁₀ to form {cyclo-[(AsMe)₇(As)Re(CO)₄]Re₂(CO)₆} in 26% yield. The product has been structurally characterized by X-ray methods. The 11 heavy atoms form a trishomocubane structure analogous to that found in [(AsMe)₉Mo₂(CO)₆]; as compensation for the additional electron of each Re(CO)₃ group (compared to Mo(CO)₃), one of the As units has, through demethylation, converted from a two-electron to a one-electron donor. Another of the positions is occupied by a Re(CO)₄ group which functions as the isolobal equivalent of a second naked As atom.

We have proposed[1] that transition-metal, main-group hybrid clusters containing a majority of main-group atoms generally form structures explicable (but not always pre-

(1) Rheingold, A. L.; Fountain, M. E.; DiMaio, A.-J. *J. Am. Chem. Soc.* 1987, *109*, 141.
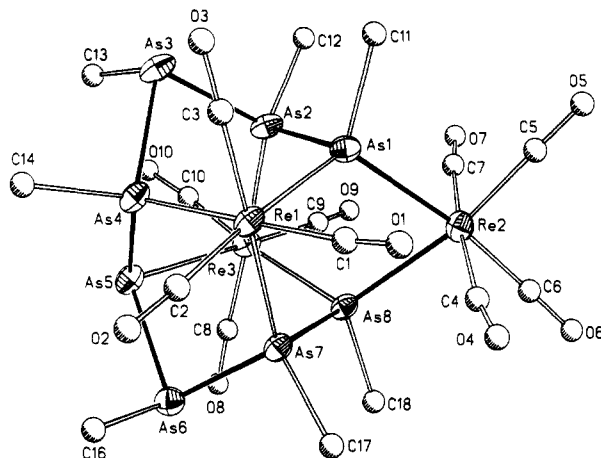
Figure 1. Molecular structure and labeling scheme for **II** as viewed approximately along the Re(1)···Re(3) vector with 40% probability thermal ellipsoids.

Table I. Selected Bond Distances and Angles for II

(a) Bond Distances (Å)

Re(1)-As(1)	2.605 (3)	As(1)-As(2)	2.443 (5)
Re(1)-As(4)	2.543 (4)	As(2)-As(3)	2.419 (5)
Re(1)-As(7)	2.567 (4)	As(3)-As(4)	2.414 (5)
Re(2)-As(1)	2.602 (4)	As(4)-As(5)	2.437 (6)
Re(2)-As(8)	2.601 (3)	As(5)-As(6)	2.406 (5)
Re(3)-As(5)	2.646 (3)	As(7)-As(8)	2.432 (5)
Re(3)-As(8)	2.612 (4)		

(b) Bond Angles (deg)

As(1)-Re(1)-As(4)	90.5 (1)	As(3)-As(4)-As(5)	104.5 (2)
As(1)-Re(1)-As(7)	84.8 (1)	As(4)-As(5)-As(6)	97.9 (2)
As(4)-Re(1)-As(7)	85.7 (1)	As(5)-As(6)-As(7)	95.4 (2)
As(1)-Re(2)-As(8)	77.7 (1)	As(6)-As(7)-As(8)	95.2 (2)
As(2)-Re(3)-As(5)	90.2 (1)	Re(1)-As(1)-Re(2)	118.7 (1)
As(2)-Re(3)-As(8)	95.3 (1)	Re(3)-As(8)-Re(2)	119.9 (1)
As(5)-Re(3)-As(8)	95.9 (1)	Re(2)-As(1)-As(2)	104.0 (2)
As(1)-As(2)-As(3)	96.3 (2)	Re(2)-As(8)-As(7)	102.7 (2)
As(2)-As(3)-As(4)	86.5 (2)		

dictable) by application of two concepts: (1) the overall cluster structure will have isolobal relationships to known (or expected) *main-group* structures and (2) the main-group component will undergo structural modifications as needed to fulfill the steric and electronic demands of the transition-metal components. We illustrated these concepts with the structure of [cyclo-(AsPh)₉Mo₂(CO)₆] (**I**) which formed an isolobal trishomocubane structure in good yield from Mo(CO)₆ and cyclo-(AsPh)₆. As a test of these concepts, we were curious to learn the results of substituting a metal center of higher electron count, e.g., Re(CO)₃ for Mo(CO)₃. If a trishomocubane structure persisted, what structural accommodations would be necessary in the main-group and transition-metal portions of the structure? To this end we now report the product of the reaction of Re₂(CO)₁₀ with cyclo-(AsMe)₅ which does lead to a trishomocubane structure, {cyclo-[(AsMe)₇(As)Re(CO)₄]Re₂(CO)₆} (**II**), but with some unusual structural accommodations needed to achieve this result.

I   II