

Silylene and disilene reactions with electron-poor 1,3-dienes: new ring systems and complete degradation of a CF₃ group^{1, 2}

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Abstract

Photolysis of (t-Bu₂Si)₃ (**1**) or (Me₃Si)₂SiR₂, R = Mes, 2,4,6-ⁱPr₃C₆H₂, in the presence of 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine (**5**) furnishes silaheterocycles having 3,4,1-diazasilole (**6**) and 2,5-dihydro-1,3,2,5-diazadisilene (**9**, **10**) ring skeletons. Irradiation of **5** in the presence of an excess of **1** leads to complete degradation of one of the CF₃ groups and to a partial rearrangement of the six-membered ring skeleton to give the new ring system **4**. Cophotolysis of **1** and 2,5-bis(trifluoromethyl)-1,3,4-oxadiazole provides the 2,6-dihydro-1,5,3,7,2,6-dioxadiazadisilocene and 2,3,6-trihydro-1,4,2,3,6-oxazatrisilene derivatives **12** and **13**. The structures of **4**, **9**, **12**, and **13** were determined by X-ray crystallography.

Keywords: Silicon; Silylene; Disilene; Defluorination; 1,3-Dienes; Crystal structure

1. Introduction

As with the C=C double bond of alkenes, the Si=Si double bond of disilenes can participate in numerous addition and cycloaddition reactions. However, these two double bond systems also exhibit differences in their behaviour. Thus, for example, the Diels–Alder reaction is one of the most well-known processes in organic chemistry, whereas neither [2 + 2]- nor [4 + 2]-cycloadditions between the stable tetraaryldisilenes and alkenes or 1,3-dienes have been observed [2].

Tetra-*tert*-butyldisilene (**2**), which is most simply prepared together with di-*tert*-butylsilylene (**3**) by photolysis of the cyclotrisilane **1**, as shown in Scheme 1, has proved to be somewhat more reactive [3]. Hence, the reaction of **2** with 2,3-dimethylbutadiene furnishes

the corresponding Diels–Alder product which can be isolated from the reaction mixture in very low yield together with the ene adduct and other compounds [4]. We recently found that [2 + 4]-cycloadducts are also accessible in low yields from the cophotolysis of **1** with cyclopentadiene or furan; the structures of these adducts were also elucidated for the first time in our laboratory [1].

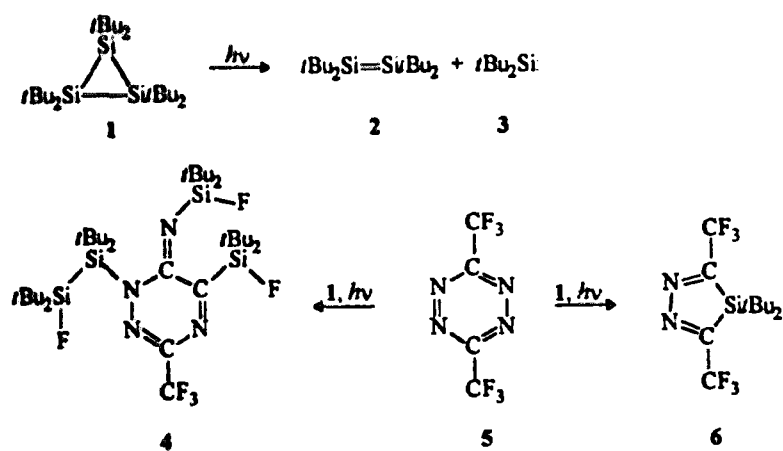
The photolysis reactions of **1** in the presence of 1,4-heterodienes such as, for example, 1,4-diazabutadienes or α -iminoketones, proceed much more readily but, surprisingly, do not give rise to the almost strain-free [1 + 4]-adducts of **3** and the diene; instead the highly strained hetero-Diels–Alder products are formed [5,6]. Apparently, **2** behaves here in a similar way to the electron-rich strained olefins, which also react preferentially with electron-poor 1,3-dienes [7].

We thus became interested in the question of whether this reaction could also be applied to 1,3-dienes possessing extremely electron-deficient carbon atoms in the positions 1 and 4 [8]. Here, we report the results from photolysis of **1** in the presence of 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine (**5**) or 2,5-bis(trifluoromethyl)-

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¹ Dedicated to Professor Robert Corriu in appreciation of his outstanding contributions to organosilicon chemistry.

² See Ref. [1].



Scheme 1.

1,3,4-oxadiazole (11), as well as the reactions of 5 with diarylsilylenes.

2. Results and discussion

Irradiation of a 1 : 2 mixture of 1 and 5 gave rise to a complex range of products from which only one compound could be isolated in the pure state. On the basis of its analytical and spectral data, this product can be identified as the 3,4,1-diazasilole 6. The formation of this five-membered ring system can be most simply explained in terms of a [1 + 4]-cycloaddition of the silylene 3 to the ring carbon atoms and concomitant loss of a molecule of nitrogen.

In further experiments of this type, an excess of 1 was allowed to react with the tetrazine in order to give not only the silylene 3 but also the disilene 2 a chance to participate in a cycloaddition at the endocyclic carbon atoms of the tetrazine 5. Again, complex mixtures of products were obtained from which, in addition to unreacted 1, one crystalline compound 4 was isolated. The analytical and spectral data were indicative of an unusual composition for the product 4. Above all, the ^{29}Si NMR spectrum proved to be of high diagnostic value: this revealed three $^1J(\text{Si},\text{F})$ and one $^2J(\text{Si},\text{F})$ couplings. We assume that the combined attack of 2 and 3 on the tetrazine 5 has effected the complete degradation of a CF_3 group under very mild conditions (Scheme 1).

An X-ray crystallographic analysis of compound 4 (Fig. 1, Tables 1 and 2) not only confirmed the interpretation of the spectroscopic data but also revealed the occurrence during the reaction of a rearrangement of the ring skeleton of 5 in which one endocyclic nitrogen atom and the carbon atom of the defluorinated CF_3 group had changed places. A further interesting spectral observation sheds further light on the structure of 4. An F,F coupling of 68 Hz between the fluorine nuclei of the two di-*tert*-butylfluorosilyl groups was observed in the ^{19}F NMR spectrum. Since a coupling of this magnitude through six bonds is highly improbable, this must

be a through-space coupling [9]. Indeed, in the solid state the two fluorine atoms 9 and 10 are very close together; a similar conformation in solution and in the crystal is feasible on account of the steric overcrowding of the silyl groups.

