

### 3. Experimental Section

#### 3.1 General procedures

##### 3.1.1 Abbreviations used

PFA	Perfluoroethene-perfluorovinylether-copolymer
n-BuLi	n-butyl-lithium
Et <sub>2</sub> O	Diethyl ether (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O
$\delta$	NMR chemical Shift (given in ppm)
-o, -m, -p	Ortho, meta and para positions of an aromatic ring.
s, d, t, qu., q, m.	Multiplicity of the NMR signals (singlet, doublet, triplet, quartet, quintet and multiplet)
a-HF	anhydrous HF
F-11	Freon-11 (CCl <sub>3</sub> F)
EtCN	CH <sub>3</sub> CH <sub>2</sub> CN
AcetD	(CD <sub>3</sub> ) <sub>2</sub> CO

##### 3.1.2 Instruments used

###### Glove Box

Water and Oxygen sensitive substances were handled in a glove box (Firma Braun GmbH, Graching Type MB 150 B/G or Type MB 200) with automatic argon gas flow over a Copper-catalyst which provides an H<sub>2</sub>O and O<sub>2</sub> content level lower than 1 ppm.

###### Raman Spectrometer

Samples were placed inside sealed PFA tubes (4 mm). Raman spectra were recorded on a Bruker RFS 100 FT-Raman spectrometer which operates with a Nd-YAG-Laser ( $\lambda$  1064 nm, 10-550 mW).

### NMR-Spectrometer

NMR spectra were recorded using a JEOL JNM-LA 400 spectrometer ( $^1\text{H}$  at 399.65 MHz,  $^{13}\text{C}$  at 100.40 MHz and  $^{19}\text{F}$  at 376.00 MHz).  $\text{F}_5\text{W}(\text{OC}_6\text{F}_5)$  at 20°C and 184°C was recorded using a JEOL F 90 Q instrument ( $^{19}\text{F}$  at 84.25 MHz). Chemical shift values are reported with respect to TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{BF}_3\cdot\text{Et}_2\text{O}$  ( $^{11}\text{B}$ ) and  $\text{CCl}_3\text{F}$  ( $^{19}\text{F}$ ).<sup>[68]</sup> Deuterated solvents were used as received. NMR spectra were recorded at room temperature, otherwise stated. The samples for  $^{19}\text{F}$  NMR dynamic spectra were measured inside 4 mm PFA tubes and using  $\text{C}_2\text{D}_2\text{Cl}_4$  as solvent, occasionally  $\text{CD}_2\text{Cl}_2$  was used.

### Single Crystal Diffractometer

Single crystals were handled in a special device, cut to an appropriate size, and mounted on a Bruker SMART CCD 1000 TU diffractometer, using Mo  $K\alpha$  irradiation, a graphite monochromator, a scan width of  $0.3^\circ$  in  $\omega$ , and a measuring time of 20 s per frame. After semiempirical absorption corrections (SADABS) by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinement.<sup>[96]</sup> All atoms except hydrogen are refined anisotropically. Hydrogen atoms have been located by difference Fourier maps and refined independently from other atomic positions, however, with a single isotropic displacement parameter for all hydrogen atoms. Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 218240 ( $\text{C}_6\text{F}_5\text{-O-MoF}_5$ ) and CCDC 218241 ( $(\text{CF}_3\text{CH}_2\text{O})_2\text{MoF}_4$ ). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

### 3.1.3 DFT Calculations

DFT calculations were performed with the program GAUSSIAN revision A7, 1998.<sup>[43]</sup> Method Becke 3LYP<sup>[41,42]</sup> and basis sets: 6-311G(d,p) for C, H, O, and F as implemented in the program. The relativistically corrected pseudo potentials and basis sets for Mo, and W were obtained from the Institute für Theoretische Chemie, Universität Stuttgart ([www.theochem.uni-stuttgart.de/pseudopotentials/clickpse.html](http://www.theochem.uni-stuttgart.de/pseudopotentials/clickpse.html)). Mo: 28 core electrons; W: 60 core electrons, 8s 7p 6d valency basis for each metal.

### 3.1.4 $^{19}\text{F}$ -NMR Simulations

The program gNMR<sup>[67]</sup> was used for the simulation of the dynamic NMR spectra.

### 3.1.5 Elemental Analysis

Elemental analyses were performed by Beller Co., Göttingen, Germany.

### 3.1.6 Experimental

All reactions were carried out under dry argon atmosphere using Schlenk technique.<sup>[97]</sup> Solvents were dried by standard methods<sup>[98]</sup> and kept over Molecular sieve (4 nm). Commercially available chemicals (see section 3.1.7) were used as received. 2,2,2-Trifluoroethanol was distilled twice before use. Diphenyl zink and Phenyl lithium were first used as they were; later they were sublimed. Antimontrifluoride was sublimed before it was used.

### 3.1.7 Reactants used

$\text{CF}_3\text{CH}_2\text{OH}$	Fa. Merck
$(\text{CH}_3)_3\text{SiCl}$	Fa. Merck
$\text{C}_6\text{F}_5\text{OH}$	Fa. Aldrich
$(\text{CF}_3)_3\text{COH}$	Fa. Apolo Scientific LTD.
$[(\text{CH}_3)_3\text{Si}]_2\text{NH}$	Fa. Aldrich
$(\text{C}_6\text{F}_5)\text{B}(\text{OH})_2$	Fa. Aldrich
$\text{KHF}_2$	Fa. Aldrich
$\text{BF}_3$	Available in stock
$(\text{C}_6\text{H}_5)_3\text{SiCl}_3$	Fa. Aldrich
Mg	Available in stock
$(\text{C}_6\text{F}_5)\text{Br}$	Fa. Aldrich
$\text{Si}(\text{OCH}_2\text{CH}_3)_4$	Available in stock
$\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$	Fa. Aldrich

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$\text{SbF}_3$	Available in stock
$(\text{CH}_3)_3\text{SnCl}$	Available in stock
$\text{F}_2$	Available in stock
$\text{Hg}(\text{NO}_3)_2$	Available in stock
$\text{Li}(\text{C}_6\text{H}_5)$	Available in stock
n-BuLi	Fa. Acros Organics
LiH	Available in stock
$(\text{CH}_3)_4\text{NF}$	Available in stock
$\text{MoF}_6$	Fa. Merck
$\text{WF}_6$	Fa. Merck
$\text{WCl}_6$	Available in stock
$\text{Zn}(\text{C}_6\text{H}_5)_2$	Available in stock
$(\text{CH}_3)_3\text{Si}(\text{OCH}_2\text{CF}_3)$	Synthesized according to ref. [99].
$(\text{CH}_3)_3\text{Si}(\text{OC}_6\text{F}_5)$	Synthesized according to ref. [100].
$(\text{CH}_3)_3\text{Si}(\text{OC}(\text{CF}_3)_3)$	Synthesized exactly like $(\text{CH}_3)_3\text{Si}(\text{OC}_6\text{F}_5)$ and $(\text{CH}_3)_3\text{Si}(\text{OCH}_2\text{CF}_3)$ were prepared.
$\text{LiOC}(\text{CF}_3)_3$	Synthesized according to ref. [101].
$(\text{C}_6\text{F}_5)\text{BF}_2$	Synthesized according to ref. [102].
$(\text{C}_6\text{H}_5)\text{SiF}_3$	Synthesized according to ref. [103].
$(\text{C}_6\text{F}_5)\text{SiCl}_3$	Synthesized according to ref. [104].
$(\text{C}_6\text{F}_5)\text{Sn}(\text{CH}_3)_3$	Synthesized according to ref. [105, 106].
$\text{HgF}_2$	Synthesized from $\text{F}_2$ and $\text{Hg}(\text{NO}_3)_2$ [107]
$\text{Hg}(\text{SCF}_3)_2$	Synthesized according to ref. [108].

