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.

Acknowledgment. Support of this work by Deutsche Forschungsgemeinschaft (to N.W. and G.M.) is gratefully acknowledged.

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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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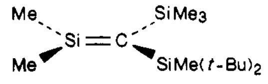
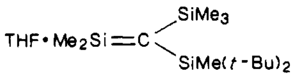
The stable silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$ (**1**) forms adducts with a variety of neutral and anionic Lewis bases as, e.g., tetrahydrofuran (THF), NMe_3, pyridine, and F^-, with the donor atoms being coordinated in all cases to the unsaturated Si atom. The structure of the F^- adduct (in $[Li(12\text{-crown-}4)_2]^+[FMe_2Si\ddot{C}(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)]^-$ (**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, $\alpha = 88.65$ (1)°, $\beta = 95.62$ (1)°, $\gamma = 97.71$ (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 $(Me_3Si)_2Si{=}C(OSiMe_3)(1\text{-adamantyl})$,[4] where both unsaturated centers showed straightforward sp^2 hybridization.

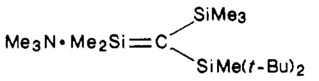


1



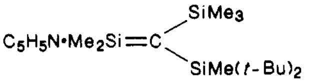
$THF\cdot Me_2Si{=}C(SiMe_3)(SiMe(t\text{-}Bu)_2)$

2



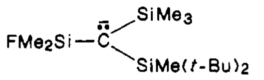
$Me_3N\cdot Me_2Si{=}C(SiMe_3)(SiMe(t\text{-}Bu)_2)$

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

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

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.

[‡] Universität München.

[§] Technische Universität München.

(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.

imines), i.e., compounds containing Si=N bonds, also could be shown to form stable THF adducts whose structures are astonishingly similar to those of the silaethene–THF adduct **2**.[5a,b] On the other hand, the unstable (at −100 °C) silaethene $Me_2Si{=}C(SiMe_3)_2$ gives an adduct with trimethylamine which is stable at room temperature.[5c]

In order to characterize further these novel adducts, we report here the synthesis, properties, and reactivity of several other donor adducts of **1**, viz., the Me_3N, pyridine, and F^- adducts **3**–**5**, as well as further reactivity studies on **2**. A structural analysis of **5** (as its $[Li(12\text{-crown-}4)_2]^+$ salt) is also presented in this paper and serves to elucidate the peculiar bonding situation in the adducts, as **5** shows surprising structural similarities to **2**.[6] A structural comparison of **1**, **2**, and **5** confirms the bonding model proposed previously for **2**.[3]

Experimental Section

All manipulations were carried out under strict exclusion of air and moisture under an atmosphere of purified argon or nitrogen. Conventional vacuum line and/or Schlenk tube techniques were used. Solvents were dried according to standard methods. $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$ (**1**)[2a] and $Me_2SiFCLi(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)\cdot n$THF[2b] were prepared according to the literature. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on JEOL FX 90Q at 89.55, 22.49, and 17.75 MHz (**4**–**6**) and Bruker WP 200 at 200.13, 50.289, and 39.761 MHz (**2** and **3**), respectively. Mass spectra: Varian CH7.

Preparation of 2–5. Tetrahydrofuran adduct 2, $THF\cdot Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$, was formed in quantitative yield by adding stoichiometric amounts of THF to stirred solutions of **1** in pentane at room temperature. After the solvent was distilled off in vacuo, the remaining solid residue was recrystallized twice from ether at −78 °C: colorless crystals; mp 87–91 °C dec. Identification was made by comparison with an authentical sample, prepared according to ref 2a: ^{1}H NMR ($C_6D_5CD_3$, 28 °C) δ 0.343 (br, $SiMe_3$ + $SiMe_2$ + SiMe) 1.19 (s, 2*t*-Bu), 1.22 + 3.58 (m, THF); ^{13}C NMR ($C_6D_5CD_3$, 28 °C) δ −0.781 (br, SiMe), 6.86 (br, $SiMe_2$), 8.32 (br, $SiMe_3$), 22.21 (CMe_3), 24.84 (THF), 31.18 (CMe_3), 70.78 (THF), ? (CSi_3); ^{29}Si NMR (Et_2O, 28 °C) δ −7.50 (SiMe-*t*-Bu_2), 7.58 ($SiMe_3$), 52.39 (br, $SiMe_2$); MS (EI, 70 eV), superposition of the spectra of **1**[2a] and THF.

Trimethylamine adduct 3, $Me_3N\cdot Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$, was prepared by condensing a slight excess of NMe_3 into a frozen solution of **2** in Et_2O (ca. 0.5 M) at −198 °C. After the solution was warmed to room temperature (quantitative yield according to ^{1}H NMR) and all volatile components were evaporated in vacuo, the residue was recrystallized three times from pentane at −78 °C: colorless crystals; mp 86–90 °C dec; ^{1}H NMR ($C_6D_5CD_3$, 28 °C) δ 0.191 (s, SiMe), 0.238 + 0.278 (two singlets, $SiMe_2$, area ratio 1:1), 0.457 (s, $SiMe_3$), 1.32 (s, 2*t*-Bu), 1.75 (s, NMe_3); ^{1}H NMR ($(C_2D_5)_2O$, 28 °C) δ 0.103 (s, SiMe), 0.165 (br, $SiMe_3$), 0.503 (br, $SiMe_2$), 1.03 (s, 2*t*-Bu), 2.62 (s, NMe_3); ^{13}C NMR ($C_6D_5CD_3$, 28 °C) δ 1.8 (SiMe), 5.8 ($SiMe_2$), 10.2 ($SiMe_3$), 22.7 (CMe_3), 31.8 (CMe_3), 48.0 (NMe_3), ? (CSi_3); ^{29}Si NMR (pentane, 28 °C) δ 5.83 (s, SiMe-*t*-Bu_2), 10.80 (s, $SiMe_3$), 34.70 (s, $SiMe_2$); MS (EI, 70 eV), superposition of the spectra of **1**[2a] and NMe_3; further characterization by reaction with methanol (see below).