The most important aspect of this reaction is the degradation of the CF_3 group with simultaneous rearrangement of the ring skeleton, both occurring at room temperature. Although various methods for the reduction of perfluoroalkyl groups proceeding under mild conditions are already known [10], this is probably the first example in which the joint attack of a silylene and a disilene have caused such a degradation. Since the very low yield of 4 could have been indicative of a coincidental result, this experiment was repeated several times and found to produce comparable amounts of 4 each time.

In spite of the application of numerous separation methods, it has not yet been possible to isolate other products, for example those with partially reduced CF_3 groups, from the reaction mixture. Since it is known that the replacement of the *tert*-butyl groups in 2 or 3 by aryl groups usually leads to the formation of better crystallizing products, the tetrazine was allowed to react with the acyclic trisilanes 7 and 8 which smoothly liberate dimesitylsilylene or bis(2,4,6-triisopropylphenyl)silylene respectively, under photolytic conditions (Scheme 2).

However, irradiation of 7 or 8 in the presence of 5 did not furnish the ring systems 4 or 6, instead the compounds 9 and 10 with the 1,3-diaza-2,5-disilacyclohexa-1,3-diene skeleton were obtained. The assigned constitutions were again based on the spectral and analytical data and, in the case of 9, confirmed by X-ray crystallography (Fig. 2, Tables 3 and 4).

The ring skeleton of 9 and 10 is not new, but was previously obtained from the reaction of 1 with pivaloyl

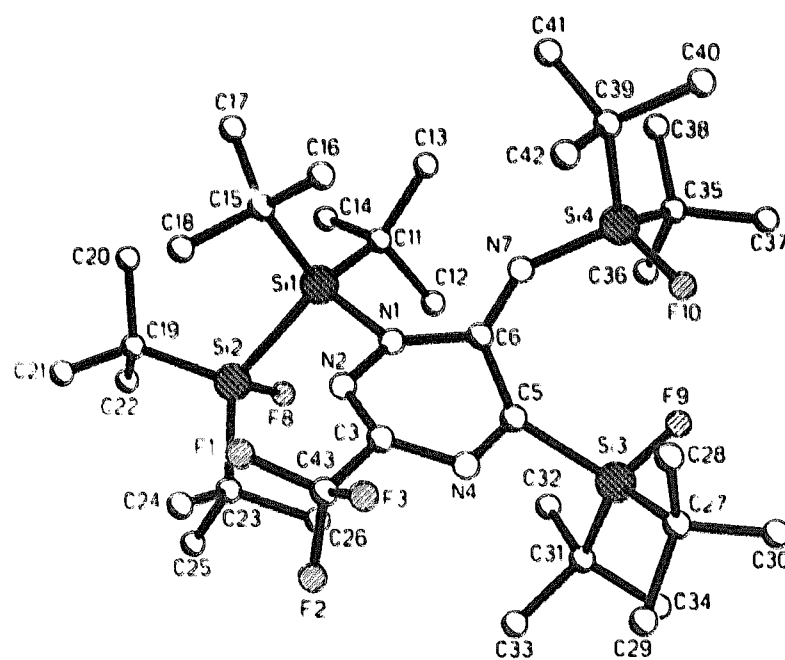


Fig. 1. Molecular structure of 4 in the crystal (hydrogen atoms omitted).

Table 1
Atomic parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{pm}^2 \times 10^{-1}$) for 4

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Si(1)	8280(1)	1969(1)	2614(1)	37(1)
Si(2)	7781(1)	2645(1)	1200(1)	46(1)
Si(3)	7435(1)	3525(1)	5693(1)	45(1)
Si(4)	7978(1)	1596(1)	5962(1)	42(1)
N(1)	8419(1)	2510(1)	3653(1)	34(1)
N(2)	9030(1)	2972(1)	3538(1)	39(1)
C(3)	9220(2)	3430(1)	4156(1)	40(1)
N(4)	8744(1)	3572(1)	4819(1)	44(1)
C(5)	8186(2)	3125(1)	4977(2)	39(1)
C(6)	8199(2)	2462(1)	4554(2)	34(1)
N(7)	8054(1)	1916(1)	4907(1)	40(1)
F(8)	6724(1)	2547(1)	1043(1)	64(1)
F(9)	6847(1)	2982(1)	6057(1)	56(1)
F(10)	8117(1)	2158(1)	6744(1)	60(1)
C(11)	7319(2)	1379(1)	2642(2)	48(1)
C(12)	6547(2)	1785(2)	2855(2)	60(1)
C(13)	7528(2)	814(1)	3342(2)	63(1)
C(14)	7015(2)	1055(2)	1686(2)	69(1)
C(15)	9435(2)	1589(1)	2729(2)	47(1)
C(16)	9864(2)	1503(2)	3752(2)	65(1)
C(17)	9400(2)	901(1)	2270(2)	69(1)
C(18)	10030(2)	2037(2)	2277(2)	65(1)
C(19)	8058(2)	2335(2)	48(2)	62(1)
C(20)	8249(3)	1601(2)	28(2)	93(2)
C(21)	8839(3)	2698(2)	-210(2)	90(2)
C(22)	7243(3)	2462(2)	-721(2)	89(2)
C(23)	7878(2)	3572(1)	1345(2)	55(1)
C(24)	8825(2)	3830(2)	1520(2)	72(1)
C(25)	7343(3)	3929(2)	492(2)	79(1)
C(26)	7451(2)	3766(2)	2166(2)	65(1)
C(27)	8100(2)	3954(1)	6727(2)	67(1)
C(28)	8961(3)	3598(2)	7095(3)	90(2)
C(29)	8318(3)	4670(2)	6522(3)	101(2)
C(30)	7556(3)	3957(2)	7493(2)	98(2)
C(31)	6595(2)	4004(2)	4855(2)	67(1)
C(32)	6117(2)	3503(2)	4150(3)	89(2)
C(33)	6977(3)	4549(2)	4333(3)	94(2)
C(34)	5912(3)	4306(2)	5364(3)	108(2)
C(35)	6862(2)	1214(1)	5957(2)	52(1)
C(36)	6144(2)	1546(2)	5252(2)	67(1)
C(37)	6639(2)	1304(2)	6919(2)	82(1)
C(38)	6836(2)	477(1)	5727(3)	77(1)
C(39)	8976(2)	1067(1)	6374(2)	55(1)
C(40)	8973(2)	817(2)	7357(2)	77(1)
C(41)	9072(2)	472(2)	5759(2)	75(1)
C(42)	9785(2)	1511(2)	6413(2)	77(1)
C(43)	9914(2)	3921(2)	4063(2)	56(1)
F(1)	10433(1)	3718(1)	3503(1)	83(1)
F(2)	9581(1)	4491(1)	3743(2)	91(1)
F(3)	10431(1)	4042(1)	4870(1)	97(1)

