Dipheno-silyliminoquinones – A 14π-system

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Abstract

Lithium salts of 2.6-dialkylanilines react with di-*tert*-butylfluorosilanes to give mono (**1**–**3**) – and bis (**7**, **8**)-(2.6-dialkylphenyl-amino)silanes. Amino-2.6-dimethylphenyl-(di-*tert*-butylfluoro)silane (**1**) forms with BuLi a dimeric lithium salt (**4**) containing an eight-membered (LiFNSi)$_2$ ring system. Thermally, **4** loses LiF and a bicyclic compound (**9**) via iminosilenes is obtained. The lithium salt of the bulkier amino-2.6-diisopropylphenyl-(di-*tert*-butylfluorosilanes) (**5**–**7**) thermally loses LiH and iminosilanes (**10**–**12**) with a 14π-system are isolated. The reaction mechanisms and crystal structures are discussed.
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Keywords: Lithium-fluorosilylamides; Iminosilenes; En-reaction; Bicycle; 14π-system; Iminosilanes

1. Introduction

Normally, imines are formed by aldehydes or ketones with most primary amines. Imines formed by ammonia are unstable but can be detected in solution. CH$_2$=NH, for example, oligomerizes to give hexamethylene-tetramine.

HN=C$\lesssim$ imines are only stable enough to isolate if the carbon atom of the imine double bond bears an aromatic substituent. Enamines are formed by aldehydes or ketones with secondary amines. Enamines of primary amines or even of ammonia also exist, but only in equilibrium with an imine isomer. Partly, they are stabilized with AlCl$_3$ as adducts [1].

Stability of compounds with double bonds can often be achieved by the use of bulky substituents which prevent further reactions, e.g., bis(silyl)diazenes [2], silenes [3], disilenes [4,5], and iminosilenes [6,7] have been isolated as stable compounds at room temperature and were reported in the 1980s and 1990s [3–7]. We found that lithium derivatives of bulky aminofluorosilanes crystallize as LiF-adducts of iminosilenes [6,7]. Attempts to eliminate LiF lead to

dimerization or rearrangement of the polar iminosilene formed, e.g. [6,7]:

(1)
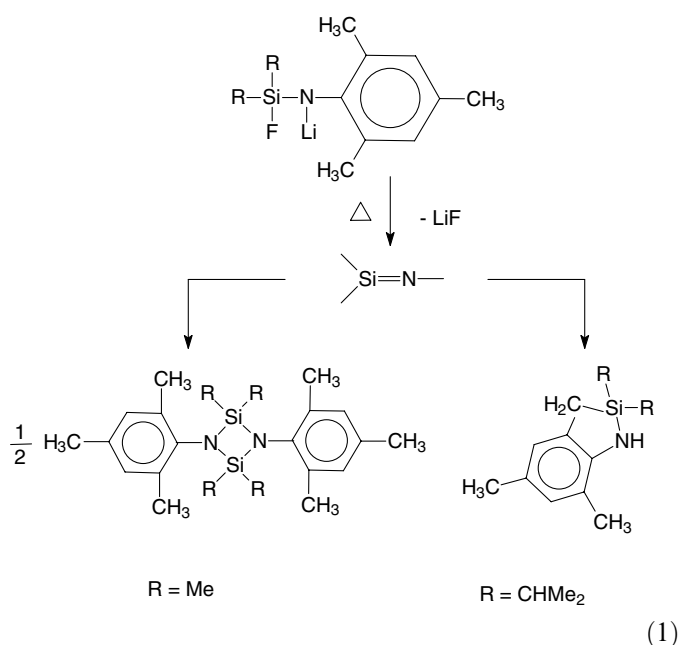
The only known iminosilenes stabilized by an aryl group are

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R = iPr₂ [6, 7, 8], tBu [9]
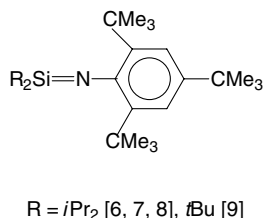
2. Results and discussion

2.1. Arylsilylamines, lithiumsalts

In order to prepare bulky substituted arylaminosilanes, we started with di-*tert*-butyl-fluorosilanes and the lithium salts of 2.6-dimethylaniline and 2.6-diisopropylaniline and synthesized **1**, **2** [10] and **3**, Eq. (2). **1** and **2** should be suitable precursors for the synthesis of iminosilenes. In reactions of the arylaminosilanes **1**, **2**, and **3** with *n*-BuLi, we isolated the lithium silylamides **4**, **5**, and **6**, Eq. (3).
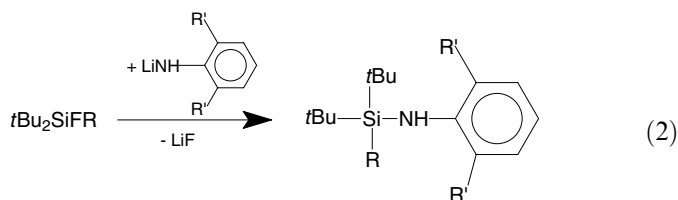
1, 2 [4], **3**
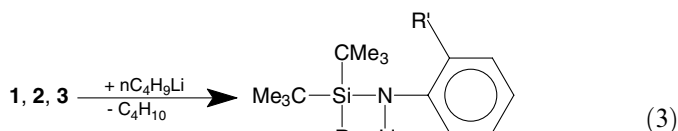
4, 5, [10], **6**

	1,4	**2,5** [10]	**3,6**
R	F	F	Me
R′	Me	iPr	iPr

Crystal structure of (Me₃C)₂SiFLiNC₆H₃Me₂ (4)

Compound **4** (Fig. 1, Table 1) crystallizes from THF in the monoclinic space group *P2₁/c* (Table 1) as dimer forming an eight-membered (SiFLiN)₂ ring which has no symmetry. The long Li–N and Si–F and short Si–N and Li–F distances with large angles at the fluorine atoms are remarkable.

