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SILYLENE COMPLEXES STABILIZED BY SULPHUR SUBSTITUENTS; A STRUCTURE AND REACTIVITY STUDY

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Abstract—A new base-stabilized silylene (silanediyl) complex $(t\text{-}BuS)_2(HMPA)Si{=}Fe(CO)_4$ (**9b**) has been prepared from $Na_2Fe(CO)_4$ and $(t\text{-}BuS)_2SiCl_2$ (**2b**) in the presence of HMPA (hexamethylphosphoric triamide). An X-ray structure analysis of **9b** shows the silylene coordinated to the iron atom [Fe—Si = 2.278(1) Å]. The HMPA is bound via its oxygen atom to the unsaturated silicon [O—Si 1.734(2) Å], which adopts a distorted tetrahedral coordination geometry. A comparison of **9b** with the analogous oxo compound $(t\text{-}BuO)_2(HMPA)Si{=}Fe(CO)_4$ (**9a**) indicates an almost identical stabilizing effect of the electron-deficient silicon atom in **9b** by π-mesomeric and polarization effects of the t-BuS substituents. The conformation of the substituents found at the silicon atom is reproduced by a force field calculation. A base-free silylene complex $(t\text{-}BuS)_2Si{=}Fe(CO)_4$ (**10**) has been observed directly by NMR spectroscopy (^1H NMR: δ 1.70, s; ^{29}Si NMR: δ 83.2, s) and was further characterized by a derivatization reaction with HMPA to form **9b**. The HMPA adduct **9b** is a valuable model compound for mechanistic investigations: photolysis of **9b** in the presence of 2,3-dimethylbutadiene as trapping reagent yields 1,4-addition of the silylene to the butadiene. In the absence of any trapping reagents, polysilanes are formed. The experiments provide evidence for a silylene cleavage mechanism.

Interest in organometallic silicon chemistry has considerably increased,[1,2] since the recent discovery of stable coordination compounds with low-valent silicon ligands.[3,4] This refers, in particular, to silylene (silanediyl) complexes (**A**) and their donor adducts (**B**), which are known for the metals iron, ruthenium, chromium and tungsten.[5] Furthermore, cationic silylene complexes (**C**)[4] and cyclic bissilylene complexes (**D**) have been realized with the compounds $Cp^*\overline{FeSiMe_2OMeSi}(OMe)Me$[6] and $Cp\overline{FeCOSiMe_2NH_2Si}Me_2$,[7] as well as base adducts of metallasilaallenes (**E**).[8] In a wider sense, the recently isolated complexes of disilaethenes (**F**)[9] and silaethenes (**G**)[10] have also to be considered (Scheme 1).

Base-stabilized silylene complexes are model compounds for extremely reactive, base-free complexes which are proposed as key intermediates in a variety of catalytic reactions. These are, for example, the dehydrogenative coupling of primary silanes to disilanes[11] or the polymerization of silanes by early transition metal catalysts.[12]

A great many research activities have been invested into stable base adducts of silylene (silanediyl) complexes by X-ray structure analysis, NMR and Mössbauer spectroscopy.[1] An X-ray structure study shows important interdependencies between bond lengths, coordination geometry and substituent effects at the silicon atom.[3,5] The bond lengths, as well as the coordination geometry at silicon, are a function of the electronic saturation of silicon, which is given by the respective substituents. Stabilizing substituents induce an elongation of both the metal–silicon and donor–silicon bonds and lead to a stronger distortion of the tetrahedral coor-

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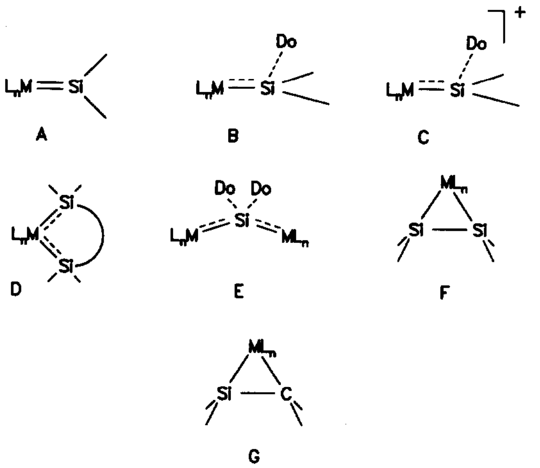


Scheme 1.

dination sphere. Thus, data from X-ray structures are a valuable indicator of the magnitude of the metal–silicon interaction. On the grounds of the extended set of parameters, a fairly good assignment of the effects of particular substituents is possible.[5]

This work describes the effects involved when sulphur is directly bonded to silicon in the coordination compound (t-BuS)$_2$(HMPA)Si=Fe(CO)$_4$ (**9b**). Sulphur, in particular, has been proposed as a stabilizing substituent for low coordinated and low-valent silicon species. Important for the stabilization are π-mesomeric effects, but a strong polarization interaction between sulphur and silicon is also important.[13] Investigations of the stable system [(i-Pr)$_2$S]$_3$Si$^+$ClO$_4^-$ have been reported and are in support of a significant stabilization effect; however, systematic data on sulphur-containing silicon species are still rare.[14] This refers also to the direct observation of silylenes (silanediyls) in a matrix, where exact measurements of the spectroscopic properties of sulphur-substituted silylenes have not been made so far.[14]

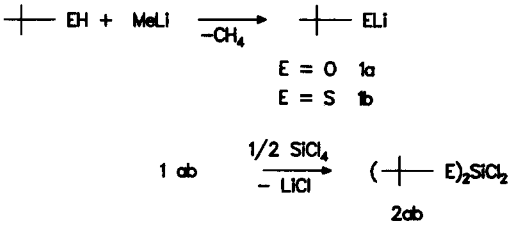
A major reason for this lack of information are the great difficulties involved with the synthesis of silicon compounds due to the inherent kinetic lability of the sulphur–silicon bond, which gives rise to an enhanced nucleophilic displacement of the thio substituents by ligand exchange reactions or hydrolysis.