Pyridine adduct 4, $py\cdot Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$, was prepared by adding a slight excess of C_5H_5N to a stirred solution of **2** or **3** in Et_2O (ca. 1 M) at −78 °C. The solution immediately turned dark red, resulting from the quantitative (^{1}H NMR) formation of **4**. The thermolability of **4** (see below) has thus far prevented its isolation: ^{1}H NMR (Et_2O, −50 °C) δ −0.090 (s, SiMe + $SiMe_3$), 0.223 + 0.255 (s, $SiMe_2$), 0.616 (br, 2*t*-Bu), 7.943 + 8.352 + 9.423 (m, py, area ratio 2:1:2); further characterization by reaction with acetone (see below).

Fluoride adduct 5, as its $Li(12\text{-crown-}4)_2$ salt $[Li(12\text{-crown-}4)_2][Me_2SiF\ddot{C}(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)]$, was formed on addition of an excess of 12-crown-4 to a 0.1 M solution of $Me_2SiFCLi(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)\cdot n$THF in Et_2O at room temperature (quantitative yield according to ^{1}H NMR). On cooling to −30 °C, pale yellow crystals formed which proved suitable for X-ray structure analysis (see below): ^{1}H NMR (Et_2O, 28 °C) δ −0.038 (s, $SiMe_3$), −0.002 (s, SiMe), 0.080 (d, J = 7.4 Hz, $SiMe_2$), 0.954 (s, 2*t*-Bu), 3.685 (s, 12-crown-4).

Thermolysis of 2–5. The tetrahydrofuran adduct **2** decomposes in solution at room temperature in the course of several weeks[2a] (about 20% decomposition in ether in 2 weeks; THF seemed to catalyze the process). Thermolysis of the trimethylamine adduct **3** took slightly longer. At 60 °C in benzene decomposition was only minor after 36 h; at 100 °C **3** decomposed rapidly.[7] Much more thermally stable was the fluoride adduct **5**, which was stable in Et_2O at 100 °C (sealed tube). The pyridine adduct **4**, however, was far more unstable. In Et_2O it isomerized even below 0 °C quantitatively into the pyridine derivative **6**, which may be isolated as a colorless oil by fractional distillation of the reaction mixture at 110 °C under high vacuum. Anal. Calcd for $C_{20}H_{41}NSi_3$ (**6**) (379.7): C, 63.20; H, 10.88; N, 3.70. Found: C, 63.01; H, 10.81; N, 3.34. **6**: ^{1}H NMR (CCl_4) δ −0.076 (s, CH), −0.024 (s, SiMe), 0.027 (s, $SiMe_3$), 0.435 + 0.475 (two singlets, $SiMe_2$, area ratio 1:1), 1.01 + 1.05 (two singlets, *t*-Bu + *t*-Bu), 7.08 + 7.42 + 8.65 (m, py, area ratio 1:2:1); MS (EI, 15 eV), m/z (relative intensity) 364 (M^+ − Me, 6.1), 322 (M^+ − *t*-Bu, 100), 301 (M^+ − py, 9.8), 259 (73.2), 250 (82.9), 217 (8.5), 203 (17.1).

Reactions of 2–4. To a 0.1 M solution of the tetrahydrofuran adduct **2** in Et_2O at −78 °C (for the gaseous reactants: to a frozen solution at −196 °C) were added/condensed equimolar amounts of the following reactants: H_2O, propene, isobutene, methanol in Et_2O, acetic acid in Et_2O, acetone in Et_2O, $BF_3\cdot Et_2O$ in Et_2O, 1,3-butadiene, tri-*tert*-butylazidosilane in Et_2O. After the reaction mixture was warmed to room temperature and worked up as described in ref 2a, products **8**–**15** and **17** are obtained (Scheme I) (characterization: cf. ref 2a).

For the reaction with bromine, 0.53 mmol of **2** in 2 mL of Et_2O at −78 °C was combined with 0.1 mL of Br_2. After the mixture was warmed to room temperature and all volatile components were evaporated in vacuo, a yellowish residue remained which consisted of **18** and **19** in a molar ratio of 55:45 (^{1}H NMR). **18** was obtained by fractional sublimation at 60–70 °C under high vacuum (mp 160–164 °C; characterization by comparison with an authentical probe[2a]). **19** decomposed on attempted distillation and, therefore, could not be purified further. **19**: ^{1}H NMR (CCl_4) δ 0.305 (s, SiMe), 0.343 (s, $SiMe_3$), 0.411 + 0.449 (s, $SiMe_2$, area ratio 1:1), 1.149 + 1.196 (s, *t*-Bu, area ratio 1:1), 1.764 (m, $-CH_2CH_2-$), 3.351 (t, CH_2O), 3.659 (t, CH_2Br).

To a 0.3 M solution of the trimethylamine adduct **3** in Et_2O at room temperature was added an equimolar amount of methanol. Under warming and gas evolution (NMe_3) **11** was formed: characterization by comparison with an authentic probe.[2a]

To a 0.7 M solution of the red pyridine adduct **4** in Et_2O at −78 °C was added an equimolar amount of acetone. On warming to −25 °C the red color disappeared within 15 min and **13** was formed: characterization by comparison with an authentic probe.[2a]

X-ray Structure Determination of 5. Single crystals of **5** were obtained from Et_2O at −30 °C. Crystal preparation and data collection procedures followed closely those described in ref 1 and 8. Crystal data and a summary of parameters pertinent to intensity data collection and structure refinement are given in Table I. The structure was solved by direct methods (MULTAN 80) and completed by difference Fourier syntheses. Refinement was first carried out isotropically with unit weights and all parameters held in one block. After conversion to anisotropic thermal parameters refinement was done with statistical weights and the parameters in four large blocks (GFMLX[9]). At this stage

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(5) (a) Wiberg, N.; Schurz, K.; Fischer, G. *Angew. Chem.* **1985**, *97*, 1085. (b) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591. (c) Wiberg, N.; Köpf, H. *J. Organomet. Chem.* **1986**, *315*, 9.

(6) The unsuitability of single crystals of **3** and the high thermal instability of **4** prevented structural characterization as yet.

(7) Present evidence (identical products in the thermolysis of **1**, **2**, and **3**) indicates that decomposition of **2** and **3** proceeds via the donor-free silaethene **1**, which then decomposes further. Further work to clarify this point is in progress.