Lithium salts with an eight-membered (SiFLiN)₂ ring skeleton have been found in oxygen containing compounds, e.g., in lithium-fluorosilyl-furanylsilylamides [13] or lithium-fluorosilyl-amidosiloxanes. [11,14]

The deviations of the atoms from the least squares plane are shown in Fig. 2a and b and measured with (pm):
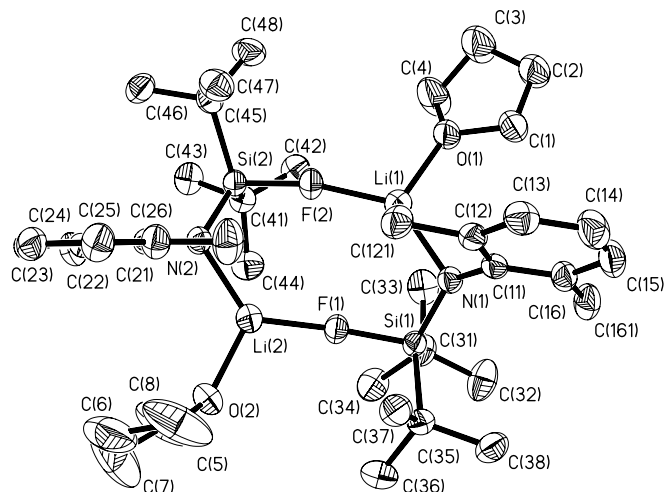

Fig. 1. Crystal structure of **4**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 164.44(19), Si(1)–F(1) 168.40(12), Si(1)–C(35) 189.3(3), F(1)–Li(2) 187.1(4), F(2)–Li(1) 192.0(4), N(1)–C(11) 140.3(3), N(1)–Li(1) 200.4(4), N(2)–C(21) 140.5(3), N(2)–Li(2) 195.7(5), Li(1)–O(1) 189.9(4); N(1)–Si(1)–F(1) 106.18(8), N(1)–Si(1)–C(35) 116.95(10), Si(1)–F(1)–Li(2) 170.24(17), Si(1)–N(1)–Li(1) 109.56(15), Si(2)–N(2)–Li(2) 114.24(16).

Si (1): +0.31,	Si (2): 0.34,
Si (1): +0.23,	F (2): 0.08,
N (1): −0.39,	N (2): −0.36,
Li (1): −0.07,	Li (2): −0.15.

The fluorine atoms are two coordinated and the lithium atoms are three coordinated. The coordination sphere of the lithium is made up of one fluorine atom, one nitrogen atom, and one THF molecule. The sum of the angles around Li(2) is measured 360° and around N(2) 356.9°.

The Li(2)–F(1) contact (187.1 pm) effects a lengthening of the of the Si(1)–F(1) bond (168.4 pm). The Si(1)–N(1) distance (164.4 pm) lies between a typical single and double bond [6,7].

2.2. Bis(phenylamino)silnes

In the synthesis of **1** and **2**. bis(2,6-dialkylphenylamino)-silanes were isolated as by-products Eq. (4).

R = Me (**7**)
R = *i*Pr [10] (**8**)
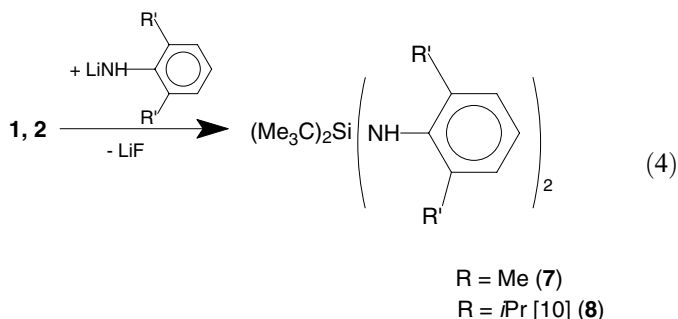
Lithium salts of aminofluorosilanes were found to react as amides or iminosilenes [6,7]. Structure investigations on these compounds have repeatedly furnished astonishing

Table 1
Crystal data and structure refinements for compounds **4**, **7** and **8**