In this article the synthesis of a new silylene coordination compound (t-BuS)$_2$(HMPA)Si=Fe(CO)$_4$ (**9b**) is introduced, together with a crystallographic investigation and a preliminary reactivity study.[15] The given data allow the accurate measurement of the silicon–sulphur interaction and a qualitative assignment of the stabilizing effects which occur.

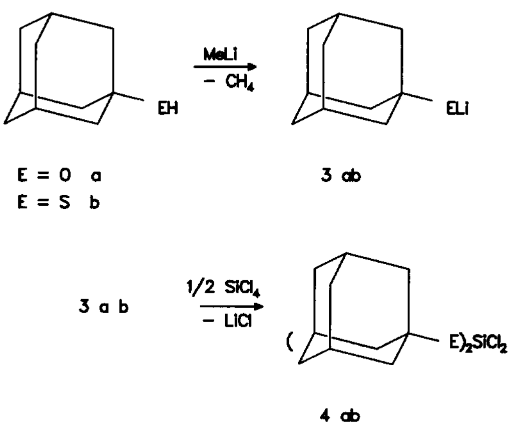
RESULTS AND DISCUSSION

Synthesis of silylene complexes

A very efficient route to coordination compounds of silylenes is provided via the salt elimination reaction of carbonylate dianions with halosilanes. This reaction is versatile and allows variation of both the metals and the introduced silanes.[3] The required silanes are conveniently synthesized by treatment of the appropriate lithium organyls with SiCl$_4$ at low temperatures.



(1)



(2)

$$2\ \mathrm{AdaSMgBr(THF)} \rightleftharpoons \mathrm{(AdaS)_2Mg \times MgBr_2 \times 2\ THF} \qquad (3)$$

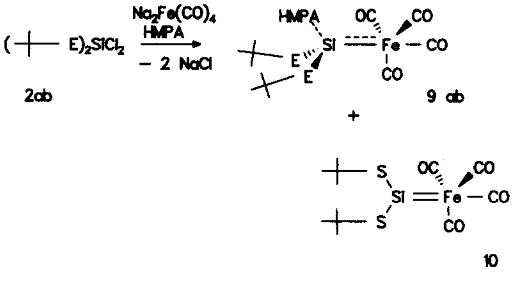
5 5'

$$\mathrm{MesLi \times LiBr \times THF} \xrightarrow{1/8\ \mathrm{S_8}} \mathrm{MesSLi \times LiBr \times THF}$$

6 7

$$7 \xrightarrow{1/2\ \mathrm{SiCl_4}} \mathrm{(MesS)_2SiCl_2} \qquad (4)$$

8



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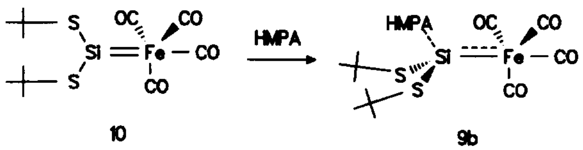

(6)

The observed selectivities for the dichlorosilanes vary and are highest for bis-t-butylthiodichlorosilane (**2b**). $MesS_2SiCl_2$ (**8**) can be obtained in moderate yields from a reaction of lithium mesitylthiolate (**7**) with silicon tetrachloride; the thiolate **7** is prepared from MesLi+LiBr and sulphur. 1-AdaSMgBr (**5**) forms a Schlenk equilibrium, $\mathbf{5} \rightleftharpoons \mathbf{5}'$, according to eq. (3).

The chlorosilanes, R_2SiCl_2, obtained are purified by fractional crystallization. However, for R = MesS, 1-AdaS, a slow exchange reaction, $2R_2SiCl_2 \rightleftharpoons RSiCl_3 + R_3SiCl$, occurs, which renders further reactions of the halosilanes with metalate anions difficult. The t-butylthio compound $(t\text{-}BuS)_2SiCl_2$ (**2b**), purified by preparative gas chromatography, is much better suited for further conversion with $Na_2Fe(CO)_4$ in the presence of HMPA to $(t\text{-}BuS)_2(HMPA)Si{=}Fe(CO)_4$ (**9b**) in 30% yield. Compound **9b** is a colourless, crystalline compound, sensitive to air and moisture.

The preparation of $(t\text{-}BuO)_2SiCl_2$ (**2a**) and its subsequent reaction to $(t\text{-}BuO)_2(HMPA)Si{=}Fe(CO)_4$ (**9a**) have already been described,[3b] but **9a** is included for comparison.

