APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 601–603
DOI:10.1002/aoc.1271

(3-Aminopropyl)trifluorosilanes and their *N*-substituted derivatives†

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Received 28 March 2007; Accepted 28 March 2007

***N*-substituted (3-aminopropyl)trifluorosilanes RR′NCH$_2$CH$_2$CH$_2$SiF$_3$ I–V were synthesized in order to investigate the effect of the substituents at the nitrogen atom on the N → Si intramolecular interaction. Compounds I–V were prepared by the reaction of KF with F$_3$BN(CH$_2$CH$_2$CH$_2$SiF$_3$)RR′ or H(RR′NCH$_2$CH$_2$CH$_2$SiF$_4$). The structures of compounds were confirmed by ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR and IR spectroscopy. The spectral data suggest a pentacoordination at silicon in compounds I (R = R′ = H) and II (R = R′ = Me) resulting from a relatively strong N → Si intramolecular bonding. Copyright © 2007 John Wiley & Sons, Ltd.**

KEYWORDS: *N*-substituted (3-aminopropyl)trifluorosilanes; NMR

INTRODUCTION

A wide variety of stable N → Si hypervalent silicon compounds with aminofunctional aryl groups has been intensively studied.[1–4] It has been shown that amino group is effectively coordinated with the trifluorosilyl group whereas the trialkoxysilanes do not show any evidence of N → Si intramolecular coordination.[5,6] The existence of an intramolecular bonding between the N and Si atoms in (aminoalkyl)silanes is still debatable. A dative N → Si interaction is absent in (dimethylaminomethyl)trifluorosilane, Me$_2$NCH$_2$SiF$_3$.[7] However an intramolecular N → Si coordination was assumed to explain the reactivity of (dialkylaminopropyl)trialkoxysilane.[8] The NMR data indicate a higher coordination at silicon in (3-dimethylaminopropyl)trifluorosilane, Me$_2$NCH$_2$CH$_2$CH$_2$SiF$_3$ induced by an N–Si interaction.[9]

In order to study the effect of the substituents at nitrogen on the coordination behavior of such compounds we prepared (3-aminopropyl)trifluorosilane and series of its *N*-substituted derivatives. The results obtained are reported below.

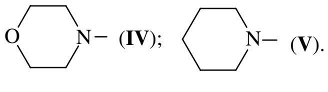
RESULTS AND DISCUSSION

The target compounds were synthesized in a two-step sequence in high yields using a procedure described in Chernov *et al*.[9] Fluorination of (3-aminopropyl)trimethoxysilanes by boron trifluoride etherate gave complexes F$_3$B · (NCH$_2$CH$_2$CH$_2$SiF$_3$)RR′, which were converted into (3-aminopropyl)trifluorosilanes (**I**) and its *N*-substituted derivatives (**II–V**) by treatment with an excess of KF.

$$\mathrm{RR'NCH_2CH_2CH_2Si(OMe)_3 + 2\,Et_2O\cdot BF_3 \longrightarrow F_3BN(CH_2CH_2CH_2SiF_3)RR' + B(OMe)_3 + 2\,Et_2O}$$

$$\mathrm{F_3BN(CH_2CH_2CH_2SiF_3)RR' + KF \longrightarrow KBF_4 + \underset{\textbf{I-V}}{RR'NCH_2CH_2CH_2SiF_3}}$$

R = R′ = H (**I**); R = R′ = Me (**II**); R = Ph, R′ = H (**III**);

RR′N =


Compounds **I–V** were also formed in 56% yield by heating KF with the corresponding tetrafluorosilicates H(RR′NCH$_2$CH$_2$CH$_2$SiF$_4$), which were obtained by the treatment of (3-aminopropyl)trialkoxysilanes with 40% solution of HF at −10 °C.[10]

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†Dedicated to the memory of Professor Des Cunningham.

Contract/grant sponsor: INTAS; Contract/grant number: 03-51-4164.
Contract/grant sponsor: Fund of President of Russian Federation; Contract/grant number: Science Schools' Grant 4575.2006.3.

Compounds **I–V** were isolated as moisture-sensitive colourless liquids. They were completely characterized by elemental analysis and spectroscopic studies (IR, ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR). The observation of intense Si–F stretching vibrations Si–F$_{eq}$ (ν_{as} 900, 880 cm^{-1}, ν_s SiF$_{eq}$ 844, 824 cm^{-1}) and SiF$_{ax}$ (ν745, 720 cm^{-1}) in the IR spectra of compounds **I** and **II** is indicative of the N → Si coordination bond in their molecules. In the IR spectra of compounds **III–V** Si–F stretching vibrations were shifted to higher wavenumbers ($\nu_{as} \sim 940$ cm^{-1} and $\nu_s \sim 880$ cm^{-1}) and are typical of tetravalent silanes. Such a difference in structure of compounds **I–II** and **III–V** resulted from the low basicity of the nitrogen atom in compounds **III** and **IV** and from steric factors in compound **V**.

