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UNSATURATED SILICON COMPOUNDS

VII *. PREPARATION AND STRUCTURE OF A SILAETHENE TETRAHYDROFURANATE **

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Summary

The compound $^tBu_2SiF{-}CLi(SiMe_3)_2 \cdot 4THF$, accessible by a multistep synthesis, decomposes in diethyl ether at room temperature to give initially $Me_2SiF{-}CLi(SiMe_3)(SiMe^tBu_2) \cdot nTHF$, and finally a colourless crystalline tetrahydrofuran adduct of the silaethene $Me_2Si{=}C(SiMe_3)(SiMe^tBu_2)$. The adduct may be sublimed (with partial decomposition, the gas phase containing both discrete silaethene and THF). The crystals are orthorhombic, space group $P2_12_12_1$ with lattice constants a 10.000(5), b 15.386(8), c 15.509(8) Å, V 2386.23 Å^3 and d_{calcd} 1.038 g/cm^3 for $Z = 4$ ($T = -45\,°C$). Full-matrix least-squares refinements of 208 parameters based on 1991 observed reflections ($F_o \geq 4.0\ \sigma(F_o)$) converged at $R = 0.052$. The THF molecule is clearly coordinated to the Si atom, which thereby adopts a distorted tetrahedral geometry. The trigonal planar sp^2 geometry expected for both the Si and C atoms of the silaethene molecule is retained only for the latter. However, the bond distance between these atoms (1.747(5) Å) is the shortest Si–C bond ever observed. The dative Si–O bond from the THF molecule, with a length of 1.878(4) Å, is significantly longer than ordinary Si–O bonds involving two- or three-coordinated oxygen. The implications of the structural parameters for the description of the bonding are discussed, and it is concluded that the adduct may be regarded as a zwitterion the formal charges of which are being located at the oxygen and the sp^2 carbon atoms, respectively. Strong support for this concept is provided by a comparison with relevant structural data for silaethenes and phosphorus ylids.

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[*] For Part VI and V see ref. 1 and 3. Also Part LVIII of Compounds of Silicon and its Group Homologues; for LVII see N. Wiberg, R. Meyers, S.K. Vasisht and H. Bayer, Chem. Ber., 117 (1984) in press. This work was supported by the Deutsche Forschungsgemeinschaft.

[**] Dedicated to Prof. M. Kumada.

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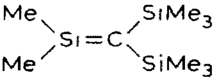
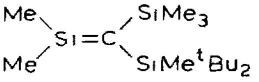
Introduction

Detailed investigations have shown that the simple silaethene I is probably formed only as a short-lived reaction intermediate and the evidence for its transitory existence is based on kinetic investigations and trapping experiments [2,3].


(I)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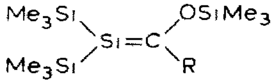
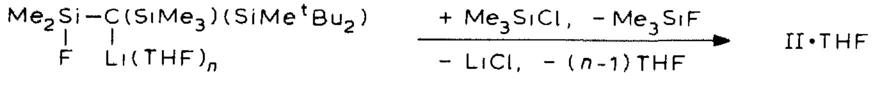

(III)

With increasing bulk of the silicon-bonded alkyl groups in I, the kinetic stability of the unsaturated silicon compound is increased. Thus the silaethene II, derived from I by formal replacement of a $\mathrm{SiMe_3}$ by a $\mathrm{SiMe^tBu_2}$ group, was stable enough to be isolated [1]. These findings parallel those of Brook et al. for the silaenol ethers III, which are more stable under normal conditions as the bulk of R is increased (e.g. R = adamantyl, $\mathrm{CEt_3}$) [4]. No single crystals of the silaethene II suitable for X-ray crystallography have yet been obtained, but as briefly indicated recently [1], the molecule forms a crystalline tetrahydrofuran adduct, II · THF. The preparation, properties and structure, of this adduct, and consideration of the bonding in it, are discussed in this paper.

