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# Reaction of phenyltrifluorosilane with 8-hydroxy- or 8-mercapto-quinoline and their derivatives as a route to new heterocyclic compounds of pentacoordinate silicon†

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**The protodesilylation of phenyltrifluorosilane with 8-hydroxy- and 8-mercapto-quinoline $NC_9H_6YH$ (Y: O, 1a; S, 1b) affords the novel intramolecular pentacoordinate silanes (N $\longrightarrow$ Si) 8-(trifluorosiloxy)- and (N $\longrightarrow$ Si) 8-(trifluorosilylthio)-quinoline respectively. The (N $\longrightarrow$ Si) 8-(Phenyldifluorosiloxy)- and (N $\longrightarrow$ Si) 8-(phenyldifluorosilylthio)-quinolines prepared by the transsilylation reaction of trimethylsilyl derivatives of heterocycles 1a and 1b by phenyltrifluorosilane possess a similar pentacoordinate structure. Copyright © 2005 John Wiley & Sons, Ltd.**

**KEYWORDS:** 8-(trifluorosiloxy(thio))quinoline; 8-(phenyldifluorosiloxy(thio))quinoline; phenyltrifluorosilane; protodesilylation; pentacoordinate silicon

## INTRODUCTION

In the last two decades, intramolecular complexes containing Group 14 or 15 elements (silicon, tin, lead, phosphorus) and mono- or poly-dentate heterocyclic fragments have attracted considerable interest. Among these are organometallic derivatives of 8-hydroxy- and 8-mercapto-quinoline (**1a**, **b**).[1–5] It has been shown that the substitution reactions take place by treatment of lithium 8-hydroxyquinolinate with methylchlorosilanes, $Me_{4-n}SiCl_n$.[1] In the case that $n = 1$ or 2, 8-(trimethylsiloxy)- or 8-(dimethylchlorosiloxy)-quinolines with a tetracoordinated silicon are formed respectively. However, when $n = 3$ or 4 the complex compounds $(NC_9H_6O)_2SiMeCl$ and $(NC_9H_6O)_2SiCl_2$ are obtained. According to X-ray crystallography, the first complex is characterized by a distorted octahedrally coordinated silicon.[2] Bidentate oxyquinoline ligands are arranged nearly perpendicular. The nitrogen atoms of both ligands are dative bonded to the silicon centre, take up the equatorial plane and are in the cis position to the chloro substituent and the methyl group lying on the same site. The axial positions of the distorted octahedron are occupied by the oxygen atoms. The N $\longrightarrow$ Si and O–Si are slightly elongated (to 0.28 Å and 0.13 Å respectively) in comparison with those in tetracoordinated silicon compounds.[3,4] All the above compounds are highly sensitive to moisture.

The reactions between **1a** or **1b** and $Cl_2SnR_2$ (R = Bu, Bn, Ph) yielded the intramolecular complexes $(NC_9H_6O)_2SnR_2$. The central tin atom is hexacoordinate, being bound to two bidentate quinoline ligands.[5] Also described have been the intramolecular complex compounds $(NC_9H_6S)MPh_3$ (M = Sn, Pb) that were synthesized by treatment of **1b** with $Ph_3SnCl$ or $Ph_3PbCl$.[6] The reaction of 8-(trimethylsiloxy)quinoline **3a** with $PhPF_4$ gave cyclic intramolecular complex $(NC_9H_6O)PPhF_3$, with the hexacoordinate phosphorus atom arising via elimination of $Me_3SiF$.[7]

Previously, we described the reaction of **3a** with dimethyl(chloromethyl)chlorosilane and methyl(chloromethyl)difluorosilane.[8] In the case of $ClCH_2SiMe_2Cl$, trimethylchlorosilane and 8-[dimethyl(chloromethyl)siloxy]quinoline (**A**) are formed in the first reaction step (Scheme 1).

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†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

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The latter compound is unstable and identified by $^1$H, $^{13}$C and $^{29}$Si NMR spectroscopy only. The intermediate is rapidly cyclized into *N*-methyl(dimethylsilyl-8-oxyquinolinyl)chloride containing the tetracoordinated silicon atom.