|	**4**	**7**	**8**
Empirical formula	$C_{40}H_{70}F_2Li_2N_2O_2Si_2$	$C_{24}H_{38}N_2Si$	$C_{32}H_{54}N_2Si$
Formula weight	719.04	382.65	494.86
Temperature (K)	133(2)	133(2)	133(2)
Wave length (pm)	71.073	71.073	71.073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$
Unit cell dimensions			
a (pm)	2518.40(14)	2147.4(2)	863.13(4)
α (°)	90	90	90
b (pm)	951.67(5)	879.21(4)	1129.13(4)
β (°)	111.201(4)	130.085(6)	97.58(3)
c (pm)	1916.56(10)	1587.03(16)	3129.24(13)
γ (°)	90	90	90
Volume (nm_3)	4.2825(4)	2.2925(3)	3.0231(2)
Z	4	4	4
Density (calculated) (Mg/m_3)	1.115	1.109	1.087
Absorption coefficient (mm_{-1})	0.125	0.113	0.099
$F(000)$	1568	840	1096
Crystal size (mm^3)	$0.30 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.10$	$0.30 \times 0.20 \times 0.20$
θ Range for data collection (°)	1.73–24.85	2.48–24.81	1.31–25.20
Index ranges	$-29 \leqslant h \leqslant 29, -11 \leqslant k \leqslant 10,$ $-20 \leqslant l \leqslant 22$	$-25 \leqslant h \leqslant 25, -10 \leqslant k \leqslant 10,$ $-14 \leqslant l \leqslant 18$	$-10 \leqslant h \leqslant 10, -13 \leqslant k \leqslant 13,$ $-37 \leqslant l \leqslant 37$
Reflections collected	22806	16740	30924
Independent reflections	7370 [$R_{(int)} = 0.0540$]	1966 [$R_{(int)} = 0.0332$]	5332 [$R_{(int)} = 0.0441$]
Completeness (%)	99.2	99.0	97.9
Maximum and minimum transmission	0.9755 and 0.9635	0.9888 and 0.9561	0.9804 and 0.9708
Refinement method	Full-matrix least-squares on F_2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7370/0/467	1966/0/128	5332/0/330
Goodness-of-fit on F^2	0.995	1.021	1.042
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0478$ $wR_2 = 0.1151$	$R_1 = 0.0362,$ $wR_2 = 0.0989$	$R_1 = 0.0363,$ $wR_2 = 0.0975$
R indices (all data)	$R_1 = 0.0759$ $wR_2 = 0.1241$	$R_1 = 0.0400$ $wR_2 = 0.1012$	$R_1 = 0.0436,$ $wR_2 = 0.1013$
Largest difference in peak and hole (e $Å^{-3}$)	0.688 and −0.330	0.409 and −0.466	0.253 and −0.423
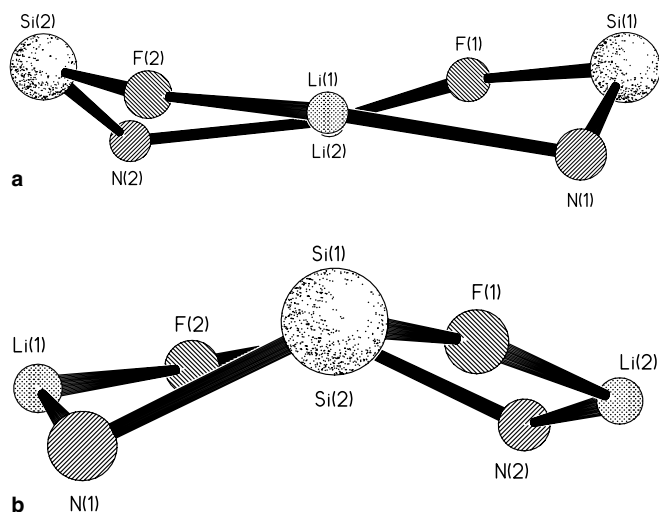
Fig. 2.

results. The structural types found so far include (SiFNLi) four- and eight-membered rings via the LiN- or LiF-bond. LiF-adducts of iminosilenes or amides, tricyclic and pentacyclic compounds [6,7,11]. The high reactivity of the lithiated aminofluorosilanes allows the step-by-step synthesis of numerous bis and tris (silyl)amines and chain com-

pounds [6]. Free iminosilenes are isolated by salt elimination [7,12].

Crystal structure of (Me₃C)₂Si(NHC₆H₃Me₂)₂ (7)

Compound **7** (Fig. 3, Table 1) crystallized from *n*-hexane in the space group *C2/c* (Table 1).

The bond lengths and angles are found in a normal range. Only the C(11)–N(1)–Si(1) and the N(1)–Si(1)–N(11) angles are a little bulged.

Crystal structure of (Me₃C)₂Si(NHC₆H₃i-Pr₂)₂ (8)

Single crystals of **8** were obtained from a solution in *n*-hexane. (Table 1) (see Fig. 4).

The bond lengths and angles of **8** are in a normal range.

2.3. Bicyclus (9)

Attempts to eliminate LiF from **4** led to the formation of a crystalline compound with the molecular weight of the dimer of an iminosilene; however, the NMR-data were not consisting with such a cyclodisilazane. According to the results of the X-ray structure analysis we had isolated the bicyclic compound **9** which may be formed following mechanism (Scheme 1):

At first, LiF-elimination leads to the formation of an iminosilene. Two iminosilene molecules react with each
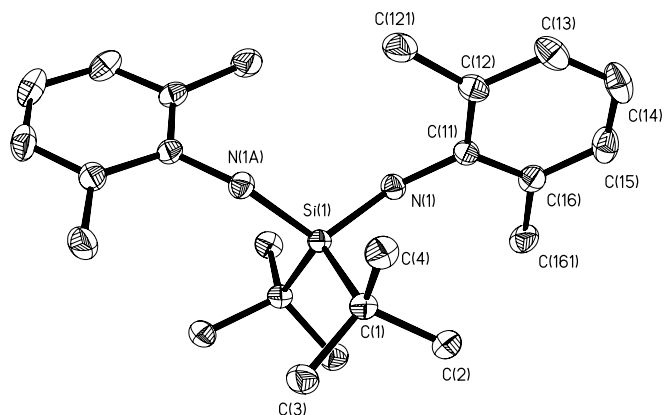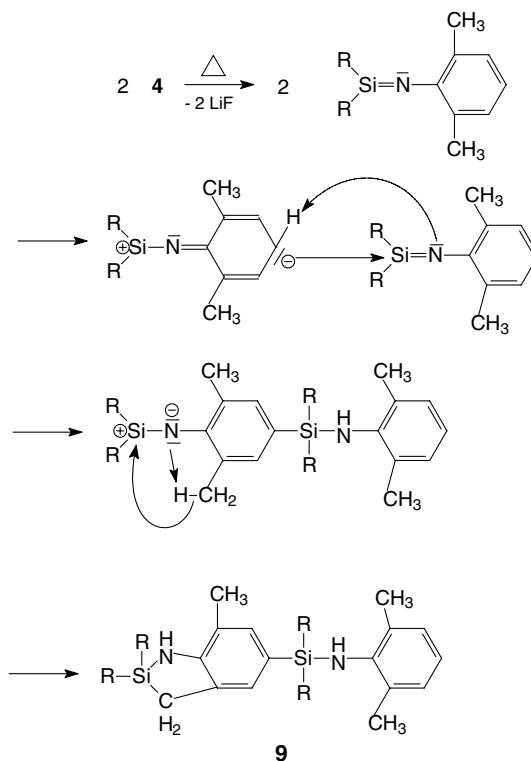
Fig. 3. Crystal structure of **7**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 174.27(12), Si(1)–C(1) 191.46(14), N(1)–C(11) 142.62(18); N(1)–Si(1)–N(1)#1 115.60(8), C(11)–N(1)–Si(1) 135.20(10).