Preparation of II · THF

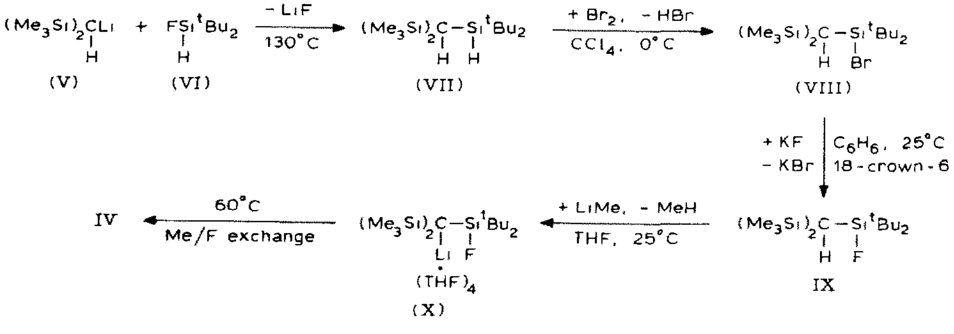
As previously found for other silaethenes [2], II may be obtained by the "thermal salt elimination" according to the scheme $\rangle\mathrm{SiX{-}CLi}\langle \rightarrow \rangle\mathrm{Si{=}C}\langle + \mathrm{LiX}$ (X = electronegative group or atom). The tetrahydrofuran adduct IV serves as a convenient precursor. IV readily undergoes elimination of LiF in diethyl ether at 100 °C (sealed tube), but the product formed under these conditions were unstable. However, in the presence of trimethylchlorosilane, II · THF is formed even at room temperature, where it is sufficiently thermostable to be isolated.



$$\underset{\mathrm{F}}{\mathrm{Me_2Si}}-\underset{\mathrm{Li(THF)}_n}{\mathrm{C}}\mathrm{(SiMe_3)(SiMe^tBu_2)} \xrightarrow[-\,\mathrm{LiCl},\ -\,(n-1)\mathrm{THF}]{+\,\mathrm{Me_3SiCl},\ -\,\mathrm{Me_3SiF}} \mathrm{II{\cdot}THF}$$

(IV)

The lithium compound IV is available from a multistep synthesis which is summarized below and described in detail in the experimental section:



Description of the structure of II · THF

Figure 1 depicts the molecular structure of II · THF. The most interesting feature is that there is an essentially planar, sp^2-hybridized carbon atom (C(1)) engaged in bonding with a tetracoordinate silicon atom of unusual geometry. It is specifically this silicon atom (Si(1)) with its two methyl groups which is clearly approached by the oxygen atom of the coordinated THF molecule. The Si(1)–C(1) bond length of 1.747(5) Å is drastically shorter than Si–C single bonds with sp^3- or sp^2-hybridized C atoms which range typically from 1.87 to 1.94 Å [5]. It is even slightly shorter than the 1.764(3) Å found in the silaenol ether III [4], although this difference may not be significant in the light of the e.s.d.'s. More important, it comes close to the range of 1.69–1.73 Å predicted on the basis of MO calculations for sterically unhindered Si=C double bonds [6].

Geometry at C(1). The planarity of C(1) is indicated by the sum of its bond angles (358.8°) and by the smallness of the deviation, only 0.11 Å, of C(1) from the Si(1),Si(2),Si(3) plane. The large discrepancies between the angles at C(1) (Tab. 2) are probably due to steric interactions between the substituents. The largest angle Si(1)–C(1)–Si(3) (126.7(3)°) is associated with the extremely bulky SiMe^{t}Bu$_2$ group, the corresponding Si(3)–C(8) and Si(3)–C(12) bonds of which adopt a gauche conformation relative to Si(1)–C(1) (for torsion angles see Tab. 2). The other angles at C(1), both smaller than that expected for sp^2, obviously compensate for this. The much smaller methyl groups, although involved in various eclipsing conformations, clearly induce far less severe strain. Facile bond angle distortion due to steric crowding seems to be a general phenomenon for sp^2-hybridized C atoms [7], and has also been observed in the silaenol ether III [4].

