$[\mathrm{Me_3Si(CF_3)F}]^-$ and $[\mathrm{Me_3Si(CF_3)_2}]^-$: Reactive Intermediates in Fluoride-Initiated Trifluoromethylation with $\mathrm{Me_3SiCF_3}$— An NMR Study**

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Trimethyl(trifluoromethyl)silane (**1**) is widely used especially in organic synthesis in fluoride-initiated reactions for nucleophilic trifluoromethylation.[1] Although many pentacoordinated organosilicates have been detected and in part fully characterized,[2] trifluoromethylsilicates formed in the system $\mathrm{Me_3SiCF_3/F^-}$ have not been observed so far. The reaction of **1**/$\mathrm{F^-}$ and MeCN was described recently;[3] however, only the intermediate $[\mathrm{Me_3Si(CH_2CN)F}]^-$ was detected in solution by ^{19}F and ^{1}H NMR and IR spectroscopy.

In our investigations on the synthesis of highly coordinated trifluoromethyl–element compounds,[4] we found that polar trifluoromethylations of **1**/$\mathrm{F^-}$ proceed depending on the amount of fluoride via intermediates $[\mathrm{Me_3Si(CF_3)_2}]^-$ (**2**) and $[\mathrm{Me_3Si(CF_3)F}]^-$ (**3**). The anion **2** forms in reactions where the **1**/$[\mathrm{Me_4N}]$F ratio is >1:1 [Eq. (1)], whereas anion **3** forms selectively when an excess of fluoride is used [Eq. (2)] (Figure 1).

$$> 1\ \underset{\mathbf{1}}{\mathrm{Me_3SiCF_3}} + [\mathrm{Me_4N}]\mathrm{F} \xrightarrow[-90\,^{\circ}\mathrm{C}/-60\,^{\circ}\mathrm{C}]{\mathrm{THF}} \underset{\mathbf{2}}{[\mathrm{Me_4N}][\mathrm{Me_3Si(CF_3)_2}]} + \mathrm{Me_3SiF} \tag{1}$$

$$< 1\ \underset{\mathbf{1}}{\mathrm{Me_3SiCF_3}} + [\mathrm{Me_4N}]\mathrm{F} \xrightarrow[-90\,^{\circ}\mathrm{C}/-60\,^{\circ}\mathrm{C}]{\mathrm{THF}} \underset{\mathbf{3}}{[\mathrm{Me_4N}][\mathrm{Me_3Si(CF_3)F}]} \tag{2}$$

Although carefully dried THF and $[\mathrm{D_8}]$THF have been used as solvents, considerable amounts of $\mathrm{CF_3H}$ and $\mathrm{CF_3D}$, respectively, were formed. The quantity of $\mathrm{CF_3H}$ ($\mathrm{CF_3D}$) formed depends on the temperature of the addition of **1** to the $[\mathrm{Me_4N}]$F suspension. At −90 °C only traces of $\mathrm{CF_3H}$ ($\mathrm{CF_3D}$) were detected, whereas at −60 °C the ratio of $\mathrm{CF_3H}$ ($\mathrm{CF_3D}$) to **2** and **3**, respectively, approximated to 1:1. Simultaneously, a colorless solid precipitated which was insoluble in common organic solvents; elemental analysis revealed the solid contained 38.7 % C, 6.8 % H, 7.4 % N, 38.7 % F. In light of the recently published results,[3] it seems plausible that the product is formed by $\mathrm{H^+}$ and $\mathrm{D^+}$ abstraction, respectively, from the solvent.

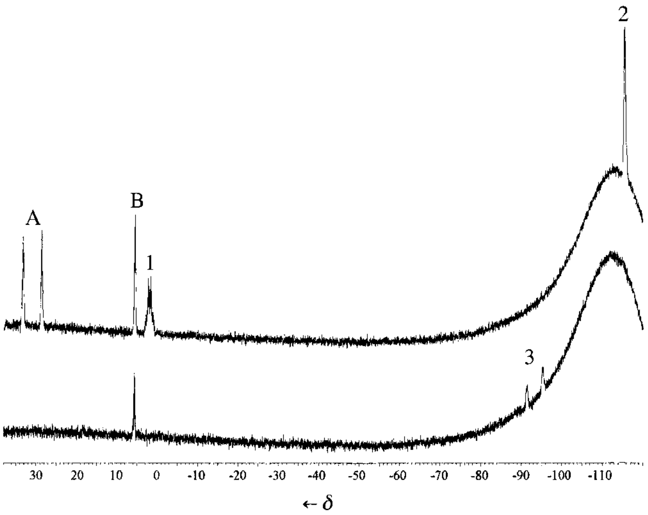

Figure 1. ^{29}Si NMR spectra of the reactions of $[\mathrm{NMe_4}]$F and **1**; top: stoichiometry according to Equation (1); bottom: stoichiometry according to Equation (2) (A: $\mathrm{Me_3SiF}$, B: by-product; temperature −60 °C).