Spectroscopic investigations

All compounds have been fully characterized by NMR and IR spectroscopy (see Experimental). In particular, the ^1H NMR spectrum of **9b** shows characteristic shifts [δ 1.63, s, 18H, t-BuS; δ 2.77, d, $^3J(^{31}P^1H) = 29.0$ Hz, 18H, HMPA]. The ^{29}Si NMR spectrum [δ 74.4, $^2J(^{31}P^{29}Si) = 33.1$ Hz] is also of diagnostic value. The observed IR bands for the $\nu(CO)$ stretching vibration are typical for an axial coordination of the silylene ligand (C_{3v}). A comparison of the $\nu(CO)/cm^{-1}$ A_1 and E vibrational data and the respective force constants $k_0(^{12}CO)/Nm^{-1}$ [For **9a**: $\nu(CO)$ 2005(w), 1920(s), 1883(s); $k_0(^{12}CO)$ 1623, 1489, 1432. For **9b**: $\nu(CO)$ 1995(w), 1910(s), 1870(s); $k_0(^{12}CO)$ 1607, 1473, 1412] indicates a stronger donor capacity of the coordinated silylene in the sulphur compound **9b**.[16]

The spectroscopic analysis of the reaction mixture [eq. (5)] gives, in addition to **9b**, direct evidence for the presence of a donor-free complex **10** [^1H NMR (C_6D_6): δ 1.70, s, 18H, t-BuS; ^{29}Si NMR: δ 83.2, singlet], with no further impurities present. The ^{29}Si resonance clearly excludes a dimeric species.* According to the intensity distribution of both the ^{29}Si and ^1H NMR signals, **10** is formed in a ratio of 1 : 1.6 (**10**/**9b**). Compound **10** decomposes at −30°C into $[(t\text{-}BuS)_2Si]_n$ and $Fe_3(CO)_{11}H^-$ with a half-life time of 12 h.† The polysilane has been isolated. By addition of a 10-fold excess of HMPA, **10** is converted to **9b** quantitatively.‡

Molecular structure of 9b

An X-ray structure analysis of **9b** (Tables 1 and 2) confirms the proposed molecular structure (Fig. 1). The coordination geometry at the iron centre is trigonal bipyramidal with the silicon ligand occupying an apical coordination site. The Fe—Si bond [2.278(1) Å] in **9b** is short compared with the known Fe—Si single bond distances. The Fe—Si bond lengths of donor-stabilized silylene complexes range from 2.289(2) Å in **9a**[3a] to 2.214(1)/2.221(1) Å in $Cl_2(HMPA)Si{=}Fe(CO)_4$[3c] for acyclic complexes, and 2.207(3)/2.222(3) Å in Cp*Fe(CO)SiMe(OMe)-OMe-SiMe$_2$.[6] A rough estimate of the Fe=Si bond lengths of an uncomplexed double bond on the grounds of covalent radii gives 2.18 Å.[3b]

The coordination sphere of the silicon is completed to a distorted tetrahedron by the addition of a HMPA molecule [Si—O 1.734(2) Å]. The HMPA

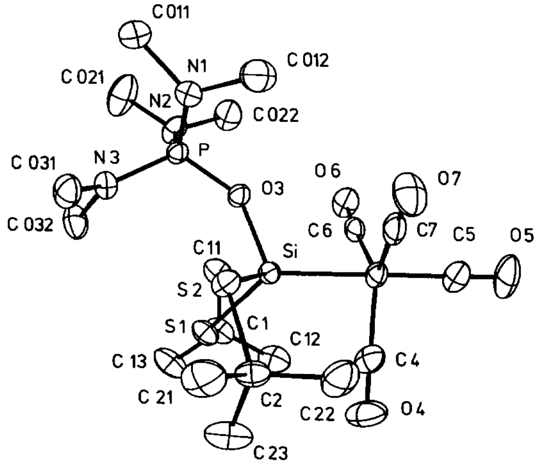

Fig. 1. ORTEP view of **9b**. Displacement ellipsoids at the 50% probability level.

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* For $(OC)_4Fe\text{-}SiMe_2\text{-}Fe(CO)_4\text{-}SiMe_2$, ^{29}Si NMR δ 161.0 ppm has been measured, which is typical for metallasilacyclobutanes.

† A dimeric silylene complex would be stable.

‡ This trapping experiment provides further evidence for the presence of a monomeric silylene complex **10**, since the retro-cleavage of a dimeric silylene complex species by a base to a monomeric coordination compound is not known in the literature.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **9b** ($U_{eq} = \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j a_i a_j$)

