azide (not isolated) was diluted (10^{-3} M) in cold DMF, made slightly basic with DIEA, and stored at 4 °C for 2 days. The product, purified on a column of silica gel (MeOH in $CHCl_3$ as eluent), was isolated as a homogeneous material which crystallized from MeOH: ether as a complex with 2 equiv of NaOAc: 40%, mp 218–219 °C, $[\alpha]^{23}_{D}$ +40° (*c* 0.5, MeOH). The peptide was desalted on a column of Rexyn I-300 with 50% ETOH as eluent to give VII, cyclo-(Glu^1-Pro^2-Gly^3-Lys^4-Pro^5-Gly^6)-cyclo-(1γ → 4ε)-Leu^7-Phe^8-Ala^9, which crystallized from MeOH–ether as fine, soft needles: mp 215–216 °C. Mass spectrum $(M + H)^+$ 879 (field desorption and fast atom bombardment). No ninhydrin or fluorescamine reaction with this compound was observed. Satisfactory amino acid and elemental analyses were obtained in all cases for this peptide and the synthetic intermediates.

The above described synthesis resulted in a homogeneous bicyclic peptide in respectable yield. This strategy and methods are being used for the preparation of analogous peptides.

Conformational and metal binding studies are being performed. Initial circular dichroism measurements (in acetonitrile) indicate that the bicyclic peptide binds Zn^{2+} in a 2:1 peptide to Zn^{2+} ratio. Changes in NMR spectra (^{13}C and ^1H) have also occurred upon addition of Zn^{2+}. These changes, as well as those caused by other metal ions, are being investigated.

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Evidence for the Intermediacy of Hexamethyl-1,4-disilabenzene[1]

Jonathan D. Rich and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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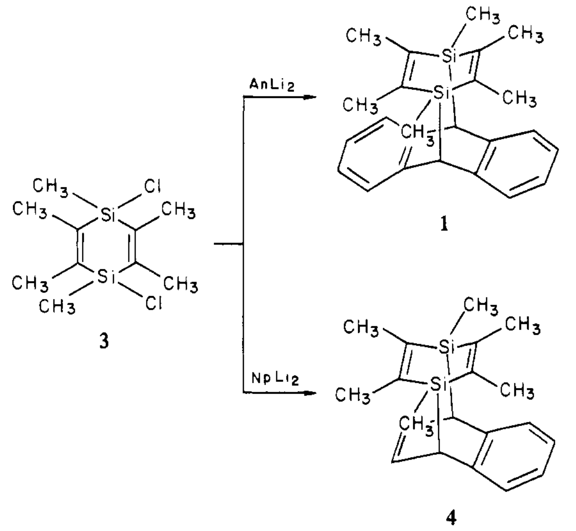
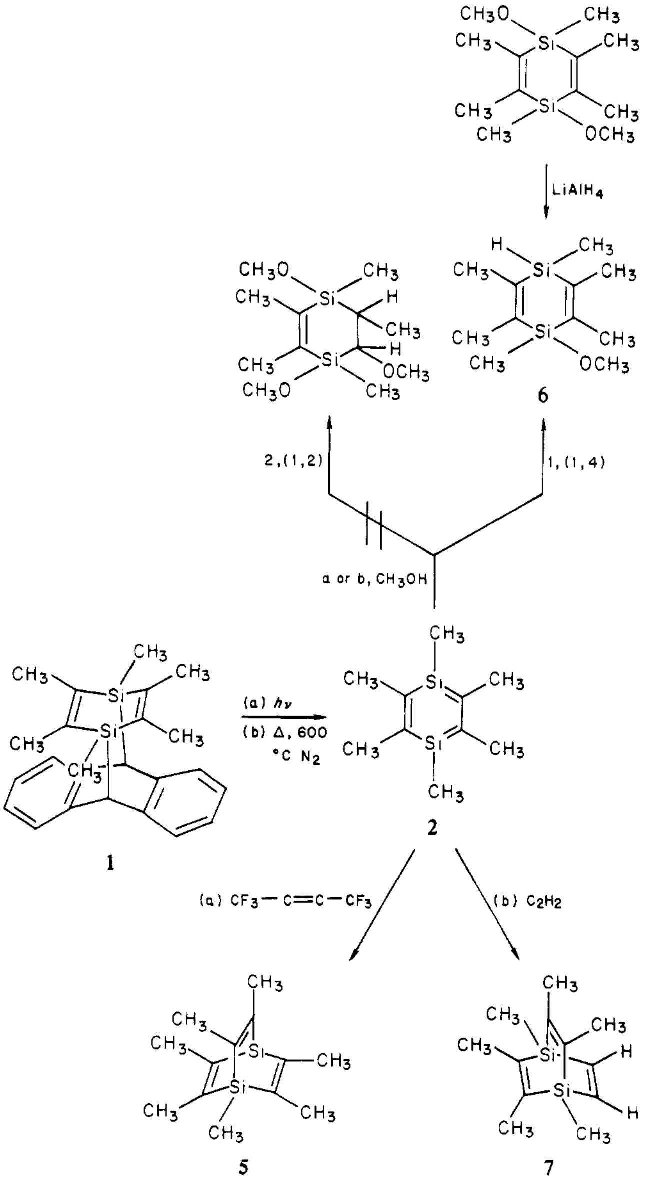
The pioneering work of Barton and co-workers on the generation of silatoluene[2] provided the first example of a potentially aromatic, silicon-containing analogue of benzene. Two other examples of silabenzene intermediates have recently been described.[3] We now report evidence for the existence of the first polysilabenzene, hexamethyl-1,4-disilabenzene (**2**) obtained by photochemical or thermal fragmentation of the precursor **1**.

