Organometallics **1987**, *6*, 1977–1984

tified to promote C–C bond formation in the isocyanide systems therefore had to be applied to a greater degree in the CO case. A more electron-rich substrate complex was needed, closer nonbonded carbon–carbon contacts had to be developed, a stronger reducing agent and an R group (Me_3Si) preferential for oxygen were used, and Lewis acid activation to reduce the C≡O bond order was found to be necessary. That these factors favoring reductive coupling could be extrapolated from the isocyanide to the carbonyl case suggests that it might be possible to couple reductively other linear ligands, for example NO, carbenes, carbynes, CN^-, or acetylides.

Acknowledgment. This work was supported by National Science Foundation Grant NSF CHE85-42205.

Registry No. 1, 109467-49-4; 2, 99797-93-0; 4, 109467-51-8; 5, 66507-17-3; 6, 61916-36-7; $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2I]$, 109467-50-7; $[(C_5Me_5)_2ZrCl_2]$, 54039-38-2; $Me_3SiOSO_2CF_3$, 27607-77-8.

Supplementary Material Available: Tables S1–S8 containing non-hydrogen atom thermal parameters and hydrogen atom positional parameters for 1–4 (4 pages); listings of structure factors for 1–4 (47 pages). Ordering information is given on any current masthead page.

Ab Initio Calculations on Some C_3SiH_4 Isomers

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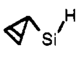
Restricted Hartree–Fock ab initio calculations have been performed on various isomers of silacyclobutadiene (C_3SiH_4). Geometry optimizations were performed by using various basis sets. Geometric results were similar, but proper description of relative energies required the larger 6-31G* basis. Calculations treating election correlation at the MP2 level were performed on the seven lowest energy structures. These calculations gave similar results. The most stable species found is 2-methylsilacycloprop-2-en-1-ylidene. Silacyclobutadiene is almost 60 kcal mol^{-1} less stable, while silatetrahedrane lies a further 32 kcal mol^{-1} higher in energy. The most stable isomer with normal valence is 2-silabut-1-en-3-yne, 28.2 kcal mol^{-1} above the global energy minimum.

Introduction

There is currently much interest in the thermal isomerization of organosilicon molecules that are strained or possess an unsaturated silicon atom. The isomers of C_3SiH_4 are particularly relevant in this context, since many of them contain these structural features and the analogous hydrocarbons such as cyclobutadiene, methylenecyclopropene, and tetrahedrane have been the object of many investigations. The experimental work of one of us involves the photochemical generation of cyclopropenylsilylenes (substituted derivatives of a C_3SiH_4 isomer) and their subsequent transformations. In connection with this work, ab initio molecular orbital calculations have been performed on a number of isomers of the parent, C_3SiH_4, system. Species studied include the parent cyclopropenylsilylene, **1**, silacyclobutadiene, **2**, silatetrahedrane, **3**, silylidenecyclopropene, **4**, 2-silabicyclo[1.1.0]butanylidene, **5**, 2-methyl-1-silacycloprop-2-en-1-ylidene, **6**, 2-methylenesilacycloprop-1-ylidene, **7**, silacyclobut-2-en-1-ylidene, **8**, and 1- and 2-silamethylenecyclopropene, **9** and **10**. For comparison, eight isomeric acyclic silenes and silylenes were studied: 1- and 2-propynylsilylene, **11** and **12**, methylethynylsilylene, **13**, 1-sila-1-buta-1,3-dienyldiene, **14**, 1,2-propadienylsilylene, **15**, 1-silabutatriene, **16**, and 1- and 2-silabut-1-en-3-yne, **17** and **18**. Calculations on several other isomers showed them to be higher in energy; they are not reported here. Our primary intent was to discover the energetic global minimum of the system and to determine how destabilized the other isomers were in relation to it. We were particularly interested in the relative stabilities of **1** and some of its possible isomerization products, such as **2**, **3**, **4**, and **5**.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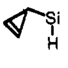
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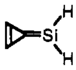
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5

The relative stabilities of the isomers will be governed by various principles. First, the weakness of π bonding involving silicon should disfavor structures with silicon–carbon double bonds and especially those with silicon–carbon triple bonds. Where possible, alkyl substitution on silicon provides more stabilization than hydrogen substitution. The stability of silylenes (divalent silicon species) compared to tetravalent silicon is greater than that of carbenes compared with tetravalent carbon.[2] Finally, silacyclobutadiene may be somewhat destabilized due to antiaromaticity. Due to the poor π overlap noted above, this effect is liable to be small.

Several theoretical studies have been performed on silaethylene and its isomer, methylsilylene. Schaefer and co-workers[5] examined these compounds, along with silylmethylene, in both the singlet and triplet states. This study found silaethylene and methylsilylene to be close in energy, while the carbene isomers and all of the triplet

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(1) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163–168.
(2) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–252.
(3) Gordon, M. S. *Chem. Phys. Lett.* **1978**, *54*, 9–13.
(4) Hood, D. M.; Schaefer, H. F., III *J. Chem. Phys.* **1978**, *68*, 2985–2986.
(5) Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 7644–7650.