Atom	X/A	Y/B	Z/C	*U* (eq.)
Fe	0.64056(3)	0.78213(3)	0.70252(2)	0.031
C(4)	0.7209(3)	0.8985(3)	0.6854(2)	0.042
O(4)	0.7713(2)	0.9735(2)	0.6732(1)	0.052
C(5)	0.5776(2)	0.7928(3)	0.6109(2)	0.050
O(5)	0.5363(2)	0.7974(2)	0.5518(1)	0.081
C(6)	0.6773(2)	0.6442(3)	0.6845(1)	0.031
O(6)	0.6966(2)	0.5543(2)	0.6694(1)	0.053
C(7)	0.5261(2)	0.7997(3)	0.7583(2)	0.042
O(7)	0.4515(2)	0.8090(2)	0.7921(1)	0.066
Si	0.72317(5)	0.76789(6)	0.81885(4)	0.025
S(1)	0.88651(5)	0.78771(6)	0.83115(4)	0.036
S(2)	0.67603(5)	0.86429(5)	0.91890(4)	0.031
C(1)	0.9637(2)	0.7083(3)	0.7591(2)	0.045
C(2)	0.6801(2)	1.0159(2)	0.9026(2)	0.037
C(11)	0.9373(2)	0.5860(3)	0.7615(2)	0.054
C(12)	0.9526(3)	0.7548(3)	0.6779(2)	0.053
C(13)	1.0731(2)	0.7253(3)	0.7887(2)	0.064
C(21)	0.6505(3)	1.0632(3)	0.9818(2)	0.053
C(22)	0.6021(3)	1.0519(3)	0.8426(2)	0.061
C(23)	0.7872(2)	1.0525(3)	0.8804(2)	0.058
P	0.70945(5)	0.57608(6)	0.93787(4)	0.027
O(3)	0.6968(1)	0.6419(1)	0.86173(9)	0.029
N(1)	0.5961(2)	0.5751(2)	0.9771(1)	0.035
N(2)	0.7550(2)	0.4576(2)	0.9099(1)	0.043
N(3)	0.7874(2)	0.6200(2)	1.0038(1)	0.034
C(011)	0.5797(2)	0.5112(3)	1.0492(2)	0.040
C(012)	0.5027(2)	0.6008(3)	0.9355(2)	0.064
C(021)	0.7873(4)	0.3747(3)	0.9672(2)	0.087
C(022)	0.7177(3)	0.4072(3)	0.8383(2)	0.053
C(031)	0.7571(2)	0.6942(2)	1.0669(2)	0.042
C(032)	0.8994(2)	0.6058(3)	0.9983(2)	0.055

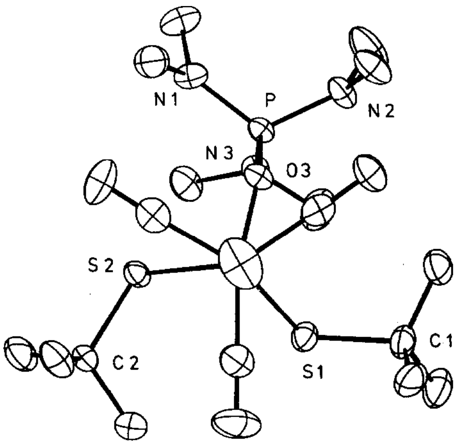


Fig. 2. ORTEP view of **9b** down the Fe—Si axis.

O—Si bond lengths of **9b** and **9a** [Si—O 1.730(3) Å] are identical within the usual three-fold standard deviations. The Si—S distances are relatively short, 2.158(1) and 2.170(1) Å, and indicate a substantial mesomeric π-interaction between the silicon and the sulphur atom, while metal–silicon bond lengths are even shorter due to the more electrophilic silicon atom (π-backbonding).[3c] Thus, a comparison of the Fe—Si bond lengths in **9a** and **9b** allows the conclusion that stabilizing O → Si π-effects are slightly more important in **9a** than S → Si effects are in **9b**. The coordination geometry at the silicon centre shows typical distributions from an ideal tetrahedron, with relatively large bond angles, t-BuS—Si—Fe 123.1(1)/121.3(1)°, and a small angle, t-BuS—Si—S(t-Bu) 98.2(1)°. The sum of the angles between the substituents at silicon, R—Si—R, Fe—Si—R and R—Si—Fe, is virtually the same in **9a** (342.1°) and **9b** (342.6°).

It has been shown that the donor–silicon interaction occurs through the LUMO of the Si=Fe double bond and is strongly influenced by substituent effects.[3c,d] The discussed structural features may be used as a probe for the degree of electronic saturation at silicon and allow a qualitative assignment of the stabilizing effect of sulphur, which is only slightly smaller in **9b** than in the oxo compound **9a**, and substantially greater than in alkyl-substituted silylene complexes.[1]

Table 2. Selected bond distances (Å) and angles (°) in the structure of **9b** (ESDs in units of the last significant digit in parentheses)

	Bond distances (Å)		
Fe—Si	2.278(1)	P—O(3)	1.542(2)
Si—S(1)	2.158(1)	S(1)—C(1)	1.866(3)
Si—S(2)	2.170(1)	S(2)—C(2)	1.865(3)
Si—O(3)	1.734(2)		
	Bond angles (°)		
Fe—Si—S(1)	123.1(1)	Fe—Si—O(3)	110.2(1)
Fe—Si—S(2)	121.3(1)	S(1)—Si—O(3)	104.7(1)
S(1)—Si—S(2)	98.2(1)	S(2)—Si—O(3)	94.8(1)