## 3.2 Synthesis, Spectroscopic data, and Crystal structure analysis

### 3.2.1 (CF<sub>3</sub>CH<sub>2</sub>O)Si(CH<sub>3</sub>)<sub>3</sub>

2,2,2-Trifluoroethoxy-trimethyl-silane was prepared using a literature procedure.<sup>[99]</sup> To a previously dried three-necked flask equipped with a reflux condenser bis(trimethylsilyl)amine (45 ml, 0.212 mol) and two drops of chlorotrimethylsilane were added under argon pressure. With the aid of a syringe 2,2,2-trifluoroethanol (30 ml, 0.417 mol) was added dropwise while the mixture was stirred slowly. After refluxing for three hours the liquid was distilled at atmospheric pressure giving a mixture of (CF<sub>3</sub>CH<sub>2</sub>O)Si(CH<sub>3</sub>)<sub>3</sub> and [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>NH (84% and 16% respectively as shown by the <sup>1</sup>H NMR integrals). The mixture was evacuated at -30 °C and with the aid of a double cold trap (-60 °C / -196 °C) 59.58 g (83% yield) of (CF<sub>3</sub>CH<sub>2</sub>O)Si(CH<sub>3</sub>)<sub>3</sub> were collected as a colorless liquid in the -196 °C trap. <sup>19</sup>F NMR [CDCl<sub>3</sub>]: δ = -77.4 (3F, t, <sup>3</sup>J<sub>FH</sub> = 7.7 Hz, -CF<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} [CDCl<sub>3</sub>]: δ = 124.3 (1C, q, <sup>1</sup>J<sub>CF</sub> = 278.6 Hz, -CF<sub>3</sub>), 61.2 (1C, q, <sup>2</sup>J<sub>CF</sub> = 35.7 Hz, -CH<sub>2</sub>-), -0.9 (3C, s, -CH<sub>3</sub>). <sup>1</sup>H [CDCl<sub>3</sub>]: δ = 3.9 (2H, q, <sup>3</sup>J<sub>FH</sub> = 8.66 Hz, -CH<sub>2</sub>-), 0.1 (9H, s, -CH<sub>3</sub>).

### 3.2.2 (C<sub>6</sub>F<sub>5</sub>O)Si(CH<sub>3</sub>)<sub>3</sub>

Pentafluorophenoxy-trimethylsilane was prepared in a similar manner to the procedure described above, as the reaction between pentafluorophenol and chlorotrimethylsilane according to the literature proved to be unreliable.<sup>[100]</sup> Pentafluorophenol (30.0 g, 0.163 mol) was added to a previously dried three-necked flask equipped with a reflux condenser. [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>NH (18 ml, 84.7 mmol) was dropped slowly into the flask followed by stirring as soon as there was enough liquid. The reaction mixture was refluxed for 4 h. After distillation, the mixture contained 85% (C<sub>6</sub>F<sub>5</sub>O)Si(CH<sub>3</sub>)<sub>3</sub> and 15% bis(trimethylsilyl)-amine. Vacuum distillation from -30 °C into a -196 °C trap gave 25.05 g (60% yield) of the pure compound as a colorless liquid. <sup>19</sup>F NMR [CDCl<sub>3</sub>]: δ = -159.7 (2F, d, <sup>3</sup>J<sub>FF</sub> = 18.4 Hz, -*o*), -165.8 (2F, t, <sup>3</sup>J<sub>FF</sub> = 21.3 Hz, -*m*), -168.2 (1F, t, <sup>3</sup>J<sub>FF</sub> = 21.3 Hz -*p*). <sup>13</sup>C{<sup>19</sup>F} [CDCl<sub>3</sub>]: δ = 138.6 (1C, s, C<sub>2,6</sub>), 135.640 (1C, s, -C<sub>3,5</sub>), 133.7 (1C, s, -C<sub>4</sub>), 128.1 (1C, s, -C<sub>1</sub>), -1.6 (3C, q, <sup>1</sup>J<sub>CH</sub> = 119.5 Hz, -CH<sub>3</sub>). <sup>1</sup>H [CDCl<sub>3</sub>]: δ = 0.1 (9H, s, -CH<sub>3</sub>).

### 3.2.3 ((CF<sub>3</sub>)<sub>3</sub>CO)Si(CH<sub>3</sub>)<sub>3</sub>

Perfluoro-*tert*-butoxy-trimethyl-silane was prepared successfully from HOC(CF<sub>3</sub>)<sub>3</sub> and [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>NH using the same procedure described in 3.2.1 and 3.2.2. <sup>19</sup>F NMR [CDCl<sub>3</sub>]: δ = -75.3 (9F, s). <sup>13</sup>C{<sup>19</sup>F} [CDCl<sub>3</sub>]: δ = 122.6 (3C, s, -CF<sub>3</sub>), 80.3 (1C, s, -OC), 1.0 (3C, qu, <sup>1</sup>J<sub>CH</sub> = 119.5 Hz, -CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} [CDCl<sub>3</sub>]: δ = 122.6 (3C, qu, <sup>1</sup>J<sub>CF</sub> = 290.9 Hz, -CF<sub>3</sub>), 80.3 (1C, m, <sup>2</sup>J<sub>CF</sub> = 31.5 Hz, -OC), 1.0 (3C, s, -CH<sub>3</sub>). <sup>1</sup>H [CDCl<sub>3</sub>]: δ = -0.3 (9H, s, -CH<sub>3</sub>).

### 3.2.4 LiOC(CF<sub>3</sub>)<sub>3</sub>

Lithium perfluoro-*tert*-butoxide was prepared in a similar manner according to a literature procedure.<sup>[101]</sup> To a previously dried three-necked flask equipped with a reflux condenser Lithium Hydride (1.0g, 125.8 mmol) was added. 30 ml Et<sub>2</sub>O were added into the flask and the mixture was stirred. With the aid of a syringe Perfluoro-*tert*-butanol (11.1 ml, 79.7 mmol) was added dropwise under argon over a period of 2 h, while the mixture was stirred and kept at 0°C. The mixture was allowed to reach room temperature after which it was refluxed for 30 min. Volatile materials were pumped off and a yellowish oily material remained in the flask. After subliming the material (48 hrs/150°C/10<sup>-3</sup> mbar) 11.6 g (60.2% yield) of a white crystalline material identified as LiOC(CF<sub>3</sub>)<sub>3</sub> were recovered. <sup>19</sup>F NMR [Et<sub>2</sub>O/CDCl<sub>3</sub>]: δ = -77.3 (9F, s, -CF<sub>3</sub>). <sup>13</sup>C{<sup>19</sup>F} [Et<sub>2</sub>O/CDCl<sub>3</sub>]: δ = 122.1 (3C, s, -CF<sub>3</sub>), 81.1 (1C, s, -OC).

### 3.2.5 (C<sub>6</sub>F<sub>5</sub>)BF<sub>2</sub>

Bor-pentafluorophenyl-difluoride was prepared in similar way as described in the literature.<sup>[102]</sup> Yields of this many steps reaction were lower than 15%. To achieve a better yield, the reaction was started from commercially available Pentafluorobenzene boronic acid (C<sub>6</sub>F<sub>5</sub>)B(OH)<sub>2</sub> (10g, 47.2 mmol) and worked out exactly like in [102]. A transparent liquid (81% yield) extremely sensitive to air and moisture was obtained. <sup>19</sup>F NMR [CCl<sub>3</sub>F]: δ = -74.8 (2F, s, -BF<sub>2</sub>), -128.6 (2F, d, -o), -144.2 (2F, t, -m), -161.3 (1F, t, -p). <sup>11</sup>B NMR [CCl<sub>3</sub>F]: δ = 22.4 (1, s).