8-[Methylfluoro(chloromethyl)siloxy]quinoline is easily formed by a similar reaction between **3a** and $ClCH_2SiMeF_2$ at ambient temperature (Scheme 2). On heating at 50 °C, compound **B** is rapidly and quantitatively converted into *N*-[methyl(methyl-8-quinolyloxy)silyl-8-oxyquinolinyl]chloride containing a pentacoordinated silicon that is bonded to the nitrogen atom by donor–acceptor interaction.

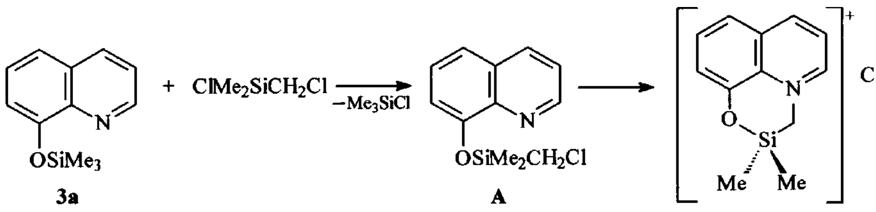
The synthesis and electronic structure of organosilicon derivatives of **1b** of the type $(NC_9H_6S)CH_2SiMe_{3-n}F_n$ ($n = 2$, 3) have been reported.[9,10] The compounds were obtained by the reaction of (chloromethyl)trimethoxysilane or (chloromethyl)methyldimethoxysilane with sodium 8-quinolylthiolate followed by treatment with boron trifluoride diethyl etherate (Scheme 3). The silicon atom in these compounds is tetracoordinated, even in the trifluoro derivative ($n = 3$), which is highly sensitive to moisture.

Following our research on hypervalent organosilicon compounds, in this paper we report on some new heterocyclic compounds with the pentacoordinate silicon atom arising from **1a** and **1b**.

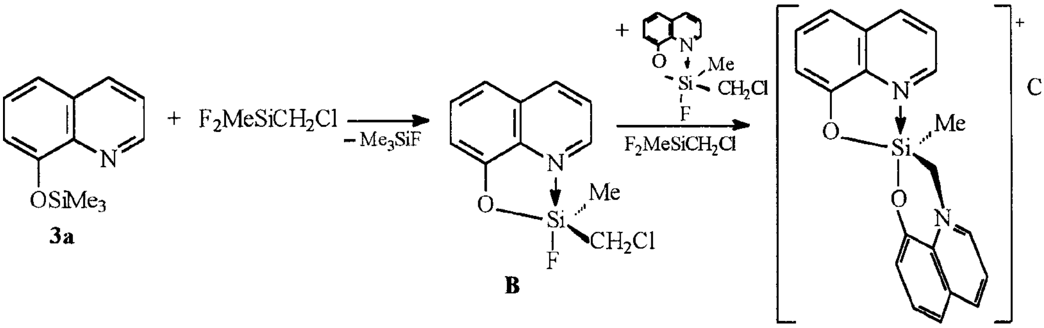
## RESULTS AND DISCUSSION

We found that treatment of **1a** or **1b** with phenyltrifluorosilane resulted in the cleavage of the Ph–Si bond to give new heterocyclic derivatives of pentacoordinate silicon, (N ⟶ Si) 8-(trifluorosiloxy)quinoline (**2a**) and (N ⟶ Si) 8-(trifluorosilylthio)quinoline (**2b**) (Scheme 4).

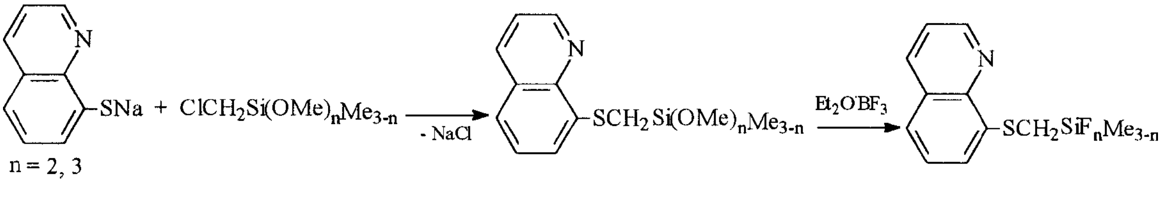
We suggest that the first reaction step involves the coordination of phenyltrifluorosilane with the nitrogen atom of the $NC_9H_6YH$ fragment, due to its higher nucleophilicity compared with that of oxygen or sulfur atoms, to give intermediate **C**. Subsequent ready attack of the internal nucleophilic YH group on the silicon atom is due to the enhancement in its electrophilicity and weakening Si–C bond by going to a pentacoordinated silicon state. Previously, it was shown that protolytic cleavage of the Ph–Si bond proceeded by treatment of phenyltrifluorosilane with $NH_4F{\cdot}HF$.[11] We would like to emphasize the considerable contribution of