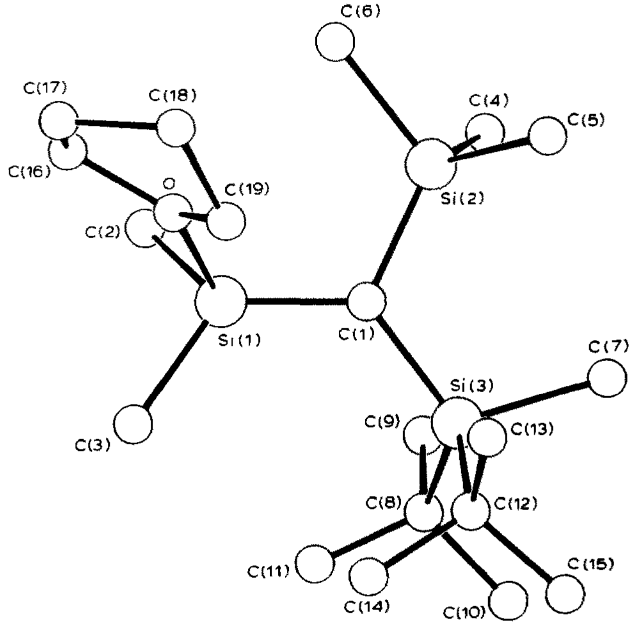


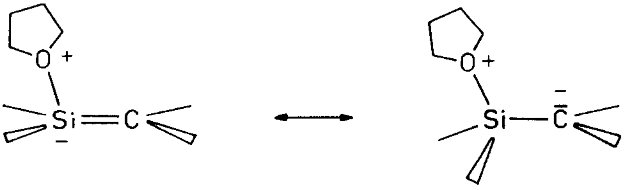
Fig. 1. Ball and stick model (ORTEP) of II·THF together with the numbering scheme used.

Geometry at Si(1). Deviations from perfect tetrahedral geometry, not easily explained in terms of steric crowding, are apparent at Si(1). The C(1)–Si(1)–C(2)/C(3) angles (119.7(3) and 124.1(3)°, respectively) show surprisingly little deviation from the 120° normal for an sp^2-hybridized atom, which is assumed to represent the bonding model for the free silaethene II in the absence of complexing THF. Relative to this model, the angle C(2)–Si(1)–C(3) (104.9(3)°) is significantly compressed, and is even smaller than the tetrahedral angle. The angles involving the THF oxygen atom may be divided into two groups: the O–Si(1)–C(1) angle, of 107.9(2)° is much larger than the O–Si(1)–C(2)/C(3) angles to the methyl groups, which are 97.9(2) and 96.5(2)°, respectively. The Si(1)–O distance is 1.878(4) Å, much longer than the 1.63–1.66 Å found for Si–O bonds with two-coordinated O atoms [8]. Even Si–O bonds involving three-coordinated O atoms, such as in aluminosiloxanes, are noticeably shorter (1.66(2)–1.76(3) Å [9]), although it should be kept in mind that in some of these examples the O atom is incorporated into a strained AlOAlO four-membered heterocycle.

The lengths of the Si(1)–C(2) and Si(1)–C(3) bonds (1.850(5) and 1.858(5) Å, respectively) agree reasonably well with those of the C(1)–Si(2) and C(1)–Si(3) bonds (1.835(5) and 1.836(5) Å). The latter are slightly shorter than the Si–Me bonds (1.879(6)–1.907(6) Å) in silyl groups in which both atoms show straightforward sp^3 hybridization. The Si–^{t}Bu bonds, (1.939(5), 1.927(6) Å) are even larger, and this must be attributed solely to steric strain.

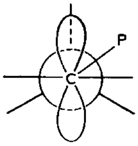
Discussion of the structure of II · THF

The bonding situation in II · THF can be described in terms of the resonance formulation XIa ↔ XIb.