### 3.2.6 (C<sub>6</sub>H<sub>5</sub>)SiF<sub>3</sub>

Phenyl-trifluoro-silane was prepared by the reaction of (C<sub>6</sub>H<sub>5</sub>)SiCl<sub>3</sub> and SbF<sub>3</sub> using a similar procedure as described in literature for (C<sub>6</sub>F<sub>5</sub>)SiF<sub>3</sub>.<sup>[103]</sup> Phenyl-trichloro-silane (11.85 g, 56.0 mmol) and an excess of Antimontrifluoride (12.3 g, 68.8 mmol) were given into a glass ampoule equipped with a magnetic stirrer. The ampoule was sealed and the reaction mixture was heated and stirred at 80 °C for 18 h. After opening the reaction vessel inside the glove box the mixture was evacuated at room temperature for 6 h. A transparent liquid (8.87 g, 54.7 mmol, 97.7% yield) was recovered in the -196°C trap. <sup>19</sup>F NMR [CDCl<sub>3</sub>]: δ = -141.9 (3F, s, -SiF<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR [CDCl<sub>3</sub>]: δ = -134.6 (2C, s, -o), -128.7 (2C, s, -m), -133.5 (1c, s, -p), -120.5 (1C, s, -*ipso*C). <sup>29</sup>Si NMR [CDCl<sub>3</sub>]: δ = -73.1 (1Si, qu., -SiF<sub>3</sub>, <sup>1</sup>J<sub>Si-F</sub> = 3.36 Hz).

### 3.2.7 (C<sub>6</sub>F<sub>5</sub>)SiF<sub>3</sub>

Attempts to prepare Pentafluorophenyl-trifluoro-silane from (C<sub>6</sub>F<sub>5</sub>)Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> and a-HF using a modified Grignard method like described in the literature [104] proved to be unsuccessful mainly because mixtures of (C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4-n</sub> (n = 1, 2, or 3) were obtained, and upon reaction with a-HF, C<sub>6</sub>F<sub>5</sub>H was detected (<sup>19</sup>F NMR) as the main product.

(C<sub>6</sub>F<sub>5</sub>)Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> (19.2g, 85% yield) was successfully synthesized in the following manner: To a three-necked flask equipped with a reflux condenser Bromopentafluorobenzene (0.12 mol), magnesium turnings (0.1 mol), and Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> (0.36 mol) were added and stirred at 40 °C. Diethyl ether (60 ml) was added dropwise over a period of 1h. The reaction mixture was refluxed for 24 h. Continuing the procedure like in the literature [104] gave a light brown liquid identified as Pentafluorophenyl-triethoxy-silane. <sup>19</sup>F-NMR [CDCl<sub>3</sub>]: δ = -124.24 (2F, d, -o), -148.94 (1F, t, -p), -159.64 (2F, t, -m). <sup>13</sup>C{<sup>19</sup>F} NMR [CDCl<sub>3</sub>]: δ = 109.31 (1C, s, -*ipso*C), 141.37 (1C, s, -m), 146.77 (2C, s, -p), 153.55 (2C, s, -o).

Pentafluorophenyl-trichloro-silane was obtained by the reaction of Pentafluorophenyl-triethoxy-silane (6.86g, 20.8 mmol), SOCl<sub>2</sub> (0.3 l), and some Pyridinium hydrochloride in a glass ampoule equipped with a magnetic stirrer.<sup>[103]</sup> The ampoule was sealed and the mixture was stirred and refluxed at 80 °C for 12 h, and to ensure completeness of the

reaction, refluxing for 24 more hours at 100 °C was needed. After opening the reaction vessel inside the glove box and pumping off the excess solvent, a mixture of compounds ((C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>Si(Cl)<sub>3-n</sub> n = 1 and 2 from <sup>19</sup>F NMR) containing mainly (C<sub>6</sub>F<sub>5</sub>)SiCl<sub>3</sub> remained in the ampoule. This mixture was treated as in **3.2.6**, the ampoule was evacuated between -30 °C and -10 °C over a period of 6 hours to give a colorless liquid in the -196 °C trap identified as (C<sub>6</sub>F<sub>5</sub>)SiF<sub>3</sub>. <sup>19</sup>F NMR [CDCl<sub>3</sub>]: δ = -128.1 (2F, d, -o), -146.6 (1F, t, -p), -162.5 (2F, t, -m), -137.6 (3F, s, -SiF<sub>3</sub>). <sup>13</sup>C{<sup>19</sup>F} NMR [CDCl<sub>3</sub>]: δ = 94.6 (1C, s, -*ipso*C), 137.6 (1C, s, -m), 145.4 (2C, s, -p), 149.8 (2C, s, -o).

### 3.2.8 (C<sub>6</sub>F<sub>5</sub>)Sn(CH<sub>3</sub>)<sub>3</sub>

Trimethyl-pentafluorophenyl-tin was prepared by the reaction of (CH<sub>3</sub>)<sub>3</sub>SnCl and C<sub>6</sub>F<sub>5</sub>MgBr<sup>[109]</sup> using literature procedures.<sup>[105,106]</sup> The only modification to the procedure was the use of (CH<sub>3</sub>)<sub>3</sub>SnCl instead of (CH<sub>3</sub>)<sub>3</sub>SnBr since only the former was available in stock for use. To a previously dried 3-necked flask equipped with a reflux condenser Bromopentafluorobenzene (40.5 g, 164 mmol), magnesium turnings (4g, 165 mmol) and 100 ml diethyl ether were added and stirred. The reaction mixture was refluxed for 24 hours after which hexane was added to precipitate the magnesium salts. The oily brown solution was filtered and ¾ of the solvent were pumped off under vacuum. 25 ml of Et<sub>2</sub>O were added and the solution was transferred to a 3-necked flask equipped with a reflux condenser. The mixture was stirred and trimethyltinchloride (15.35g, 77 mmol) in diethyl ether (25 ml) was added. The reaction mixture was refluxed for 72 h after which 30 ml of a 10% aqueous NH<sub>4</sub>Cl and 15 ml more of Et<sub>2</sub>O were added. The mixture was stirred for 12 h and the organic layer was transferred to a new flask. 100 ml more of diethyl ether and 30 ml more of 10% aqueous NH<sub>4</sub>Cl were used to wash the flask. Both organic phases were combined and were dried with MgSO<sub>4</sub>. The organic phase was filtered and the flask containing it was evacuated at room temperature for 4 h. A <sup>19</sup>F NMR of the trap showed signals corresponding to a mixture of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, C<sub>6</sub>F<sub>5</sub>Br and (C<sub>6</sub>F<sub>5</sub>)Sn(CH<sub>3</sub>)<sub>3</sub>. An <sup>19</sup>F NMR of the remaining liquid in the flask showed very little traces of the desired compound and lots of impurities. It was discarded immediately.



Fractional distillation of the liquid mixture at 30 mbar afforded two main portions which contained the desired material (yield can be estimated to be less than 5%).  $^{19}\text{F}$  NMR [ $\text{CDCl}_3$ ]:  $\delta = -122.2$  (2F, m, *-o*),  $-153.5$  (1F, m, *-p*),  $-161.3$  (2F, m, *-m*).  $^{13}\text{C}\{^{19}\text{F}\}$  NMR [ $\text{CDCl}_3$ ]:  $\delta = 110.8$  (1C, s, *-ipsoC*),  $136.8$  (1C, s, *-m*),  $141.5$  (2C, s, *-p*),  $148.7$  (2C, s, *-o*),  $-7.6$  (3C, q,  $-\text{CH}_3$ )

### 3.2.9 Hg(SCF<sub>3</sub>)<sub>2</sub>

Bis-(trifluoromethylthio)-mercury was prepared successfully from the reaction of  $\text{HgF}_2$ <sup>[107]</sup> and  $\text{CS}_2$  like described in the literature.<sup>[108]</sup> Mercury (II) fluoride (12.4 g, 52.0 mmol) and carbon disulfide ( $\approx 6.5$  ml, 108 mmol) were heated at 250 °C for 4 h in a metal autoclave. After cooling to room temperature, the carbon disulfide solution of the mercury salt was separated from mercury (II) sulfide by filtration. The solvent was pumped off and the low melting solid residue remaining in the flask was heated with an air-gun and recovered as a light brown crystalline material in another flask. 14.7g (70% yield) of the material identified as  $\text{Hg}(\text{SCF}_3)_2$  were obtained.  $^{19}\text{F}$  NMR [ $\text{CH}_2\text{Cl}_2/\text{AcetD}$ ]:  $\delta = -23.3$  (6F, s,  $-\text{CF}_3$ ).  $^{13}\text{C}\{^{19}\text{F}\}$  NMR [ $\text{CH}_2\text{Cl}_2/\text{AcetD}$ ]:  $\delta = 132.9$  (2C, s,  $-\text{CF}_3$ ).