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states were much less stable. Further, the results of calculations with and without treatment of electron correlation were similar when polarized basis sets were employed. When electron correlation was included the double-bonded structure was favored relative to the silylene by about 4 kcal mol^{-1}.[6] Finally, a large barrier for interconversion of the two (41.0 kcal mol^{-1} at the best level of theory) was predicted.

Schaefer has also studied silacyclobutadiene.[7] His studies focused on its geometry and the relative energies of its lowest singlet and triplet states. He concluded that this compound was a ground-state singlet. Force constants, obtained by finite difference, suggested that the molecule was planar.

Earlier, Gordon had studied silatetrahedrane and silacyclobutadiene.[8] His calculations involved geometry optimization with the split-valence 3-21G basis set, followed by single-point energy calculations using the polarized 6-31G* basis (RHF/6-31G*//RHF/3-21G). He concluded that silacyclobutadiene lay 33.3 kcal mol^{-1} lower in energy than silatetrahedrane and 56.3 kcal mol^{-1} lower than the dissociation products, acetylene and silaacetylene. (Note that silavinylidene, rather than silaacetylene, is the most stable isomer of that dissociation product.[9])

In a subsequent study of disilatetrahedrane isomers,[10] silylenes were found not only to be stable species but also to be the most stable species. In fact, the only local minimum found which was not a silylene was disilatetrahedrane, although it lay more than 80 kcal mol^{-1} above the most stable isomer.

Barthelat, Trinquier, and Bertrand studied several isomers of C_2SiH_4 by using a pseudopotential basis set.[11] A result pertinent to the present work is that the species with sp hybridization at silicon, 2-silapropyne, and 2-silaallene were extremely high in energy relative to the most stable species studied, 3-silapropyne. Related work by Gordon and Koob[12] confirmed these results and used bond separation reactions to estimate substituent effects on the stabilities of the silylenes and silenes.

A later study of silabutadienes and isomeric silylenes by Trinquier and Malrieu[13] again found that silenes and silylenes were comparable in energy and that for both species the silicon preferred the inner rather than terminal position. These results will be compared below with those for acyclic C_3SiH_4 species.

Computational Methods

All of the calculations reported here were done by using the GAUSSIAN-82 suite of programs.[14] Geometries were optimized by using the Berny method[15] at both the 3-21G*[16] (RHF/3-21G*//RHF/3-21G*) and 6-31G*[17] (RHF/6-31G*//RHF/6-31G*) levels, using the symmetry restrictions noted. Vibrational frequency calculations were not performed. Such calculations would determine whether the structures obtained were true minima or other types of stationary points, such as transition states. The Berny algorithm produces approximate second derivatives, and, in every case, these suggest that the structures obtained are true minima. Since these structures incorporate many very different types of bonds (localized and delocalized π bonds, bonds in strained rings, and nonbonding lone pairs in silylenes), it is possible that electron-correlation corrections could be important. For the seven isomers of lowest energy, correlated calculations at the MP2 level[18] were performed at the 6-31G* optimized geometries. (These calculations used a slightly different polarized basis set for silicon,[1] but this produces only small changes in the energies, and should not change the relative energies by more than 1 kcal mol^{-1}.)

Table I. Relative Energies of Various Isomers (kcal mol^{-1})

compd	symmetry	3-21G*	6-31G*	MP2
1a	C_S	67.3	59.5	
1b	C_S	67.7	59.8	
2	C_S	55.9	59.5	
3	C_{3V}	94.5	91.5	
4	C_{2V}	70.3	59.2	
5	C_S	30.4	25.1	
6	C_S	(0)[a]	(0)[b]	(0)[c]
7	C_S	23.3	27.1	
8	C_S	7.6	10.2	12.0
9	C_{2V}	36.2	43.6	
10	C_S	64.4	66.9	
11	C_S	12.0	17.8	23.6
12	C_S	20.8	35.1	
13	C_S	7.2	18.0	21.6
14	C_S	18.3	20.4	20.4
15	C_S	23.6	26.3	32.9
16	C_{2V}	28.9	36.9	
17	C_S	30.1	35.9	
18	C_S	15.3	28.2	26.9

[a] Calculated energy: −402.697 648 1 au. [b] Calculated energy: −404.772 375 0 au. [c] Calculated energy: −405.223 89 au.

Several of the compounds studied can exist in different conformations. The propynyl- and propadienylsilylenes all preferred the anti conformations shown. Both the syn and anti conformations are reported for cyclopropenylsilylene. The conformations of 2-methylsilacycloprop-2-en-1-ylidene and 2-silylcyclopropenylidene with one methyl hydrogen syn to the double bond are lowest in energy. In the cases of 1-propynylsilylene and methylethynylsilylene, the orientation shown for the methyl group was the only one studied.

Symmetry requirements were imposed upon several of the structures. These include requiring silacyclobutadiene, the cyclopropenyl- and cyclobutenylsilylenes and the sila-substituted methylenecyclopropenes, as well as all of the acyclic isomers, to have a plane of symmetry, silatetrahedrane to have C_{3v} symmetry, and 2-silabicyclo[1.1.0]butanylidene to have a mirror plane. In the case of cyclopropenylsilylene, the assumption of C_s symmetry was tested. After the geometries with C_s symmetry were optimized, the silicon–hydrogen bond was rotated a few degrees from its symmetric position syn or anti to the three-membered ring. Optimization of all geometric parameters from those starting points returned to the C_s

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(6) At very high levels (MP4(SDQT) with a triple-ζ + polarization functions basis at an MP2/6-31G(d)-optimized geometry and including zero-point energy corrections), silaethylene is found to lie 3.2 kcal mol^{-1} below methylsilylene (Truong, T. N.; Gordon, M. S. submitted for publication in *J. Am. Chem. Soc.*

(7) Schaefer, H. F., III *Faraday Symp. Chem. Soc.* **1984**, *19*, 39–48.