Fig. 4. Crystal structure of **8**; selected bond lengths (pm) and angles (°): Si(1)–C(31) 189.70(14), Si(1)–N(1) 174.27(11), N(2)–C(11) 142.35(17); N(2)–Si(1)–N(1) 106.62(5), C(1)–N(1)–Si(1) 135.00(9), C(11)–N(2)–Si(1) 132.20(9).

other forming a C–Si-bond of the C(4)-atom of one aryl group. The proton migrates to the nitrogen of the iminosilene. The other Si=N-bond undergoes an ene reaction with one of the ortho CH$_3$-groups of the aryl ring forming a bicyclic unit.

Addition reactions of H-acidic compounds and intramolecular ene-reactions of unsaturated heavier main group systems are well known [6,7]. They occur when the substituents of the unsaturated compounds prevent a dimerization because of bulkiness and an acidic C–H hydrogen exists. The formation of **9** may be a borderline case between dimerization and ene-reaction.

Crystal structure of (Me$_3$C)$_2$SiNH(CH$_2$)C$_6$H$_2$MeSi-(CMe$_3$)$_2$NHC$_6$H$_3$Me$_2$ (9)

Crystals of **9** were obtained from a solution of *n*-hexane. **9** crystallizes in the space group $P\bar{1}$ (Fig. 5, Table 2). The bicyclus lies in a plane.

Scheme 1. Formation mechanism of **9**.

2.4. Dipheno-silyliminoquinones

In order to prevent sterically this reaction (Scheme 1) of the intermediate iminosilene, we carried out the analogous reaction with the lithium salt of amino-2,6-diisopropylbenzene-(di-*tert*-butylfluorosilane) (**5**) [10] and isolated in a strange reaction red crystals with the composition of compound **10**.

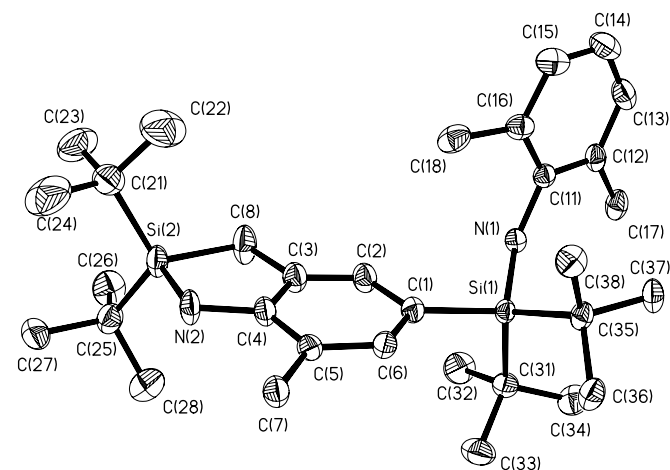The formation of **10** occurs in a lithium hydride elimination of **5** which was proved in the hydrogenation of

Fig. 5. Crystal structure of **9**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 175.39(18), Si(1)–C(1) 188.6(2), Si(1)–C(31) 192.0(3), Si(2)–N(2) 175.1(2), Si(2)–C(8) 189.4(3), Si(2)–C(25) 190.2(3), N(1)–C(11) 141.3(3), N(2)–C(4) 140.1(3), C(3)–C(4) 140.5(3); N(1)–Si(1)–C(1) 108.66(10), N(2)–Si(2)–C(8) 93.01(10), C(11)–N(1)–Si(1) 133.42(16), C(4)–N(2)–Si(2) 113.23(16).

Table 2
Crystal data and structure refinements for compounds **9**, **10** and **11**

	9	10	11
Empirical formula	$C_{32}H_{54}N_2Si_2$	$C_{40}H_{68}F_2N_2Si_2$	$C_{48}H_{84}N_2Si_2$
Formula weight	522.95	671.14	745.35
Temperature (K)	133(2)	203(2)	133(2)
Wave length (pm)	71.073	71.073	71.073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Unit cell dimensions			
a (pm)	834.70(6)	920.19(12)	1005.16(7)
α (°)	102.178(6)	90	90
b (pm)	1369.02(10)	1046.14(19)	1449.62(9)
β (°)	98.189(6)	99.230(13)	102.880(3)
c (pm)	1488.30(11)	2208.9(4)	1692.93(7)
γ (°)	99.289(6)	90	90
Volume (nm^3)	1.6129(2)	2.0989(6)	2.4047(2)
Z	2	2	2
Density (calculated) (Mg/m^3)	1.077	1.062	1.029
Absorption coefficient (mm^{-1})	0.132	0.121	0.1051
$F(000)$	576	736	828
Crystal size (mm^3)	$0.30 \times 0.30 \times 0.10$	$1.00 \times 0.80 \times 0.80$	$0.20 \times 0.10 \times 0.10$
θ Range for data collection (°)	1.55–24.85	3.70–25.00	1.87–24.82
Index ranges	$-9 \leqslant h \leqslant 9, -16 \leqslant k \leqslant 16,$ $-17 \leqslant l \leqslant 17$	$-10 \leqslant h \leqslant 10, -12 \leqslant k \leqslant 12,$ $-26 \leqslant l \leqslant 26$	$-11 \leqslant h \leqslant 11, -17 \leqslant k \leqslant 16,$ $-19 \leqslant l \leqslant 19$
Reflections collected	23 977	6265	34 937
Independent reflections	5547 [$R_{(int)} = 0.0892$]	3683 [$R_{(int)} = 0.0725$]	4137 [$R_{(int)} = 0.0707$]
Completeness (%)	99.1	99.6	99.7
Maximum and minimum transmission	0.9870 and 0.9616	0.9098 and 0.8890	0.9896 and 0.9793
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5547/0/340	3683/0/218	4137/0/246
Goodness-of-fit on F^2	1.017	1.081	0.990
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0490$ $wR_2 = 0.1090$	$R_1 = 0.0674$ $wR_2 = 0.1784$	$R_1 = 0.0407$ $wR_2 = 0.1019$
R indices (all data)	$R_1 = 0.0787$ $wR_2 = 0.1186$	$R_1 = 0.0704$ $wR_2 = 0.1824$	$R_1 = 0.0629$ $wR_2 = 0.1085$
Largest difference in peak and hole (e Å^{-3})	0.342 and −0.335	0.616 and −0.531	0.585 and −0.527

