indicated absolute configuration to be that shown in Figure 1 (n = 1.04 (4)). Refinement of the inverted structure leads to significantly higher R values (R = 0.0389 vs. 0.0244 and R_w = 0.0406 vs. 0.0250), confirming the absolute configuration. Reasonable positions for all hydrogen atoms were located on difference maps, but calculated hydrogen positions were used in structure refinement. The largest peaks of the final difference map were 0.5 to 0.7 e Å^{-3} and were less than 1.5 Å from the platinum position.

Acknowledgment. We thank Montana State University, the National Science Foundation (CHE 7826160, 8115565, 8306254), the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the CRISS Center at Montana State University (XPS work) for support of this research. Also, we wish to acknowledge Johnson-Matthey for their generous loan of platinum.

Registry No. **5**, 98772-92-0; **6**, 105280-91-9; **7**, 105280-92-0; **8**, 105280-93-1; **9**, 105369-27-5; **10**, 105280-94-2; CH_2N_2, 334-88-3; CH_3CHN_2, 1117-96-0; Zeise's dimer, 12073-36-8; ethyl diazoacetate, 623-73-4.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen positions, and least-squares planes and atomic deviations therefrom (2 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(19) Rogers, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, 734–741.

Structure of the Stable Silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$[†]

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The structure of the stable, solid silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$ (**4**) has been determined by X-ray crystallography (orthorhombic, $P2_12_12_1$, a = 8.109 (1) Å, b = 14.886 (2) Å, c = 16.470 (2) Å, V = 1988.10 Å^3, D_{calcd} = 1.005 g cm^{-3} for Z = 4 at −35 °C; R_w = 0.053, $w = 1/\sigma^2(F_o)$ for 163 refined parameters and 2447 observables with $I \geq 2.0\sigma(I)$). The double-bond geometry in **4** is essentially planar, with a twist about Si=C of only 1.6°. The silicon–carbon double-bond length (1.702 (5) Å) is substantially shorter than that in the previously reported sila enol ether $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl) (**3**) (1.764 (3) Å) but in excellent agreement with theoretical figures based on ab initio calculations. The difference must be attributed mainly to the different polarity of the double bonds in **3** and **4**, caused by the $-OSiMe_3$ substituent, and to the generally larger bulk of the substituents in **3**.

Introduction

The recent synthesis of stable compounds containing multiple bonds of the p_π–p_π type to heavier main-group elements demonstrated that the kinetic stability of such compounds may be dramatically improved, provided sufficiently bulky substituents are used.[1,2] This is especially true for unsaturated phosphorus where a great variety of compounds could recently be synthesized for the first time and shown to be stable in condensed phase under ordinary conditions.[3]

Far less is known about multiple bonds involving silicon.[4] Their greater instability, as compared to phosphorus, has been attributed to the smaller gap between their π and π^* orbitals and, in the case of silicon–carbon double bonds, to their greater polarity.[5] Nevertheless, compounds with silicon–silicon,[4a,c,6] silicon–carbon,[4c,7] and silicon–nitrogen[8] double bonds could be successfully synthesized and structurally characterized.[9] The latter studies[6g–i,7b,c,e,8b] showed double bonds involving silicon to be closely related structurally to their carbon analogues. In particular, they were found to be significantly shorter than the respective single bonds, and three-coordinate silicon showed only small[6g,i] deviations from planarity, indicative of substantial p orbital overlap mandatory for "real" π bonds.[10]

In addition to laying the experimental ground for a description of the bonding, structure determinations may

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[†] Unsaturated Silicon Compounds. 18. Compounds of Silicon. 70. Parts 17 and 69: Wiberg, N.; Schurz, K.; Fischer, G. *Chem. Ber.* 1986, *119*, 3498.

[‡] Universität München.

[§] Technische Universität München.

(1) (a) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386; (b) *Polyhedron* **1984**, *3*, 389.

(2) Apparent exceptions to the "double-bond rule" have been known for almost 200 years, e.g., CS_2: Lampadius, W. A. *Neues J. Phys. Gren.* **1796**, 304.