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

Table I. Crystal Structure Data for 5

formula	$C_{31}H_{68}FLiO_8Si_3$
M_r	679.08
cryst system	triclinic
space group	$P\bar{1}$
a, Å	10.245 (1)
b, Å	18.126 (2)
c, Å	22.175 (3)
α, deg	88.65 (1)
β, deg	95.62 (1)
γ, deg	97.71 (1)
V, Å^3	4060.9
Z	4
D_{calcd}, g/cm^3	1.111
T, °C	−40
μ(Mo Kα), cm^{-1}	1.6
$F(000)$, e	1488
radiatn	Mo Kα
λ, Å	0.71069
scan type	ω
scan width, deg	0.9
scan speed, deg/min	0.9–29.3
scan range (θ), deg	1.0–22.5
hkl range	$h,\pm k,\pm l$
measd data	11525
unique data	10564
R_{int}[a]	0.044
obsd data [$I \geq 2.0\sigma(I)$]	6939
ref params	793
R[b]	0.071
R_w[c]	0.077
(shift/error)$_{max}$	0.29
$\Delta\rho_{fin}$(max), e/Å^3	+0.72

[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] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

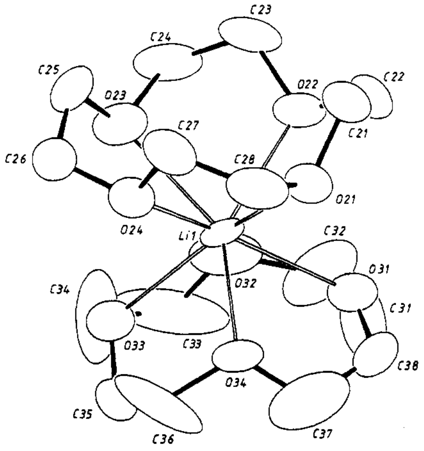

Figure 1. Structure of one of the two crystallographically independent $[Li(12\text{-crown-}4)_2]^+$ cations in 5 (ORTEP, thermal ellipsoids at the 50% probability level, H atoms omitted for clarity).

24 hydrogen atoms out of a total of 136 could be located and served to determine the conformations of all methyl groups. The remainder was calculated at idealized geometrical positions (XANADU). Final refinement was done by block-diagonal least squares with fixed H atoms and the parameters of each non-H atom held in one block (GBDL[10]). Relatively high anisotropic thermal parameters for some of the crown ether methylene groups strongly indicated static disorder of these atoms. Refinement of split models failed, however. The anisotropic treatment of these atoms leads to an artificial shortening of the bonds involved. Table II contains the final atomic coordinates of the non-H atoms. Tables III and IV summarize important bond distances and angles together with those of 1[1] and 2.[3] Figures 1 and 2 depict the molecular structure (ORTEP). Reference 8 contains the sources of the scattering factors and the programs used.

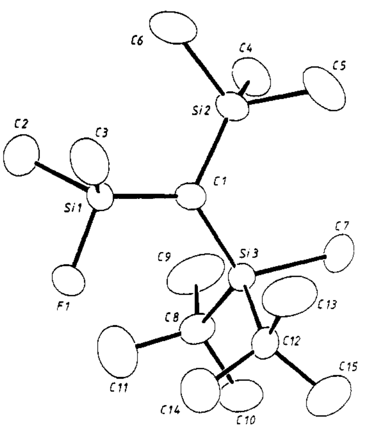

Figure 2. Structure of one of the independent carbanions in 5 and atomic numbering scheme used (ORTEP, H atoms omitted).

Results and Discussion

Thermal and Complex Stability of 2–5. Similar to the *tetrahydrofuran adduct* 2,[3] the *trimethylamine adduct* 3 forms colorless, air- and moisture-sensitive crystals, which are soluble in organic solvents and may be sublimed under partial decomposition. According to mass spectrometry, the gas phase of 2 and 3 contains the discrete molecules 1 and THF or NMe_3, respectively. The donor molecule is more tightly bound in 3 than in 2, as follows from the complete substitution of THF by NMe_3 (eq 1) This reaction also serves as the best preparative route to 3. Adduct 3 is somewhat more stable thermally than 2 and decomposes at 65 °C in solution during 3–4 days (at 100 °C during 4–5 h). Because the thermal decomposition presumably proceeds via the dissociation of the adducts into the donor molecules and the free silaethene 1,[7] the increase in thermal stability from 2 to 3 also points to an increase in complex stability in the same direction. Even more stable thermally is the pale yellow, air- and moisture-sensitive *fluoride adduct* 5 which does not decompose up to 100 °C. It is markedly less soluble in organic solvents which points to a more ionic structure, as verified by the X-ray structure analysis (see below). Due to the insolubility of the crown ether complex of LiF, the relative complex stability of 5 may not be determined directly by substitution of NMe_3 in 3 by F^-. To judge from its thermal stability, the complex stability of 5 is most probably higher than that of 3. Compound 3, as does 2, reacts with pyridine in Et_2O to give the burgundy-red *pyridine adduct* 4[11] (eq 2). This establishes the following sequence of increasing Lewis basicity toward the silaethene 1: THF < NMe_3 < C_5H_5N, F^-. Except for the thermolabile pyridine adduct 4, the thermal stability of the adducts increases in the same order: 2 < 3 < 5. The reason for the markedly reduced thermal stability of 4 has to be sought in the fact that 4 does not decompose in the regular manner by formation

$$\underset{\mathbf{2}}{THF{\cdot}Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)} + NMe_3 \rightarrow \underset{\mathbf{3}}{Me_3N{\cdot}Me_2Si{=}(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)} + THF \quad (1)$$

$$\underset{\mathbf{3}}{Me_3N{\cdot}Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)} + C_5H_5N \rightarrow \underset{\mathbf{4}}{C_5H_5N{\cdot}Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)} + NMe_3 \quad (2)$$

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(9) GFMLX, a highly modified version of ORFLSD, by Hirshfeld, Coppens, Leiserowitz, and Rabinovich for full-matrix least squares with blocking option and enantiopol refinement (by Flack).

(10) GBDL, Davis' block-diagonal least-squares program as modified from the Kartha S version of the Sparks–Trueblood BDLSQ program.