### 3.2.10 Tungsten pentafluoride (2,2,2-trifluoroethoxide), $\text{F}_5\text{W}(\text{OCH}_2\text{CF}_3)$

A mixture of  $(\text{CF}_3\text{CH}_2\text{O})\text{Si}(\text{CH}_3)_3$  (1.590 g, 9.23 mmol) with a few drops of 2,2,2-trifluoroethanol was added into a previously dried PFA tube equipped with a magnetic stirrer. An excess of  $\text{WF}_6$  (7.41 g, 24.91 mmol) was condensed inside. The reaction vessel was kept at  $-90$  °C. The temperature was raised up to  $-30$  °C over a period of 3 h while the mixture was being stirred. At this point a light pink solution was observed. The mixtures was kept at  $-30$  °C and stirred for 1 more hour. The PFA tube was kept between  $-40$  °C and  $-30$  °C while it was evacuated for 5 h. 3.313 g (95% yield) of transparent liquid, highly sensitive to moisture and slightly volatile at room temperature, remained inside the tube. m.p.  $-55.5$  °C;  $^{19}\text{F}$  NMR [ $\text{CDCl}_3$  ext.]:  $\delta = 129.2$  (4F, d,  $^2J_{\text{FF}} = 64.0$  Hz,  $F_{\text{eq.}}$ ),  $107.5$  (1F, q,  $^2J_{\text{FF}} = 66.3$  Hz,  $F_{\text{ax.}}$ ),  $-75.6$  (3F, s,  $-\text{CF}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  [ $\text{CDCl}_3$  ext.]:  $\delta = 121.4$  (1C, q,  $^1J_{\text{CF}} = 278.9$  Hz,  $-\text{CF}_3$ ),  $76.7$  (1C, q,  $^2J_{\text{CF}} = 40.2$  Hz,  $-\text{CH}_2-$ ). Raman:  $\nu = 3022(4)$ ,  $2971(14)$ ,  $2864(1)$ ,  $2772(1)$ ,  $1437(12)$ ,  $1395(5)$ ,  $1279(15)$ ,  $1145(38)$ ,  $950(7)$ ,  $841(41)$ ,  $732(100)$ ,  $638(16)$ ,  $618(41)$ ,  $528(29)$ ,  $360(28)$ ,  $306(59)$ ,  $247(12)$ ,  $187(9)$ ,  $123(33)$   $\text{cm}^{-1}$ . Elemental analysis: C 6.93% H 0.65%, calcd C 6.36%, H 0.53%.

**3.2.11 Molybdenum pentafluoride (2,2,2-trifluoroethoxide),  $F_5Mo(OCH_2CF_3)$** 

A mixture of  $(CF_3CH_2O)Si(CH_3)_3$  (0.901 g, 5.23 mmol) with a few drops of 2,2,2-trifluoroethanol was added into a previously dried PFA tube equipped with a magnetic stirrer. An excess of  $MoF_6$  (2.779 g, 13.24 mmol) was condensed inside. At  $-78\text{ }^\circ\text{C}$  various colors (yellow, light brown, light green) were observed at the contact surface between the two reactants. The mixture was kept and stirred at  $-50\text{ }^\circ\text{C}$  for 2 h. The PFA tube with the dark brown mixture was evacuated between  $-75\text{ }^\circ\text{C}$  and  $-60\text{ }^\circ\text{C}$  for 3 h. Three more hours at  $-30\text{ }^\circ\text{C}$  of evacuation were needed to pump off all unreacted  $MoF_6$ . 1.432 g (94.4% yield of a light yellow liquid, very moisture sensitive and slightly volatile at room temperature, remained inside the tube. m.p.  $-31.0\text{ }^\circ\text{C}$ ;  $^{19}\text{F}$  NMR [ $CDCl_3$  ext.]:  $\delta=$  234.8 (4F, d,  $^2J_{\text{FF}} = 82.4\text{ Hz}$ ,  $F_{\text{eq}}$ ), 207.5 (1F, q,  $^2J_{\text{FF}} = 87.7\text{ Hz}$ ,  $F_{\text{ax}}$ ),  $-71.1$  (3F, s,  $-CF_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  [ $CDCl_3$  ext.]:  $\delta=$  122.9 (1C, q,  $^1J_{\text{CF}} = 280.13\text{ Hz}$ ,  $-CF_3$ ), 84.8 (1C, q,  $^2J_{\text{CF}} = 39.98\text{ Hz}$ ,  $-CH_2-$ ). Raman:  $\nu =$  30.10(6), 2953(21), 2838(1), 2747(1), 1424(14), 1382(14), 1267(19), 1098(82), 944(8), 840(44), 701(100), 641(41), 608(65), 530(45), 383(41), 357(22), 324(66), 302(56), 246(21), 172(18), 122(56)  $\text{cm}^{-1}$ . Elemental analysis: C 8.73%, H 0.76%, calcd C 8.28%, H 0.69%.

**3.2.12 Molybdenum bis(2,2,2 trifluoroethoxide) tetrafluoride,  $cis-(CF_3CH_2O)_2MoF_4$** 

In an attempt to synthesize  $(CF_3CH_2O)MoF_5$  as described in the literature<sup>[28]</sup> a mixture of compounds with the molecular formula  $(CF_3CH_2O)_nMF_{6-n}$ ,  $n = 1, 2,$  and  $3$  (as shown by the  $^{19}\text{F}$  NMR) was obtained. After standing for a few days at room temperature, some yellow crystals were observed on the walls of the reaction flask. The crystals were suitable for X-ray diffraction (see tables 20-23). The crystal structure obtained was  $cis-(CF_3CH_2O)_2MoF_4$ . Attempts to crystallize the *trans*-derivative or the other higher members of the series from this mixture failed, and no other substance could be isolated.  $^{19}\text{F}$  NMR [ $CDCl_3$  ext]: 171.3 (2F,t, $^2J_{\text{FF}} = 91.5\text{ Hz}$ ), 151.9 (2F,t, $^2J_{\text{FF}} = 91.5\text{ Hz}$ ),  $-74.6$  (3F,s).

**Table 20.** Crystallographic data for *cis*-(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>MoF<sub>4</sub>

Compound	<i>cis</i> -(CF <sub>3</sub> CH <sub>2</sub> O) <sub>2</sub> MoF <sub>4</sub>
Description	Yellow plates
Empirical formula	C <sub>4</sub> H <sub>4</sub> F <sub>10</sub> Mo O <sub>2</sub>
Formula weight	370.01 g/mol
Temperature	-100 °C
Wavelength	71.073 pm
Crystal system, space group	Triclinic, P $\bar{1}$
Unit cell dimensions	a = 1008.63(12) pm $\alpha$ = 73.499(2)° b = 1041.28(12) pm $\beta$ = 74.614(2)° c = 1085.93(13) pm $\gamma$ = 89.603(2)°
Volume	1.4052(2) nm <sup>3</sup>
Z	4
Calculated density	2.337 Mg/m <sup>3</sup>
Absorption coefficient	1.380 mm <sup>-1</sup>
F(000)	704
Crystal size	0.1 x 0.3 x 0.3 mm <sup>3</sup>
Theta range for data collection	2.03° to 30.57°
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected / unique	13077 / 6340 [R(int) = 0.0495]
Completeness to 2theta = 30.57°	98.1%
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6340 / 0 / 308
Goodness-of-fit on F <sup>2</sup>	0.953 < 41
Final R indices [I > 2sigma(I)]	R1 = 0.0674, wR2 = 0.1829
R indices (all data)	R1 = 0.0993, wR2 = 0.2065
Largest diff. peak and hole	5.067 and -1.049 e. Å <sup>-3</sup>