(8) Gordon, M. S. *J. Chem. Soc., Chem. Commun.* **1980**, 1131–1132.

(9) Hoffmann, M. R.; Yoshioka, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 1084–1088.

(10) Holme, T. A.; Gordon, M. S.; Yabushita, S.; Schmidt, M. W. *Organometallics* **1984**, *3*, 583–586.

(11) Barthelat, J.-C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1979**, *101*, 3785–3789.

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(16) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039–5048.

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(18) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1981; pp 38–40.

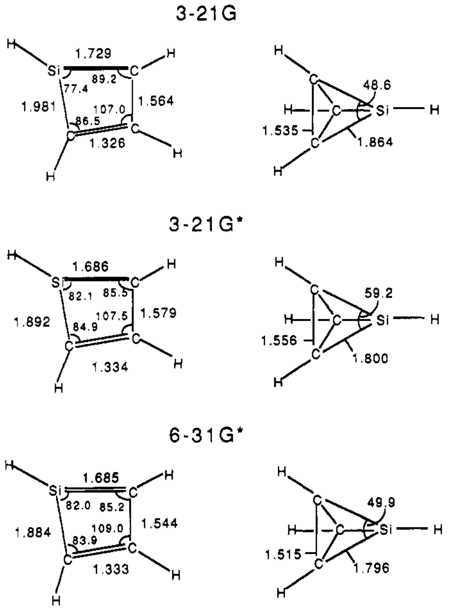

Figure 1. Comparison of silacyclobutadiene and silatetrahedrane geometries obtained with various basis sets. Distances are given in Angstroms, angles in degrees.

geometries. (Due to the numerical thresholds employed, geometric parameters varied from symmetrical values by tiny amounts.) In order to check for another minimum far from C_s symmetry, the silicon–hydrogen bond was rotated 50° from the transoid form. Optimization again returned it to the symmetrical form.

Results

The energies for all species studied are given in the Table I. The optimized geometric parameters are shown in Table II. Figure 1 shows the geometric results for silatetrahedrane and silacyclobutadiene, along with Gordon's earlier 3-21G optimized geometries. All three basis sets give similar geometries. Relative energies, on the other hand, change when polarization functions are used. It is known that polarization functions are required to describe the energies of small ring compounds properly.[19] The compounds with carbocyclic three-membered rings have no polarization functions in the 3-21G* basis set, but do in the 6-31G*. As would be expected, these are treated differently by the two basis sets. For example, the relative energies of silylidenecyclopropene and 2-methylenesilacyclopropene invert depending upon the basis set used. In fact, the compounds containing a carbocyclic three-membered ring (**1**, **3**, **4**, and **5**) are stabilized by an average of 12 kcal mol^{-1} more than the others on going to the larger basis set.

The global minimum of the system was found to be the cyclic silylene, 2-methylsilacycloprop-2-en-1-ylidene, **6**.

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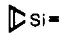

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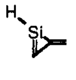

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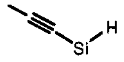
This compound contains a three-membered ring, but the vacant p orbital at silicon can interact with the double bond to form an aromatic system. The isomeric silylene **7**, which lacks this aromatic stabilization lies 27 kcal mol^{-1} higher in energy. The larger ring silylene **8** is also competitive in energy, only 12 kcal mol^{-1} above the global minimum. In a recent pyrolysis study,[20] Ishikawa and co-workers found that a silacyclobutene which could undergo either a 1,1-elimination reaction to form a derivative of **8** or a 1,2 elimination to form a silacyclobutadiene preferred the former path. As will be seen below, the parent silacyclobutadiene is calculated to be substantially less stable than **8**.

Among the other cyclic isomers, 1-silamethylenecyclopropene, **9**, is the most stable, 43.6 kcal mol^{-1} above the global minimum. The other two sila-substituted methylenecyclopropenes, **4** and 2-silamethylenecyclopropene, **10**, lie 15.9 and 23.3 kcal mol^{-1} higher in energy, respectively. We have no convincing rationalization to offer for the energy ordering of these similar structures.

Cyclopropenylsilylene, **1**, can exist in two conformers of roughly equal energy. Each of them has C_s symmetry like the bisected geometry of the cyclopropylcarbinyl cation.[21] In fact, the LUMO's of these compounds both show an interaction of a silicon p orbital with the out-of-phase combination of the cyclopropenyl σ orbitals. Compounds **1** and **2** are both nearly equal to **4** in energy, while silatetrahedrane, **3**, lies about 20 kcal mol^{-1} higher.