The anion **2** is detected in the ^{29}Si NMR spectrum at $\delta = -112.1$ (Table 1). The complex spin system is reduced to a septet in the $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR spectrum and to a decet in the $^{29}\mathrm{Si}\{^{19}\mathrm{F}\}$ NMR spectrum. Multiplicities confirm the expected trigonal-bipyramidal structure with two axial $\mathrm{CF_3}$ groups and three equatorial methyl groups. Besides the resonance of **2**, the signals of $\mathrm{Me_3SiF}$ and **1** were detected in the ^{29}Si NMR spectrum. A further multiplet at $\delta = +8.0$ became a sharp singlet on ^{1}H decoupling. This signal is assigned to a reaction product of silicates **2** and **3** with THF. Compounds such as $\mathrm{Me_3SiOCH_2CH_2CH{=}CH_2}$, $\mathrm{Me_3SiO(CH_2)_4F}$, or $\mathrm{Me_3Si[O\text{-}(CH_2)_4]_{\mathit{n}}[OC_4H_8]^+F^-}$ seem probable. NMR spectroscopic evidence for the formation of $[\mathrm{Me_3SiF_2}]^-$ was not found in any case.

The ^{19}F NMR signals of the $\mathrm{CF_3}$ groups are only slightly shifted to lower field compared with those of **1** (Table 1). However, the differences in the absolute values of the coupling constants are remarkable: a decrease in ^{2}J(Si,F) coupling (6.0 Hz compared with 36.2 Hz in **1**) as well as an

Table 1. Selected NMR data of **1**–**3**.

	1	**2**	**3**
^{19}F-NMR:			
$\delta(\mathrm{CF_3})$	−65.8	−62.6	−63.9
^{1}J(F,C)	322	378	375
^{2}J(Si,F)	36.2	6.0	4.5
δ(F)[a]			−50.4
^{1}J(Si,F)			235
^{3}J(F,F)			13
^{29}Si-NMR:			
δ	+5.4	−112.1	−94.0
^{13}C-NMR:[b]			
δ(Me)	1.4	–[c]	1.7
^{2}J(F,C)			47
$\delta(\mathrm{CF_3})$	131.5	144.7	141.8

[a] For comparison: $\mathrm{Me_3SiF}$: $\delta(\mathrm{F}) = -155.89$, $^{1}J(\mathrm{Si,F}) = 275$ Hz. [b] δ-($[\mathrm{NMe_4}]^+$) = 53.5. [c] Signals of **1**, **2**, and $\mathrm{Me_3SiF}$ overlap.

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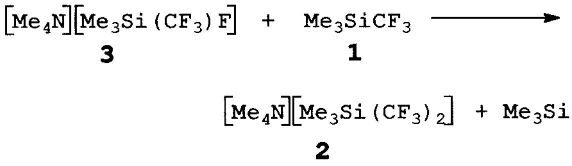
increase in ^{1}J(F,C) coupling (378 Hz compared with 322 Hz in **1**). This effect appears to be characteristic for ^{1}J(F,C) couplings in highly coordinated compounds with linear CF_3-element-CF_3 units.[5]

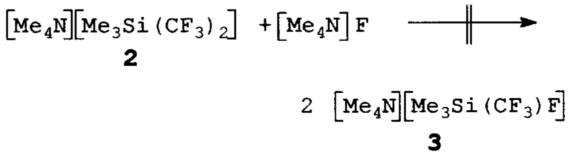
In the $^{13}C\{^{1}H\}$ NMR spectrum the CF_3 groups were detected as expected as a quartet of quartets (Table 1). The unsymmetrical anion **3** displays a doublet of multiplets at $\delta = -94.0$ in the ^{29}Si NMR spectrum. The above-mentioned by-product was also detected as an additional product. Two signals are detected in the ^{19}F NMR spectrum of **3**, a quartet centered at $\delta = -50.4$ and a doublet at $\delta = -63.9$. The Me_3Si resonance in the ^{13}C NMR spectrum shows an additional doublet splitting (^{2}J(C,F) = 47 Hz).