**Table 21.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for *cis*-(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>MoF<sub>4</sub>. U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

Atom	x	y	z	U(eq)
Mo(1)	9796(1)	7241(1)	837(1)	27(1)
F(13)	10990(4)	5895(4)	767(5)	62(1)
F(14)	8691(4)	8660(4)	644(5)	63(1)
F(11)	11226(4)	8335(4)	-476(4)	65(1)
F(12)	9320(5)	6942(5)	-594(4)	71(1)
O(11)	10380(4)	7763(4)	2053(4)	43(1)
O(12)	8466(4)	6009(4)	1958(5)	42(1)
C(11)	11226(7)	8749(8)	2210(7)	56(2)
C(12)	10488(7)	9190(7)	3385(6)	48(2)
C(13)	7625(7)	4888(6)	2070(7)	47(2)
C(14)	7570(9)	3819(8)	3320(7)	60(2)
F(15)	9308(7)	9655(7)	3274(7)	111(2)
F(16)	11231(6)	10128(6)	3537(6)	98(2)
F(17)	10191(7)	8216(6)	4491(5)	102(2)
F(18)	7086(10)	4149(7)	4375(5)	158(4)
F(19)	8813(8)	3473(8)	3333(11)	76(5)
F(110)	6812(6)	2755(5)	3412(5)	95(2)
Mo(2)	15267(1)	7747(1)	-899(1)	28(1)
F(21)	14036(4)	6342(4)	-658(5)	62(1)
F(22)	16436(4)	9099(4)	-876(5)	60(1)
F(23)	14047(4)	8059(5)	572(4)	68(1)
F(24)	16032(4)	6659(4)	357(4)	59(1)
O(21)	16514(4)	7255(4)	-2159(5)	44(1)
O(22)	14523(4)	8993(4)	-1969(4)	41(1)
C(21)	17596(8)	6414(8)	-2395(7)	55(2)
C(22)	17369(8)	5676(7)	-3343(7)	49(2)
C(23)	13832(6)	10195(6)	-2036(6)	42(1)
C(24)	14508(7)	11252(7)	-3298(6)	49(2)
F(25)	18372(6)	4891(6)	-3577(6)	102(2)
F(26)	16201(6)	4977(6)	-2917(7)	103(2)
F(27)	17384(6)	6525(5)	-4507(5)	82(2)
F(28)	15853(5)	11439(6)	-3434(7)	101(2)
F(29)	13952(6)	12398(4)	-3298(5)	90(2)
F(210)	14411(6)	10988(6)	-4365(5)	90(2)

**Table 22.** Bond lengths [pm] and angles [°] for *cis*-(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>MoF<sub>4</sub>

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Mo(1)-O(12)	178.8(4)
Mo(1)-O(11)	179.2(4)
Mo(1)-F(14)	184.1(4)
Mo(1)-F(13)	184.7(4)
Mo(1)-F(12)	184.8(4)
Mo(1)-F(11)	184.9(4)
O(11)-C(11)	141.4(7)
O(12)-C(13)	140.5(7)
C(11)-C(12)	148.9(9)
C(12)-F(17)	129.8(9)
C(12)-F(15)	130.3(8)
C(12)-F(16)	130.9(8)
C(13)-C(14)	147.8(9)
C(14)-F(18)	126.2(10)
C(14)-F(19)	130.5(10)
C(14)-F(110)	131.6(9)
Mo(2)-O(22)	178.6(4)
Mo(2)-O(21)	178.7(4)
Mo(2)-F(21)	184.0(4)
Mo(2)-F(24)	184.7(4)
Mo(2)-F(23)	184.9(4)
Mo(2)-F(22)	185.3(4)
O(21)-C(21)	141.1(7)
C(21)-C(22)	150.9(9)
O(22)-C(23)	142.1(7)
C(22)-F(26)	129.0(9)
C(22)-F(25)	131.4(8)
C(22)-F(27)	131.8(8)
C(23)-C(24)	148.8(8)
C(24)-F(210)	129.2(8)
C(24)-F(29)	131.5(8)
C(24)-F(28)	133.5(8)
O(12)-Mo(1)-O(11)	98.3(2)
O(12)-Mo(1)-F(13)	89.1(2)
O(12)-Mo(1)-F(14)	96.3(2)
O(11)-Mo(1)-F(13)	94.9(2)
O(11)-Mo(1)-F(14)	90.6(2)
F(14)-Mo(1)-F(13)	171.8(2)
O(12)-Mo(1)-F(12)	89.7(2)
F(13)-Mo(1)-F(12)	88.0(2)
O(12)-Mo(1)-F(11)	171.3(2)
O(11)-Mo(1)-F(11)	88.5(2)
O(11)-Mo(1)-F(12)	171.5(2)

Continuation table 22.

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F(14)-Mo(1)-F(12)	85.8(2)
F(14)-Mo(1)-F(11)	89.1(2)
F(13)-Mo(1)-F(11)	84.9(2)
F(12)-Mo(1)-F(11)	83.7(2)
C(11)-O(11)-Mo(1)	143.2(4)
C(13)-O(12)-Mo(1)	144.1(4)
O(11)-C(11)-C(12)	109.4(5)
F(17)-C(12)-F(15)	105.1(7)
F(17)-C(12)-F(16)	107.6(6)
F(15)-C(12)-F(16)	108.2(7)
F(17)-C(12)-C(11)	112.7(7)
F(15)-C(12)-C(11)	112.1(7)
F(16)-C(12)-C(11)	110.9(6)
O(12)-C(13)-C(14)	110.4(6)
F(18)-C(14)-F(19)	105.9(9)
F(18)-C(14)-F(110)	107.1(7)
F(19)-C(14)-F(110)	108.7(8)
F(18)-C(14)-C(13)	114.8(8)
F(19)-C(14)-C(13)	109.7(7)
F(110)-C(14)-C(13)	110.5(6)
O(22)-Mo(2)-O(21)	98.2(2)
O(22)-Mo(2)-F(21)	96.4(2)
O(21)-Mo(2)-F(21)	91.9(2)
O(22)-Mo(2)-F(24)	170.75(19)
O(21)-Mo(2)-F(24)	88.44(19)
F(21)-Mo(2)-F(24)	89.8(2)
O(22)-Mo(2)-F(23)	89.67(19)
O(21)-Mo(2)-F(23)	172.04(19)
F(21)-Mo(2)-F(23)	86.1(2)
F(24)-Mo(2)-F(23)	83.8(2)
O(22)-Mo(2)-F(22)	88.4(2)
O(21)-Mo(2)-F(22)	94.1(2)
F(21)-Mo(2)-F(22)	171.7(2)
F(24)-Mo(2)-F(22)	84.67(19)
F(23)-Mo(2)-F(22)	87.2(2)
C(21)-O(21)-Mo(2)	144.7(4)
C(23)-O(22)-Mo(2)	142.3(4)
O(21)-C(21)-C(22)	109.5(5)
F(26)-C(22)-F(25)	109.5(7)
F(26)-C(22)-F(27)	106.3(7)
F(25)-C(22)-F(27)	106.4(6)
F(26)-C(22)-C(21)	113.2(6)
F(25)-C(22)-C(21)	110.3(6)
F(27)-C(22)-C(21)	110.9(6)

Continuation table 22.

O(22)-C(23)-C(24)	110.3(5)
F(210)-C(24)-F(29)	106.9(6)
F(210)-C(24)-F(28)	106.3(7)
F(29)-C(24)-F(28)	108.1(7)
F(210)-C(24)-C(23)	114.2(7)
F(29)-C(24)-C(23)	110.1(6)
F(28)-C(24)-C(23)	111.0(6)

**Table 23.** Anisotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for *cis*-( $\text{CF}_3\text{CH}_2\text{O}$ ) $\text{MoF}_4$ .