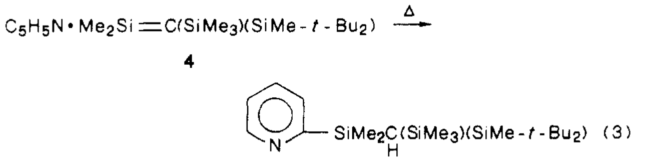
(11) Deeply colored adducts of pyridine with decaborane have been known for a long time: Graybill, B. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 2673.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for 5[a]

atom	x/a	y/b	5^d	U_{eq}, Å^2	atom	x/a	y/b	5^d	U_{eq}, Å^2
Si1	0.6037 (1)	0.1793 (1)	−0.0572 (1)	0.027	C11	0.3133 (7)	0.1411 (4)	0.0365 (3)	0.061
Si1′	0.6769 (1)	0.3128 (1)	0.4581 (1)	0.034	C11′	0.3672 (5)	0.3397 (3)	0.5293 (2)	0.039
Si2	0.7981 (1)	0.2614 (1)	0.0386 (1)	0.036	C12	0.4030 (5)	0.3419 (3)	−0.0133 (2)	0.034
Si2′	0.5306 (1)	1.850 (6)	0.3487 (1)	0.037	C12′	0.4788 (5)	0.1445 (2)	0.5417 (2)	0.029
Si3	0.4982 (1)	0.2768 (1)	0.0404 (1)	0.028	C13	0.5039 (7)	0.3905 (4)	−0.0466 (3)	0.064
Si3′	0.4132 (1)	0.2032 (1)	0.4736 (1)	0.024	C13′	0.5917 (6)	0.1064 (3)	0.5217 (2)	0.042
F1	0.4475 (2)	0.1640 (1)	−0.0838 (1)	0.038	C14	0.3016 (7)	0.3005 (3)	−0.0595 (3)	0.057
F1′	0.6768 (3)	0.3239 (1)	0.5316 (1)	0.045	C14′	0.5290 (6)	0.1883 (3)	0.5986 (2)	0.039
O21	0.3547 (4)	0.5590 (2)	0.3049 (1)	0.051	C15	0.3280 (7)	0.3941 (4)	0.0182 (3)	0.064
O22	0.1826 (4)	0.6605 (2)	0.2754 (1)	0.048	C15′	0.3722 (6)	0.0821 (3)	0.5606 (2)	0.042
O23	−0.0142 (4)	0.5820 (2)	0.3378 (1)	0.058	C21	0.3958 (6)	0.6346 (3)	0.3191 (2)	0.053
O24	0.1609 (4)	0.4809 (2)	0.3667 (1)	0.048	C22	0.3211 (6)	0.6793 (3)	0.2749 (2)	0.051
O31	0.2050 (4)	0.5553 (2)	0.1780 (1)	0.057	C23	0.1302 (7)	0.6980 (3)	0.3208 (3)	0.055
O32	−0.0511 (5)	0.5725 (2)	0.1965 (2)	0.073	C24	−0.0077 (7)	0.6610 (3)	0.3248 (3)	0.055
O33	−0.0543 (4)	0.4397 (2)	0.2614 (1)	0.057	C25	0.0157 (7)	0.5643 (4)	0.3984 (3)	0.058
O34	0.1987 (4)	0.4263 (2)	0.2422 (1)	0.048	C26	0.0530 (7)	0.4875 (3)	0.4009 (3)	0.055
O41	0.0916 (3)	0.0354 (2)	0.6515 (1)	0.049	C27	0.2848 (7)	0.5039 (3)	0.3982 (2)	0.052
O42	−0.1017 (3)	0.0983 (2)	0.7027 (1)	0.050	C28	0.3839 (6)	0.5091 (3)	0.3536 (3)	0.054
O43	−0.1226 (4)	−0.0245 (2)	0.7774 (1)	0.053	C31	0.1242 (9)	0.5662 (6)	0.1299 (3)	0.092
O44	0.0700 (4)	−0.0879 (2)	0.7265 (2)	0.056	C32	0.024 (1)	0.6029 (5)	0.1440 (3)	0.083
O51	0.2989 (3)	0.0333 (2)	0.7609 (1)	0.049	C33	−0.1492 (9)	0.5202 (5)	0.1830 (5)	0.085
O52	0.1462 (3)	−0.0178 (2)	0.8513 (1)	0.046	C34	−0.1718 (7)	0.4700 (6)	0.2304 (3)	0.072
O53	0.0282 (3)	0.1094 (2)	0.8389 (1)	0.047	C35	−0.030 (1)	0.3768 (4)	0.2380 (4)	0.079
O54	0.1811 (4)	0.1616 (2)	0.7470 (1)	0.050	C36	0.0990 (8)	0.3644 (3)	0.2504 (4)	0.057
C1	0.6280 (5)	0.2390 (3)	0.0068 (2)	0.030	C37	0.2468 (9)	0.4294 (5)	0.1885 (4)	0.091
C1′	0.5393 (4)	0.2498 (3)	0.4282 (2)	0.026	C38	0.2898 (9)	0.4985 (4)	0.1690 (4)	0.075
C2	0.6414 (6)	0.0816 (3)	−0.0474 (2)	0.053	C41	−0.0157 (6)	0.0514 (4)	0.6143 (3)	0.061
C2′	0.6855 (6)	0.4122 (3)	0.4323 (3)	0.053	C42	−0.0634 (6)	0.1141 (3)	0.6406 (2)	0.043
C3	0.6779 (6)	0.2135 (4)	−0.1277 (2)	0.054	C43	−0.2245 (6)	0.0591 (4)	0.7052 (3)	0.060
C3′	0.8468 (6)	0.2870 (4)	0.4545 (3)	0.054	C44	−0.2271 (5)	0.0242 (4)	0.7653 (3)	0.049
C4	0.8394 (6)	0.2279 (3)	0.1190 (3)	0.047	C45	−0.1582 (7)	−0.0928 (4)	0.7524 (3)	0.061
C4′	0.3860 (6)	0.2628 (3)	0.3008 (2)	0.049	C46	−0.0377 (6)	−0.1319 (3)	0.7583 (3)	0.043
C5	0.8677 (6)	0.3631 (3)	0.0410 (2)	0.048	C47	0.0610 (7)	−0.0998 (3)	0.6663 (3)	0.061
C5′	0.5280 (6)	0.1298 (4)	0.3279 (2)	0.054	C48	0.1398 (6)	−0.0358 (3)	0.6382 (3)	0.045
C6	0.9210 (6)	0.2207 (5)	−0.0037 (3)	0.069	C51	0.3386 (6)	−0.0214 (3)	0.8070 (2)	0.044
C6′	0.6765 (7)	0.2773 (4)	0.3105 (3)	0.067	C52	0.2848 (6)	−0.0115 (3)	0.8647 (3)	0.053
C7	0.5665 (6)	0.3417 (3)	0.1060 (2)	0.044	C53	0.0796 (6)	0.0098 (3)	0.8988 (2)	0.050
C7′	0.2954 (5)	0.1309 (3)	0.4275 (2)	0.038	C54	0.0852 (6)	0.0911 (4)	0.8961 (2)	0.056
C8	0.3788 (5)	0.2021 (3)	0.0790 (2)	0.033	C55	0.0568 (6)	0.1888 (3)	0.8231 (3)	0.051
C8′	0.2944 (5)	0.2691 (3)	0.4983 (2)	0.031	C56	0.1858 (7)	0.2053 (3)	0.7972 (3)	0.059
C9	0.4639 (7)	0.1653 (4)	0.1283 (3)	0.059	C57	0.3110 (6)	0.1553 (4)	0.7277 (3)	0.052
C9′	0.2192 (5)	0.2956 (3)	0.4401 (2)	0.042	C58	0.3807 (6)	0.1006 (4)	0.7646 (3)	0.054
C10	0.2707 (5)	0.2329 (3)	0.1095 (2)	0.047	Li1	0.124 (1)	0.5315 (5)	0.2707 (4)	0.036
C10′	0.1914 (5)	0.2334 (3)	0.5395 (2)	0.045	Li2	0.0784 (9)	0.0356 (5)	0.7592 (4)	0.036