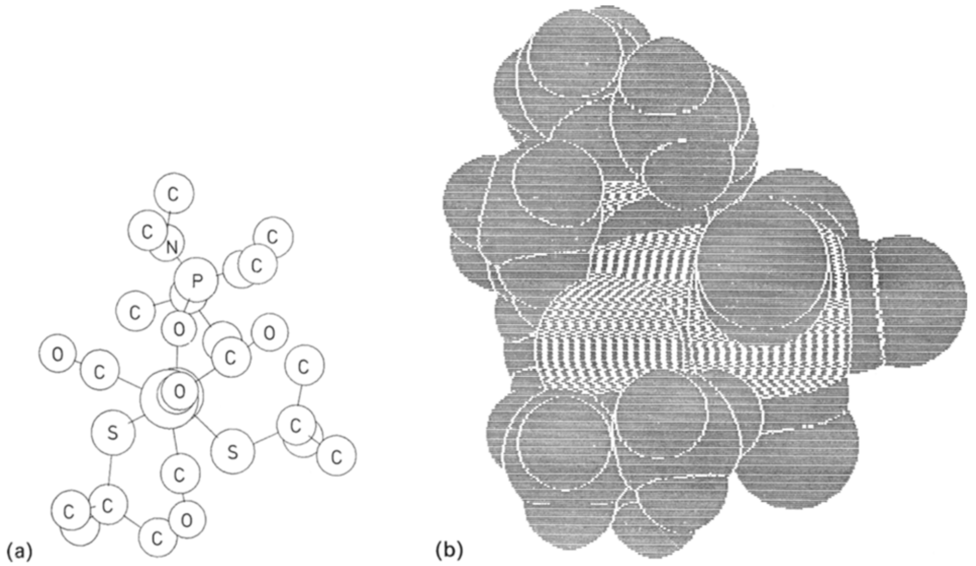


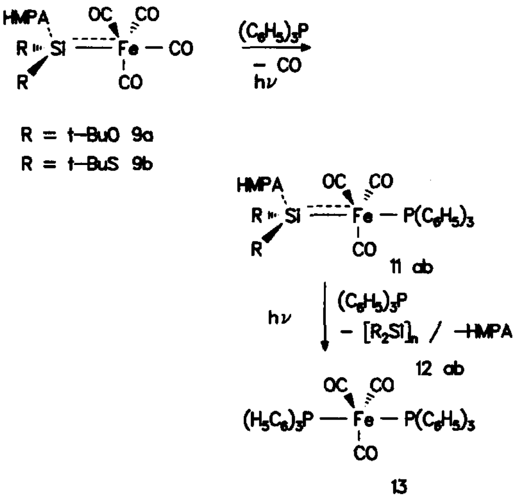
Fig. 3. (a) Projection down the Fe—Si axis of the structure of **9b** obtained by a force field calculation (hydrogen atoms omitted for clarity). (b) View of the van der Waals' surface of **9b** obtained by the force field calculation.

The bond lengths and the coordination geometry at silicon are primarily a result of electronic effects. However, the relative conformation of the organic substituents at the silicon atom represents a minimum of steric interactions. An ORTEP view of the molecule down the Fe—Si bond (Fig. 2) shows that **9b** contains no mirror plane, but the two t-BuS substituents together with HMPA form an asymmetric conformation, which is apparently a minimum of energy. This rotamer is reproduced by a force field calculation.[17] The obtained conformation and van der Waals' surface are depicted in Fig. 3.

Reactions

Previous experiments have shown that coordinated silylenes (with an additional base at silicon) can be activated photochemically or thermally in silylene transfer reactions.[3c]

A reactivity study of **9a,b** provides similar results: photolysis of the complexes $R_2(HMPA)Si{=}Fe(CO)_4$ (R = t-BuO, t-BuS) in the presence of triphenylphosphine leads, after photolytic activation of CO, to the *trans*-phosphine complexes **11a,b**, and subsequently to the displacement of the silylene ligand by a further phosphine to produce the bis-phosphine complex **13**. The liberated silylenes polymerize instantaneously; for **12a**, R = t-BuO, the molecular weight has been determined as 550. $[(t\text{-BuS})_2Si]_n$ (**12b**) is a white, air-sensitive material, soluble in toluene and insoluble in THF. The coordinated HMPA is split off from the silicon during the second step of the photolysis reaction and can be recovered quantitatively.



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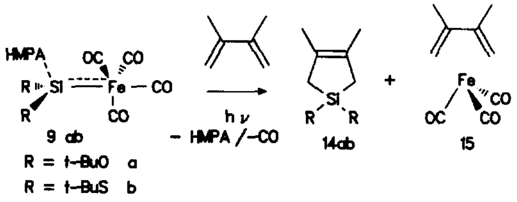

(8)

Trapping experiments of the silylenes with 2,3-dimethylbutadiene have been successful for R = t-BuO and R = t-BuS and yield the products **14a,b** and **15**. The photolysis reaction can be monitored by IR spectroscopy [ν(CO) **9a**: 2005, 1920, 1883 cm^{-1}, ν(CO) **15**: 2045, 1971 cm^{-1}], which shows the disappearance of the ν(CO) bands of **9a** or **9b** together with a simultaneous increase of the bands of **15**. The reaction follows a (pseudo) first-order rate law. The observed reactivity pattern documents the potential of complexes **9a,b** to react as a silylene source and also provides evidence for a silylene polymerization mechanism. Further experiments concerning the reactivity and spectroscopic properties of $[(t\text{-}BuS)_2Si]$ are underway.

Summary

The obtained results provide a set of data for both a "donor-free" silylene complex, $(t\text{-}BuS)_2Si{=}Fe(CO)_4$ (**10**), and its HMPA adduct, $(t\text{-}BuS)_2(HMPA)Si{=}Fe(CO)_4$ (**9b**). An X-ray structure analysis of **9b** allows the estimation of the stabilizing effect of the sulphur substituents at silicon. The bond distances Si—S, Si—Fe, Si—O and the overall coordination geometry at silicon show a substantial stabilization of the electron-deficient silicon by sulphur due to mesomeric π-interaction and polarization effects. The observed effects are slightly smaller than in the oxo compound **9a** and allow the assignment of the following gradation of ligand stabilization capacity: $O > S \gg C$. This gradation is consistent with results from ^{29}Si NMR and IR spectroscopy.