The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [ h^2 a^{*2}$

$U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Mo(1)	26(1)	22(1)	36(1)	-11(1)	-9(1)	0(1)
F(13)	59(2)	51(2)	76(3)	-23(2)	-14(2)	27(2)
F(14)	56(2)	48(2)	87(3)	-22(2)	-22(2)	25(2)
F(11)	55(2)	61(3)	60(3)	-4(2)	3(2)	-25(2)
F(12)	77(3)	93(4)	59(3)	-37(3)	-29(2)	-12(3)
O(11)	43(2)	42(2)	49(2)	-21(2)	-12(2)	-6(2)
O(12)	38(2)	39(2)	49(2)	-16(2)	-8(2)	-12(2)
C(11)	48(4)	66(5)	58(4)	-38(4)	2(3)	-24(3)
C(12)	50(4)	57(4)	40(3)	-24(3)	-7(3)	0(3)
C(13)	59(4)	35(3)	47(3)	-2(3)	-24(3)	-22(3)
C(14)	72(5)	56(5)	44(4)	0(3)	-21(4)	-14(4)
F(15)	107(5)	131(5)	143(6)	-93(5)	-59(4)	67(4)
F(16)	113(4)	104(4)	91(4)	-72(4)	0(3)	-40(3)
F(17)	157(5)	99(4)	37(2)	-10(3)	-13(3)	-30(4)
F(18)	272(10)	128(6)	40(3)	-32(3)	26(4)	-115(6)
F(19)	109(6)	121(6)	240(11)	76(6)	-90(7)	0(5)
F(110)	157(5)	49(3)	65(3)	5(2)	-27(3)	-49(3)
Mo(2)	28(1)	21(1)	39(1)	-11(1)	-12(1)	3(1)
F(21)	55(2)	44(2)	88(3)	-17(2)	-26(2)	-18(2)
F(22)	64(3)	42(2)	75(3)	-15(2)	-25(2)	-19(2)
F(23)	62(3)	88(3)	53(2)	-29(2)	-6(2)	26(2)
F(24)	64(3)	53(2)	61(3)	-3(2)	-33(2)	15(2)
O(21)	40(2)	44(3)	56(3)	-22(2)	-17(2)	14(2)
O(22)	43(2)	33(2)	51(3)	-12(2)	-20(2)	10(2)
C(21)	64(4)	70(5)	62(4)	-48(4)	-38(4)	43(4)
C(22)	61(4)	52(4)	45(4)	-23(3)	-21(3)	14(3)
C(23)	39(3)	32(3)	46(3)	-3(2)	-5(3)	13(2)

Continuation table 23.

C(24)	56(4)	43(4)	38(3)	1(3)	-11(3)	6(3)
F(25)	142(5)	111(4)	108(4)	-85(4)	-71(4)	88(4)
F(26)	103(4)	84(4)	122(5)	-58(4)	-1(4)	-36(3)
F(27)	126(4)	78(3)	49(3)	-21(2)	-32(3)	24(3)
F(28)	60(3)	89(4)	115(5)	30(3)	-21(3)	-26(3)
F(29)	134(5)	39(2)	81(3)	6(2)	-31(3)	26(3)
F(210)	135(5)	91(4)	46(3)	-20(3)	-30(3)	31(3)

### 3.2.13 Tungsten pentafluoride pentafluorophenoxide, $F_5W(OC_6F_5)$

Attempts to synthesize a pure sample according to reported procedures<sup>[31,33,34]</sup> were all unsuccessful. Even modifications on the procedure like the use of a solvent ( $CH_2Cl_2$ ,  $CCl_3F$ ), higher reaction temperatures and longer reaction times gave either unreacted  $WF_6$  and  $(C_6F_5O)Si(CH_3)_3$  or a mixture of compounds with molecular formula  $F_{6-n}W(OC_6F_5)_n$ ,  $n = 1, 2, 3$  as shown by the  $^{19}F$  NMR. No purification of the desired compound was achieved.

A solution of  $(C_6F_5O)Si(CH_3)_3$  (3.610 g, 14.09 mmol) and  $C_6F_5OH$  (0.099g, 0.54 mmol) were given into a previously dried PFA tube equipped with a stainless steel valve. An excess of  $WF_6$  (12.119 g, 40.69 mmol) was condensed into the tube. The reaction mixture was stirred at  $-5\text{ }^\circ C$  for 7 days. The reaction vessel was evacuated at  $-45\text{ }^\circ C$  for 4 h. Two more hours of evacuation at  $-30\text{ }^\circ C$  were needed to pump off all the remaining  $WF_6$ . A red-orange solid (6.44 g) remained inside the tube.  $CCl_3F$  at  $-30\text{ }^\circ C$  was added with a Teflon tube to the reaction vessel, most of the material was insoluble at this temperature, but at  $-15\text{ }^\circ C$  almost everything dissolved. The solution was transferred at  $-15\text{ }^\circ C$  to a new PFA tube via a Teflon tube, and  $^{19}F$  and  $^{13}C$  NMR of the sample were carried out at the same temperature showing signals of only one kind of  $-OC_6F_5$  compound. The PFA tube was evacuated at  $-15\text{ }^\circ C$  for 6 h. A red solid material 6.081 g (89.9% yield), extremely reactive towards moisture, remained in the tube. m.p.  $-1.5\text{ }^\circ C$ ;  $^{19}F$  NMR (376 MHz,  $20\text{ }^\circ C$ ) [ $CDCl_3$  ext.]:  $\delta = 144.3$  (4F, d,  $^2J_{FF} = 64.3$  Hz,  $^1J_{WF} = 40$  Hz,  $F_{eq.}$ ),  $136.6$  (1F, q,  $^2J_{FF} = 65.6$  Hz,  $F_{ax.}$ ),  $-150.6$  (1F, t,  $^3J_{FF} = 18.5$  Hz,  $-p$ ),  $-151.7$  (2F, d,  $^3J_{FF} = 12$  Hz,  $-o$ ),  $-160.7$  (2F, t,  $^3J_{FF} = 17.0$  Hz,  $-m$ ).  $^{13}C\{^{19}F\}$  [ $CDCl_3$  ext.]:  $\delta = 143.2$  (1C, s,  $-C_4$ ),  $142.4$  (2C, s,  $-C_{2,6}$ ),  $137.0$  (2C, s,  $-C_{3,5}$ ),  $134.2$  (1C, s,  $-C_1$ ).  $^{19}F$  NMR (84.25 MHz,  $184\text{ }^\circ C$ ,



1.04 M) [CCl<sub>2</sub>DCCl<sub>2</sub>D]:  $\delta$ = 145.7 (5F, s,  $^1J_{WF}$  = 40 Hz). Raman:  $\nu$  = 1641(15), 1535(3), 1517(3), 1466(100), 1325(33), 1263(3), 118(31), 1160(4), 1051(18), 1041(22), 1018(5), 787(6), 765(33), 720(18), 714(27), 653(4), 641(6), 583(5), 501(15), 452(7), 423(13), 406(6), 377(9), 336(10), 307(9), 297(8), 280(20), 262(12), 224(6), 201(6), 185(6), 155(11), 120(8) cm<sup>-1</sup>. Elemental analysis: C 16.46%, calcd C 15.60%.