Me$_3$SiCl. To our knowledge, there is no precedent in the literature where an anilinofluorosilyl-compound has been lithiated at the C(4)-atom of the aryl ring. Carbenes or some oxidants may be involved in the formation of **10**, however, no evidence was found for it. To exclude these types of mechanisms we carried out further reactions which led to the formations of **11** and **12**.
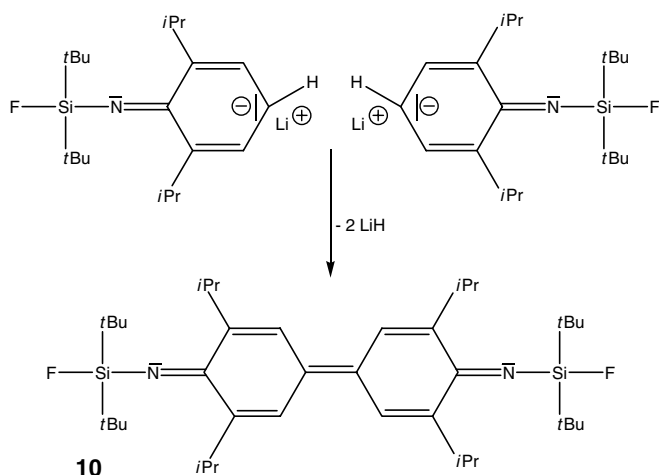
(5)

10 presents an unknown silicon containing 14π electron system.

*Crystal structure of $((Me_3C)_2SiFNC_6H_2i\text{-}Pr_2)_2$ (**10**)*

10 (Fig. 6, Table 2) crystallizes from *n*-hexane in the monoclinic space group $P2_1/n$. To our knowledge neutral compounds with quinonoid character and silyl groups bonded to the nitrogen atom are unknown, so far. In literature, diphenoquinonimines have been described as precursors of polymers [14], and they were stabilized as arylamido complexes, e.g., of platinum [15].

Detailed comparisons of the platinum complex [15], **10** and biphenyl [16] show the significantly quinonoid character of **10** judged by the external C=N bond and compared with biphenyl the substantial shortening of the C–C bond linking the rings.

Comparative bond distances (pm)

	Ring end	Ring centre	External	External
	C–C	C–C	C–C	C=N
10	144.7	135.2	140.7	127.9
Platinum complex	142.7	135.5	143.1	132.6
Biphenyl	137.9 139.8	138.7	149.7	–

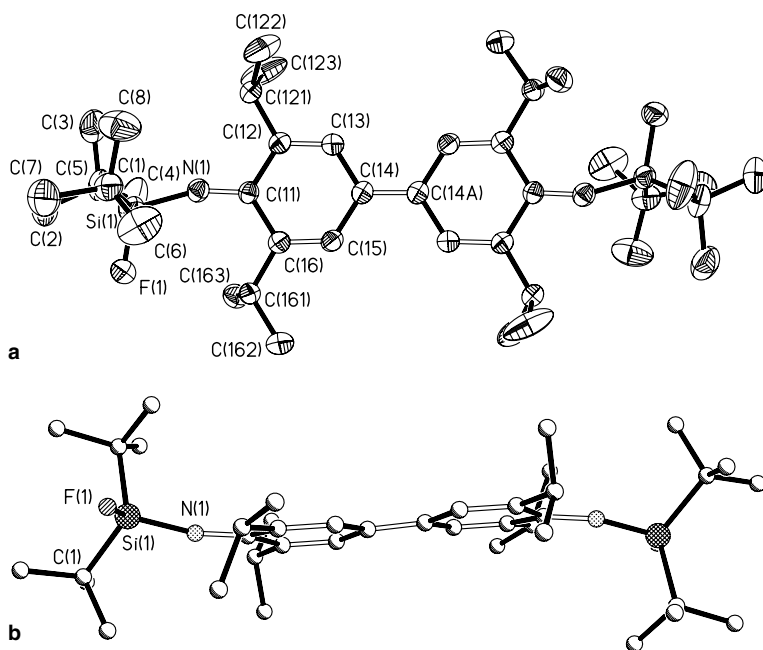Fig. 6. (a, b) Crystal structure of **10**; selected bond lengths (pm) and angles (°): Si(1)–F(1) 161.60(15), Si(1)–N(1) 167.91(18), Si(1)–C(1) 189.0(3), N(1)–C(11) 127.9(3), C(11)–C(12) 148.7(3), C(12)–C(13) 135.2(3), C(12)–C(121) 151.9(3), C(13)–C(14) 144.7(3), C(14)–C(14)#1 140.7(4); F(1)–Si(1)–N(1) 114.55(8), C(5)–Si(1)–C(1) 120.96(12), C(11)–N(1)–Si(1) 159.74(17), N(1)–C(11)–C(12) 119.64(19), C(16)–C(11)–C(12) 116.54(17), C(13)–C(12)–C(11) 120.0(2), C(14)#1–C(14)–C(15) 122.1(2).

The Si–N bond lengths (167.9 pm) are extremely short, all C-atoms of the six-membered rings have a planar environment, the C–C bond lengths differ from 135.2 pm (C(12)–C(13)) to 148.4 pm (C(16)–C(11)). The angle at the imine-nitrogen C(11)–N(1)–Si(1) is measured 159.7°. The N(1)–C(11) bond length is a double bond length. A small excess of BuLi in solution led to the substitution of the fluorine atoms by *n*-C₄H₉-groups and the formation of **11**. In the purification process of **10** a small amount of crystals from **11** was found.