On the basis of NMR data, anions **2** and **3** are unambiguously identified as the intermediates in reactions of **1** with $[Me_4N]F$ in THF. Attempts to isolate **2** and **3** by condensing off all low-boiling components at a maximum temperature of −20 °C failed. After the volume was reduced to approximately one third of the original volume, spontaneous decomposition occurred with formation of a highly viscous brown residue.

It is noteworthy that addition of **1** to a solution of **3** enhances the formation of **2** [Eq. (3)], whereas addition of $[Me_4N]F$ to a solution of **2** does not give any evidence for the formation of **3** [Eq. (4)].



$$\underset{\mathbf{3}}{[Me_4N][Me_3Si(CF_3)F]} + \underset{\mathbf{1}}{Me_3SiCF_3} \longrightarrow \underset{\mathbf{2}}{[Me_4N][Me_3Si(CF_3)_2]} + Me_3SiF \qquad (3)$$



$$\underset{\mathbf{2}}{[Me_4N][Me_3Si(CF_3)_2]} + [Me_4N]F \not\longrightarrow 2\ \underset{\mathbf{3}}{[Me_4N][Me_3Si(CF_3)F]} \qquad (4)$$

The addition of cyclohexanone either to a solution of **2** or **3** leads spontaneously to 1-trifluoromethylcyclohexan-1-olates, which after treatment with acids are converted into the corresponding alcohol, 1-trifluoromethylcyclohexan-1-ol. The NMR data of the alcohol match well with literature values.[6]

These and further results[4, 5] demonstrate that **2** and **3** are the reactive intermediates in nucleophilic trifluoromethylations.

Experimental Section

2: $[Me_4N]F$ (0.25 g, 2.7 mmol) was suspended in a 10 mm NMR tube in a mixture of THF (4 mL) and [D$_8$]THF (2 mL). At −90 °C **1** (0.80 mL, 0.76 g, 5.4 mmol) was added. The mixture was warmed to −60 °C and stirred for 1 h. A colorless solution of **2** was obtained which was investigated by NMR spectroscopy at −60 °C.

3: $[Me_4N]F$ (0.25 g, 2.7 mmol) was suspended in THF (3 mL) in an 8 mm NMR tube. At −90 °C **1** (0.20 mL, 0.19 g, 1.3 mmol) was added. After warming to −60 °C and stirring for 1 h, the colorless solution was investigated by NMR spectroscopy (external lock [D$_6$]acetone).

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[5] For comparison: $[I(CF_3)_2]^-$: ^{1}J(F,C) = 442 Hz (CF_3I: ^{1}J(F,C) = 344 Hz); $[Te(CF_3)_3]^-$ (axial): ^{1}J(F,C) = 414 Hz ($Te(CF_3)_2$: ^{1}J(F,C) = 354 Hz); N. Maggiarosa, W. Tyrra, D. Naumann, N. V. Kirij, Yu. L. Yagupolskii, unpublished results.

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Rapid Screening of Olefin Polymerization Catalyst Libraries by Electrospray Ionization Tandem Mass Spectrometry**

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Herein we report the use of electrospray ionization tandem mass spectrometry (ESI-MS/MS) and gas-phase ion–molecule reactions for the rapid screening of Brookhart-type Pd^{II} olefin polymerization catalysts.[1, 2] Whereas the preparation and testing of individual catalysts has long been pursued, the screening of catalyst libraries is a recent phenomenon. Screening of libraries of compounds, either natural products or synthetic molecules which may have been combinatorially prepared, has been extensively applied in biological systems and for the discovery of lead compounds in medicinal chemistry. Attempts to apply the general idea of screening to organometallic catalysts[3] have only recently appeared, with thermographic,[4] fluorescence quenching,[5] conventional microwell parallel reactions,[6] and polymer-supported "bead" methods[7] having been tried. Only the last of these has been attempted for polymerization reactions catalyzed by organometallic complexes, the other methods being inapplicable for a variety of technical reasons. Even the polymer-supported bead method, when applied to polyolefin catalyst screening, suffers from a nonoptimal encoding procedure that limits its usefulness. The experiment reported here has the advantages

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