Reaction of a 1:1 mixture of *cis*- and *trans*-1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene (**3**) with lithium and either anthracene or naphthalene gave the corresponding bridged adducts **1** and **4** in 25% yields.[4] Both of the adducts fragment under mass spectroscopic conditions in a manner consistent with formation of the disilabenzene; **1** gives a peak with *m/e* 194 (corresponding to the elements of **2**) as the base peak, while **4** gave *m/e* 194 as 27% of the base peak, naphthalene. Subsequent studies were carried out on the anthracene adduct **1**, which is easily recrystallized from THF.[6]



Scheme I



Photolysis of **1** in THF at 254 nm gave anthracene as the only volatile product. When **1** was irradiated in the presence of hexafluoro-2-butyne, anthracene was again isolated but now the disilabarralene derivative **5** was also formed in 88% yield (Scheme

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[1] Preliminary results of this work were presented at the 16th Symposium on Organosilicon Chemistry, Midland, MI, June 16, 1982.

[2] (a) Barton, T. J.; Banasiak, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5199. (b) Barton, T. J.; Burns, G. T. *Ibid.* **1978**, *100*, 5246.

[3] (a) For a review of previous attempts to generate silabenzenes see: Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 232. (b) 1,4-Di-*tert*-butylsilabenzene: Märkl, G.; Hofmeister, P. *Ibid.* **1979**, *18*, 780. (c) Parent silabenzene: Maier, G.; Mihm, G.; Reisenauer, H. P. *Ibid.* **1980**, *19*, 52. (d) Photoelectron spectra of silabenzene: Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Ibid.* **1980**, *19*, 51.

[4] Compound **3** is conveniently synthesized from the corresponding dimethoxy derivative[5] and acetyl chloride.

[5] Atwell, W.; Weyenberg, D. *J. Am. Chem. Soc.* **1968**, *90*, 3848.

[6] Anthracene adduct **1**: mp 246–247.5 °C; NMR (CCl_4, Me_4Si) δ 6.8–6.9 (m, 8 H), 3.5 (s, 2 H), 1.4 (s, 12 H), 0.4 (s, 6 H); mass spectrum *m/e* 372 (8.2), 194 (100), 179 (18).