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

of pyridine and the thermolysis products of 1.[7] Instead, it isomerizes well below 0 °C under formation of an insertion product of 1 into an ortho CH bond of pyridine (eq 3).



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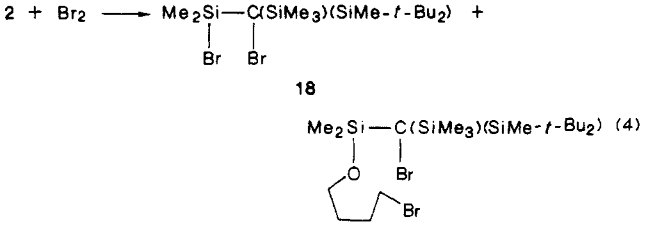
(3)

6

Reactivity of 2–5. The reactions of 2–5 probably proceed in most cases via the "free" silaethene 1 which is formed by primary dissociation of the adducts. This is evident from the fact that most reactions of the THF adduct 2, which by far is the best studied compound of 2–5 as yet, lead to identical products as those of "free" 1. This is exemplified by the insertion reactions into the O–H or B–F bonds of H_2O, MeOH, $MeCO_2H$, and BF_3 leading to 7, 8, 11, 12, and 14, by the ene reaction products 9, 10, and 13 from reactions with propene, isobutene, and acetone and by the cycloaddition product 15 from the reaction with 1,3-butadiene (Scheme I).

Tri-*tert*-butylazidosilane probably also forms a cycloaddition product 16 which then decomposes into the stable silaketimine (silanimine) 17 and the corresponding diazomethane (cf. Scheme I and ref 5b). Particularly indicative for the proposed dissociation/addition mechanism is the reaction of an equimolar mixture of MeOH and $MeCO_2H$ with 1 and 2. Compounds 11 and 12 are formed in a constant molar ratio of 3:2, independent of whether "free" 1 or its THF adduct 2 is used.[3] Present evidence indicates that these observations for the THF adduct 2 are in part also valid for the NMe_3 adduct 3 and also for the C_5H_5N adduct 4. This is clearly seen from the reaction of 4 with acetone leading to the ene product 13 (for the mechanism of the reaction of 3 with MeOH, leading to 11, cf. ref 5c). On the other hand, the reactions of 1 and 2 with bromine lead in part to different products. Bromination of 1 yields exclusively the expected dibromo adduct 18.[2a] 2 reacts with bromine to form 18 and 19 in about 1:1 ratio (eq 4). 19 points to electrophilic addition of bromine to



18

(4)