Various acyclic species, which might prove more stable due to the lack of ring strain, were studied. Those containing carbenes, silicon–carbon triple bonds, or silicon as the central atom of an allene are likely to be quite high in energy, as shown by Barthelat et al., and were neglected here. We considered eight isomers as candidates: 1- and 2-propynylsilylene, **11** and **12**, ethynylmethylsilylene, **13**, 1-sila-1-buta-1,3-dienylidene, **14**, 1,2-propadienylsilylene, **15**, silabutatriene, **16**, 1-silabut-1-en-3-yne, **17**, and 2-silabut-1-en-3-yne, **18**.



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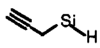

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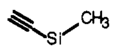

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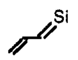

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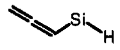

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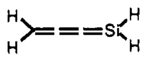

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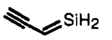

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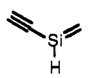

18

Of these, the first proved to be the lowest in energy. It is about 7.6 kcal mol^{-1} above the global minimum. The nonconjugated silylene **12** is considerably less stable. In addition to the conjugation, methyl substitution on the sp-hybridized carbon probably also contributes to the greater stability of **11**. The isomeric silylene **13** is only about 0.2 kcal mol^{-1} and the silavinylidine **14** only 2.6 kcal mol^{-1} less stable than **11**. Propadienylsilylene lies more than 16 kcal mol^{-1} above **11**. The two isomeric silenes lie still higher in energy, with silicon again preferring the internal position in the molecule. Silabutatriene is about equal in energy to the corresponding alkyne. These results parallel those of Trinquier and Malrieu[13] for silabutadienes. They found 2-silabutadiene to be about 6 kcal mol^{-1} more stable than the 1-sila- isomer, close to the 8 observed here. On the other hand, methylvinylsilylene, the most stable isomer that those authors found, was only 2 kcal mol^{-1} more stable than its corresponding silene. In our case the difference is over 10 kcal mol^{-1}. It may prove that in general a carbon–carbon triple bond is more effective than a carbon–carbon double bond at stabilizing an adjacent divalent silicon atom.

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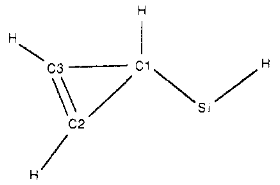
(19) Reference 18, p 293.

(20) Ishikawa, M.; Sugisawa, H.; Akitomo, H.; Matsusaki, K.; Kamitori, S.; Hirotsu, K.; Higuchi, T. *Organometallics* **1986**, *5*, 2447–2451.

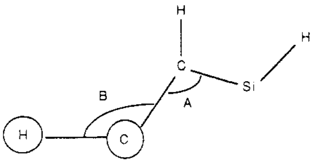
(21) For a summary of theoretical studies on the cyclopropylcarbinyl cation, see ref 18, pp 390–394.

Table II. Optimized Geometries of C_3SiH_4 Isomers[a]

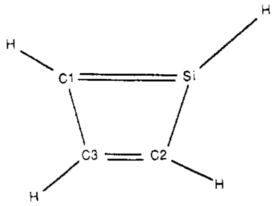


1a

parameter	3-21G*	6-31G*
C1-Si	1.863	1.883
C1-C2	1.578	1.536
C2-C3	1.276	1.263
Si-H	1.514	1.516
C1-H	1.078	1.085
C2-H	1.058	1.067
C1-Si-H	97.08	97.08
Si-C1-H	122.30	119.15
Si-C1-C2	117.76	119.46
C3-C1-C2	47.36	48.53
C1-C2-C3	66.32	65.73
C1-C2-H	141.99	142.03
C3-C2-H	151.65	152.20

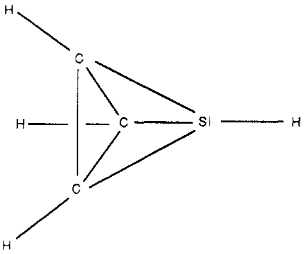


parameter	3-21G*	6-31G*
A	120.57	122.64
B	177.56	177.46



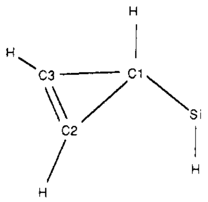
2

parameter	3-21G*	6-31G*
Si-C1	1.686	1.685
Si-C2	1.892	1.884
C1-C3	1.579	1.544
C2-C3	1.334	1.333
Si-H	1.470	1.472
C1-H	1.063	1.067
C2-H	1.065	1.068
C3-H	1.073	1.079
C1-Si-C2	82.10	82.00
Si-C2-C3	84.93	83.91
Si-C1-C3	85.45	85.17
C2-C3-C1	107.52	109.01
C1-Si-H	141.33	141.24
Si-C1-H	148.66	148.57
C3-C2-H	130.22	130.55
C2-C3-H	128.33	127.20



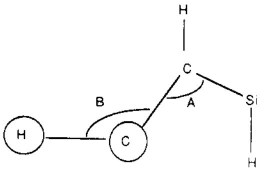
3

parameter	3-21G*	6-31G*
Si-C	1.800	1.796
C-C	1.556	1.515
Si-H	1.452	1.452
C-H	1.060	1.067
C-Si-C	51.22	49.91
C-Si-H	150.06	150.85
Si-C-H	158.20	159.03