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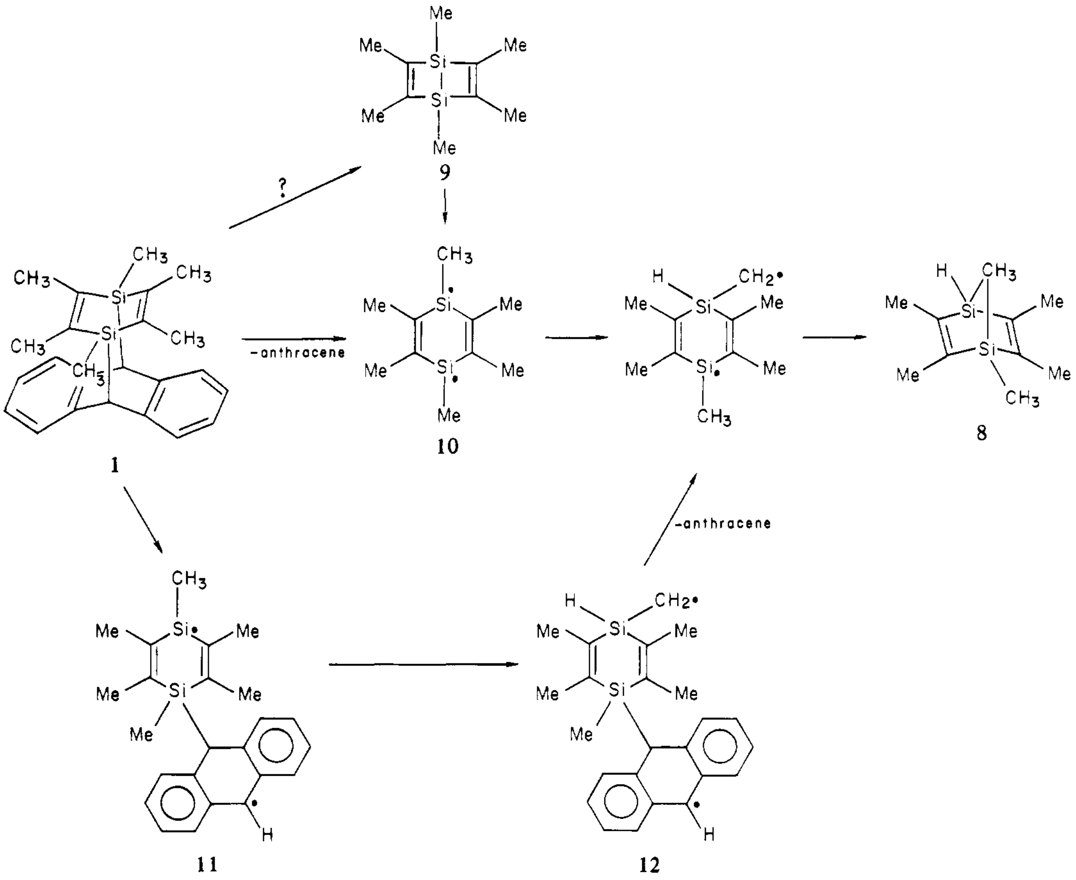
Scheme II



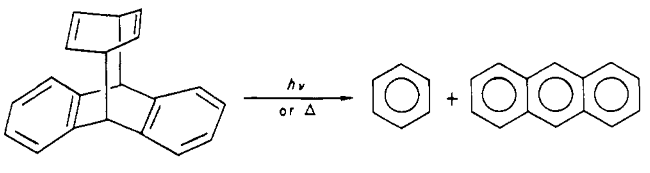
I).[7] This compound can be explained as arising from a Diels–Alder [4 + 2] reaction of 1,4-disilabenzene and hexafluoro-2-butyne.

Methanol is a commonly used trapping reagent for silicon–carbon doubly bonded intermediates.[8] If disilabenzene were trapped with methanol, two competing reactions could be envisioned: the two silicon–carbon double bonds could react separately to give the product arising from two 1,2-additions, or methanol could add in a conjugate 1,4-addition to yield a 1-methoxy-4-hydrodisilacyclohexadiene. As shown in Scheme I, photolysis of **1** in THF with an excess of methanol gives *only the 1,4-adduct* **6** as a 1:1 mixture of cis and trans isomers in >95% yield based on anthracene formed. Copyrolysis of **1** and methanol at 600 °C in a nitrogen flow reactor also gives a 38% yield of **6**, again as a 1:1 mixture of isomers. The structure of **6** was proven by independent synthesis from the careful reduction of 1,4-dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene with lithium aluminum hydride.