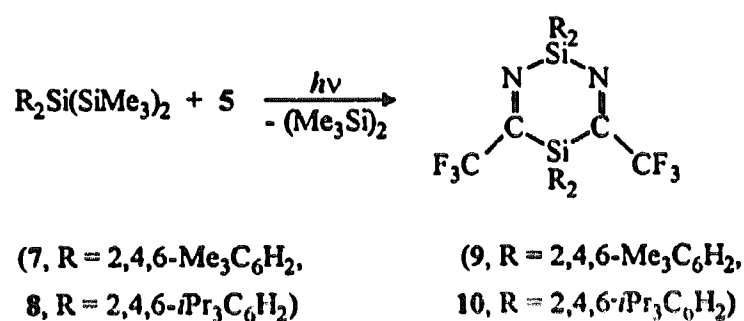
nitrile, presumably by way of the [1 + 2]-cycloadduct of 3 with the C≡N triple bond and subsequent σ -dimerization [11]. The formation of this ring system upon photolysis of 7 or 8 in the presence of 5 is still a subject of speculation. One possibility is the [1 + 4]-cycloaddition of the respective silylene at the ring carbon atoms, with the intermediate formation of a compound of the type 6

Table 2
Selected bond lengths (pm) and bond angles (deg) (standard deviations in parentheses) for 4

Si(1)–Si(2)	249.2(2)	Si(1)–N(1)	186.6(2)
N(1)–N(2)	136.9(3)	N(2)–C(3)	129.7(3)
C(3)–N(4)	136.9(3)	N(4)–C(5)	130.8(3)
C(5)–C(6)	148.8(3)	C(6)–N(7)	126.6(3)
N(7)–Si(4)	171.5(2)	C(5)–Si(3)	190.5(3)
C(6)–N(7)–Si(4)	139.2(2)	C(6)–C(5)–N(4)	119.5(2)
C(5)–N(4)–C(3)	116.7(2)	N(4)–C(3)–N(2)	125.1(2)
C(3)–N(2)–N(1)	118.2(2)	N(2)–N(1)–C(6)	117.3(2)
N(1)–C(6)–C(5)	110.6(2)		

and subsequent insertion of a second silylene molecule into the N–N single bond.

As with the reaction of 1 with the tetrazine 5, photolysis of the cyclotrisilane in the presence of the 1,3,4-oxadiazole 11 (Scheme 3) also took an unexpected course. Initially, pale yellow crystals separated from the reaction mixture and gave spectral and analytical data indicative of the eight-membered ring system 12. Ac-



Scheme 2.

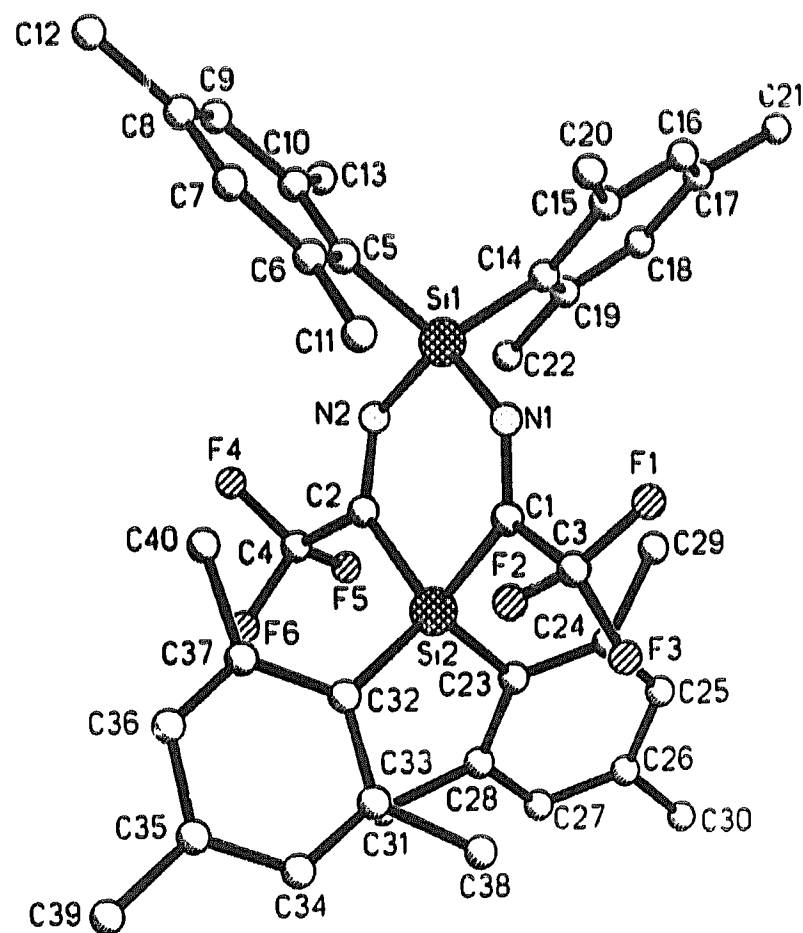


Fig. 2. Molecular structure of 9 in the crystal (hydrogen atoms omitted).