(3) (a) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem.* **1981**, *93*, 771. (b) Becker, G.; Becker, W.; Mundt, O. *Phosphorus Sulfur* **1983**, *14*, 267.

(4) (a) West, R. *Science (Washington, D.C.)* **1984**, *225*, 1109. (b) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (c) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (d) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

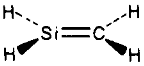
(5) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

(6) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. (b) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992. (c) Masamune, S.; Hanazawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *Ibid.* **1982**, *104*, 1150. (d) Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1464. (e) Masamune, S.; Tobita, H.; Murakami, S. *J. Am. Chem. Soc.* **1983**, *105*, 6524. (f) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. (g) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Ibid.* **1983**, 1010. (h) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333. (i) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Ibid.* **1984**, *3*, 793. (j) Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821.

(7) (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (c) Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1632. (d) Wiberg, N.; Wagner, G. *Angew. Chem.* **1983**, *95*, 1027. (e) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem.* **1985**, *97*, 220. (f) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467.

0276-7333/87/2306-0032$01.50/0

play a crucial role in assessing the validity of previous theoretical investigations. A particularly long-lasting controversy between theory and experiment arose about the silicon–carbon double-bond length where a series of theoretical studies of various degree of sophistication was culminated by the prediction of 1.69–1.71 Å for the Si=C bond in small, unhindered silaethenes (silenes) like 1 or 2.[11] Although these values were obtained from "state of the art" ab initio calculations and were thus considered to be most reliable, the first experimental Si=C bond length determination on 2, by electron diffraction, yielded 1.83 ± 0.04 Å,[12] substantially longer than the theoretical figures. Although this study is now generally considered to be erroneous,[5] the first reliable experimental Si=C distance of 1.764 (3) Å (in 3, by X-ray diffraction)[7b,c] was still far outside the range predicted by theory. Furthermore, the double bond in 3 was found to be noticeably twisted (by 14.6°).[7b,c] Subsequent theoretical work indicated that the double-bond geometry in 3 should be severely influenced by steric and electronic substituent effects.[5]



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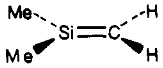

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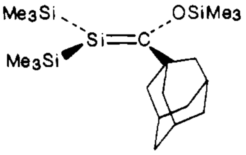

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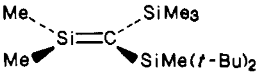

4

We report here on the structure of the stable silaethene 4, which not only bears completely different and substantially less bulky substituents than 3 but also shows a reactivity resembling much more closely that of small silaethenes.[7d,f] A preliminary report has appeared.[7e]

Experimental Section

X-ray Structure Determination. Single crystals of 4, prepared from its tetrahydrofuran (THF) adduct as described in ref 7e,f, were obtained by cooling a solution of 1.5 mmol of 4 in 1 mL of pentane first to −90 °C for 2–3 days (formation of crystal seeds) and then to −78 °C. The solvent was decanted off at −78 °C, and the crystals were dried in vacuo. Due to their low melting point and high degree of air and moisture sensitivity, they were mounted at dry ice temperature under an atmosphere of dry argon into glass capillaries and immediately transferred to the diffractometer (Syntex P2$_1$) equipped with a low-temperature device. Cell symmetry and space group were determined by diffractometer measurements. Exact cell dimensions were obtained by least-squares refinement of the parameters of the orientation matrix to the setting angles of 15 high order reflections from various parts of reciprocal space. Crystal data and a summary of intensity data collection and structure refinement are given in Table I. Data collection and refinement procedures followed closely those described in ref 13.

Table I. Crystal Structure Data for 4

formula	$C_{15}H_{36}Si_3$
M_r	300.71
cryst system	orthorhombic
space group	$P2_12_12_1$
a, Å	8.109 (1)
b, Å	14.886 (2)
c, Å	16.470 (2)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1988.1
Z	4
D_{calcd}, g/cm^3	1.005
T, °C	−35
μ(Mo K$_\alpha$), cm^{-1}	2.2
F(000), e	672
radiatn	Mo K$_\alpha$
λ, Å	0.710 69
scan type	ω
scan width, deg	1.0
scan speed, deg/min	0.9–29.3
scan range (θ), deg	1.0–24.0
hkl range	hkl, $\bar{h}\bar{k}\bar{l}$
measd data	3378
unique data	2928
R_{int}[a]	0.023
obsd data [$I \geq 2.0\ \sigma(I)$]	2447
ref params	163
R[b]	0.055
R_w[c]	0.053
(shift/error)$_{max}$	0.01
$\Delta\rho_{fin}$(max/min), e/Å^3	+0.45/−0.36