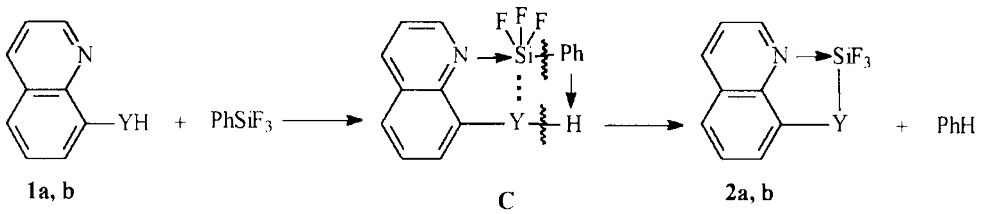
Scheme 1.



Scheme 2.

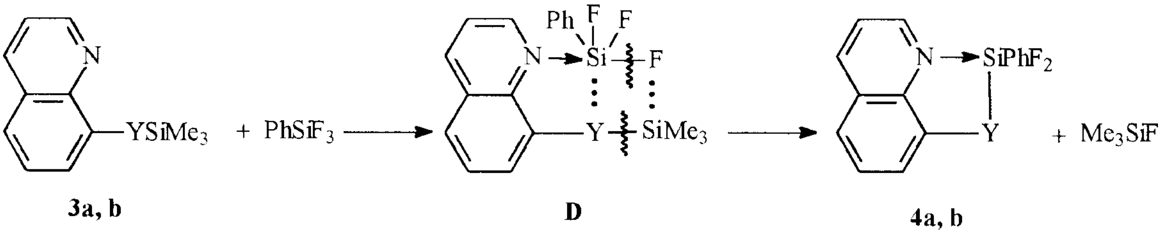


Scheme 3.



Y = O (**1a**, **2a**); S (**1b**, **2b**).

**Scheme 4.**



Y = O (**3a**, **4a**); S (**3b**, **4b**).

**Scheme 5.**

Professor C. Eaborn to research of aryl–Si bond cleavage[12–14] which has stimulated our studies in this field, too.[15]

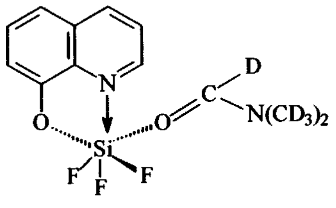
Trans-silylation reactions between *O*- (**3a**) or *S*-trimethylsilylsubstituted (**3b**) of the above heterocycles and phenyltrifluorosilane afford (N $\longrightarrow$ Si) 8-(phenyldifluorosiloxy) quinoline (**4a**) or (N $\longrightarrow$ Si) (phenyldifluorosilylthio)quinoline (**4b**) respectively (Scheme 5). It seems likely that the reaction occurs via an intramolecular attack of a fluoride ion leaving coordinated silicon to another silicon atom, followed by the elimination of $Me_3SiF$ and five-membered ring closure.

Intramolecular complex compounds **2a, b** and **4a, b** are yellowish crystals. The compounds **2a, b** and **4a, b** have a structure with a five-membered ring with a donor–acceptor N $\longrightarrow$ Si bond and covalent Si–O or Si–S bonds. Their structures are similar to those of dragonoids.[16]

The $^{29}Si$ resonance of compound **4b** is significantly upfield (−79.8 ppm) relative to tetracoordinate difluorosilanes.[17] The presence of two fluorine atoms in compound **4b** leads to a splitting of the $^{29}Si$ NMR signal to a triplet with $J_{Si-F} = 264$ Hz, which is smaller than the related value (290 Hz) for tetracoordinate silicon.[17] The magnitude of the change in the chemical shift and in the coupling constant suggests the existence of an N $\longrightarrow$ Si dative bond in **4b**.