19

Scheme I

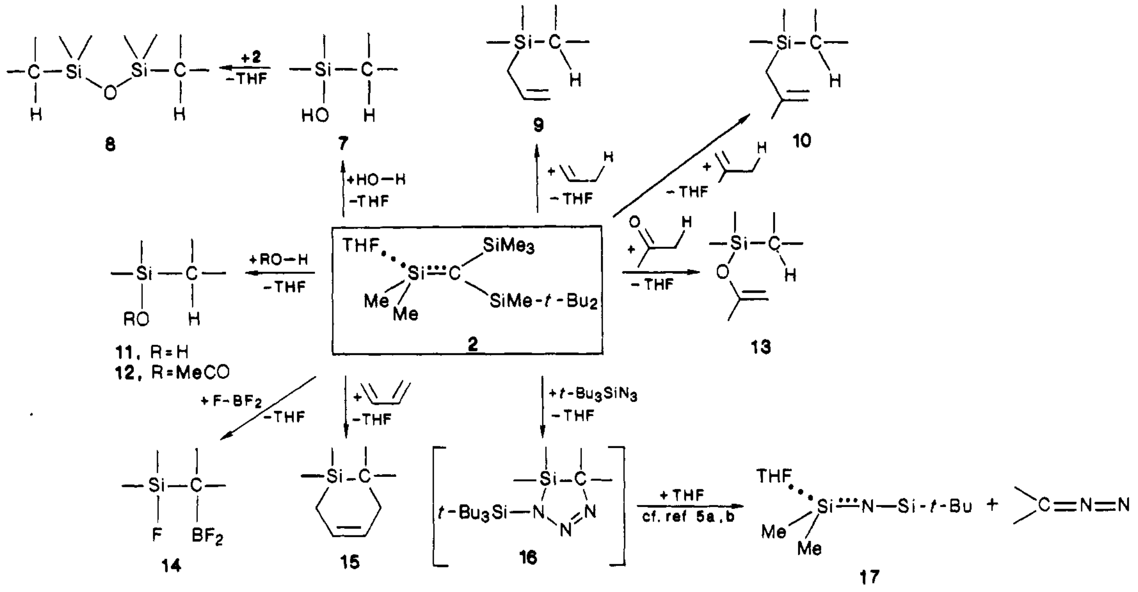


Table III. Important Interatomic Distances[a] (Å) for 1,[b] 2,[c] and 5

	1	2	5[d]
Si1–C1	1.702 (5)	1.747 (5)	1.782 (6)/1.777 (6)
Si2–C1	1.865 (5)	1.835 (5)	1.812 (6)/1.796 (5)
Si3–C1	1.890 (5)	1.836 (5)	1.806 (6)/1.822 (5)
Si1–C2	1.851 (5)	1.850 (6)	1.867 (7)/1.871 (7)
Si1–C3	1.842 (5)	1.858 (6)	1.863 (7)/1.872 (6)
Si1–O		1.878 (4)	
Si1–F1			1.640 (3)/1.647 (4)
Si2–C4	1.879 (5)	1.879 (6)	1.897 (7)/1.888 (7)
Si2–C5	1.892 (6)	1.885 (6)	1.887 (7)/1.890 (7)
Si2–C6	1.864 (6)	1.898 (7)	1.876 (8)/1.883 (8)
Si3–C7	1.893 (5)	1.907 (6)	1.910 (7)/1.901 (6)
Si3–C8	1.934 (5)	1.939 (5)	1.941 (6)/1.938 (6)
Si3–C12	1.909 (5)	1.927 (6)	1.944 (6)/1.946 (5)
C8–C9	1.533 (8)	1.53 (1)	1.529 (9)/1.538 (8)
C8–C10	1.526 (7)	1.513 (9)	1.525 (8)/1.532 (8)
C8–C11	1.529 (8)	1.45 (1)	1.514 (9)/1.535 (8)
C12–C13	1.544 (7)	1.44 (1)	1.51 (1)/1.531 (8)
C12–C14	1.532 (7)	1.51 (1)	1.520 (9)/1.517 (8)
C12–C15	1.548 (7)	1.522 (9)	1.519 (9)/1.544 (8)
O–C16		1.474 (6)	
O–C19		1.480 (6)	
C16–C17		1.508 (9)	
C17–C18		1.504 (9)	
C18–C19		1.488 (9)	
Li1–O21			2.40 (1)
Li1–O22			2.34 (1)
Li1–O23			2.43 (1)
Li1–O24			2.32 (1)
Li1–O31			2.30 (1)
Li1–O32			2.49 (1)
Li1–O33			2.30 (1)
Li1–O34			2.27 (1)
Li2–O41			2.41 (1)
Li2–O42			2.51 (1)
Li2–O43			2.27 (1)
Li2–O44			2.36 (1)
Li2–O51			2.26 (1)
Li2–O52			2.33 (1)
Li2–O53			2.38 (1)
Li2–O54			2.41 (1)

[a] Eds in units of the last significant figure in parentheses. [b] Reference 1. [c] Reference 3. [d] Both values for the two independent anions are given.

the Si–C "double bond" in 2 before the dissociation into 1 and THF. The Br^- ion formed in this step is then able to attack the THF C atoms vicinal to O (formation of 19).

Table IV. Important Interatomic Angles (deg) for 1,[a] 2,[b] and 5

	1	2 (X = O)	5 (X = F)[c]
C1–Si1–C2	127.0 (3)	119.7 (3)	119.2 (3)/117.5 (3)
C1–Si1–C3	129.0 (2)	124.1 (3)	118.3 (3)/118.3 (3)
C2–Si1–C3	104.0 (3)	104.9 (3)	104.7 (3)/105.9 (3)
C1–Si1–X		107.9 (2)	111.8 (2)/112.0 (2)
X–Si1–C2		97.9 (2)	100.2 (3)/99.7 (3)
X–Si1–C3		96.5 (2)	99.5 (2)/100.7 (3)
Si1–C1–Si2	119.5 (3)	114.9 (3)	115.3 (3)/116.4 (3)
Si1–C1–Si3	122.8 (3)	126.7 (3)	125.0 (3)/123.8 (3)
Si2–C1–Si3	117.7 (2)	117.2 (3)	119.7 (3)/119.8 (3)
C1–Si2–C4	113.2 (2)	114.9 (2)	116.7 (3)/115.4 (3)
C1–Si2–C5	110.8 (2)	114.7 (3)	116.6 (3)/116.3 (3)
C1–Si2–C6	115.9 (3)	115.3 (2)	114.1 (3)/113.8 (3)
C4–Si2–C5	108.4 (3)	107.1 (3)	103.2 (3)/105.1 (3)
C4–Si2–C6	102.9 (3)	101.5 (3)	102.1 (3)/102.5 (3)
C5–Si2–C6	104.9 (3)	101.6 (3)	102.0 (3)/101.9 (3)
C1–Si3–C7	111.0 (2)	110.7 (3)	111.9 (3)/111.2 (3)
C1–Si3–C8	112.8 (2)	113.3 (2)	113.6 (3)/113.2 (2)
C1–Si3–C12	111.3 (2)	114.0 (2)	114.1 (3)/115.3 (2)
C7–Si3–C8	102.8 (2)	102.9 (3)	102.3 (3)/102.2 (2)
C7–Si3–C12	103.0 (2)	102.4 (3)	101.8 (3)/102.3 (3)
C8–Si3–C12	115.1 (2)	112.4 (3)	111.9 (2)/111.3 (2)
Si1–O–C16		126.7 (3)	
Si1–O–C19		121.1 (3)	
C16–O–C19		110.4 (4)	

[a] Reference 1. [b] Reference 3. [c] Both values for the two independent anions are given.

Whether 18 is formed directly from $2{\cdot}Br^+Br^-$ under substitution of THF or by bromination of 1 cannot be decided, however.

Structure of $[Li(12\text{-crown-}4)_2]^+[FMe_2Si\ddot{C}(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)]^-$ (5). The structure of 5 consists of discrete $[Li(12\text{-crown-}4)_2]^+$ cations (Figure 1) and tris(silyl)methanide anions (Figure 2), the asymmetric unit being composed of two formula units. The shortest Li···F and Li···C1 distances are longer than 4.0 Å.