Table 3
Atomic parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{pm}^2 \times 10^{-1}$) for **9**

	x	y	z	U_{eq}
Si(1)	8772(1)	4767(1)	2375(1)	42(1)
Si(2)	11462(1)	4679(1)	2774(1)	43(1)
N(1)	9519(3)	5532(3)	2884(2)	42(1)
N(2)	9553(3)	3943(3)	2125(2)	50(1)
C(1)	10484(3)	5538(3)	3024(3)	42(1)
C(2)	10519(4)	3846(3)	2286(3)	49(2)
C(3)	10886(4)	6294(3)	3507(3)	58(2)
C(4)	10941(5)	3009(4)	2007(4)	69(2)
C(5)	7870(3)	4237(3)	2944(3)	44(2)
C(6)	7862(4)	4366(3)	3689(3)	50(2)
C(7)	7155(4)	3946(4)	4040(3)	64(2)
C(8)	6458(4)	3368(4)	3722(4)	63(2)
C(9)	6457(4)	3234(3)	2995(4)	64(2)
C(10)	7140(4)	3661(3)	2595(3)	53(2)
C(11)	8583(5)	4967(4)	4132(3)	68(2)
C(12)	5717(5)	2895(5)	4154(4)	91(3)
C(13)	7060(5)	3469(4)	1811(3)	75(2)
C(14)	8154(4)	5376(3)	1585(3)	45(2)
C(15)	7451(4)	6030(3)	1719(3)	49(2)
C(16)	6994(4)	6532(3)	1156(3)	57(2)
C(17)	7178(5)	6406(4)	468(3)	62(2)
C(18)	7853(4)	5753(3)	331(3)	60(2)
C(19)	8345(4)	5237(3)	865(3)	53(2)
C(20)	7157(5)	6219(4)	2444(3)	66(2)
C(21)	6704(6)	6960(4)	-138(3)	86(2)
C(22)	9033(5)	4535(5)	641(3)	75(2)
C(23)	12308(4)	5028(3)	2072(3)	50(2)
C(24)	12023(4)	5713(3)	1597(3)	56(2)
C(25)	12668(5)	5976(4)	1112(3)	64(2)
C(26)	13579(5)	5558(4)	1033(4)	73(2)
C(27)	13855(4)	4895(4)	1482(3)	73(2)
C(28)	13250(4)	4596(4)	1997(3)	60(2)
C(29)	11020(5)	6194(4)	1591(3)	83(3)
C(30)	14257(6)	5857(5)	474(4)	111(4)
C(31)	13667(5)	3839(4)	2414(4)	91(3)
C(32)	12126(4)	4301(3)	3677(3)	49(2)
C(33)	13073(4)	4649(3)	3981(3)	55(2)
C(34)	13554(4)	4311(4)	4622(3)	63(2)
C(35)	13145(4)	3658(4)	4975(3)	66(2)
C(36)	12185(4)	3355(3)	4701(3)	60(2)
C(37)	11674(4)	3655(3)	4068(3)	54(2)
C(38)	13627(4)	5385(4)	3666(3)	76(2)
C(39)	13687(6)	3309(5)	5680(3)	103(3)
C(40)	10615(4)	3274(4)	3850(3)	76(2)
F(1)	10256(3)	6944(2)	3481(2)	92(2)
F(2)	11070(4)	6054(3)	4176(2)	100(2)
F(3)	11775(3)	6597(3)	3327(3)	108(2)
F(4)	13261(3)	2388(2)	1937(3)	110(2)
F(5)	11277(4)	3118(3)	1381(3)	133(3)
F(6)	11727(3)	2694(2)	2452(2)	105(2)

Table 4
Selected bond lengths (pm) and bond angles (deg) (standard deviations in parentheses) for **9**

Si(1)–N(1)	175.3(4)	Si(1)–N(2)	173.9(4)
N(1)–C(1)	125.9(6)	N(2)–C(2)	127.3(6)
C(1)–Si(2)	194.7(5)	C(2)–Si(2)	194.6(5)
N(1)–Si(1)–N(2)	110.1(2)	Si(1)–N(2)–C(2)	128.5(4)
N(2)–C(2)–Si(2)	126.0(4)	C(2)–Si(2)–C(1)	100.1(2)
Si(2)–C(1)–N(1)	127.9(4)	C(1)–N(1)–Si(1)	126.9(3)
C(5)–Si(1)–C(14)	115.7(2)	C(23)–Si(2)–C(32)	117.6(2)

confirmed by X-ray crystallography (Fig. 3, Tables 5 and 6).

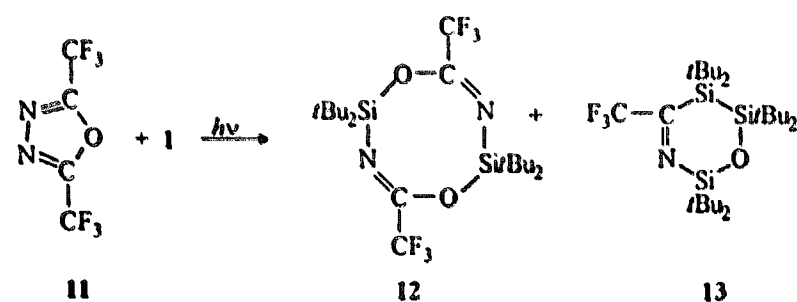
When the starting materials are compared with the isolated molecule **12**, it became apparent that the $\text{CF}_3\text{C(N)O}$ fragment remaining after cleavage of trifluoroacetonitrile from **11** had undergone a formal addition with the silylene **3** followed by a cyclodimerization to furnish the eight-membered ring product **12**.

When the solution remaining after separation of compound **12** was kept for several weeks at -30°C , a second crop of crystals was obtained, for which the analytical and spectral data were indicative of the six-membered ring product **13**. Thus, for example, there were three signals in the ^{29}Si NMR spectrum, one singlet in the ^{19}F NMR spectrum, and the typical signal pattern for a $\text{C}-\text{CF}_3$ group in the ^{13}C NMR spectrum. Final confirmation of the structure was again provided by an X-ray crystallographic analysis (Fig. 4, Tables 7 and 8), which also revealed some unexpected details.

Particularly conspicuous is the extremely large Si–Si bond length of 254.2(1) pm; this bond length is equal to that of the $-\text{tBu}_2\text{Si}-\text{Si}^t\text{Bu}_2-$ bonds in the extremely strained hepta-*tert*-butylcyclotetrasilane [12,13] and, together with the latter, constitutes the longest Si–Si bond currently known in the cyclooligosilanes. As expected, the smallest endocyclic bond angles are found at the silicon atoms, while the C–N–Si(3) angle, and especially the angle of the disiloxane unit, Si(1)–O–Si(3), are appreciably widened.