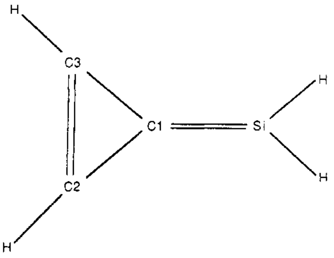


1b

parameter	3-21G*	6-31G*
C1-Si	1.865	1.885
C1-C2	1.574	1.533
C2-C3	1.268	1.263
Si-H	1.509	1.513
C1-H	1.079	1.086
C2-H	1.058	1.067
C1-Si-H	96.22	95.99
Si-C1-H	117.38	114.58
Si-C1-C2	122.59	123.81
C3-C1-C2	47.50	48.67
C1-C2-C3	66.25	65.67
C1-C2-H	142.02	142.13
C3-C2-H	151.74	152.19



parameter	3-21G*	6-31G*
A	126.03	127.64
B	181.29	178.44



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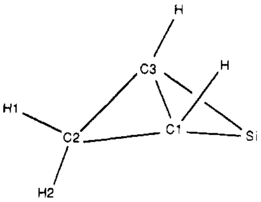
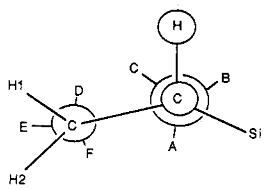
parameter	3-21G*	6-31G*
C1-Si	1.692	1.715
C1-C2	1.464	1.434
C2-C3	1.295	1.292
Si-H	1.463	1.463
C2-H	1.058	1.067
C1-Si-H	120.81	120.10
C2-C1-Si	153.74	153.21
C2-C1-C3	52.51	53.58
C3-C2-C1	63.74	63.21
C1-C2-H	146.36	146.29
C2-C3-H	149.90	150.49



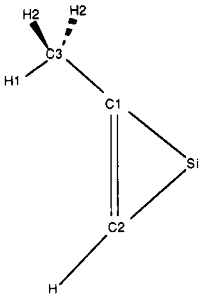
5

parameter	3-21G*	6-31G*
Si-C1	1.835	1.833
C1-C2	1.514	1.488
C1-C3	1.664	1.599
C1-H	1.071	1.076
C2-H1	1.077	1.081
C2-H2	1.073	1.078
C3-Si-C1	53.93	51.72
Si-C1-C3	63.04	64.14
C1-C2-C3	66.66	65.00
C2-C1-C3	56.67	57.50
C3-C1-H	127.86	126.79
Si-C1-H	131.82	129.93
C1-C2-H1	115.95	116.52
C1-C2-H2	119.06	119.65

Table II (Continued)

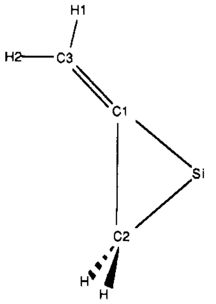


parameter	3-21G*	6-31G*
A	131.40	132.01
B	123.52	121.88
C	105.44	106.11
D	121.59	121.97
E	125.54	125.91
F	112.87	112.12



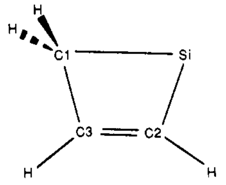
6

parameter	3-21G*	6-31G*
Si–C1	1.819	1.816
Si–C2	1.804	1.801
C1–C2	1.345	1.338
C1–C3	1.493	1.493
C2–H	1.070	1.076
C3–H1	1.085	1.086
C3–H2	1.085	1.085
C1–Si–C2	43.58	43.40
Si–C1–C2	67.64	67.70
C1–C2–Si	68.77	68.90
Si–C1–C3	156.07	155.64
Si–C2–H	156.73	156.71
C1–C3–H1	112.04	112.31
C1–C3–H2	109.92	110.08
H2–C3–H2	107.16	106.91



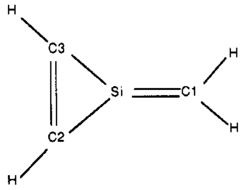
7

parameter	3-21G*	6-31G*
Si–C1	1.837	1.843
Si–C2	1.914	1.925
C1–C2	1.507	1.488
C1–C3	1.314	1.319
C2–H	1.082	1.083
C3–H1	1.075	1.077
C3–H2	1.077	1.080
C1–Si–C2	47.33	46.46
Si–C1–C2	69.02	69.68
C1–C2–Si	63.65	63.86
Si–C1–C3	153.02	151.82
Si–C2–H	119.34	119.08
H–C2–H	112.06	111.72
C1–C3–H1	121.58	121.44
C1–C3–H2	122.31	122.40



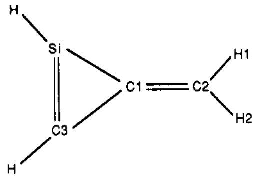
8

parameter	3-21G*	6-31G*
Si–C1	1.962	1.964
Si–C2	1.876	1.872
C1–C3	1.536	1.515
C2–C3	1.342	1.340
C1–H	1.086	1.087
C2–H	1.072	1.076
C3–H	1.078	1.084
C1–Si–C2	73.97	73.76
Si–C1–C3	85.17	85.01
C1–C3–C2	106.54	107.40
C3–C2–Si	94.32	93.80
Si–C1–H	117.03	117.31
H–C1–H	108.30	107.50
C3–C1–H	113.97	114.29
C1–C3–H	125.49	125.23
C2–C3–H	127.97	127.37
C3–C2–H	126.08	126.14
Si–C2–H	139.60	140.02