The molecular structures of both crystallographically independent cations differ with regard to details in the Li coordination and the conformations of the 12-crown-4 molecules. They have in common a "puckered sandwich" structure with an eightfold oxygen coordination at Li in the form of an irregular square antiprism with relatively long Li–O distances (2.27 (1) – 2.51 (1) Å; Table III). As similar $[Li(12\text{-crown-}4)_2]^+$ cations have already been structurally characterized,[12] they shall not be described in

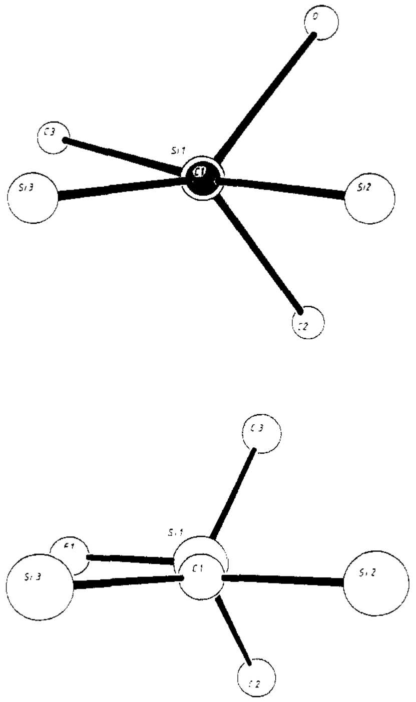


Figure 3. "Newman projections" of the central skeleton of 2 and 5, as seen down the C1–Si1 axis (ORTEP, atoms with arbitrary radii).

greater detail here.

The structures of the independent carbanions, which are of more importance for the scope of the present study, do not differ significantly (Tables III and IV). The carbanionic C atom C1 is strictly trigonally planar coordinated by two trialkylsilyl and one dialkylfluorosilyl group (sum of the valence angles at C1 = 360°). The C1–Si bonds range between 1.777 (6) and 1.822 (5) Å, with the bonds to the fluoro-substituted Si atoms marginally (but consistently) shorter. Whereas the valence angles at the trialkylsilyl groups Si2 and Si3 do not show major deviations from the tetrahedral standard, those at Si1 do. Most noteworthy are the angles C1–Si1–C2/C3 — larger by ca. 10°— whereas C2–Si1–C3 is compressed to 104.7 (3)/105.9 (3)°. The angles involving fluorine are close to tetrahedral in the case of F1–Si1–C1; the angles F1–Si1–C2/C3 are significantly compressed to about 100°. As the substituents at Si1 are by no means stereochemically demanding, the particular bonding geometry points to an electronic origin. The only apparent stereochemical preference seems to be the conformation of the FMe$_2$Si group with respect to rotation about C1–Si1. It is the smallest substituent (F1) which is closest to the *t*-Bu groups at Si3 (torsion angles Si3–C1–Si1–F1 = 1.7/0.0°; see Figure 3).

Structural Comparison of 1, 2, and 5. It is the close structural similarity between the fluoride adduct **5** and the previously described THF adduct **2** which allows important conclusions to be drawn as to the puzzling bonding situation indicated by the molecular structure of **2**[3] (Tables III and IV; Figure 4). Actually, the markedly irregular tetrahedral substituent geometry at the "unsaturated" Si atoms Si1 in **2** and **5** is most conspicuous, as steric reasons for this effect can almost certainly be ruled out. A comparison of the bond angles at Si1 in both compounds (Table IV) reveals the similarity of the distortions, with

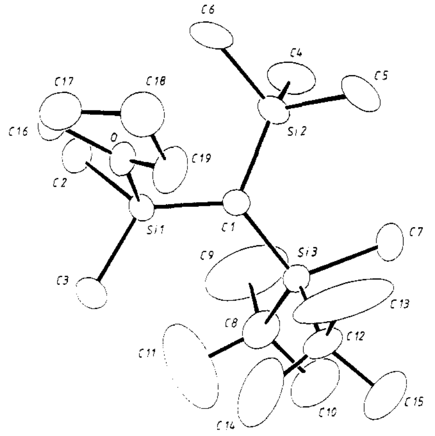


Figure 4. Molecular structure of **2**[3] (ORTEP, H atoms omitted).

the substituent geometry at Si1 in **5** to be somewhat closer to tetrahedral. Intuitively, one might argue that the observed Si1 geometries look as if the approach of the donor molecules (THF, F$^-$) to the unsaturated Si atom on the reaction coordinate is stopped short before the fully tetrahedral geometry is reached. This is supported particularly (a) by the angles C1–Si1–C2/C3 in **5** and **2** which increasingly resemble those in **1**, (b) by the unchanged angles C2–Si1–C3 in **1**, **2**, and **5**, and (c) by the angles X–Si1–C2/C3 (X = F or O) which are closer to 90° in **2** than in **5**. In line with this view are the Si1–X distances in **2** and **5** which both are unusually long. This is especially true for Si1–O in **2** (1.878 (4) Å) which has no precedence in the literature.[13] For Si1–F in **5** (1.640 (3)/1.647 (4) Å) the difference to normal Si–F bonds (cf. Si–F = 1.57 Å in Me$_3$SiF[14]) is less dramatic but still noteworthy. Although the reason for such an "incomplete" addition reaction is unclear as yet, it points to a pronounced energetic preference of the silicon–carbon double bond.

As Figure 3 shows, the most noticeable difference in the geometries of **2** and **5** arises from a different conformation of the silyl group Si1 with respect to rotation about Si1–C1. Apparently these groups are rotated into a position of least steric hindrance with the differently sized substituents Si2 and Si3 at C1. It is the smallest substituent at Si1 (F in **5**, Me in **2**) which is closest to the SiMe-*t*-Bu$_2$ groups.

Particularly informative are the trends in the bond lengths at Si1 in **2** and **5** (Table III). In **5** Si1–C1 (1.782 (6)/1.777 (6) Å) are slightly shorter than C1–Si2/Si3 and lie halfway between Si–C double (1.70 Å) and single (1.87 Å) bonds.[15] In the THF adduct **2** Si1–C1 is noticeably shorter (1.747 (5) Å), but C1–Si2/Si3 are longer and approach the Si–C single bond value. As discussed in the preceding paper,[1] in the silaethene **1** the Si1–C1 distance is even shorter, whereas the C1–Si2/Si3 bond lengths are essentially those of "normal" Si–C single bonds.