XIa XIb

The canonical form XIa implies adduct formation between THF and the Si atom engaged in a Si=C double bond. Because of this interaction, the Si atom has to accomodate 10 valence electrons, which necessarily means *d*-orbital participation. The other canonical formula XIb involves a 1,3-charge separation as a consequence of a strong adduct formation. The Si-decet state is avoided by generation of a carbanionic center (lone pair of electrons). Molecules of formula XIb can be regarded as structurally related to phosphorus ylids $R_3\overset{+}{P}-\overset{-}{\bar{C}}R_2$. The rather long Si–O bond in II · THF is consistent with a relatively weak adduct XIa, in which suitable *d* functions at Si permit overlap with O donor orbitals. Although significantly distorted, the approximately tetrahedral substituent geometry around Si(1), on the other hand, is consistent with a zwitterionic species, as in XIb. The Si(1)–C(1) bond length itself gives no direct guide to the bonding. The distance is comparable to that in uncomplexed silaethenes such as III, in which it is roughly equal in length to the sum of hypothetical C and Si double bond radii [4]. Although at first glance this agreement seems to point to an essentially doubly bonded Si atom, as in XIa, it should also be noted, that the short ylidic bond in R_3PCR_2 molecules can be accounted for in terms of $(p\text{–}d)_\pi$ overlap of the lone pair at the ylidic C atom with suitable *d* orbitals at phosphorus [10], and electrostatic attraction between the localized partial charges of the zwitterionic molecule [11]. It should be kept in mind, however, that in phosphorus ylids the formal charges are located on adjacent atoms, whereas XIb implies a charge separation over two bonds. Much structural data are available for phosphorus ylids, and both experimental observations and theoretical investigations point to essentially free rotation about the ylidic P–C bond in solution [10]. In the solid state P ylids with sterically non-demanding substituents at P and the ylidic C atom seem to prefer the conformation shown below, in which one substituent at P is in an eclipsed conformation with respect to the ylidic p_z-lone pair at C [10,12]:



When the steric bulk of the substituents is increased, however, deviations from such a conformation are observed [13]. For II · THF, the conformation in the solid state also seems to be exclusively determined by steric interactions of the substituents at Si(1) and C(1). In particular, the small torsion angle C(3)–Si(1)–C(1)–Si(3) of 22.4° seems to minimize the steric interactions between the Me groups C(3) at Si(1) and C(11)/C(14) of the ^{t}Bu groups at Si(3) (see Fig. 2 and Fig. 1). For the silaenol ether III the NMR spectroscopic nonequivalence of the Si substituents

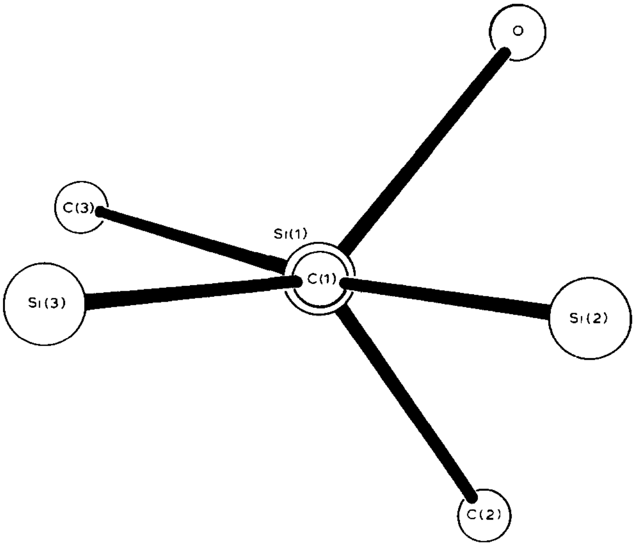


Fig. 2. View along the C(1)–Si(1) bond of II·THF ("Newman projection"). Only the atoms bonded to Si(1)/C(1) are shown.

pointed to a rigid structure on the NMR time scale, i.e. restricted rotation about the Si=C double bond in solution [4]. The adduct II · THF, on the other hand, shows equivalent Me groups at Si(1) in THF at 30 °C. This result is a strong support for the significance of form XIb, for which ylide-type bonding requires free rotation around the Si(1)–C(1) bond.