### 3.2.14 Molybdenum pentafluoride pentafluorophenoxide, F<sub>5</sub>Mo(OC<sub>6</sub>F<sub>5</sub>)

Into a previously dried PFA tube, equipped with a magnetic stirrer, MoF<sub>6</sub> (1.830 g, 8.72 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (1.160g, 13.82 mmol) were condensed. A solution of (C<sub>6</sub>F<sub>5</sub>O)Si(CH<sub>3</sub>)<sub>3</sub> (1.311 g, 5.12 mmol) and C<sub>6</sub>F<sub>5</sub>OH (0.069g, 0.37 mmol) was added drop wise with a syringe, while the reaction mixture was being stirred and kept at -20 °C. An additional amount of CH<sub>2</sub>Cl<sub>2</sub> (1.32g, 15.73 mmol) was dropped inside to wash down the inner walls of the tube. After stirring the dark purple solution for 2 weeks at -20 °C a black precipitate was observed. The PFA tube was evacuated first at -50 °C for 1 h and then at -20 °C for 5 h. 1.69g (82.5% yield) of a black solid crystalline material, extremely reactive to moisture, remained in the tube. m.p. 57.3 °C – 58 °C. Crystals suitable for X-ray diffraction were taken from this sample, see tables 24-27. <sup>19</sup>F NMR (-20 °C, 0.35 M) [Cl<sub>2</sub>CDCDCl<sub>2</sub>]:  $\delta$ = 254.5 (4F, d,  $^2J_{FF}$  = 82.0 Hz,  $F_{eq}$ ), 250.2 (1F, q,  $^2J_{FF}$  = 88.5 Hz,  $F_{ax}$ ), -134.9 (1F, t,  $^3J_{FF}$  = 20.0 Hz, -*p*), -140.8 (2F, d,  $^3J_{FF}$  = 15 Hz, -*o*), -154.9 (2F, t,  $^3J_{FF}$  = 18.5 Hz, -*m*). <sup>13</sup>C{<sup>19</sup>F} (-20 °C, 0.35 M) [Cl<sub>2</sub>CDCDCl<sub>2</sub>]:  $\delta$ = 147.2 (1C, s, -C<sub>4</sub>), 145.2 (2C, s, -C<sub>2,6</sub>), 136.8 (2C, s, -C<sub>3,5</sub>). Raman:  $\nu$  = 1636(25), 1507(6), 1424(45), 1397(49), 1380(15), 1320(77), 1183(57), 1039(75), 1017(21), 789(9), 732(100), 697(45), 669(60), 640(12), 622(10), 604(23), 580(40), 496(84), 447(12), 405(11), 384(23), 366(25), 353(20), 306(53), 290(48), 252(13), 226(14), 208(15), 196(16), 178(17), 156(12), 111(16) cm<sup>-1</sup>. Elemental analysis: C 18.34%, calcd C 19.27%.

**Table 24.** Crystallographic data for F<sub>5</sub>Mo(OC<sub>6</sub>F<sub>5</sub>).

Compound	F <sub>5</sub> Mo(OC <sub>6</sub> F <sub>5</sub> ).
Description	black needles.
Empirical formula	C <sub>6</sub> F <sub>10</sub> Mo O
Formula weight	374.00 g/mol
Temperature	-100 °C
Wavelength	71.073 pm
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /n
Unit cell dimensions	a = 647.63(14) pm    α = 90° b = 1256.6(3) pm    β = 91.400(4)° c = 1123.1(2) pm    γ = 90°
Volume	0.9137(3) nm <sup>3</sup>
Z	4
Calculated density	2.719 Mg/m <sup>3</sup>
Absorption coefficient	1.583 mm <sup>-1</sup>
F(000)	704
Crystal size	0.1 x 0.1 x 0.2 mm <sup>3</sup>
Theta range for data collection	2.43° to 30.58°
Index ranges	-9 ≤ h ≤ 9, -17 ≤ k ≤ 17, -16 ≤ l ≤ 16
Reflections collected / unique	11150 / 2802 [R(int) = 0.0457]
Completeness to 2theta = 30.58°	99.9%
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2802 / 0 / 163
Goodness-of-fit on F <sup>2</sup>	0.952 < 41
Final R indices [I > 2sigma(I)]	R1 = 0.0286, wR2 = 0.0615

Continuation table 24.

R indices (all data) R1 = 0.0480, wR2 = 0.0675

Largest diff. peak and hole 0.714 and -0.725 e. Å<sup>-3</sup>

**Table 25.** Atomic coordinates (  $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for  $\text{F}_5\text{Mo}(\text{OC}_6\text{F}_5)$ . U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Mo(1)	991(1)	9490(1)	7198(1)	20(1)
F(1)	3748(2)	9445(1)	7578(2)	34(1)
F(2)	-1789(2)	9402(1)	6895(2)	32(1)
F(3)	1009(3)	8023(1)	7262(2)	34(1)
F(4)	1546(3)	9311(1)	5605(1)	30(1)
F(5)	464(3)	9595(1)	8784(1)	36(1)
F(11)	-1970(3)	12416(1)	6539(2)	33(1)
F(12)	-1464(3)	13970(1)	4889(2)	38(1)
F(13)	1985(3)	14019(1)	3606(2)	41(1)
F(14)	5058(3)	12601(1)	4002(2)	40(1)
F(15)	4589(3)	11055(1)	5665(2)	36(1)
O	1014(3)	10915(2)	6879(2)	25(1)
C(1)	1302(4)	11709(2)	6118(2)	22(1)
C(2)	-239(4)	12475(2)	5930(2)	23(1)
C(3)	11(4)	13254(2)	5092(2)	26(1)
C(4)	1790(4)	13281(2)	4440(2)	27(1)
C(5)	3351(4)	12551(2)	4630(2)	26(1)
C(6)	3111(4)	11762(2)	5467(2)	24(1)

**Table 26.** Bond lengths [pm] and angles [°] for F<sub>5</sub>Mo(OC<sub>6</sub>F<sub>5</sub>).

---

Mo(1)-F(5)	182.66(17)
Mo(1)-F(1)	182.70(16)
Mo(1)-O	182.72(19)
Mo(1)-F(2)	182.73(16)
Mo(1)-F(3)	184.41(17)
Mo(1)-F(4)	184.72(16)
F(11)-C(2)	133.0(3)
F(12)-C(3)	132.8(3)
F(13)-C(4)	132.6(3)
F(14)-C(5)	132.8(3)
F(15)-C(6)	132.1(3)
O-C(1)	133.0(3)
C(1)-C(2)	139.8(4)
C(1)-C(6)	139.8(4)
C(2)-C(3)	137.1(4)
C(3)-C(4)	138.0(4)
C(4)-C(5)	137.8(4)
C(5)-C(6)	137.7(4)
F(5)-Mo(1)-F(1)	88.80(8)
F(5)-Mo(1)-O	97.06(8)
F(1)-Mo(1)-O	93.62(8)
F(5)-Mo(1)-F(2)	88.81(8)
F(1)-Mo(1)-F(2)	174.10(8)
O-Mo(1)-F(2)	92.03(8)
F(5)-Mo(1)-F(3)	92.07(8)
F(1)-Mo(1)-F(3)	87.43(8)
O-Mo(1)-F(3)	170.83(8)
F(2)-Mo(1)-F(3)	87.26(8)
F(5)-Mo(1)-F(4)	177.15(8)
F(1)-Mo(1)-F(4)	90.60(8)
O-Mo(1)-F(4)	85.76(8)
F(2)-Mo(1)-F(4)	91.53(7)
F(3)-Mo(1)-F(4)	85.11(7)
C(1)-O-Mo(1)	149.78(18)
O-C(1)-C(2)	120.2(2)
O-C(1)-C(6)	120.2(2)
C(2)-C(1)-C(6)	119.5(2)
F(11)-C(2)-C(3)	120.5(2)
F(11)-C(2)-C(1)	119.5(2)
C(3)-C(2)-C(1)	119.9(3)
F(12)-C(3)-C(2)	120.3(3)
F(12)-C(3)-C(4)	120.0(3)
C(2)-C(3)-C(4)	119.7(3)

Continuation table 26.