^1H NMR and ^{29}Si NMR data, as well as trapping experiments with HMPA, give evidence for a labile, "base-free" complex $(t\text{-}BuS)_2Si{=}Fe(CO)_4$ (**10**). Both **10** and the HMPA adducts **9a,b** undergo silylene cleavage reactions with subsequent polymerization of the silylenes in solution. This mechanism is supported by trapping experiments of the silylenes with 2,3-dimethylbutadiene.

EXPERIMENTAL

All experiments have been performed in an atmosphere of dry nitrogen or argon, respectively. The solvents were dried by conventional techniques (NaK alloy, P_4O_{10}), and residual water contents were in all cases below 3.5 ppm (detected by Karl Fischer titration). Elemental analyses were carried out at Mikroanalytisches Laboratorium der Technischen Universität München. NMR spectra were obtained on Jeol GX 400 and Jeol FX 270 spectrometers, IR spectra on a Nicolet FT–IR-5DX spectrometer and GC–MS analysis was performed on Hewlett–Packard 5890 A and 5970 B instruments with a column CP SIL 5CB (50 m; 0.32 mm).

Bis(t-butylthio)dichlorosilane, $(t\text{-}BuS)_2SiCl_2$ (**2b**)

To a solution of t-butylthiol (33.8 cm^3, 0.3 mol) in 100 cm^3 of pentane, n-BuLi (190 cm^3, 0.3 mol) (1.71 M solution in hexane) was added at -40°C. The reaction mixture was stirred for a further 2 h at room temperature. After removal of the solvent *in vacuo*, lithium-t-butylthiolate (27.6 g, 0.287 mol) was isolated as a white solid (96%). Further reaction to the chlorosilane was accomplished by the addition of a solution of the thiolate (27.6 g, 0.287 mol) in 100 cm^3 of THF at -60°C to $SiCl_4$ (16.6 cm^3, 0.144 mol) dissolved in 100 cm^3 of THF. After completion of the addition, the reaction mixture was stirred at room temperature for a further 2 h. The LiCl was removed by filtration and the THF stripped off *in vacuo*. The residual colourless oil was contaminated with LiCl and was therefore purified by vacuum distillation or by prep. GC (retention time: 9.7 min; MS analysis: $M^+ = 276.3\%$). Compound **2b** is a colourless liquid. Yield: 10.6 g (27%); b.p. 90°C/1 mbar. ^1H NMR ($CDCl_3$): δ 1.2 (s). ^{29}Si NMR (C_6D_6): δ 4.4.

Bis(1-adamantyloxo)dichlorosilane, $(AdaO)_2SiCl_2$ (**4a**) *and bis-(1-adamantylthio)dichlorosilane*, $(AdaS)_2SiCl_2$ (**4b**)

To magnesium chips (1.69 g, 69.7 mmol) in 50 cm^3 of ether, 1-AdaBr (15.0 g, 69.7 mmol) dissolved in 100 cm^3 of ether was added dropwise. The Grignard reaction was initiated by external local heating of the mixture. After 30 min, the heat formed is self-sufficient for further reaction. After completion of the halide addition, the mixture was refluxed for 3 h and kept at room temperature for 10 h. Then, sulphur (2.23 g, 69.7 mmol) was added portionwise through a special device and the obtained mixture refluxed for a further 5 h. The slightly cloudy, yellow solution was filtrated and the THF removed *in vacuo*. The brown residue obtained was purified by dissolving it repeatedly in 40 cm^3 of THF and precipitating the product by addition of 40 cm^3 of pentane. Compound **4b** formed as a yellow powder (8.96 g; yield: 48%). ^1H NMR (C_6D_6): **4b**, δ 1.5 (m, α-methylene-H): 2.3 (m, β-CH); 3.9 (m, γ-methylene-H).

Compound **4a** was prepared by deprotonation of 1-adamantol with methyllithium and subsequent conversion to the chlorosilane by $SiCl_4$ (Yield: 62%).

Synthesis of bis(2,4,6-trimethylphenylthio)dichlorosilane [bis(mesitylthio)dichlorosilane], $(MesS)_2SiCl_2$ (**8**)

Mesityllithium·LiBr. The synthetic procedure given in ref. 18 was slightly modified. Mesitylbromide (30.1 cm^3, 0.2 mol) was dissolved in 250 cm^3 of diethyl ether. Then, n-BuLi (250 cm^3, 0.4 mol) (1.71 M solution in hexane) was added under vigorous stirring over a period of 1 h. If necessary, the reaction flask was cooled externally by an ice bath. A white precipitate of **6** formed, which increased during a further hour of refluxing of the reaction mixture. The product was isolated by filtration and dried in high vacuum (10^{-3} torr). Yield: 31.8 g (75%).