Crystal structure of ((Me₃C)₂SinC₄H₉NC₆H₂i-Pr₂)₂ (11)

11 (Fig. 7, Table 2) crystallizes in the space group *P2₁/c*

Bond lengths and angles of **11** are comparable to those of **10**. In order to control the easy formation of such 14π-

systems, we prepared **3** and its lithium salt **6** (Eqs. (2) and (3)). **6** was tempered like **4** and **5** at 150 °C. The raw product was solved in *n*-hexane, crystallized from *n*-hexane and characterized as **12** by X-ray determination.

Crystal structure of ((Me₃C)₂SiMeNC₆H₂iPr₂)₂ (12)

12 crystallizes in the space group *P2₁/n* (Table 3) (see Fig. 8).

The distances and angles of **11** and **12** have values comparable with **10**.

3. Experimental

All experiments were carried out under exclusion of moisture under dry N₂ or Ar. – MS: CH-5 Varian. – NMR: solutions in C₆D₆; TMS int., C₆F₆ ext., Bruker-AM-250. – The
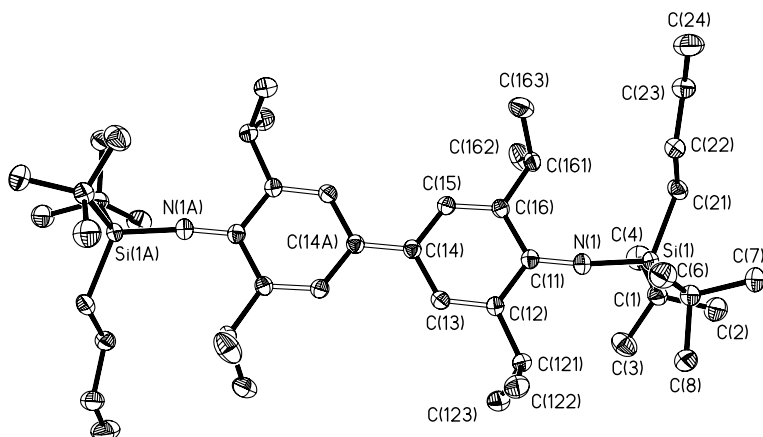

Fig. 7. Crystal structure of **11**; Selected bond lengths (pm) and angles (°): Si(1)–N(1) 169.31(16), N(1)–C(11) 128.3(2), C(11)–C(12) 147.7(2), C(12)–C(13) 134.9(2), C(13)–C(14) 144.3(2), C(14)–C(14)#1 140.2(3); C(11)–N(1)–Si(1) 170.54(15), C(14)#1–C(14)–C(15) 123.00(19).

Table 3
Crystal data and structure refinements for compound **12**

	12
Empirical formula	$C_{42}H_{74}N_2Si_2$
Formula weight	663.21
Temperature (K)	133(2)
Wave length (pm)	71.073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (pm)	1008.44(7)
α (°)	90
b (pm)	1392.43(12)
β (°)	100.362(6)
c (pm)	1577.60(12)
γ (°)	90
Volume (nm^3)	2.1791(3)
Z	2
Density (calculated) (Mg/m^3)	1.011
Absorption coefficient (mm^{-1})	0.109
$F(000)$	736
Crystal size (mm^3)	$0.20 \times 0.20 \times 0.10$
θ Range for data collection (°)	1.96–24.71
Index ranges	$-11 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 18$
Reflections collected	21 886
Independent reflections	3694 [$R_{(int)} = 0.1350$]
Completeness (%)	99.5
Maximum and minimum transmission	0.9892 and 0.9785
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3694/0/219
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1285$, $wR_2 = 0.2586$
R indices (all data)	$R_1 = 0.2025$, $wR_2 = 0.2976$
Largest difference in peak and hole (e Å^{-3})	1.277 and -1.113

purity of the isolated compounds was determined by spectroscopy.

3.1. Aminophenyl-(di-tert-butyl)silanes (1, 2 [4], 3, 7, 8 [4])

To a solution of 0.1 mol of the phenylamine in 100 ml of *n*-hexane 0.1 mol of *n*-BuLi (23% in hexane) was added. The mixture was heated at reflux for 2 h. When the lithia-

tion was complete the solution was cooled to 20 °C and 0.1 mol of *t*Bu$_2$SiFR (R = F (1,2); Me = (3)) was introduced. The reaction mixture was subsequently heated at reflux for 5 h and then the solvent was removed by distillation. The product was condensed at 0.01 mbar into a cooling trap and purified by distillation and/or crystallization from *n*-hexane.

3.1.1. Amino-2,6-dimethylphenyl-(di-tert-butylfluoro)silane (1)

Yield: 23.5 g (84%), b.p. 81 °C/0.01 mbar. – MS (EJ), *m/z* (%): 281 (32) M$^+$; – IR: ν (NH) = 3384 cm^{-1}; – ^{1}H NMR (C$_6$D$_6$): $\delta = 0.97$ (d, C (CH$_3$)$_3$, $^4J_{HF} = 0.98$ Hz, 18 H), 2.3 NH, 6.6–6.9 C$_6$H$_3$; – ^{13}C NMR: $\delta = 20.38$ (d, CC$_3$, $^2J_{CF} = 18.15$ Hz), 27.71 3,5-C_2C_6 128.82 4-C$_6$, 133.48 2,6-C$_6$, 141.85 (d, 1-C$_6$, $^3J_{CF} = 1.5$ Hz); – ^{15}N NMR: – 331.12 (d, d, $J_{NH} = 73.6$ Hz, $^2J_{NF} = 9.8$ Hz); ^{19}F NMR: $\delta = 11.78$; ^{29}Si NMR: $\delta = -6.32$ ($J_{SiF} = 312.98$ Hz).

C$_{16}$H$_{28}$FNSi (281.5): Calcd. C, 68.3; H, 10.0. Found: C, 69.3; H, 10.9%.