Some properties of II · THF

The adduct II · THF decomposes at room temperature during several days to give unidentified products. At 100 °C this decomposition is very fast. II · THF may be sublimed with partial decomposition at 10^{-4} Torr at room temperature. The mass spectrum indicates that the gas phase consists of discrete molecules II and THF. Clearly the bonding between II and THF is not very strong and is reversible. Reactions of II · THF with molecular oxygen, water, methanol, acetic acid, boron trifluoride, or acetone yield the same products as the analogous reactions with uncomplexed II, although the reactions of the latter are obviously faster. Apparently the reactive species in both cases is II, which exists in solution in a rapid equilibrium with II · THF:

$$\mathrm{II \cdot THF} \rightleftharpoons \mathrm{II + THF}$$

The equilibrium concentration and lifetime of the adduct are below the experimental limits of NMR spectroscopy, however. Further proof for II as the reactive species was obtained by allowing II · THF to react with an equimolar mixture of methanol and acetic acid, which yielded the MeOH and MeCOOH adducts of II in a molar ratio of 3/2 [14]. In the case of a direct reaction with II · THF, i.e. with a zwitterionic species, as in XIb the more acidic component should react faster.

Unsaturated silicon compounds may probably react generally with THF or other donor molecules as shown for II. Accordingly, the insertion of silaethenes $\rangle Si{=}C\langle$ into the O–H bond of alcohols could well proceed through initial formation of a silaethene alcohol adduct with an O–Si donor–acceptor bond. The final product $\mathrm{RO}{\geq}\mathrm{Si}{-}\overset{/}{\underset{\backslash}{\mathrm{C}}}\mathrm{H}$ would than be formed in a second step by hydrogen migration [15].

Experimental

Preparation of V

A solution of 1000 mmol LiBu in 600 ml hexane is added dropwise to a mixture of $CHBr_3$ and Me_3SiCl in 500 ml THF at −78 °C. Subsequently the solvent and the BuBr formed are evaporated off at 10 Torr. The residue is then fractionally distilled in high vacuum to yield 101.2 g (423 mmol, 85%) $(Me_3Si)_2CHBr$ at 75–85 °C/10 Torr. (Identity by comparison with an authentic sample [16]). 210 mmol LiBu in 130 ml hexane are dropped rapidly to a solution of 50 g (210 mmol) $(Me_3Si)_2CHBr$ in 200 ml Et_2O at −78 °C. Removal of all the volatiles at 10^{-2} Torr with gradual warming from −78 to 65 °C leaves solid colourless V (85%). ^1H NMR (C_6H_6): $\delta(Me_3Si)$ 0.172 ppm, $\delta(CH)$ −2.367 ppm.

Preparation of VI

Compound VI was prepared by a published method [17].

Preparation of VII

V, prepared as described above from 50 g (210 mmol) $(Me_3Si)_2CHBr$ is heated with 34 g (210 mmol) VI to 130 °C for 12 h. Subsequent distillation at 10^{-2} Torr and 80–120 °C yields solid colourless VII (yield: 90%, m.p. 40–60 °C), consisting of two rotamers (*gauche,trans*) in 1/1 molar ratio. Anal. Found: C, 59.36; H, 12.23. $C_{15}H_{38}Si_3$ calcd.: C, 59.51; H, 12.65%. ^1H NMR (CH_2Cl_2): $\delta(Me_3Si)$ 0.190 and 0.141 ppm; $\delta(^tBu)$ 1.098 and 1.013 ppm; $\delta(SiH)$ 3.703 ppm; $\delta(CH)$ −0.610 ppm.

Preparation of VIII

16 g (100 mmol) Br_2 in 100 ml CCl_4 are added dropwise to 30 g VII (99.3 mmol) in 100 ml CCl_4 at 0 °C. After evaporation of the solvent and the excess Br_2, VIII is obtained by sublimation at 10^{-2} Torr at temperatures > 120 °C in almost quantitative yield (m.p. 156 °C). Anal. Found: C, 47.80; H, 10.21. $C_{15}H_{37}BrSi_3$ calcd.: C, 47.21; H, 9.77%. ^1H NMR (C_6H_6): $\delta(Me_3Si)$ 0.310 ppm; $\delta(CH)$ −0.092 ppm; $\delta(^tBu)$ 1.133 ppm; (CCl_4): $\delta(Me_3Si)$ 0.282 ppm; $\delta(CH)$ −0.050 ppm; $\delta(^tBu)$ 1.140 ppm.