Lithium mesitylthiolate, LiSMes·THF (**7**). To a solution of MesLi·LiBr (**6**) (31.8 g, 0.2 mol) in 250 cm^3 of THF, S_8 (4.8 g, 150 mmol) was added portionwise over a period of 30 min at -20°C. The sulphur dissolved completely, and the yellow solution which formed was kept at room temperature for a further 3 h. The obtained crude lithium mesitylthiophenolate was purified by derivatization to the thiophenol. Therefore, the THF was first replaced by ether, and subsequently the thiophenolate was converted to the thiol by addition of 0.1 M sulphuric acid at 0°C. The thiophenol was extracted from the water phase with ether. After removal of ether, the thiol was isolated as a yellow oil with a characteristic odour. Yield: 20.4 g (90%); b.p. 106°C. ^{1}H NMR ($CDCl_3$): δ 2.2 (Br, 6H, 3H; o-CH_3, p-CH_3); 2.8 (s, 1H, SH); 6.7 (s, 2H, aryl-H).

To a solution of mesitylthiophenol (20.4 g, 134 mmol) dissolved in 200 cm^3 of THF, n-BuLi (74 cm^3, 134 mmol) (1.71 M solution in n-hexane) was added. The colour of the solution changed from yellow to orange during the addition. The mixture obtained was then stirred for a further 3 h at room temperature. After removal of the THF *in vacuo*, **7** was isolated in 70% yield (22.7 g).

Bis(2,4,6-*trimethylphenylthio*)*dichlorosilane*, $(MesS)_2SiCl_2$ (**8**)

To a stirred solution of silicon tetrachloride (5.1 cm^3, 45 mmol) in 100 cm^3 of THF, **7** (22.7 g, 93 mmol) dissolved in 100 cm^3 of THF was added at -25°C (3% access of $SiCl_4$), and the reaction mixture turned slightly yellow. After refluxing for a further 6 h, the lithium halides were removed and the solvent stripped off *in vacuo*. The resulting paste was again dissolved in 100 cm^3 of a 3 : 1 mixture of pentane–ether. After filtration from the residual lithium halides and removal of the solvent, a yellow oil was obtained, which is sensitive to hydrolysis and oxidation. Yield: 12.2 g (70%). ^{29}Si NMR data show the presence of two reaction products in the ratio 4 : 1 $(MesS)_2SiCl_2$/$(MesS)_3SiCl$. Compound **8** could not be further enriched by either fractional crystallization or Kugelrohr distillation due to ligand exchange reactions. ^{1}H NMR ($CDCl_3$): **8** δ 2.3 (m, 9H, o-CH_3, p-CH_3); 6.9 (s, broad, 2H, aryl H). ^{29}Si NMR (C_6D_6): δ 26.7. MS: m/z 400 (M^+; 1.7%)

Reaction of **2b** *with* $Na_2[Fe(CO)_4]$ *to form* $(t\text{-}BuS)_2Si{=}Fe(CO)_4$ (**9b**) *and* $(t\text{-}BuS)_2(HMPA)Si{=}Fe(CO)_4$ (**10**)

To a solution of $Na_2[Fe(CO)_4]$ (3.3 g, 9.6 mmol) in a mixture of 100 cm^3 of THF and 15 cm^3 of HMPA, **2b** (2.7 g, 9.6 mmol) was added at -50°C. The reaction mixture was stirred for 12 h, filtered, and THF and HMPA were subsequently removed at high vacuum (10^{-4} torr). The crude product contained **9b** and **10** in a 1 : 1.6 ratio. Compound **10** can be converted to **9b** by addition of 2 cm^3 of HMPA. Alternatively, the mixture could be purified by column chromatography on silica gel (2.5 cm diameter, 40 cm height) with a cooled (-15°C) chromatography column. However, **10** decomposed during chromatography into $HFe_3(CO)_{11}^-$ and polysilane **12b**. Analytical data for **9b**: Found (Calc.): C, 38.98 (39.04); H, 6.59 (6.51); N, 7.62 (7.59). IR for **9b** (KBr): 1995 (w), 1910 (s), 1870 (s) [ν(CO) in cm^{-1}]. MS: $m/z = 553$ (M^+; 1.5%). ^{1}H NMR (C_6D_6): δ 1.63 (s, br, 18H), δ 2.77 [d, $^2J(^{31}P^{29}Si) = 29.0$, 18H]. ^{29}Si NMR ($C_6D_6$): δ 74.0, **9b**.

^{1}H NMR (C_6D_6): 1.70; ^{29}Si NMR (C_6D_6): δ 83.2, **10**.

Crystal structure analysis of **9b***

Crystal data and a summary of data pertinent to data collection and refinement are colleced in Table 3. Exact cell dimensions were obtained by least-squares refinement of the Bragg angles of 15 selected reflections centred on the diffractometer. Reduced cell calculations did not reveal symmetry higher than orthorhombic. Three standard reflections, measured after every 50 reflections, showed only random intensity fluctuations. Therefore, a correction for crystal decay was not considered necessary, neither was one for absorption. Refinement was carried out with anisotropic displacement parameters. The methyl groups were treated as rigid groups (H atoms with U_{iso} fixed at 0.05 Å^2). To ensure that the chirality of the single crystal under investigation and that of the coordinate set were identical, the inverse coordinate set was also refined.

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*A complete list of fractional atomic coordinates including hydrogen atoms and a list of observed and calculated structure factors ($F_o - F_c$) have been deposited together with the manuscript.