Further evidence for the generation of a 1,4-disilabenzene as an intermediate in the thermolysis of **1** comes from its reaction with acetylene. Pyrolysis of **1** in a flow system at 600 °C using a mixture of nitrogen and acetylene as the carrier gas gives the Diels–Alder trapping adduct **7** in low yield.[9]

When **1** was flash vacuum pyrolyzed at 700 °C (5×10^{-5} torr), anthracene was formed along with a new compound in 8% yield. NMR and mass spectrometry evidence leads us to assign the minor product as 1,2,3,5,6-pentamethyl-1,4-disilabicyclo[2.2.1]hepta-2,5-diene, **8**.[10] Some possible mechanisms for formation of this product are outlined in Scheme II. Cleavage of **1** might lead either directly or through the Dewar isomer **9** to a cyclodisilane diradical **10**, which could then undergo a hydrogen transfer and ring closure to give the observed norbornadiene product. An alternative that cannot be ruled out involves initial silicon–carbon bond cleavage to give the diradical **11** followed by hydrogen migration and cleavage of the other silicon–carbon bond to give **12**, which leads to the observed product.

It is clear from our experiments that hexamethyl-1,4-disilabenzene is being generated from the thermal and photochemical extrusions of anthracene from **1**. The high yields of the photochemical trapping products compared with the lower yields in the thermolysis are consistent with orbital symmetry arguments, whereby fragmentation of **1** to **2** is allowed photochemically but forbidden thermally. They also agree with the recent results of Yang and co-workers on the analogous all-carbon molecule **13**, which similarly fragments to benzene and anthracene, in high yield photochemically and in low yield thermally.[11]



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[7] **5** was isolated by preparative VPC; NMR (C_6D_6) δ 1.65 (s, 12 H), 0.55 (brs, 6 H); mass spectrum calcd $C_{14}H_{18}Si_2F_6$, 356.0851; obsd 356.0850.

[8] Bush, R. D.; Golino, C. M.; Homer, G. D.; Sommer, C. H. *J. Organomet. Chem.* **1974**, *80*, 37.

[9] GC–mass spectrum *m/e* 220 (p^+, 21), 205 ($p^+ - CH_3$, 100), 166 ($p^+ - CH_3C{\equiv}CCH_3$, 4), 151 (*m/e* 166 − CH_3, 21.7).

[10] **8** was isolated by preparative VPC; NMR (200 mH, C_6D_6) δ 4.83 (s, 1 H), 1.91 (q, J = 0.01 Hz, 6 H), 1.78 (q, J = 0.01 Hz, 6 H), 0.43 (s, 2 H), 0.40 (s, 3 H). The downfield shift of the singlet resonance at δ 0.43, assigned to the bridging CH_2 group, is similar to that observed for the analogous protons in norbornadiene. The singlet at δ 0.40 assigned to Si–CH_3 has the same chemical shift as that observed in other bicyclic silanes.[2]

[11] Yang, N. C.; Chen, M.; Chen, P.; Mak, K. T. *J. Am. Chem. Soc.* **1982**, *104*, 853.

USAF, under Grant No. AFOSR 82-0067.

Registry No. **1**, 83447-53-4; *cis*-**3**, 83447-54-5; *trans*-**3**, 83447-55-6; **4**, 83447-56-7; **5**, 53447-57-8; *cis*-**6**, 83447-58-9; *trans*-**6**, 83447-59-0; **7**, 83447-60-3; **8**, 83447-61-4; anthracene, 120-12-7; naphthalene, 91-20-3; hexafluoro-2-butyne, 692-50-2; methanol, 67-56-1; 1,4-dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene, 23119-27-9; acetylene, 74-86-2.

Characterization of Catalyzed Carbon Surfaces by Derivatization and Solid-State NMR

C. A. Mims,* K. D. Rose, and M. T. Melchior

Exxon Research and Engineering Company
Linden, New Jersey 07036

J. K. Pabst

Exxon Research and Engineering Company,
Baytown, Texas 77520

Received March 29, 1982

We have investigated the active form of alkali salts involved in the catalysis of the H_2O–carbon and CO_2–carbon reactions. Using a combination of surface derivatization and solid-state ^{13}C NMR, we show that an appreciable fraction of potassium on a K_2CO_3-catalyzed carbon is bonded to the surface in the form of surface salt complexes. Included in these surface complexes are salts of surface carbon oxides that have been previously proposed as intermediates in the mechanism of catalyzed gasification.