[a] $R_{int} = [\sum(N\sum_n w(\langle F\rangle - F)^2)/\sum((N-1)\sum_n wF^2)]^{1/2}$. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for 4[a]

atom	x/a	y/b	z/c	U(eq), Å^2
Si1	0.7786 (2)	0.0284 (1)	0.8294 (1)	0.035
Si2	1.0524 (2)	0.1315 (1)	0.9199 (1)	0.041
Si3	0.9689 (2)	0.1805 (1)	0.7344 (1)	0.030
C1	0.9264 (6)	0.1096 (3)	0.8273 (3)	0.030
C2	0.7274 (9)	−0.0465 (4)	0.9155 (3)	0.063
C3	0.6328 (6)	−0.0052 (3)	0.7492 (3)	0.040
C4	1.0477 (9)	0.2523 (4)	0.9531 (3)	0.056
C5	1.2747 (6)	0.0978 (4)	0.9030 (3)	0.045
C6	0.9883 (10)	0.0702 (4)	1.0134 (3)	0.072
C7	1.1362 (6)	0.2660 (3)	0.7555 (3)	0.042
C8	0.7832 (6)	0.2547 (3)	0.7038 (3)	0.038
C9	0.7049 (9)	0.2913 (5)	0.7818 (5)	0.072
C10	0.8372 (8)	0.3356 (3)	0.6535 (4)	0.057
C11	0.6503 (6)	0.2068 (4)	0.6541 (5)	0.064
C12	1.0607 (6)	0.1101 (3)	0.6487 (3)	0.036
C13	1.2282 (6)	0.0735 (3)	0.6785 (3)	0.044
C14	0.9596 (6)	0.0270 (3)	0.6257 (3)	0.047
C15	1.0888 (8)	0.1639 (4)	0.5695 (3)	0.062

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$, where U_i are the eigenvalues of the $\mathbf{U}_{ij}$ matrix.

The structure was solved by direct methods (MULTAN 80[14]) and completed by successive difference Fourier syntheses. After anisotropic refinement of the non-hydrogen atoms 26 of the 36 H atom positions were obtained from a difference synthesis. The remainder was calculated at idealized geometrical positions (XANADU[15]). Located H atoms served to determine the confor-

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(8) (a) Wiberg, N.; Schurz, K.; Fischer, G. *Angew. Chem.* **1985**, *97*, 1058. (b) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591.

(9) For a stable compound with a Si=P bond in solution see: Smith, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011.

(10) This is at variance with the structures of distannenes and digermenes, containing formal double bonds, cf: (a) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480.

(11) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283 and references cited therein.

(12) Mahaffy, P. G.; Gutowsky, R.; Montgomery, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 2854.

(13) Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics* **1985**, *4*, 1624.

(14) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data; University of York, York, England, and University of Louvain, Louvain, Belgium, 1980.

(15) Roberts, P.; Sheldrick, G. M. XANADU; University of Cambridge: Cambridge, England, 1975.

Table III. Important Interatomic Distances (Å) and Angles (deg) for 4[a]