It would seem that the same initial steps are involved in the formation of **13** from **1** and **11** as in that of **12**: compound **11** again is apparently degraded to give a $\text{CF}_3\text{C(N)O}$ fragment, which then undergoes addition and insertion reactions with the photolysis products of **1** to furnish the final product **13** isolated.

cordingly, only one signal for each was observed in the ^{19}F and ^{29}Si NMR spectra. In addition to signals for the *tert*-butyl carbon atoms, the ^{13}C NMR spectrum contained two quartets at low field with the typical $^1J(\text{C},\text{F})$ and $^2J(\text{C},\text{F})$ coupling constants for the CF_3 group. The nature of this new ring system was unambiguously



Scheme 3.

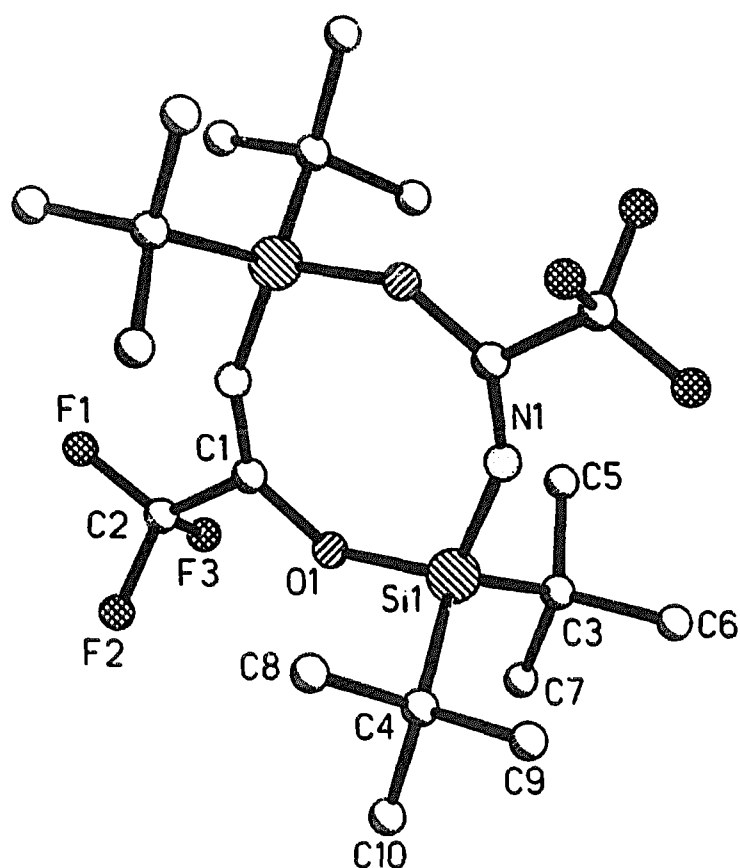


Fig. 3. Molecular structure of **12** in the crystal (hydrogen atoms omitted).

Although the actually expected Diels–Alder products have not yet been obtained from the photolysis reactions of **1** in the presence of **5** or **11**, these reactions have nevertheless given rise to some, mostly novel, silaheterocyclic systems containing one, two, or three silicon atoms in the ring skeleton. The result of the photolysis of **5** in the presence of an excess of **1** is equally surprising, in that the combined attack of the species **2**

Table 5
Atomic parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{pm}^2 \times 10^{-1}$) for **12**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Si(1)	1860(1)	1048(1)	5557(1)	48(1)
O(1)	1661(2)	−16(3)	4650(1)	69(1)
N(1)	435(2)	1256(3)	5873(2)	70(1)
C(1)	759(3)	−919(3)	4146(2)	51(1)
C(2)	1352(4)	−1681(5)	3477(3)	80(2)
C(3)	2270(3)	2938(4)	5196(2)	70(1)
C(4)	3151(3)	27(4)	6485(2)	66(1)
C(5)	1016(5)	3464(5)	4448(3)	118(2)
C(6)	2556(5)	4048(4)	5950(3)	123(3)
C(7)	3513(5)	2889(5)	4846(3)	113(2)
C(8)	2605(5)	−1531(5)	6537(3)	121(2)
C(9)	3344(5)	756(6)	7370(3)	141(3)
C(10)	4531(4)	−115(6)	6333(3)	136(3)
F(1)	522(8)	−2582(19)	2946(9)	138(4)
F(1a)	738(49)	−2927(22)	3217(32)	149(21)
F(2)	2471(10)	−2447(10)	3903(8)	125(4)
F(2a)	2567(19)	−1760(85)	3688(30)	195(20)
F(3)	1748(21)	−735(11)	3000(10)	130(5)
F(3a)	908(109)	−892(73)	2745(26)	155(24)

Table 6
Selected bond lengths (pm) and bond angles (deg) (standard deviations in parentheses) for **12**

C(1)–O(1)	129.7(3)	O(1)–Si(1)	168.1(2)
Si(1)–N(1)	168.7(3)		
C(1)–O(1)–Si(1)	138.9(2)	O(1)–Si(1)–N(1)	115.4(1)
O(1)–C(1)–N(1A)	131.9(3)	Si(1)–N(1)–C(1A)	153.0(2)

and **3** leads, albeit in low yield, to the complete degradation of one CF_3 group of **5**.

3. Experimental section

3.1. General procedures

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

The ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on a Bruker AM 300 spectrometer, whereas the ^{29}Si NMR spectra were recorded on a Bruker AMX 300 spectrometer using C_6D_6 or CDCl_3 as solvents. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. Mass spectra were obtained with Varian-MAT 212 or Finnegan-MAT 95 instruments. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

The compounds **1** [14], **5** [15], **7** [16], **8** [17], and **11** [18] were prepared according to the published procedures.