9

parameter	3-21G*	6-31G*
Si–C1	1.680	1.682
Si–C2	1.777	1.772
C2–C3	1.356	1.346
C1–H	1.075	1.074
C2–H	1.069	1.074
Si–C1–H	121.77	121.55
Si–C2–H	159.00	159.05
C2–Si–C1	157.57	157.67
C2–Si–C3	44.86	44.67
S1–C2–C3	67.57	67.67



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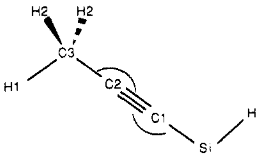
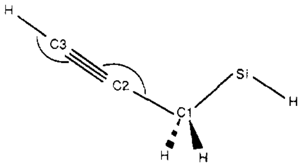
parameter	3-21G*	6-31G*
Si–C1	1.794	1.797
Si–C3	1.666	1.667
C1–C2	1.316	1.322
C1–C3	1.525	1.491
C2–H1	1.073	1.074
C2–H2	1.075	1.077
Si–H	1.461	1.461
C3–H	1.066	1.071
C1–C2–H1	121.62	121.60
C1–C2–H2	121.35	121.05
C1–Si–H	155.60	157.04
C1–C3–H	131.13	131.14
Si–C1–C3	59.63	60.07
C1–C3–Si	52.11	50.79
C3–Si–C1	68.26	69.14

Table II (Continued)



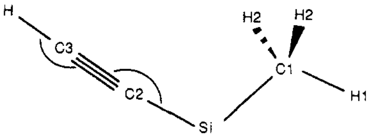
11

parameter	3-21G*	6-31G*
Si–C1	1.821	1.837
C1–C2	1.203	1.202
C2–C3	1.463	1.466
Si–H	1.505	1.508
C3–H1	1.084	1.084
C3–H2	1.085	1.084
H–Si–C1	95.70	95.94
Si–C1–C2	176.99	174.41
C1–C2–C3	180.07	179.13
C2–C3–H1	111.12	111.31
C2–C3–H2	110.04	110.14
H1–C3–H3	108.09	107.98



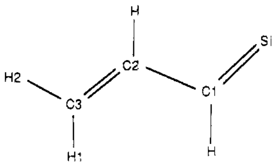
12

parameter	3-21G*	6-31G*
Si–C1	1.926	1.934
C1–C2	1.462	1.464
C2–C3	1.190	1.188
Si–H	1.511	1.514
C1–H	1.092	1.090
C3–H	1.050	1.051
Si–C1–C2	114.45	114.98
C1–C2–C3	179.01	178.50
C1–Si–H	93.63	93.37
Si–C1–H	108.31	108.02
C2–C1–H	109.92	110.07
C2–C3–H	180.20	179.94



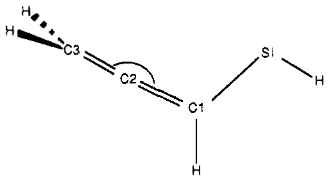
13

parameter	3-21G*	6-31G*
Si–C1	1.905	1.912
Si–C2	1.845	1.859
C2–C3	1.201	1.199
C1–H1	1.085	1.085
C1–H2	1.090	1.089
C3–H	1.052	1.058
Si–C1–H1	111.77	111.83
Si–C1–H2	110.73	110.75
H1–C1–H2	108.45	108.39
H2–C1–H2	106.54	106.44
C1–Si–C2	98.00	98.01
Si–C2–C3	183.17	184.84
C2–C3–H	180.31	179.81



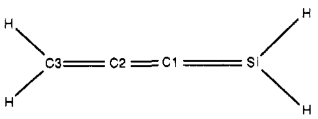
14

parameter	3-21G*	6-31G*
Si–C1	1.711	1.716
C1–C2	1.465	1.462
C2–C3	1.325	1.327
C1–H	1.088	1.088
C2–H	1.076	1.079
C3–H1	1.074	1.076
C3–H2	1.073	1.075
Si–C1–C2	131.13	132.06
Si–C1–H	114.79	113.48
C1–C2–C3	124.86	125.12
C3–C2–H	118.37	118.07
C2–C3–H1	121.83	121.86
C2–C3–H2	121.53	121.53



15

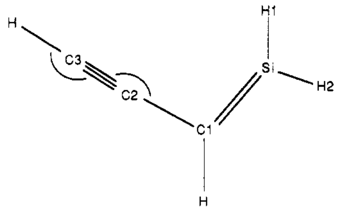
parameter	3-21G*	6-31G*
Si–C1	1.876	1.880
C1–C2	1.306	1.309
C2–C3	1.291	1.294
Si–H	1.510	1.513
C1–H	1.080	1.080
C3–H	1.074	1.075
H–Si–C1	95.80	95.98
Si–C1–C2	118.67	118.09
C1–C2–C3	177.93	177.98
C2–C1–H	118.08	117.66
C2–C3–H	121.09	120.89
H–C3–H	117.82	118.23



16

parameter	3-21G*	6-31G*
Si–C1	1.663	1.673
C1–C2	1.261	1.266
C2–C3	1.303	1.307
Si–H	1.462	1.463
C3–H	1.073	1.075
C1–Si–H	122.55	122.31
C2–C3–H	121.10	120.89