These observations lend ample support to a zwitterionic/π-bonding model for **2** and **5** which is essentially a resonance formulation between the zwitterionic structure A and the no-bond structure B.[16] The importance of a

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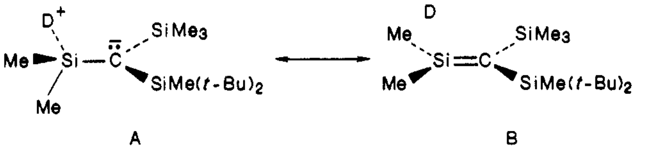
(12) (a) Hope, H.; Olmstead, M. M.; Power, P. P.; Xu, X. *J. Am. Chem. Soc.* **1984**, *106*, 819. (b) Olmstead, M. M.; Power, P. P. *Ibid.* **1985**, *107*, 2174. (c) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *Ibid.* **1985**, *107*, 4337.

(13) See ref 3 for a discussion.

(14) Wilkins, C. J.; Sutton, L. E. *Trans. Faraday Soc.* **1954**, *50*, 783.

(15) Typical Si–C distances in silyl-substituted carbanions where the carbanion participates in close Li–C contacts range between 1.78 and 1.95 Å. See, e.g.: Atwood, J. L.; Fjeldberg, T.; Lappert, M. F.; Luong-Thi, N. T.; Shakir, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1163. (b) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *Ibid.* **1983**, 1390, 827. (c) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 311. (d) Engelhardt, L. M.; Leung, W.-P.; Raston, C. L.; Twiss, P.; White, A. H. *Ibid.* **1984**, 321. (e) Hacker, R.; Reber, G.; Müller, G.; Schleyer, P. v. R.; Brandsma, L. *J. Organomet. Chem.*, in press.

(16) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.



zwitterionic contribution to the bonding in **2** was previously proposed on a tentative basis to account for the peculiar structure of **2**.[3] With increasing Lewis basicity of the donor D (D = THF < F^-) toward the Lewis acidic center Si1, the weight of the zwitterionic form A is expected to increase. In other words, the Si–C bond length changes observed upon going from "free" **1** to the THF adduct **2** to the fluoride adduct **5** result from an increased negative charge buildup at the former olefinic C atom C1 which causes the Si=C bond to lengthen (by increasingly less p orbital overlap) and the C1–Si2/Si3 bonds to shorten (mainly because of their greater polarity).

In summary, the structures of the silaethene **1** and its Lewis base adducts **2** and **5** form a concise picture of the silicon–carbon double bond in that (a) **1** closely resembles in reactivity and structure short-lived silaethenes, (b) **1** forms stable adducts with even weak donor molecules such as THF, whose structures show resemblances to that of **1**. They are best described by a zwitterionic/π-bonding model with the charge separation increasing with increasing donor character of the Lewis base toward the olefinic Si atom. The increased charge separation leads to an elongation of the former Si=C p_π–p_π bonds due to reduced p orbital overlap. They are still significantly shorter than Si–C single bonds, however, because of their high polarity (bond ionicity) as is best seen in the fluoride adduct **5**. The structures of the trimethylamine and pyridine adducts **3** and **4** are expected to be intermediate between **2** and **5**. A prerequisite for adduct formation seems to be a polar Si=X double bond as neither Brook's sila enol ether $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl), which has a largely nonpolar silicon–carbon double bond,[4] nor West's[17] or Masamune's[18] (symmetrical) disilenes have been reported to form stable adducts.

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Registry No. **1**, 87937-47-1; **2**, 93228-68-3; **3**, 105253-42-7; **4**, 105253-43-8; **5**, 105369-28-6; **6**, 105280-95-3; **8**, 100207-12-3; **9**, 100207-13-4; **10**, 105280-97-5; **11**, 87937-50-6; **12**, 100207-16-7; **13**, 87937-52-8; **14**, 87937-51-7; **15**, 87937-53-9; **17**, 100229-17-2; **18**, 87937-49-3; **19**, 105280-96-4; $Me_2SiFCLi(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$, 87937-48-2.

Supplementary Material Available: Complete tables of atomic and thermal parameters for **5** (10 pages); a listing of observed and calculated structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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Uranium–Carbon Multiple-Bond Chemistry. 7.[1] The Reaction of $Cp_3UCHP(CH_3)(C_6H_5)_2$ with Diphenylamine and the Structure of $Cp_3UN(C_6H_5)_2$

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The reaction between $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$ and $HN(C_6H_5)_2$ produces $Cp_3UN(C_6H_5)_2$ in good yield. The X-ray structure of this product, which is the first Cp_3U amide to be structurally characterized (space group $P2_1$, $a = 8.875$ (1) Å, $b = 8.402$ (1) Å, $c = 14.280$ (1) Å, $\beta = 99.68$ (1)°, $V = 1049$ (1) Å^3, and $Z = 2$, $R_1 = 0.054$ and $R_2 = 0.065$), shows the U–N bond distance to be 2.29 (1) Å and indicates a U–N bond order near 2.

While the Cp_3U^+ moiety (Cp = η-$C_5H_5^-$) is common in organouranium chemistry and the first uranium amides were characterized during the 1940s by Gilman's group,[2] no Cp_3U amides were known until several were mentioned[3] as byproducts in the preparation of $Cp_2U(NR_2)_2$. $Cp_3UN(C_2H_5)_2$ and $Cp_3UN(C_6H_5)_2$ were further reported in 1985.[4] It has been noted[4] that the synthesis of the amides is not as straightforward as that of most other Cp_3U–X systems. For example $Cp_3UN(C_6H_5)_2$ was obtained via an acid–base reaction

$$Cp_3UP(C_6H_5)_2 + HN(C_6H_5)_2 \rightarrow Cp_3UN(C_6H_5)_2 + HP(C_6H_5)_2$$

using $Cp_3UP(C_6H_5)_2$, which itself is not easily prepared.[4] An analogous reaction between $Cp_3UN(C_2H_5)_2$ and $HN(C_6H_5)_2$ failed to produce $Cp_3UN(C_6H_5)_2$, even though $HN(C_6H_5)_2$ is a stronger acid than $HN(C_2H_5)_2$[4] and the reaction of $U[N(C_2H_5)_2]_4$ with $HN(C_6H_5)_2$ has been used to synthesize $U[N(C_6H_5)_2]_4$.[5]

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