Compound **2a** in deuterated dimethylformamide (DMF-$d_7$) solution exhibits a $^{29}Si$ resonance at −173.9 ppm (quintet, $J_{Si-F} = 140$ Hz) in the hexacoordinate silicon range. It can be assumed that the intermolecular complex **D** is formed by the interaction of pentacoordinate compound **2a** with DMF-$d_7$ molecule.

In the $^{19}F$ NMR spectrum of **4b** there is a narrow resonance signal observed at −136.9 ppm. The chemical shift is characteristic of pentacoordinate silicon and, hence, is further evidence for intramolecular coordination N $\longrightarrow$ Si in the compound.



**complex D**

The $^{19}F$ NMR spectrum of **2a** in DMF-$d_7$ solution shows three resonance signals at −137.43, −118.94 and 139.46 ppm, with the ratio of the first two signals being 2 : 1. These resonances were assigned to two equatorial and one axial fluorine atom respectively in the hexacoordinate intermolecular complex **D**. The $^{19}F$ resonance at −137.43 ppm is due to silicon pentacoordination in compound **2a**.

The IR spectra of compounds **2a** and **4b** are similar to those reported for pentacoordinated silicon compounds. The IR spectrum of **2a** shows bands at 680 ($Si-F_{ax}$), 720 and 820 cm$^{-1}$ ($Si-F_{eq}$) (cf. Ref. 18). The IR spectrum of **4b** is essentially similar to that of **2a**, showing absorption at 670, 750, 880 cm$^{-1}$ (cf. Ref. 10). The IR spectra of **2a** and **4b** do not display the bands at 930–960 cm$^{-1}$ due to $\nu_{as}$ Si–F that are characteristic of tetracoordinate silicon compounds. These data strongly suggest the pentacoordinate structure of **2a** and **4b**.

## EXPERIMENTAL

### General procedures and materials

All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvent.

NMR spectra were recorded on a Bruker DPX-400 spectrometer. The compounds were fully characterized by $^{1}$H (400.13 MHz), $^{13}$C (100.61 MHz), $^{19}$F (376.50 MHz) and $^{29}$Si (79.50 MHz) NMR spectroscopy. Because of low solubility of **2a**, NMR spectra are recorded using DMF-$d_7$ as solvent.

IR spectra were recorded on a Specord 75 IR spectrometer in pellets with KBr.

8-(Trimethylsiloxy)quinoline compound **3a** was prepared as described in Ref. 19.

### Synthesis of 8-(trifluorosiloxy)quinoline (2a)

To a solution of **1a** (1.41 g, 10 mmol) in dry chloroform, $PhSiF_3$ (3.24 g, 20 mmol) was added. The reaction mixture was stirred for 5 h. The crystalline precipitate formed was filtered and washed with chloroform to give **2a** (71%); m.p. 104 °C. Anal. Found: C, 47.16; H, 2.64; Si, 12.25. F, 24.86; N, 6.11; Calc. for $C_9H_6F_3NOSi$: C, 47.03; H, 2.78; F, 24.97; N, 6.05; Si, 12.57%. Benzene was identified in the reaction mixture by gas-phase chromatography. $\delta_H$ (400.13 MHz, DMF-$d_7$) 9.08 (br. s), 7.87 (d, $J = 8$ Hz), 8.80 (br. m), 7.61 (br. m), 7.37 (d, $J = 5.6$ Hz); $\delta_C$ (100.61 MHz, DMF-$d_7$) 145.94, 122.28, 142.42, 118.52, 129.56, 114.13, 150.74, 128.82, 141.29; $\delta_{Si}$ (79.49 MHz, DMF-$d_7$) −173.9 (q, $J = 140$ Hz).

Compound **2b** was prepared following the same procedure; m.p. 135 °C (54%). Anal. Found: C, 44.07; H, 2.47; F, 23.24; N, 5.71; Si, 11.45. Calc. for $C_9H_6F_3NSSi$: C, 43.91; H, 2.58; F, 23.10; N, 5.52; Si, 11.54%.