	Bond Distances		
Si1-C1	1.702 (5)	Si3-C8	1.934 (5)
Si2-C1	1.865 (5)	Si3-C12	1.909 (5)
Si3-C1	1.890 (5)	C8-C9	1.533 (8)
Si1-C2	1.851 (5)	C8-C10	1.526 (7)
Si1-C3	1.842 (5)	C8-C11	1.529 (8)
Si2-C4	1.879 (5)	C12-C13	1.544 (7)
Si2-C5	1.892 (6)	C12-C14	1.532 (7)
Si2-C6	1.864 (6)	C12-C15	1.548 (7)
Si3-C7	1.893 (5)		
	Bond Angles		
C1-Si1-C2	127.0 (3)	C4-Si2-C5	108.4 (3)
C1-Si1-C3	129.0 (2)	C4-Si2-C6	102.9 (3)
C2-Si1-C3	104.0 (3)	C5-Si2-C6	104.9 (3)
Si1-C1-Si2	119.5 (3)	C1-Si3-C7	111.0 (2)
Si1-C1-Si3	122.8 (3)	C1-Si3-C8	112.8 (2)
Si2-C1-Si3	117.7 (2)	C1-Si3-C12	111.3 (2)
C1-Si2-C4	113.2 (2)	C7-Si3-C8	102.8 (2)
C1-Si2-C5	110.8 (2)	C7-Si3-C12	103.0 (2)
C1-Si2-C6	115.9 (3)	C8-Si3-C12	115.1 (2)

[a] Esd's in units of the last significant figure in parentheses.

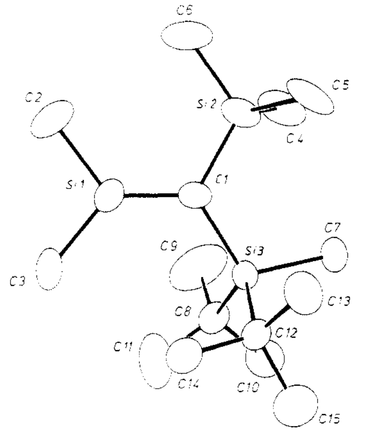

Figure 1. Molecular structure of 4 and atomic numbering scheme used (ORTEP, thermal ellipsoids at the 50% probability level, H atoms omitted for clarity).

mations of all methyl groups. Refinement was carried out by full-matrix least squares with anisotropic thermal parameters for all non-H atoms and all H atoms as fixed-atom contributions (SHELX 76[16]). Refinement of the inverse coordinate set did not yield significantly different R values nor were the derived structural parameters different. The function minimized was $\sum w(|F_o| - |F_c|)^2$. "Unobserved" data were not used in the refinement. The sources of the scattering factors are included in ref 13. Table II contains the final atomic coordinates of the non-H atoms, and Table III summarizes important bond distances and angles. Figures 1 and 2 depict the molecular structure (ORTEP[17]).

Description of the Structure

The observed silaethene geometry of 4 (Figure 1) shows great resemblances to that of ethenes. Both unsaturated centers (Si1, C1) are three-coordinate. As is best seen in the "side on" view of Figure 2, the double-bond geometry is essentially planar (sum of the angles at Si1 and C1 = 360°) with only a minimal twist of 1.6° about Si=C.[18] Deviations from the sp^2 standard are observed for some of the bond angles, however (Table III). In particular, the angles C1-Si1-C2/C3 (127.0 (3)/129.0 (2)°) are noticeably larger than 120°, while the C2-Si1-C3 bond angle (104.0 (3)°) compensates for this. The bond angle deformations at C1 are much less pronounced.

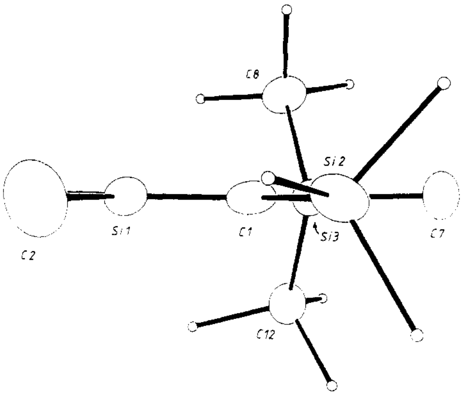

Figure 2. View of the molecular geometry of 4 approximately perpendicular to the double-bond plane (ORTEP, H atoms omitted, methyl groups at Si2, C8, C12 with arbitrarily small radii).

The most significant structural feature of 4 is the short silicon-carbon double bond length of 1.702 (5) Å, the shortest Si-C bond reported ever. All other Si-C bonds in 4 are substantially longer and similar to 1.867 Å, established as the Si-C single-bond distance in methylsilane H_3Si-CH_3.[19] The slightly shorter Si1-C2/C3 bonds are probably due to the smaller covalent radius of sp^2-hybridized silicon. The longer Si3-C8/C12 bonds to the *tert*-butyl groups certainly reflect their greater steric bulk.