Table 3. Crystal structure data for **9b**

Crystal dimensions (mm^3)	0.40 × 0.45 × 0.50
Formula	$C_{18}H_{36}FeN_3O_5PS_2Si$
M_r	553.540
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a (Å)	13.066(2)
b (Å)	12.155(1)
c (Å)	17.181(3)
V (Å^3)	2728.6
Z	4
d_{calc} (g cm^{-3})	1.347(7)
μ(Mo-K_α) (cm^{-1})	8.3
F(000) (e)	1168
T (°C)	−50
Diffractometer	Syntex-P2$_1$
Radiation	Mo-K_α, $\lambda = 0.71069$ Å
Monochromator	Graphite
Scan	ω
Scan width (in ω)	0.6
Scan speed (° min^{-1})	0.7–29.3
$(\sin/\lambda)_{max}$ (Å^{-1})	0.572
hkl range	+14, +13, ±19
Standard reflections	020, 006, 200
Reflections (measured/unique)	4721/4238
R_{int}	0.021
Reflections observed [$F_o \geqslant 4.0\sigma(F_o)$]	4022
Structure solution	Direct methods (SHELXS-86)
Hydrogen atoms (found/calc)	33/3
Parameters refined	316
r^a	0.026
Rw^b	0.028
$(\text{Shift/error})_{max}$	0.016
$\Delta\rho_{fin}$(max/min) (e/Å^3)	0.57/−0.28

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

[b] $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. Function minimized: $\Sigma w(|F_o| - |F_c|)^2$.

It yielded substantially higher R values, however ($R/R_w = 0.039/0.044$).

Atomic form factors for neutral, isolated atoms were taken from Cromer and Waber,[19] and those for hydrogen were based on the bonded spherical atom model of Stewart *et al.*[20] Corrections for anomalous scattering were applied for all atoms except hydrogen.[21] The programs used included SHELXS-86[22] (structure solution), SHELXS-76[23] (refinement), ORTEP[24] (molecular drawings), as well as locally written routines. All calculations were performed on a VAX 8200.

Molecular modelling of the structure of 9b

The molecule was optimized by the ALCHEMY minimizer program with $E_{tot} = E_{str} + E_{ang} + E_{tor} + E_{vdw}$. E_{tot} = total energy, $E_{str} = \Sigma_i^N k^d{}_i/2(d_i - d^0{}_i)^2$, $d^0{}_{FeSi} = 2.300$ Å, $k_{FeSi} = 1500$ kcal mol^{-1} Å^2; $E_{ang} = \Sigma_i^N k^\theta{}_i/2(\theta_i - \theta^0{}_i)^2$, $\theta_{0FeSiO} = 115°$, $k^\theta{}_{FeSiO} = 0.03$ kcal mol^{-1} deg^2; $E_{tor} = \Sigma_i^N k_i/2[1 + \sin(\text{per}_i) \times \cos(|\text{per}_i|\omega_i)]$, $\omega_{SiFe**} = 0.1$ kcal mol^{-1} deg^2; $E_{vdw} = \Sigma_i^n[\Sigma_{j>i} E_{ij}(1.0/a^{12}{}_{ij} - 2.0/a^6{}_{ij})]$, $E_{FeSi} = 0.200$ kcal mol^{-1}, $a_{Fe} = 3.000$ Å, $a_{Si} = 2.000$ Å. All other parameters were used from the program without modification. A detailed description is given in ref. 5.

Photolysis of complexes 9a *and* 9b

The photolysis reaction of **9b** was carried out as described for **9a**.[3d] A solution of **9b** (1.66 g, 3 mmol) and $(C_6H_5)_3P$ (787 mg, 3 mmol) in 100 cm^3 of THF was photolysed at −40°C for 2 h (Hg high pressure lamp). Complex **11a** was isolated quantitatively.

Further irradiation of **11a** at −40°C in the presence of $(C_6H_5)_3P$ in a 2 : 1 ratio yielded the bisphosphine complex **13** and polysilane, which were separated as described in ref. 3d. ^{1}H NMR (C_6D_6): **11b** δ 1.7 (s, 18H, t-BuO), 2.5 [d, $^3J(^{31}P^1H) = 10.5$ Hz, 18H, HMPA], 7.0–7.3 (m, 15H, C_6H_5); **13** δ 7.1 (m, 18H), 7.5–8.0 (m, 12H). ^{31}P NMR (C_6D_6): **11b** δ 87.8; **13** δ 95.2.

Photolysis of **9a,b** *in the presence of* 2,3-*dimethylbutadiene*

Complex **9a** (1.54 g, 3 mmol) together with 2,3-dimethylbutadiene (5.0 g) in 100 cm^3 of THF were photolysed at -40°C. Every 30 min, an aliquot of the reaction mixture (2 cm^3) was taken and concentrated by a factor of 10 in the vacuum (10^{-2} torr). The GC–MS analysis gave two major peaks at retention time 6.2 min, 70% intensity, M = 256 M$^+$ **14a**: retention time 5.2 min, 20% intensity, M = 222, M$^+$ **15**. Furthermore, traces of HMPA, M$^+$ = 179, were present.

No further by-products were observed. Complexes **14a,b** and **15** can be separated by prep. GC. ^{1}H NMR (C_6D_6): **14a**, δ 1.74, br, 10H, CH_3, CH_2; 1.70, s, 18H, t-BuO; **14b**, δ 1.75, br, 10H, CH_3, CH_2; 1.70, s, 18H, t-BuS.[25] IR (THF): **15**, 2045 (s), 1971 (s) CO.[26]

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