Table II (Continued)



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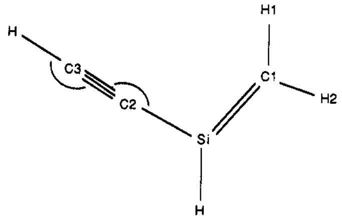

18

parameter	3-21G*	6-31G*	parameter	3-21G*	6-31G*
C2–C3	1.193	1.191	C2–C3	1.196	1.194
C1–C2	1.422	1.426	C2–Si	1.806	1.818
C1–Si	1.703	1.705	Si–C1	1.687	1.690
C3–H	1.050	1.056	Si–H	1.462	1.462
C1–H	1.078	1.078	C3–H	1.052	1.058
Si–H1	1.463	1.464	C1–H1	1.076	1.067
Si–H2	1.464	1.465	C1–H2	1.076	1.067
C2–C3–H	180.04	180.07	C1–Si–C2	123.96	123.65
C1–C2–C3	179.97	180.04	C2–C3–H	180.10	180.10
C2–C1–H	115.59	115.80	C3–C2–Si	180.36	180.65
C2–C1–Si	125.15	125.65	C2–Si–H	112.59	112.78
C1–Si–H1	123.41	123.69	Si–C1–H1	122.88	122.88
C1–Si–H2	121.11	120.67	Si–C1–H2	122.01	121.71

[a] Distances are given in angstroms, and angles are given in degrees. In cases where dihedral angles are specified, these are labeled with letters and refer to the accompanying diagrams. In those diagrams, an atom in a circle represents two symmetry-related atoms eclipsed in the view chosen. Where angles are near linear, curved lines are used to tell which angle is being specified.

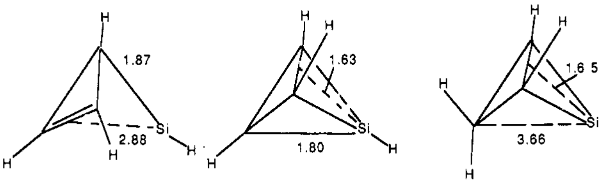

Figure 2. Comparison of the geometries of silatetrahedrane with 2-silabicyclo[1.1.0]butanylidene and cyclopropenylsilylene. Distances are given in Angstroms.

Although several different types of bonding are present in the compounds studied, inclusion of electron correlation in calculations for the lowest several isomers does not produce large changes in the relative energies. The silacyclopropenylidene **6** appears somewhat more stable relative to all but compounds **14** and **18**. Compared to the latter, it loses only 1.3 kcal mol^{-1}. Propadienylsilylene is destabilized by over 6 kcal mol^{-1}, the largest change observed.

The relative energies of the various species suggest that all of them, with the possible exception of silatetrahedrane, are reasonable synthetic targets. Of course, the relative stabilities of these molecules say nothing about their ability to react with other reagents or to dimerize. Appropriate protection or matrix isolation may be required for their observation.

Silatetrahedrane is not only the least stable isomer considered, but also is similar in structure to 2-silabicyclo[1.1.0]butanylidene, **5**. At this time, we know nothing about the activation energy for the hydrogen migration necessary for this 66.5 kcal mol^{-1} exothermic rearrangement, but it could well be small. Reversion of **3** to cyclopropenylsilylene also involves little atomic motion and is more than 32.1 kcal mol^{-1} exothermic. It may have a low activation barrier as well. It is known experimentally that addition of silylenes to olefins and the reverse reaction are often facile.[22] The geometric changes involved in these two rearrangements are illustrated in Figure 2. Isomerization of silacyclobutadiene to the cyclobutenylsilylene, **8**, is also very exothermic, but the 1,2-hydrogen migration required cannot have favorable overlap in its transition state.

The insertion of cyclopropenyl silylene into adjacent carbon–hydrogen or carbon–carbon bonds to produce silylidenecyclopropene, **4**, and silacyclobutadiene, **2**, respectively, are predicted to be nearly thermoneutral reactions. This was not anticipated at the outset of this study, but is consistent with recent experimental observations.[23] These rearrangements are liable to have appreciable barriers to reaction, analogous as they are to the interconversion of methylsilylene and silaethylene cited above.

In connection with current experimental studies, the impact of substitution of bulky alkyl or aryl groups for hydrogen must be assessed. We are unable to do this quantitatively, but point out that, as is found in tetrahedrane,[24] isomers in which bulky substituents can be located as far as possible from each other should be preferentially stabilized. Hydrogen–hydrogen distances in silacyclobutadiene are shorter than in either silatetrahedrane or cyclopropenylsilylene. Those two compounds have comparable hydrogen–hydrogen separations. Each of the remaining compounds have two or more gem hydrogens, which would be expected to lead to significant destabilization were hydrogen to be replaced by larger substituents. (In substituted systems, this may well lead to silylenes related to **6** not being the most stable isomers.)

In conclusion, we have studied 18 isomeric structures of the C_3SiH_4 system. The global minimum appears to be a silylene. In general, the silylenes studied proved more stable than classical structures, because in this highly unsaturated system isomers without divalent silicon require strained rings or multiply bonded silicon atoms. A variety of novel structures, such as silacyclobutadiene and sila-substituted methylenecyclopropenes are strained but may well be capable of existence, at least as substituted

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(22) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288–1294.