3.1.2. Amino-2,6-diisopropylphenyl-di-tert-butyl-methylsilane (3)

Yield: 26.5 g (79%), b.p.: 120 °C/0.01 mbar, – MS (EJ), *m/z* (%): 333 (13) M$^+$, 276 (100) [M – C$_4$H$_9$]$^+$ – ^{1}H NMR (C$_6$D$_6$, TMS): $\delta = 0.36$ (SiCH$_3$, 3 H), 1.00 (C(CH$_3$)$_3$, 18 H), 1.21 (d, CH(CH$_3$)$_2$, $^3J_{HH} = 6.8$ Hz, 12 H), 2.50 (NH, 1 H), 3.67 (sept., CHMe$_2$, $^3J_{HH} = 6.8$ Hz, 2 H), 7.1 (C$_6$H$_3$); – ^{13}C NMR: $\delta = -4.32$ SiCH$_3$, 21.48 SiCC$_3$, 23.55 CC$_2$, 28.30 CC$_2$, 28.81 CC$_3$, 123.37 3,5-C$_6$, 123.82 4-C$_6$, 141.05 1-C$_6$, 143.51 2,6-C$_6$; – ^{15}N NMR: $\delta = -346.69$ (d, NH, 71.4 Hz); ^{29}Si NMR: $\delta = 6.52$.

3.1.3. Bis(2,6-dimethylphenyl)amino-di-methylsilane (7)

Yield: 2.67 g (7%), m.p. 195 °C; – MS (EJ), *m/z* (%). 383 (12) M$^+$, 325 (100) [M – C$_4$H$_9$]$^+$ – ^{1}H NMR (C$_6$D$_6$): $\delta = 0.98$ (C (CH$_3$)$_3$, 18 H), 2.44 (C$_6$ (CH$_3$)$_2$, 12 H), 3.08 (NH, 2 H), 6.88–7.15 (C$_6$H$_3$, 6 H); – ^{13}C NMR (C$_6$D$_6$). $\delta = 21.29$ CC$_3$, 21.91 C$_6$C$_2$, 29.33 CC$_3$, 121.84 3,5-C$_6$, 128.32 4-C$_6$, 129.45 2,6-C$_6$, 144.33 NC; ^{15}N NMR (C$_6$D$_6$): $\delta = -323.09$ (NH, $J_{NH} = 71.1$ Hz); ^{29}Si NMR (C$_6$D$_6$): $\delta = -16.12$.
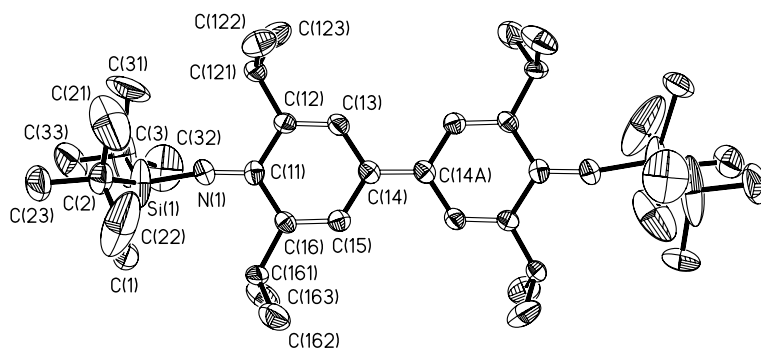

Fig. 8. Crystal structure of **12**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 167.0(5), Si(1)–C(3) 177.3(10), Si(1)–C(2) 185.8(7), Si(1)–C(1) 204.5(9), N(1)–C(11) 128.2(7), C(11)–C(16) 148.2(8), C(11)–C(12) 148.9(8), C(12)–C(13) 135.0(8), C(13)–C(14) 143.4(8), C(14)–C(14)#1140.7(12); N(1)–Si(1)–C(2) 106.5(3), C(3)–Si(1)–C(2) 126.2(5), C(3)–Si(1)–C(1) 92.8(7), C(11)–N(1)–Si(1) 169.5(5), N(1)–C(11)–C(16) 123.0(6).

$C_{24}H_{38}N_2Si$ (382.7): Calcd. C, 75.3; H, 10.0. Found: C, 75.2; H, 0.94%.

3.2. Lithium-di-tert-butylsilyl-(2,6-dimethylphenyl)amide (4, 6)

To a solution of 2.81 g (0.01 mol) of **1** resp. **3** in 20 ml of n-hexane 0.01 mol of n-BuLi was added (23% in n-hexane). The corresponding mixture was refluxed for 1 h. The lithium salt formed was dissolved in boiling THF. **4** crystallized after 1 day at 0 °C. Yield: 2.61 g (91%).

3.2.1. Lithium-di-tert-butylfluorosilyl-(2,6-dimethylphenyl)amide (4)

^1H NMR (C_6D_6): $\delta = 1.09$ (O(CH$_2$CH_2)$_2$, 4 H), 1.27 (C(CH$_3$)$_3$, 18 H), 2.54 (C_6(CH$_3$)$_2$, 6 H), 3.20 (O(CH$_2$–CH$_2$)$_2$, 4H), 6.6–7.6 (C_6H$_3$, 3 H); – ^7Li NMR (C_6D_6): = 0.2; – ^{13}C NMR (C_6D_6). $\delta = 22.34$ FSiC (d, $^2J_{CF} = 25.68$ Hz), 25.08 OC$_2$$C_2$, 27.75 $C_6$$C_2$, 29.07 C$C_3$, 68.26 O$C_2C_2$, 115.92 3.5-C$_6$, 127.72 4-C$_6$, 130.45 (2.6-C$_6$, $^4J_{CF} = 5.43$ Hz), 155.59 1-C$_6$; – ^{19}F NMR (C_6D_6): $\delta = 15.75$; ^{29}Si NMR (C_6D_6): $\delta = -16.70$ ($J_{SiF} = 286.43$). – $C_{40}H_{70}F_2LI_2N_2O_2Si_2$ (719.06).