Preparation of IX

To a solution of 95.5 g (250 mmol) VIII and 3.5 g (12.5 mmol) 18-crown-6 in 500 ml benzene dried KF is added in several portions (3 × 20 g) during 24 h. The mixture is stirred for two days at room temperature, and then filtered, and the solvent evaporated. Distillation (80–100 °C, 10^{-2} Torr) affords colourless solid IX (m.p. 70–90 °C), consisting of two rotamers (*gauche,trans*) in a 5/6 molar ratio. Anal.Found: C, 55.50; H, 11.35. $C_{15}H_{37}FSi_3$ calcd.: C, 56.17; H, 11.63%. ^1H NMR (THF): $\delta(^tBu)$ 1.116 (d,$J(^1H-^{19}F)$ 1.8 Hz) and 1.036 ppm (d,$J(^1H-^{19}F)$ 0.72 Hz); $\delta(Me_3Si)$ 0.226 (s,broad) and 0.184 ppm (d,$J(^1H-^{19}F)$ 1.7 Hz); $\delta(CH)$ −0.034 ppm (d,$J(^1H-^{19}F)$ 0.7 Hz). (CCl_4): $\delta(^tBu)$ 1.091 (d,$J(^1H-^{19}F)$ 2.2 Hz) and 1.010 (s,broad) ppm; $\delta(Me_3Si)$ 0.193 (s,broad) and 0.157 ppm (d,$J(^1H-^{19}F)$ 1.7 Hz); $\delta(CH)$ − 0.138 (s,broad) ppm.

Preparation of X

A mixture of 16 g (50 mmol) IX, 100 mmol LiMe (as the etherate) and 75 ml THF is stirred for 5 days at room temperature. The mixture is then cooled to 0 °C and 12.5 ml (100 mmol) Me_3SiCl is added. After 30 min all the volatiles are evaporated off at room temperature and 10^{-2} Torr. The residue is dissolved in Et_2O and after filtration to remove the LiCl this solution of X is used directly. ^1H NMR (Et_2O): $\delta(^tBu)$ 0.969 ppm (d,$J(^1H-^{19}F)$ 0.7 Hz); $\delta(Me_3Si)$ −0.053 ppm (d, $J(^1H-^{19}F)$ 0.3 Hz); δ(THF) 1.929(m) and 3.772(m) ppm.

Preparation of II · THF

A solution of 1.5 mmol X and 0.5 ml (4 mmol) Me_3SiCl in 2 ml Et_2O is stirred for 1 h at room temperature, and the volatiles are then evaporated off at 10^{-2} Torr. The residue is dissolved in 2 ml Et_2O and the solution is filtered to remove LiCl. Cooling of the filtrate to −30 °C with slow evaporation of some solvent, if necessary, gives colourless crystals of II · THF. After two recrystallizations from Et_2O 250 mg (0.67 mmol, 45% of theory) of analytically pure II · THF is obtained. ^1H NMR (THF, 30 °C): $\delta(Me_2Si)$ 0.446 ppm; $\delta(SiMe^tBu_2)$ 0.082 ppm; $\delta(SiMe^tBu_2)$ 0.969 ppm.

Structure determination of II · THF

A suitable single crystal of $C_{19}H_{44}OSi_3$, II · THF, was mounted under argon at dry ice temperature in a Lindemann glass capillary. According to the diffraction data (Syntex $P2_1$) it crystallizes in the orthorhombic space group $P2_12_12_1$, as uniquely determined by the systematic absences. Reduced cell calculations did not reveal any higher symmetry. The following cell constants were determined by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 high order reflections from various parts of reciprocal space (T $-45 \pm 5\,°$C): a 10.000(5), b 15.386(8), c 15.509(8) Å, $V = 2386.23$ Å^3; d_{calcd} 1.038 g/cm^3 for $Z = 4$, $M_r = 372.820$, $F(000) = 832$.