Catalysis of gas-carbon reactions by alkali metal salts has been appreciated and studied for over a century.[1] Because of the difficulties in studying gas–solid reactions in general, the reaction pathways of both catalyzed and uncatalyzed systems are still uncertain despite a significant amount of research. Many workers, beginning with Fox and White[2] and Kröger,[3] have rationalized the catalysis by a cycle of reactions in which the alkali salt reacts first with the carbon substrate and then with the gas phase. In such mechanisms the interaction between the carbon and the alkali carbonate (calculated to be the stable phase under H_2O–C reaction conditions)[4] is represented by a global reaction:

$$K_2CO_3 + 2C \rightarrow 3CO + 2K \tag{1}$$

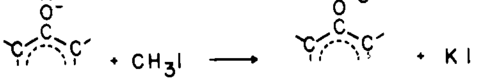
The carbonate is subsequently regenerated by a series of reactions with the gas phase:

$$2K + 2\ H_2O \rightarrow 2\ KOH + H_2 \tag{2}$$

$$2KOH + CO \rightarrow K_2CO_3 + H_2 \tag{3}$$

Others, notably Long and Sykes,[5] have postulated the existence of surface oxides, especially phenoxy analogues, as key intermediates in the catalyzed reaction. We[6] and others[7] have supported the idea that the potassium catalyst exists at gasification conditions in a highly dispersed state as surface salt complexes. We believe that this most satisfactorily explains the reproducibility of the catalytic effect and is supported by the fact that K_2CO_3 in contact with carbon or coal reacts to evolve CO_2 at ~450 °C,[6] a temperature much below the decomposition temperature of K_2CO_3.

Functionalities on "graphitic" carbon surfaces are amenable to derivatization chemistry analogous to that of simple aromatic molecules. Model reactions have been used previously to characterize surface groups on solid surfaces including coal[8] and carbons.[9] The advent of high-resolution solid-state NMR techniques[10] using cross-polarization and magic-angle sample spinning (CPMAS) greatly improved the ability to characterize the solid reaction product.[11] To test the potassium-catalyzed carbon surface for anionic functionalities formed before and during gasification, we have used methylation by CH_3I, shown here for a hypothetical surface phenolate group:



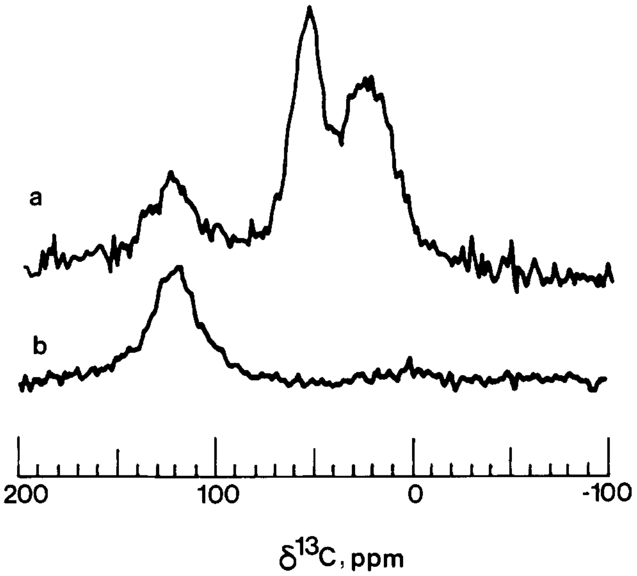


Figure 1. CPMAS ^{13}C NMR spectra of potassium-catalyzed carbon samples (a) after and (b) before methylation by reaction with $^{13}CH_3I$ (40% ^{13}C).

We prepared catalyzed carbon samples by K_2CO_3 solution impregnation of Spherocarb (Analabs, Inc.), a high purity, high surface area, nonfriable carbon. Sufficient carbonate (30 wt %) was added to give a K/C atomic ratio of 0.05. A sample of the active surface was prepared by allowing the impregnated carbon to react in a flowing H_2O/H_2 mixture (1:1 molar ratio) at 700 °C. After 15 min approximately 15% of the carbon had been gasified and a constant reaction rate had been reached. Argon was then substituted for the reactant gas, and the sample was immediately cooled and methylated at ambient temperature by slurrying the carbon in a solution of methyl iodide and anhydrous tetrahydrofuran. Air and water were excluded until the alkylation was complete. Analysis of the methylated samples was aided by the use of isotopically labeled CH_3I. $^{14}CH_3I$ (6×10^{-5} Ci/mol) followed by combustion/radioassay was used for quantitative analysis and ^{13}C enrichment (40%) afforded enhanced NMR sensitivity to the added groups.

Figure 1a shows the solid-state ^{13}C NMR spectrum of the gasified and methylated sample.[12] The resonance band at ~128

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