(23) Fink, M. J.; Puranik, D. B. *Organometallics* **1987**, *6*, 1809–1811.

(24) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520–521.

derivatives. Silatetrahedrane is predicted to be very strained and may not yield isolable derivatives.

Acknowledgment. We thank Professors Herman and Levy of the Tulane University chemistry department for making their copy of GAUSSIAN-82 available to us, Mr. August Truebig for adapting it to the IBM-3081GX, and the Tulane University and North Dakota State University Computer Centers for generous grants of computer time. M.S.G. acknowledges the support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE83-09948).

Registry No. **1**, 88986-74-7; **2**, 76893-79-3; **3**, 76893-78-2; **4**, 109584-96-5; **5**, 109584-97-6; **6**, 109584-98-7; **7**, 109584-99-8; **8**, 109585-00-4; **9**, 109585-01-5; **10**, 109585-02-6; **11**, 109585-03-7; **12**, 109585-04-8; **13**, 109585-05-9; **14**, 109585-06-0; **15**, 109585-07-1; **16**, 109585-08-2; **17**, 109585-09-3; **18**, 109585-10-6.

Communications

Conversion of (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO) to (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$): Interchange of Boron and Carbon Atom Positions

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Received April 22, 1987

Summary: The cluster (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO) (I) reacts with BCl$_3$ to produce (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$) (II), a new example of a cluster vinylidene analogue. In the formation of II the boron and carbon atoms of the BCO unit exchange positions, going from μ_3-B to μ_3-C. An X-ray crystal structure determination reveals that the C–B bond vector differs by 15° from being normal to the plane of the metal atoms, unlike the markedly tilted bonds, B–C in the cluster vinylidene analogue (μ-H)$_3$(CO)$_9$Os$_3$(μ_3-B-η^2-CH$_2$) and C–C in the cluster vinylidenes (CO)$_9$Co$_2$Ru(μ_3-C-η^2-CRH) (R = *t*-Bu, Ph).

The cluster (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO)[1] (I) reacts with BCl$_3$ to produce (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$) (II), a new example of a cluster vinylidene analogue which is noteworthy for two reasons: (1) in the formation of II the boron and carbon atoms of the BCO unit exchange positions, going from μ_3-B to μ_3-C; (2) the C–B bond vector differs by 15° from being normal to the plane of the metal atoms (Figure 1), unlike the markedly tilted bonds, B–C in the cluster vinylidene analogue (μ-H)$_3$(CO)$_9$Os$_3$(μ_3-B-η^2-CH$_2$)[2] and C–C in cluster vinylidenes.[3,4]

Preparation of II is represented by reaction 1. The Cl$_3$B$_3$O$_3$ formed decomposes[5] to BCl$_3$ and B$_2$O$_3$ when excess BCl$_3$ is removed from the system. Chemical confirmation of the formation of an Os$_3$C cluster core was provided by quantitative hydrolysis of II to (μ-H)$_3$(CO)$_9$Os$_3$(μ_3-CH) (III) and boric acid and also the conversion of II to III in glacial acetic acid.

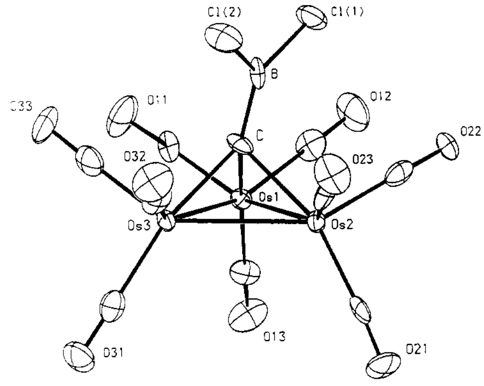
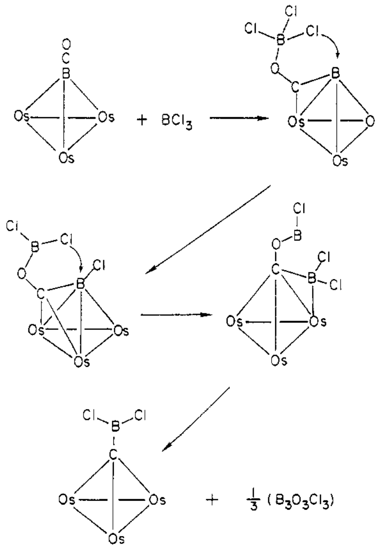


Figure 1. Structure of (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$). Selected distances (Å): Os(1)–Os(2) = 2.875 (1), Os(2)–Os(3) = 2.869 (1), Os(1)–Os(3) = 2.879 (1), Os(1)–C = 2.108 (13), Os(2)–C = 2.168 (14), Os(3)–C = 2.134 (13), C–B = 1.47 (2).

Scheme I



$$\underset{\text{I}}{(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-BCO})} + BCl_3 \xrightarrow{CH_2Cl_2} \underset{\text{II}}{(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CBCl}_2)} + {}^1/_3(Cl_3B_3O_3) \quad (1)$$

Movement of boron from a vertex site in μ_3-BCO to a terminal site in μ_3-CBCl$_2$ in the formation of II is believed

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