Intensity data: Two forms of data ($\pm h$, $+k$, $+l$; $1 \leqslant \vartheta \leqslant 24\,°$) were measured by a multispeed moving crystal-stationary counter technique where the peak height at the calculated peak position served to determine the final scan speed (ω-scans, $\Delta\omega$ 0.9°, $1.2 \leqslant \dot{\omega} \leqslant 29.3\,°$/min, graphite-monochromated Mo-K_α radiation, λ 0.71069 Å). The time spent measuring the background intensities at each end of the scan interval was half that taken to measure the peak. A monitor reflection, examined after every 50 reflections, served as a check on the centering and stability of the crystal and diffractometer system, and there was no significant change in its intensity. The intensity of a reflection and its standard deviation were calculated as $I = (S - B/\beta)\dot{\omega}$ and $\sigma(I) = (S - B/\beta^2)^{1/2}\dot{\omega}$, where S is the total scan counts, B the total background counts, and β the time ratio of total background to scan. After Lorentz and polarization corrections ($F_o = (I/\text{Lp})^{1/2}$, $\sigma(F_o) = \sigma(I)/(2F_o\text{Lp})$) 150

TABLE 1

FINAL ATOMIC COORDINATES FOR THE NON-H ATOMS OF II·THF. E.s.d.'s IN UNITS OF THE LAST SIGNIFICANT FIGURE ARE GIVEN IN PARENTHESES

Atom	x/a	y/b	z/c
Si(1)	0.1784(1)	0.1764(1)	0.2608(1)
Si(2)	0.1828(2)	0.3424(1)	0.3647(1)
Si(3)	0.3892(1)	0.3258(1)	0.2136(1)
O	0.1777(4)	0.1123(2)	0.3639(2)
C(1)	0.2597(5)	0.2749(3)	0.2807(3)
C(2)	−0.0038(5)	0.1754(4)	0.2403(4)
C(3)	0.2469(6)	0.0886(4)	0.1914(4)
C(4)	0.0791(6)	0.4354(4)	0.3236(4)
C(5)	0.3038(7)	0.3884(4)	0.4460(4)
C(6)	0.0587(7)	0.2841(4)	0.4371(4)
C(7)	0.4194(7)	0.4430(4)	0.2486(5)
C(8)	0.3370(6)	0.3382(4)	0.0938(4)
C(9)	0.2017(9)	0.3851(8)	0.0913(6)
C(10)	0.4306(8)	0.3931(6)	0.0400(5)
C(11)	0.3128(15)	0.2579(5)	0.0476(5)
C(12)	0.5638(5)	0.2744(4)	0.2262(4)
C(13)	0.5910(8)	0.2615(12)	0.3167(5)
C(14)	0.5775(7)	0.1857(5)	0.1863(9)
C(15)	0.6755(6)	0.3287(5)	0.1869(6)
C(16)	0.0788(6)	0.0463(4)	0.3899(4)
C(17)	0.1446(7)	0.0000(4)	0.4644(4)
C(18)	0.2487(8)	0.0621(4)	0.4975(4)
C(19)	0.2987(6)	0.1064(4)	0.4186(4)

structure factors with $F_o \leqslant 4.0\ \sigma(F_o)$ out of a total of 2141 unique reflections ($R_{int} = 0.02$) were deemed "unobserved" and not used in all further calculations. An absorption correction was not applied (μ(Mo-K_α) 1.97 cm^{-1}).

Structure solution and refinement. The structure was solved by direct methods (MULTAN 80) and completed by Fourier methods. Positions for 27 out of the 44 H atoms could be obtained from difference Fourier syntheses. All others were calculated at idealized geometrical positions (d(C–H) 0.95 Å). During the refinement high thermal parameters for the methyl C atoms of the ^{t}Bu groups indicated partial disorder of these groups. Difference Fourier syntheses calculated after isotropic refinement of these atoms with lower occupancy factors revealed clearly that the disorder was purely rotational in nature, but did not yield alternative positions which could be refined individually. However, since reasonable H atom positions could be partially found even for the disordered methyl groups the disorder is estimated to be not greater than 35%. Anisotropic refinement of all non-H atoms (208 parameters, H atoms as fixed atom contributions) on 1991 observed reflections (measured Friedel pairs averaged) converged at $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.052$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} = 0.057$. The function minimized was $\Sigma w(F_o -$