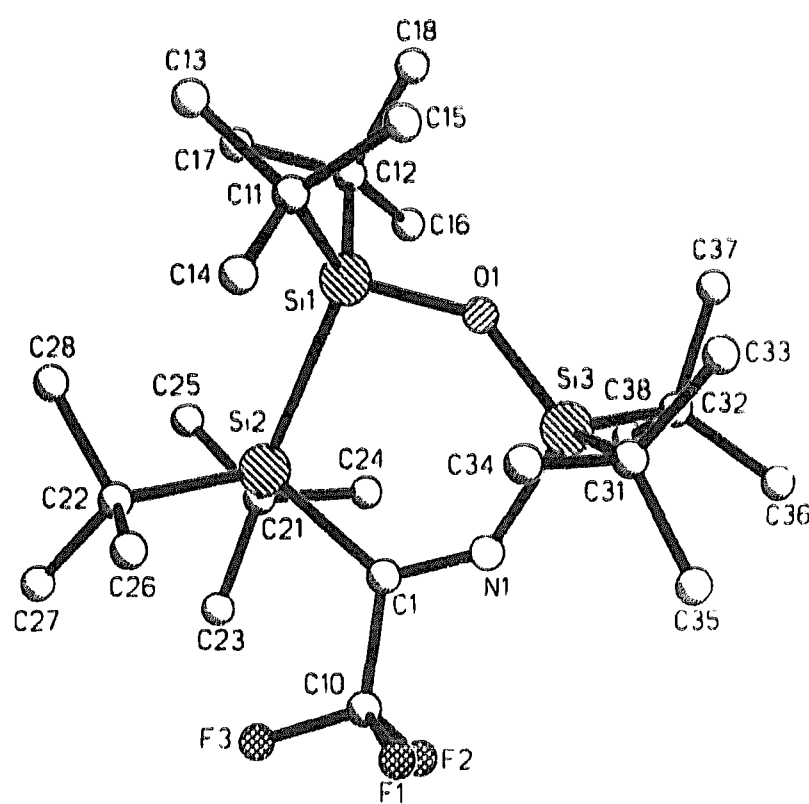


Fig. 4. Molecular structure of **13** in the crystal (hydrogen atoms omitted).

Table 7
Atomic parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{pm}^2 \times 10^{-1}$) for **13**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Si(1)	1018(1)	1255(1)	4652(1)	32(1)
Si(2)	2142(1)	1753(1)	6416(1)	35(1)
Si(3)	2424(1)	727(1)	7116(1)	36(1)
O(1)	1455(2)	873(1)	5592(1)	34(1)
N(1)	3265(3)	1104(1)	8106(2)	41(1)
C(1)	3434(3)	1446(1)	7910(3)	39(1)
F(1)	6047(3)	1444(1)	9263(3)	123(1)
F(2)	4394(4)	1588(1)	10257(2)	125(2)
F(3)	5001(3)	1973(1)	8959(2)	83(1)
C(10)	4710(5)	1616(1)	9101(4)	64(2)
C(11)	1892(4)	1172(1)	3154(3)	46(1)
C(12)	-1215(4)	1265(1)	3912(3)	47(1)
C(13)	1048(5)	1374(1)	1810(3)	68(2)
C(14)	3605(4)	1276(1)	3429(4)	64(2)
C(15)	1794(5)	748(1)	2850(3)	65(2)
C(16)	-1972(4)	1239(1)	5044(4)	65(2)
C(17)	-1800(4)	1623(1)	3102(4)	66(2)
C(18)	-1820(4)	926(1)	2991(4)	71(2)
C(21)	760(4)	2003(1)	7287(3)	51(1)
C(22)	3348(4)	2106(1)	5722(3)	48(1)
C(23)	1618(5)	2281(1)	8400(4)	90(2)
C(24)	14(5)	1727(1)	8023(4)	76(2)
C(25)	-497(4)	2223(1)	6254(4)	69(2)
C(26)	4955(4)	1937(1)	5834(4)	66(2)
C(27)	3632(5)	2493(1)	6370(4)	75(2)
C(28)	2442(4)	2176(1)	4220(3)	59(1)
C(31)	4197(4)	446(1)	7065(3)	52(1)
C(32)	1045(4)	474(1)	7894(3)	46(1)
C(33)	3727(5)	74(1)	6328(5)	77(2)
C(34)	5138(4)	663(1)	6302(4)	67(2)
C(35)	5302(4)	372(1)	8491(4)	79(2)
C(36)	1883(5)	213(1)	9074(4)	77(2)
C(37)	-84(4)	238(1)	6804(4)	65(2)
C(38)	102(4)	745(1)	8474(4)	64(2)

3.2. 1-(1,1,2,2-Tetra-*tert*-butyl-2-fluorodisilanyl)-3-trifluoromethyl-5-di-*tert*-butylfluorosilyl-1-hydro-1,2,4-triazine-6-ylidene-di-*tert*-butylfluorosilylamine (**4**)

A solution of 1.80 g (4.20 mmol) of **1** and 0.46 g (2.10 mmol) of **5** in 100 ml of *n*-hexane was irradiated for 5 h at room temperature. The solvent was distilled off and the red residue dissolved in 20 ml of *n*-pentane. Unreacted **1** (0.57 g, 32%) was filtered off and the solvent removed. Crystallization of the residue first from a minimum amount of a 1:1 mixture of ethyl

acetate-*n*-hexane and then from *n*-hexane yielded 0.043 g (3%) of **4**: yellow transparent crystals; m.p. 148°C. ¹H NMR (C₆D₆): δ 1.128 (s, 9H), 1.133 (s, 9H), 1.169 (s, 9H), 1.171 (s, 9H), 1.177 (s, 9H), 1.181 (s, 9H), 1.34 (s, 18H). ¹³C NMR (C₆D₆): δ 20.11, 20.32, 21.46, 21.61, 24.29, 24.55, 24.69, 27.75, 27.76, 29.63, 30.64, 120.64 (q, CF₃, ¹J(C,F) = 273 Hz), 149.38, 172.95 (q, C_q, ²J(F,C) = 21 Hz). ¹⁹F (CDCl₃): δ -172.13 (s, SiF), -167.57 (d, SiF, ⁿJ(F,F) = 68 Hz), -144.56 (d, SiF, ⁿJ(F,F) = 68 Hz), -69.23 (s, CF₃). ²⁹Si NMR (C₆D₆): δ -7.19 (d, ¹J(Si,F) = 330.7 Hz), 3.96 (d, ¹J(Si,F) = 320.8 Hz), 35.03 (d, ¹J(Si,F) = 336.5 Hz), 41.32 (d, ²J(Si,F) = 19.8 Hz). MS (CI, isobutane): *m/z* 788 (M⁺, 100). Found: C, 54.84; H, 9.22; N, 7.12. C₃₆H₇₂F₆N₄Si₄ (787.34). Calc.: C, 54.92; H, 8.89, N, 7.07%.