Discussion

The Si=C bond in 4 is 0.165 Å (8.8%) shorter than the before-mentioned "classical" Si—C single-bond value. For typical carbon-carbon single (1.54 Å) and double bonds (1.34 Å) the shortening is 0.20 Å or 12.9%. This strongly indicates a smaller π-bonding component of the Si=C bond caused by less efficient p orbital overlap due to the larger size of the Si atom. It should be noted that a Si=C bond length of 1.70 Å is predicted correctly if a 12.9% shortening (from the carbon analogue) is corrected for the lesser π-bond energy of the Si=C bond on the basis of empirical thermodynamic data.[11] Furthermore, the Si=C bond length in 4 agrees reasonably well with the sum of a typical covalent radius of sp^2-hybridized silicon (1.07-1.08 Å[20]) and that of carbon (0.67 Å) after a correction for polarity effects, as, e.g., by the Schomaker-Stevenson relation.[21]

The molecular structure of 4, and particularly its Si=C distance, is in excellent agreement with theoretical predictions based on ab initio calculations.[4d,5,11] This lends further credibility to those theoretical investigations which attribute the noticeably longer Si=C bond in 3[7b,c] to substituent effects.[5,22] In particular, the high σ-electronegativity of the $-OSiMe_3$ substituent in 3 reduces drastically the "natural" bond polarity of the Si=C bond (silicon positively charged and carbon negatively charged). With decreased bond ionicity the bond is expected to lengthen.[5] The π-donating properties of $-OSiMe_3$ were found to be less important but nevertheless should play a synergistic role.[5] Actually, a reduced Si=C bond polarity

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(16) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

(17) Johnson, C. K. ORTEP II, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge TN, 1976.

(18) The relatively large thermal parameters of the C atoms C2/C3 do not exclude a slight pyramidalization of Si1 with disordered methyl groups. Alternatively they point to a relatively shallow potential energy minimum of the Si1 equilibrium conformation.

(19) Kilb, R. W.; Pierce, L. *J. Chem. Phys.* 1957, *27*, 108.

(20) One half of the Si=Si bond lengths in West's or Masamune's (symmetrical) disilenes. See ref 6g-i.

(21) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* 1941, *63*, 37.

(22) Gordon, M. S.; George, C. *J. Am. Chem. Soc.* 1984, *106*, 609.

Organometallics 1987, *6*, 35–41

in **3** was already derived by the original authors from spectroscopic data, particularly from the ^{29}Si and ^{13}C NMR shifts, but was not considered to lengthen the Si=C bond significantly.[7b] The steric strain in **3**, resulting from the generally very bulky substituents, is relieved predominantly by bond angle deformations and by a twist of 14.6° about the Si=C bond. The latter effect should also be a factor contributing to the observed Si=C bond lengthening in **3**.

In **4** the substituents are far less bulky and should not exert pronounced electronic effects.[23] They result only in the observed bond angle deformations, whereas the twist about Si=C is minimal. Furthermore, calculations show that in **4** the Si=C polarization is natural (Si positive, C negative) and the π and π^* orbital energies are similar to those in small, unhindered silaethenes as **1** or **2**.[5] Both factors are clearly reflected in the ^{29}Si and ^{13}C NMR shifts of **4**, which are drastically different from the ones observed for **3**, and in its different reactivity.[7d,f] The latter actually resembles much that of nonisolable silaethenes.[7f]

We therefore believe that, apart from bond angle distorsions, the molecular structure of **4** is essentially that of small, short-lived silaethenes. This should be especially true for the Si=C distance which, in agreement with the theoretical figures, has to be taken as the standard Si=C distance. Shorter Si=C bonds are only expected for silaethenes with highly electronegative substituents at Si which further increase the Si=C bond ionicity.

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Registry No. 4, 87937-47-1.