### Synthesis of 8-(difluorophenylsilylthio)quinoline (4b)

Phenyltrifluorosilane (3.08 g, 19 mmol) was added to (trimethylsilylthio)quinoline (**3b**) (3.90 g, 17 mmol) and the resulting mixture was stirred for 5 h. The $Me_3SiF$ formed was collected in a trap, cooled at −78 °C. A precipitate was filtered, washed with chloroform to give **4b** (75%), m.p. 69 °C. Anal. Found: C, 62.70; H, 3.86; F, 13.22; N, 4.87; Si, 9.77. Calc. for $C_{15}H_{11}F_2NOSi$: C, 62.85; H, 4.01; F, 12.96; N, 5.03; Si, 9.64%. $\delta_H$ (400.13 MHz, $CDCl_3$) 8.53 (d, $J = 4.8$ Hz), 7.58 (t, $J = 8$ Hz), 8.44 (d, $J = 12$ Hz), 7.67 (d, $J = 8$ Hz), 7.54 (t, $J = 6$ Hz), 7.90 (d, $J = 7.2$ Hz); $\delta_C$ (100.61 MHz, $CDCl_3$) 147.39, 129.14, 141.55, 123.08, 122.18, 129.50, 132.89, 127.94, 149.29; $\delta_{Si}$ (79.49 MHz, $CDCl_3$) −79.8 (t, $J = 264$ Hz).

Compound **4a** was synthesized in a similar manner; m.p. 40 °C (62%). Anal. Found: C, 59.39; H, 3.66; F, 12.53; N, 4.62; Si, 9.26. Calc. for $C_{15}H_{11}F_2NSSi$: C, 59.50; H, 3.23; F, 12.24; N, 4.81; Si, 8.97%.

### Acknowledgements

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## REFERENCES

1. Hensen K, Klebe G. *J. Organometal. Chem.* 1981; **209**: 17.
2. Klebe G, Qui DT. *Acta Crystallogr.* 1984; **40**: 476.
3. Brook MA. *Silicon in Organic, Organometallic, and Polymer Chemistry*. John Wiley: New York, 2000; 30.
4. Lukevics E, Pudova O, Sturkovich R. *Molecular Structure of Organosilicon Compounds*. Ellis Horwood: Chichester, 1989; 359.
5. Tkáč I, Holeček J, Lyčka A. *J. Organometal. Chem.* 1991; **418**: 311.
6. Kravtsov DN, Peregudov AS, Rokhlina EM, Fedin EI. *J. Organometal. Chem.* 1980; **201**: 61.
7. Krebs R, Schmutzler R. *Polyhedron* 1989; **8**: 731.
8. Albanov AI, Pestunovich VA, Trofimova OM, Chernov NF, Voronkov MG. *Zh. Obshch. Khim.* 1996; **66**: 1949.
9. Voronkov MG, Chernov NF, Trofimova OM, Ovchinnikov YuE, Struchkov YuT, Gavrilova GA. *Izv. Akad. Nauk Ser. Khim.* 1993; 758.
10. Brodskay EI, Belyaeva VV, Trofimova OM, Chernov NF, Pukhnarevich VB, Voronkov MG. *Zh. Obshch. Khim.* 2000; **70**: 1139.
11. Voronkov MG, Skorik YuI. *Izv. Akad. Nauk SSSR Ser. Khim.* 1964; 1215.
12. Eaborn C, Bott RW. In *Organometallic Compounds of the Group IV Elements*, vol. 1, MacDiarmid AG (ed.). Marcel Dekker: New York, 1968; 359–437.
13. Eaborn C. *Pure Appl. Chem.* 1969; **19**: 375.
14. Eaborn C. *J. Organometal. Chem.* 1975; **100**: 43.
15. Voronkov MG, Chernov NF, Perlova EM. *J. Organometal. Chem.* 1988; **341**: 225.
16. Voronkov MG. *Izv. Akad. Nauk Ser. Khim.* 1991; 2664.
17. Farooq O. *J. Chem. Soc. Perkin Trans. 1* 1998; 661.
18. Chernov NF, Bolgova YuI, Trofimova OM, Albanov AI, Chipanina NN, Pestunovich VA, Voronkov MG, Ovchinnikov YuE, Struchkov YuT, Gavrilova GA. *Dokl. Akad. Nauk* 2000; **375**: 210.
19. Wada M, Okawara R. *Inorg. Nucl. Chem. Lett.* 1969; 355.