3.3. 1,1-Di-*tert*-butyl-2,5-bis(trifluoromethyl)-3,4,1-di-azasilole (**6**)

A solution of 0.17 g (0.38 mmol) of **1** and 0.17 g (0.78 mmol) of **5** in 100 ml of *n*-hexane was irradiated for 3 h at room temperature, after which the reaction was shown to be complete by the disappearance of **1** (TLC monitoring). The solvent was removed and unreacted **5** was sublimed off. Crystallization of the residue from 30 ml *n*-hexane afforded 0.030 g (12%) of **6**: yellow crystals, m.p. 92–94°C. ¹H NMR (C₆D₆): δ 0.75 (s). ¹³C NMR (CDCl₃): δ 20.96 (C_q), 27.63 (C_p), 127.47 (q, CF₃, ¹J(F,C) = 275 Hz), 173.07 (q, C_q, ²J(F,C) = 38 Hz). C_p and C_q refer to primary and quaternary carbon atoms. ²⁹Si NMR (CDCl₃): δ 34.59. Found: C, 43.27; H, 5.39; N, 8.34. C₁₂H₁₈F₆N₂Si (332.37). Calc.: C, 43.37; H, 5.42; N, 8.43%.

3.4. 2,2,5,5-Tetrakis(2,4,6-trimethylphenyl)-4,6-bis(trifluoromethyl)-2,5-dihydro-1,3,2,5-diazadisilole (**9**)

A solution of 0.38 g (1.80 mmol) of **5** and 1.47 g (3.60 mmol) of **7** in 100 ml of *n*-hexane was irradiated for 2.5 h, after which the reaction was shown to be complete by the disappearance of **5** (TLC monitoring). The solution was filtered and concentrated to 30 ml. Cooling to -30°C yielded 0.34 g (26%) of **9**: yellow crystals, m.p. 259–261°C. ¹H NMR (C₆D₆): δ 1.97 (s, 6H, *p*-Me), 2.04 (s, 6H, *p*-Me), 2.27 (s, 12H, *o*-Me), 2.44 (s, 12H, *o*-Me), 6.55 (s, 4H), 6.62 (s, 4H). ¹³C NMR (CDCl₃): δ 21.02 (C_p), 21.08 (C_p), 23.62 (C_p), 24.00 (C_p), 118.05 (q, CF₃, ¹J(C,F) = 287 Hz), 125.41 (CH), 126.30 (CH), 129.41 (C_q), 129.62 (C_q), 140.34 (C_q), 145.19 (C_q), 145.43 (C_q), 188.77 (q, C_q, ²J(C,F) = 33 Hz). ¹⁹F NMR (C₆D₆): δ -70.78 (s). ²⁹Si NMR (C₆D₆): δ -71.72 (s), -28.56 (s). IR (cm⁻¹): ν(C=N) 1645 (s), 1605 (s). MS (CI, isobutane): *m/z* 723 (M⁺, 19). Found: C, 66.29; H, 6.26; N, 3.85. C₄₀H₄₄F₆N₂Si₂ (722.97). Calc.: C, 66.45; H, 6.13; N, 3.87%.

Table 8
Selected bond lengths (pm) and bond angles (deg) (standard deviations in parentheses) for **13**

Si(1)–Si(2)	254.2(1)	Si(2)–C(1)	197.4(3)
C(1)–N(1)	126.2(4)	N(1)–Si(3)	173.1(3)
Si(3)–O(1)	164.4(2)	O(1)–Si(1)	165.9(2)
O(1)–Si(1)–Si(2)	100.9(1)	Si(1)–Si(2)–C(1)	100.6(1)
Si(2)–C(1)–N(1)	126.8(2)	C(1)–N(1)–Si(3)	136.1(2)
N(1)–Si(3)–O(1)	109.3(1)	Si(3)–O(1)–Si(1)	142.3(1)

3.5. 2,2,5,5-Tetrakis(2,4,6-triisopropylphenyl)-4,6-bis(trifluoromethyl)-2,5-dihydro-1,3,2,5-diazadisilole (10)

A solution of 0.38 g (1.74 mmol) of **5** and 2.00 g (3.48 mmol) of **8** in 100 ml of *n*-hexane was irradiated until **5** was no longer detectable by TLC (2.5 h). The solution was concentrated to a 20 ml. Cooling at -30°C furnished 0.46 g (24%) of **10**: orange crystals, m.p. 215–223°C. ^1H NMR (C_6D_6): δ 0.60 (dd, 12H, $^3J(\text{H,H}) = 6.5$ Hz), 0.75 (d, 6H, $^3J(\text{H,H}) = 6.5$ Hz), 0.92 (d, 6H, $^3J(\text{H,H}) = 6.2$ Hz), 1.11–1.16 (m, 30H), 1.37–1.45 (m, 18H), 2.67 (m, 4H), 2.97 (m, 4H), 3.10 (m, 2H), 4.05 (sept, 2H, $^3J(\text{H,H}) = 6.5$ Hz), 7.03 (m, 6H), 7.11 (s, 2H). ^{13}C NMR (CDCl_3): δ 22.07, 22.15, 23.11, 23.53, 23.62, 23.67, 23.84, 24.85, 25.48, 26.92, 27.47, 32.91, 34.12, 34.87, 35.89, 26.57, 117.36 (q, CF_3 , $^1J(\text{F,C}) = 288$ Hz), 121.84, 122.01, 122.34, 123.06, 127.87, 150.91, 151.52, 155.08, 156.15, 157.63, 187.70 (q, C_q , $^2J(\text{F,C}) = 32$ Hz). ^{29}Si NMR (C_6D_6): δ -76.30 (s), -31.89 (s). IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1694 (m), 1603 (m). MS (CI, isobutane): m/z 1060 (M^+ , 100). Found: C, 72.28; H, 8.64; N, 2.73. $\text{C}_{64}\text{H}_{92}\text{F}_6\text{N}_2\text{Si}_2$ (1059.62). Calc.: C, 72.50; H, 8.75; N, 2.60%.