^{1}H and ^{13}C NMR spectra of compounds **I** and **II** showed no spin–spin coupling constants ^{19}F–^{1}H and ^{19}F–^{13}C of the CH_2SiF_3 moiety. This is probably due to rather fast (on the NMR time scale) F$_{ax}$–F$_{eq}$ intramolecular exchange at the silicon which can be initiated by the HF traces. The ^{19}F and ^{29}Si NMR spectral data for compounds **I–V** and model tetravalent silane, $ClCH_2CH_2CH_2SiF_3$ (**VI**), are given in Table 1.

The coordination state of the silicon atom was measured using the ^{29}Si chemical shifts of new and model compounds. The observed ^{29}Si resonances of **I** and **II** were nearly identical and significally shifted (by ~30 ppm) towards higher field whereas their ^{19}F resonances appeared at lower field (by 2–10 ppm) as compared with that for model tetravalent silane **VI**.[11] Furthermore, the J_{Si-F} coupling constants were considerably decreased (by 37–39 Hz) in comparison to that of the model silane (**VI**; Table 1). These data suggest pentacoordination at silicon in compounds **I** and **II** resulting from an intramolecular N → Si bonding. The coordination shift $\Delta\delta^{29}$Si for **I** was greater than that found for **II**, which indicates a stronger N → Si interaction in the former compound despite the higher bacisity of the nitrogen atom in the latter.

Considerable (5-fold) dilution of compounds **I** and **II** in C_6D_6 solution did not lead to essential changes in the ^{29}Si and ^{19}F chemical shifts. This is indicative of intramolecular (not intermolecular) interaction between nitrogen and silicon atoms as well as the absence of intermolecular association due to the formation of Si–F → Si bridges.[12–17]

Table 1. ^{19}F and ^{29}Si NMR of compounds **I–V** and model $Cl(CH_2)_3SiF_3$ (**VI**)

N	RR′	δ^{19}F, ppm	δ^{29}Si, ppm	*J*(SiF), Hz	$\Delta\delta^{29}$Si
I	H_2	−127.8	−90.1	242.0	31.1
II	Me_2	−136.74	−88.8	244.1	29.8
III	Ph H	−136.92	−60.7	280.4	1.7
IV	$O(CH_2CH_2-)_2$	−136.95	−60.4	280.9	1.4
V	$(-CH_2-)_5$	−135.21	−76.2	260.5	17.2
VI	$Cl(CH_2)_3SiF_3$	−138.6	−59.0	281.0	—

At room temperature the ^{19}F resonances in trifluorides **I** and **II** were observed as singlet peaks due to the fast (on the NMR time scale) intramolecular exchange of fluorine atoms in the trigonal–bipyramidal environment of the silicon atom. Lowering the temperature of the solution in trifluorides **II** to −80 °C resulted in upfield ^{29}Si shifts (by 3.5 ppm) and a decrease in J_{SiF} (by 1.2 Hz). Further decreasing the temperature reduced the F$_{ax}$–F$_{eq}$ exchange rate and at −100 °C the ^{19}F NMR spectra showed the equatorial fluorine doublet [at −131.4 ppm ($J\,^{19}F_{ax}-^{19}F_{eq} = 30.1$ Hz) and −146.6 ppm ($J\,^{19}F_{ax}-^{19}F_{eq} = 33.0$ Hz) for **I** for **II**, respectively] and the axial fluorine triplet (−115.4 ppm for **I** and −113.8 ppm for **II**). The values of $J\,^{29}Si-^{19}F_{ax}$ (248.7 and 245.5 Hz for **I** and **II**, respectively) were higher than those for $J\,^{29}Si-^{19}F_{eq}$ (229.7 Hz for **I** and 238.6 Hz for **II**). Such a change in spectral parameters is characteristic of pentacoordinated silicon derivatives having an SiF_3 group.[11]

The free activation energies of the exchange process $\Delta G_c^{\neq}$ at coalescence temperature (−40 °C) calculated by the equation $\Delta G_c^{\neq} = 1.987 \times T_c \times [23 + \lg(T_c/\Delta\nu)]$ were 9.2 and 8.8 kcal mol^{-1} for compounds **I** and **II**, respectively. Comparison of $\Delta\delta^{29}$Si coordination shifts and the values of $\Delta G_c^{\neq}$ for compounds **I** and **II** and 2-(*N*,*N*-dimethylaminomethyl)phenyltrifluorosilane (9.9 *kcal* mol^{-1})[18] suggested a stronger the N → Si coordination bond in the latter.