3.2.2. Lithium-di-tert-butylmethylsilyl-(2,6-diisopropylphenyl)amide (6)

Synthesis like compound **4**; Yield: 28.7 g (87%), – ^1H NMR (C_6D_6, TMS): $\delta = 0.48$ (SiCH$_3$, 3 H), 1.00 (OCH$_2$CH_2, 4 H), 1.22 (C(CH$_3$)$_3$, 18 H), 121–1.28 (CH(CH$_3$)$_2$, 12 H), 2.80 (OCH_2CH$_2$, 4 H), 4.21 (CHCH$_3$, sept., $^3J_{HH} = 7.0$ Hz, 2 H), 6.83 (4 C$_6$H, $^3J_{HH} = 7.6$ Hz, 1 H); 7.17 (3.5 C$_6$H$_2$, $^3J_{HH} = 7.6$ Hz, 2 H) – ^7Li NMR: $\delta = 0.16$; – ^{13}C NMR: $\delta = -0.67$ SiC, 23.14 CC_2, 23.53 SiCC_3, 24.96 OC_2C$_2$, 27.16 CC_2, 30.11 CC_3, 68.40 OC_2C$_2$, 116.23 4-C$_6$, 123.29 3.6-C$_6$, 142.72 2.6-C$_6$, 153.52 LiNC; – ^{29}Si NMR: $\delta = -16.39$.

3.3. Bicyclic compound (9) and dipheno-silyliminoquinones (10, 11, 12)

The lithium salts of 0.1 mol 1 (**4**), 2 (**5**) [4] and **3** were tempered at 150 °C for 5 h. The reaction process was controlled by ^{19}F NMR spectroscopy. When the reactions were finished the raw products **9** and **12** were separated from LiF (**9**) resp. LiH (**10, 11, 12**) and crystallized from n-hexane. LiH has been trapped with ClSiMe$_3$ in THF. Me$_3$SiH was formed. The formation of **11** occurred by a small excess of BuLi present in solution.

3.3.1. Bicyclus (9)

IR: 3382, 3457v NH, – MS (EJ), m/z (%): 522 (2) M$^+$, 465 (100) M – C$_4$H$_9$; – NMR (C_6D_6); ^1H: $\delta = 0.95$ (C(CH$_3$)$_3$, 18 H), 0.98 (SiCH$_2$, 2 H), 1.17 (C(CH$_3$)$_3$, 18 H), 2.04 (C$_6$CH$_3$, 3 H), 2.21 (C$_6$(CH$_3$)$_2$, 6 H), 2.98 (NH, 1 H), 2.39 (NH, 1 H), 6.93 (C6H$_3$, 1 H), 6.96 (C$_6$H$_3$, 2 H), 7.54 (C$_6$H$_2$, 1H), 7.75 (C$_6$H$_2$, 1 H); – ^{13}C: $\delta = 11.93$ SiCH$_2$, 17.72 C$_6$$CH_3$, 20.34 C$C_3$, 21.53 C$C_3$, 21.95

C_6(CH$_3$)$_2$, 27.68 CC_3, 29.58 CC_3, 117.96 C$_6$H, 121.33 C$_6$, 122.95 C$_6$, 125.46 C$_6$H, 129.34 C$_6$H, 130.61 4.5-C$_6$H$_2$, 135.20 C$_6$, 135–98 C$_6$, 145.31 CN, 151.97 CN; – ^{29}Si NMR: $\delta = -3.88$, 25.67. $C_{32}H_{54}N_2Si_2$ (522.9): Calcd. C, 73.5; H, 10.4. Found: C, 74.1; H, 10.9%.

3.3.2. Dipheno-di-tert-butylfluorosilylimino-quinone (10)

Yield: 6.4 g (19%), m.p.: 190 °C. – MS (EJ), m/z (%): 670 (100) M$^+$, 613 (99) [M – C$_4$H$_9$]$^+$. IR: 2356 v C≡N, – NMR (C_6D_6, TMS): ^1H: $\delta = 1.06$ (d, C(CH$_3$)$_3$, $^4J_{HF} = 0.7$ Hz, 36 H), 1.15 (d, CH(CH$_3$)$_2$, $^3J_{HH} = 6.8$ Hz, 24 H), 3.5 (sept. CH(CH$_3$)$_2$, $^3J_{HH} = 6.8$ Hz, 4 H), 7.6 (C$_6$H$_2$, 4 H); – ^{13}C NMR: $\delta = 20.19$ (d, CC_3, 2$J_{CF} = 19.5$ Hz), 23.30 CC_2, 27.82 CC_3, 31.60 CC_2, 122.62 2.6-C$_6$, 124.60 1-C$_6$, 135.13 3.5-C$_6$, 163.38 (d, 4-C$_6$, $^3J_{HF} = 4.5$ Hz); – ^{19}F NMR: $\delta = 14.42$; – ^{29}Si NMR: $\delta = -20.48$ (d, $J_{SIF} = 335.0$ Hz).

3.3.3. Dipheno-n-butyl-di-tert-butyl-silylimino-quinone (11)

Yield. 0.3 g (1%).

3.3.4. Di(phenol-di-tert-butyl-methyl-silylimino-quinone) (12)

Yield: 21.3 g (64%); – MS (EJ), m/z (%): 664 (100) M$^+$; – NMR comparable with **10**.

3.4. X-ray structure determination of 4, 7, 8, 9, 10, 11, and 12 [17,18]

The data in Tables 1–3 were collected on a STOE AED2 four circle diffractometer with Mo Kα radiation. The structures were solved and refined using the SHELX program suite [17,18].

4. Supplementary materials

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-282975 (**4**), CCDC-282976 (**7**), CCDC-282977 (**8**), CCDC-282978 (**9**), CCDC-282979 (**10**), CCDC-282980 (**11**), CCDC-282981 (**12**). Copies of this information can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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