3.6. 2,2,6,6-Tetra-tert-butyl-4,8-bis(trifluoromethyl)-2,6-dihydro-1,5,3,7,2,6-dioxadiazadisilole (12) and 2,2,3,3,6,6-hexa-tert-butyl-5-trifluoromethyl-2,3,6-trihydro-1,4,2,3,6-oxazatrisilole (13)

A solution of 1.61 g (3.76 mmol) of **1** and 1.55 g (7.52 mmol) of **11** in 100 ml of *n*-hexane was irradiated

for 5 h, after which the reaction was shown to be complete by the disappearance of **1** (TLC monitoring). The solvent was removed, the red residue redissolved in 20 ml of *n*-pentane, and the solution was cooled to -30°C . The solid was filtered off and recrystallized from a minimum amount of *n*-pentane to yield 0.235 g (12%) of **12**: pale yellow crystals, m.p. 174–176°C. ^1H NMR (CDCl_3): δ 1.05 (s). ^{13}C NMR (CDCl_3): δ 20.21 (C_q), 26.99 (C_p), 116.1 (q, CF_3 , $^1J(\text{C,F}) = 282$ Hz), 141.74 (q, C_q , $^2J(\text{C,F}) = 40$ Hz). ^{19}F NMR (CDCl_3): δ -74.98 (s). ^{29}Si NMR (C_6D_6): δ -18.54 (s). IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1838 (s), 1802 (s). MS (CI, isobutane): m/z 507 (M^+ , 100). Found: C, 47.57; H, 7.04; N, 5.46. $\text{C}_{20}\text{H}_{36}\text{F}_6\text{N}_2\text{O}_2\text{Si}$ (506.69). Calc.: C, 47.40; H, 7.16; N, 5.53%.

After the separation of **12** the solvent was removed from the mother liquor and the red residue redissolved in a minimum amount of ethyl acetate. The solution was kept at -30°C for 5 weeks after which a yellow powder was isolated. Repeated crystallization from ethyl acetate at -30°C provided 200 mg (10%) of **13**: yellow crystals, m.p. 183–184°C. ^1H NMR (CDCl_3): δ 1.14 (s, 18H), 1.24 (s, 18H), 1.29 (s, 18H). ^{13}C NMR (CDCl_3): δ 20.96 (C_q), 22.41 (C_q), 26.09 (C_q), 29.40 (C_p), 31.13 (C_p), 32.13 (C_p), 116.41 (q, CF_3 , $^1J(\text{C,F}) = 289$ Hz), 192.92 (q, C_q , $^2J(\text{C,F}) = 33$ Hz). ^{19}F NMR (CDCl_3): δ -70.02 (s). ^{29}Si NMR (C_6D_6): δ -13.34 (s), -1.30 (s), 19.05 (s). IR (cm^{-1}): $\nu(\text{C}=\text{N})$ 1634 (m), 1603 (w). MS (CI, isobutane): m/z 538 (M^+ , 100). Found: C, 57.90; H, 10.00; N, 2.56. $\text{C}_{26}\text{H}_{54}\text{F}_3\text{NOSi}_3$ (537.93). Calc.: C, 58.12; H, 10.05; N, 2.60%.

Table 9
Crystallographic data for **4**, **9**, **12**, and **13**^a

	4	9	12 ^b	13
Empirical formula	$\text{C}_{36}\text{H}_{72}\text{N}_4\text{F}_6\text{Si}_4$	$\text{C}_{40}\text{H}_{44}\text{N}_2\text{F}_6\text{Si}_2$	$\text{C}_{20}\text{H}_{36}\text{N}_2\text{O}_2\text{F}_6\text{Si}_2$	$\text{C}_{26}\text{H}_{54}\text{F}_3\text{NOSi}_3$
Molar mass (g mol^{-1})	787.33	722.96	506.68	537.97
<i>a</i> (pm)	1551.1(7)	1306.8(3)	1019.8(1)	900.1(1)
<i>b</i> (pm)	2034.1(9)	1560.9(3)	897.3(1)	3597.3(9)
<i>c</i> (pm)	1476.7(5)	1871.7(8)	1579.9(2)	1030.5(3)
β (deg)	101.44(3)	96.57(3)	108.10(1)	107.01(2)
<i>V</i> ($\times 10^6$ pm ³)	4556(3)	3793(2)	1374.2(4)	3190.5(1)
<i>Z</i>	4	4	2	4
<i>D</i> _{calc} (g cm^{-3})	1.148	1.284	1.224	1.120
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Crystal size (mm ³)	$0.5 \times 0.5 \times 0.2$	$0.2 \times 0.25 \times 1.25$	$0.55 \times 0.55 \times 0.15$	$0.5 \times 0.5 \times 0.1$
Data collection mode	Wyckoff-scan	ω -scan	ω -scan	ω -scan
$2\theta_{\text{max}}$ (deg)	55	55	55	55
Number of reflections	11190	9395	3549	7917
Number of unique reflections	9638	8682	3159	7326
Number of reflections $F > 3\sigma(F)$	7793	5142	2341	4605
Linear abs. coefficient (mm^{-1})	0.18	0.015	0.19	0.18
Data to parameter ratio	17.24	11.38	13.23	15.00
$R(R_w)$	0.053(0.049)	0.094(0.091)	0.064(0.065)	0.062(0.054)
Residual electron density (e nm^{-3})	0.44, -0.27	0.48, -0.44	0.25, -0.24	0.34, -0.23

^a Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, upon quoting the depository numbers 404 610 (**4**), 404 608 (**9**), 404 609 (**12**), and 404 607 (**13**). ^b The fluorine atoms are disordered, occupying two positions with the occupancy factors of 0.75 and 0.25.

3.7. X-ray structure analyses of 4, 9, 12, and 13

Crystal data and numerical data of the structure determinations are given in Table 9. Single crystals were obtained from saturated solutions in *n*-hexane (4 and 9), *n*-pentane (12), or ethyl acetate (13). In each case, the crystal was mounted in a thin-walled glass capillary. Data collection was performed at room temperature on a Siemens P4 diffractometer using graphite-monochromated Mo K α radiation.

The structures were solved by direct phase determination using the Siemens SHELXTL PLUS program system and refined by full-matrix least squares techniques. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. For each structure a complete list of bond lengths and angles, and tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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