TABLE 2

IMPORTANT BOND LENGTHS (Å), BOND ANGLES AND TORSION ANGLES (°) FOR II·THF. E.s.d.'s IN UNITS OF THE LAST SIGNIFICANT FIGURE IN PARENTHESES

Bond lengths			
Si(1)–C(1)	1.747(5)	Si(1)–O	1.878(4)
Si(1)–C(2)	1.850(6)	C(1)–Si(2)	1.835(5)
Si(1)–C(3)	1.858(6)	C(1)–Si(3)	1.836(5)
Si(2)–C(4)	1.879(6)	C(8)–C(9)	1.53(1)
Si(2)–C(5)	1.885(6)	C(8)–C(10)	1.513(9)
Si(2)–C(6)	1.898(7)	C(8)–C(11)	1.45(1)
Si(3)–C(7)	1.907(6)	C(12)–C(13)	1.44(1)
Si(3)–C(8)	1.939(5)	C(12)–C(14)	1.51(1)
Si(3)–C(12)	1.927(6)	C(12)–C(15)	1.522(9)
O–C(16)	1.474(6)	O–C(19)	1.480(6)
C(16)–C(17)	1.508(9)		
C(17)–C(18)	1.504(9)		
C(18)–C(19)	1.488(9)		
Bond angles			
C(1)–Si(1)–O	107.9(2)	Si(1)–C(1)–Si(2)	114.9(3)
C(1)–Si(1)–C(2)	119.7(3)	Si(1)–C(1)–Si(3)	126.7(3)
C(1)–Si(1)–C(3)	124.1(3)	Si(2)–C(1)–Si(3)	117.2(3)
O–Si(1)–C(2)	97.9(2)		
O–Si(1)–C(3)	96.5(2)		
C(2)–Si(1)–C(3)	104.9(3)		
Torsion angles			
C(2)–Si(1)–C(1)–Si(2)	51.1	C(2)–Si(1)–C(1)–Si(3)	−115.9
C(3)–Si(1)–C(1)–Si(2)	−170.8	C(3)–Si(1)–C(1)–Si(3)	22.3
O–Si(1)–C(1)–Si(2)	−59.5	O–Si(1)–C(1)–Si(3)	133.6
Si(1)–C(1)–Si(2)–C(4)	−101.7	Si(1)–C(1)–Si(3)–C(7)	167.7
Si(1)–C(1)–Si(2)–C(5)	133.5	Si(1)–C(1)–Si(3)–C(8)	52.8
Si(1)–C(1)–Si(2)–C(6)	15.9	Si(1)–C(1)–Si(3)–C(12)	−77.4

$F_c)^2$ with $w = k/\sigma^2(F_o)$, $k = 3.0$ in the last cycle. In the final refinement cycle the maximum shift to error ratio was less than 0.05, and the final difference Fourier synthesis was essentially featureless, $\Delta\rho_{max}$ 0.35 e/Å^3. Refinement of both enantiomers on a data set with non-averaged Friedel pairs (3543 unique reflections of which 271 $\leqslant 4.0\ \sigma(F_o)$) did not yield significantly different final R values. Scattering factors for neutral, isolated, non-H atoms were taken from Cromer and Waber [18], and those of the H atoms, based on a bonded spherical atom model, from Stewart, Davidson and Simpson [19]. Corrections for $\Delta f'$ and $\Delta f''$ were applied for all atoms [20]. The computer programs used are specified in ref. 21. Table 1 lists the final atomic coordinates, important bond lengths and angles are collected in Table 2. Tables of additional crystal structure data, anisotropic thermal parameters, and observed and calculated structure factors have been deposited [22].

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22 Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2. All inquiries should be accompanied by the registry number CSD 50885, the names of the authors and the literature citation for this communication.