Supplementary Material Available: Complete lists of atomic and thermal parameters for 4 (4 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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[23] Calculations for $Me_2Si{=}C(SiH_3)_2$, a close electronic model for **4**, predict a Si=C bond length of 1.707 Å. This is based on an assumed additivity of the substituent effects[5] including a correction for the used 3-21G calculations, as based on Schaefer's calculations:[11] $r(Si{=}C) = 1.718$ (3-21G for $H_2Si{=}CH_2$) + 0.006 (addition for $2SiH_3$) − 0.004 (for $2CH_3$) − 0.013 (correction for basis set deficiencies) = 1.707 Å: Apeloig, Y., personal communication.

Donor Adducts of the Stable Silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$: Properties and Structures[†]

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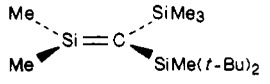
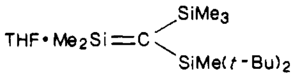
The stable silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$ (**1**) forms adducts with a variety of neutral and anionic Lewis bases as, e.g., tetrahydrofuran (THF), NMe_3, pyridine, and F^-, with the donor atoms being coordinated in all cases to the unsaturated Si atom. The structure of the F^- adduct (in $[Li(12\text{-}crown\text{-}4)_2]^+[FMe_2Si\ddot{C}(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)]^-$ (**5**)) shows a distorted tetrahedral geometry of the F-substituted Si atom (Si–F = 1.644 (4) Å) similar to that in the previously described THF adduct **2**. A comparison of the structures of **1**, **2**, and **5** confirms a partially zwitterionic description of the neutral adducts, as proposed first for **2**. Furthermore, **5** is the first structure determination of a silyl-substituted carbanion in which the central carbon atom is strictly three-coordinate. (Crystals of **5** are triclinic, space group $P\bar{1}$, with a = 10.245 (1) Å, b = 18.126 (2) Å, c = 22.175 (3) Å, α = 88.65 (1)°, β = 95.62 (1)°, γ = 97.71 (1)°, V = 4060.85 Å^3, and D_{calcd} = 1.111 g cm^{-3} for Z = 4 at −40 °C. R_w = 0.077 for 793 refined parameters and 6939 observed data.)

Introduction

In the course of our investigations which led to the synthesis and structural characterization of the stable silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$ (**1**),[1,2] we found that **1** easily forms remarkably stable adducts with even weak Lewis bases such as tetrahydrofuran (THF).[3] In the latter (**2**) the donor molecule THF coordinated exclusively to the unsaturated Si atom which thereby adopted a distorted tetrahedral coordination geometry, as was shown by X-ray structure analysis.[3] The Si–C bond length in **2** was found to be 1.747 (5) Å, slightly *shorter* than that in Brook's sila enol ether $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl),[4] where both unsaturated centers showed straightforward sp^2 hybridization.

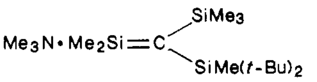


1



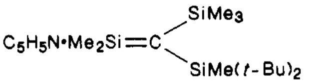
$THF\cdot Me_2Si{=}C(SiMe_3)(SiMe(t\text{-}Bu)_2)$

2



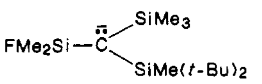
$Me_3N\cdot Me_2Si{=}C(SiMe_3)(SiMe(t\text{-}Bu)_2)$

3



$C_5H_5N\cdot Me_2Si{=}C(SiMe_3)(SiMe(t\text{-}Bu)_2)$

4



$FMe_2Si{-}\ddot{C}(SiMe_3)(SiMe(t\text{-}Bu)_2)$

5

$[Li(12\text{-}crown\text{-}4)_2]^+$

Adduct formation of unsaturated silicon is probably a more widely encountered phenomenon than initially thought. The recently synthesized silaketimines (silan-

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[†] Unsaturated Silicon Compounds. 19. Compounds of Silicon. 71. Parts 18 and 70: see ref 1.

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(1) Wiberg, N.; Wagner, G.; Riede, J.; Müller, G. *Organometallics*, preceding paper in this issue.

(2) (a) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467. (b) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1455.

(3) Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organometal. Chem.* **1984**, *271*, 381.

(4) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (b) Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1632.