EXPERIMENTAL

The starting *N*-substituted (3-aminopropyl)trimethoxysilanes were synthesized by heating (3-chloropropyl)trimethoxysilane with primary and secondary amines at 90–100 °C for 8 h in sealed ampoules. Their physical data are consistent with the literature data.[19]

^{1}I NMR, ^{13}C, ^{19}F and ^{29}Si spectra in $CDCl_3$ were recorded on a Bruker 400 DPX spectrometer at 400.13, 100.61, 376.50 and 79.49 MHz, respectively. The chemical shifts (δ) were reported with reference at 0.00 ppm (Me_4Si) or 7.26 ppm ($CHCl_3$) for the proton and at 77.00 ppm (centered on the signal of $CDCl_3$) for the carbon. IR spectra were measured on a Specord 75 JR spectrometer (microlayer).

Synthesis of (3-aminopropyl)trifluorosilane (I)

Procedure A

(3-Aminopropyl)trimethoxysilane (11 g, 61 mmol) was added under stirring to hydrofluoric acid 40%, (20 ml) at −10 °C. The crystalline precipitate formed was filtered and dried in vacuum to give tetrafluorosilicate. The mixture of tetrafluorosilicate and excess anhydrous KF was heated in vacuum to afford (3-aminopropyl)trifluorosilane **I** (70%), b.p. 124–125 °C (18 torr). Anal. found: C, 25.76; H, 6.01; F, 40.03; N, 9.24; Si, 19.32; calcd for $C_3H_8NSiF_3$: C, 25.16; H, 5.63; F, 39.80; N, 9.78; Si, 19.61. δ_H 0.87 ($J = 7$ Hz), 1.70 ($J = 6.2$ Hz), 2.75 ($J = 6.2$ Hz), 2.95 (br. s); δ_C 6.76 (br. s), 22.04, 39.32.

DOI: 10.1002/aoc

Procedure B

$BF_3 \cdot OEt_2$ (9.4 g, 66 ml) was added to (3-aminopropyl)trimethoxysilane (4 g, 22 mmol). The reaction mixture was stirred for 3 h at 36 °C. The tetrafluorosilicate was heated in vacuum with excess anhydrous KF to afford **I** (75%), b.p. 125 °C (18 torr). Compounds **III–V** were obtained following the same procedure.

Compound **II**, b.p. 139–140 °C (715 torr) (73%). Anal. found: C, 35.73; H, 7.00; F, 33.56; N, 8.12; Si, 16.36; calcd for $C_5H_{12}NSiF_3$: C, 35.07; H, 7.06; F, 33.18; N, 8.17; Si, 16.40. δ_H 0.96 ($J = 7.2$ Hz), 1.67 ($J = 7$ Hz), 2.43 ($J = 7$ Hz), 2.31 (s); δ_C 5.05 (br. s), 17.57, 58.09, 47.02.

Compound **III**, b.p. 98 °C (2 torr) (55%). Anal. found: C, 50.08; H, 5.45; F, 25.63; N, 6.00; Si, 12.64; calcd for $C_9H_{12}NSiF_3$: C, 49.29; H, 5.51; F, 25.95; N, 6.39; Si, 12.80. δ_H 0.94, 1.64, 3.36 ($J = 3.55$ Hz), 5.94 ($J = 7.47$–7.22 Hz); δ_C 3.7 ($J = 20.4$ Hz), 17.92, 52.43, 122.48, 128.68, 129.95, 137.62.

Compound **IV**, b.p. 72–74 °C (3 torr) (81%). Anal. found: C, 39.39; H, 6.25; F, 27.01; N, 6.45; Si, 13.20; calcd for $C_7H_{14}NOSiF_3$: C, 39.42; H, 6.61; F, 26.72; N, 6.56; Si, 13.16. δ_H 0.95, 1.92, 3.35, 2.96, 2.77, 3.87, 3.78; δ_C 4.30 ($J = 20.4$ Hz), 15.25, 57.19, 51.03, 60.78.

Compound **V**, b.p. 68–69 °C (2 torr) (57%). Anal. found: C, 45.81; H, 7.66; F, 26.56; N, 6.60; Si, 13.18; calcd for $C_8H_{16}NSiF_3$: C, 45.47; H, 7.63; F, 26.97; N, 6.63; Si, 13.29. δ_H 0.96, 1.64, 2.38, 1.47, 1.59, 2.53; δ_C 5.90 ($J = 12$ Hz), 17.82, 56.27, 23.94, 22.93, 53.61.

Acknowledgments

We thank INTAS (grant no. 03-51-4164) and the Fund of the President of the Russian Federation (Science Schools' Grant 4575.2006.3) for financial support.

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DOI: 10.1002/aoc