F(13)-C(4)-C(5)	119.5(3)
F(13)-C(4)-C(3)	119.1(3)
C(5)-C(4)-C(3)	121.3(3)
F(14)-C(5)-C(6)	120.4(3)
F(14)-C(5)-C(4)	120.2(3)
C(6)-C(5)-C(4)	119.4(3)
F(15)-C(6)-C(5)	120.4(3)
F(15)-C(6)-C(1)	119.6(2)
C(5)-C(6)-C(1)	120.0(3)

**Table 27.** Anisotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Mo(1)	21(1)	21(1)	18(1)	0(1)	0(1)	0(1)
F(1)	25(1)	40(1)	36(1)	3(1)	-6(1)	1(1)
F(2)	21(1)	37(1)	37(1)	-2(1)	-1(1)	-1(1)
F(3)	44(1)	22(1)	38(1)	2(1)	0(1)	0(1)
F(4)	34(1)	33(1)	22(1)	-3(1)	2(1)	2(1)
F(5)	45(1)	41(1)	21(1)	0(1)	2(1)	-2(1)
F(11)	26(1)	33(1)	39(1)	1(1)	10(1)	2(1)
F(12)	37(1)	31(1)	48(1)	7(1)	2(1)	8(1)
F(13)	52(1)	33(1)	38(1)	11(1)	6(1)	-4(1)
F(14)	31(1)	46(1)	42(1)	2(1)	16(1)	-3(1)
F(15)	26(1)	36(1)	46(1)	2(1)	4(1)	7(1)
O	28(1)	23(1)	22(1)	-1(1)	1(1)	1(1)
C(1)	25(1)	20(1)	22(1)	-3(1)	0(1)	-2(1)
C(2)	22(1)	23(1)	25(1)	-6(1)	4(1)	-3(1)
C(3)	27(2)	21(1)	30(1)	-4(1)	-2(1)	2(1)
C(4)	32(2)	23(1)	26(1)	1(1)	1(1)	-9(1)
C(5)	27(1)	27(1)	26(1)	-5(1)	5(1)	-6(1)
C(6)	23(1)	23(1)	28(1)	-6(1)	-1(1)	-2(1)

### 3.2.15 Tungsten pentafluoride-*tert*-(perfluoro)butoxide, $F_5W(OC(CF_3)_3)$

Into a previously dried PFA tube equipped with a magnetic stirrer 0.326 g (1.496 mmol) of  $LiOC(CF_3)_3$  were put inside. An excess of  $WF_6$  (1.83 g, 6.144 mmol) was condensed into the PFA tube and the mixture was stirred at room temperature for 4.5 days. A  $^{19}F$  NMR of the reaction mixture showed  $F_5W(OC(CF_3)_3)$  as the only product. The PFA tube was cooled down to  $-78\text{ }^\circ C$  and the excess of  $WF_6$  was pumped off over a period of 18 h. The PFA tube was warmed up to room temperature and evacuated for 12 more hours. A transparent liquid (0.47 g, 61.1 % yield) volatile at room temperature and slightly reactive towards moisture, was recovered in a  $-196\text{ }^\circ C$  trap. m.p.  $-59\text{ }^\circ C$ .  $^{19}F$  NMR ( $0\text{ }^\circ C$ ) [ $Cl_2CDCDCl_2$ ]:  $\delta = 150.0$  (4F, d,  $^2J_{FF} = 64.8$  Hz,  $F_{eq.}$ ),  $157.5$  (1F, q,  $^2J_{FF} = 65.18$  Hz,  $F_{ax.}$ ),  $-74.8$  (9F, s,  $-CF_3$ ).  $^{13}C\{^{19}F\}$  ( $0\text{ }^\circ C$ ) [ $Cl_2CDCDCl_2$ ]:  $\delta = 118.2$  (3C, s,  $-CF_3$ ),  $85.8$  (1C, s,  $-OC$ ). Raman:  $\nu = 1316(10)$ ,  $1273(10)$ ,  $1229(5)$ ,  $1177(23)$ ,  $986(2)$ ,  $859(12)$ ,  $761(88)$ ,  $735(100)$ ,  $674(10)$ ,  $659(14)$ ,  $539(16)$ ,  $426(4)$ ,  $333(49)$ ,  $305(67)$ ,  $284(55)$ ,  $241(19)$ ,  $134(39)$ ,  $113(24)$ .

## 3.3 $^{19}F$ NMR spectra and gNMR<sup>[67]</sup> simulations

The most important and relevant aspects of the  $^{19}F$  NMR measurements and simulations are given in detail here.

### 3.3.1 The measurements

The  $^{19}F$  NMR spectra used for the simulations were recorded for each sample as follows:

$F_5W(OCH_2CF_3)$ : Sweep width 16925.05 Hz, Offset 37597.66 Hz, Data points 5546, Digital resolution 3.05 Hz.

$F_5W(OC_6F_5)$ : Sweep width 3008.18 Hz, Offset 53391.94 Hz, Data points 21331, Digital resolution 0.14 Hz.

$F_5W(OC(CF_3)_3)$ : Sweep width 5264.14 Hz, Offset 55271.93 Hz, Data points 37328, Digital resolution 0.14 Hz.

$F_5Mo(OCH_2CF_3)$ : Sweep width 20684.81 Hz, Offset 33837.89 Hz, Data points 6778, Digital resolution 3.05 Hz.

$F_5Mo(OC_6F_5)$  in  $C_2D_2Cl_4$ : Sweep width 8272.34 Hz, Offset 88359.85 Hz, Data points 23095, Digital resolution 0.36 Hz.

$F_5Mo(OC_6F_5)$  in  $C_2D_2Cl_4$ : Sweep width 7520.15 Hz, Offset 90239.97 Hz, Data points 20995, Digital resolution 0.36 Hz.

No manual shimming of the lock signal was carried out, the machine was shimmed automatically. No weight function correction for the FID's was employed for most of the spectra in order to keep the spectra as genuine as possible. Only in some of the spectra at high temperatures ( $\geq 100$  °C) a lorentzian function correction was employed to minimize the noise to signal ratio. No baseline correction function was employed.

Phasing the A and  $B_4$  parts of the experimental spectra was tried first with both signals in the same window. In many cases a perfect phase could not be achieved for both signals at the same time, therefore a compromise had to be made and the spectrum with the best possible phase for both signals was used for the simulations.

### 3.3.2 gNMR<sup>[67]</sup> simulations

The following procedure was employed for generating all the simulated spectra.

The best resolved low temperature experimental spectrum was loaded into the gNMR program in the "spectrum window". Approximate values for: chemical shifts of the A- and  $B_4$ - parts, coupling constants  ${}^2J_{Fax-Feq}$ ,  ${}^1J_{Fax-W}$  and  ${}^1J_{Feq-W}$  (for the tungsten molecules), and half line widths were given in the "molecule window". The  ${}^2J_{Feq-Feq}$  was not seen in the experimental spectra because of the magnetic equivalence in the  $B_4$ -part, therefore it was set and kept at 0 Hz the whole time, even though it might not be necessarily 0. The desired exchange mechanism was given with the corresponding permutation operators in the "exchange window". The rate constant ( $k$ ) was set to 0. A first spectrum was generated in the "spectrum window".

A total iteration of all the variables to optimize them is meaningless. The chemical shifts of the two signals were not iterated, rather they were changed manually until the position of the A- and B<sub>4</sub>- parts of the experimental and simulated spectra were matched exactly in the “spectrum window”.

Each of the other variables in the “molecule window” has to be optimized separately and in the following manner: If a variable is open (no “-“ sign in front of it) it will be optimized, if the variable is closed (“-“ sign in front of it) it will not be optimized. Close all variables except the line width of the A-part, choose a window  $\approx 3$  times as broad as the A-part in the “spectrum window” in which the signal is placed in the center of it, iterate the variable. Close this variable and open the variables for the line width of the B<sub>4</sub>-part, choose again a window  $\approx 3$  times as broad as the B<sub>4</sub>-part in the “spectrum window” with the signal in the center of it, iterate. Repeat this procedure until the best line width for both signals is obtained. Small manual changes of the value of these variables will give a better result.

Do the same procedure for  ${}^2J_{\text{Fax-Feq}}$ , and  ${}^1J_{\text{F-W}}$  ( in the case of the tungsten molecules). If the A-part is well resolved it is better to optimize  ${}^2J_{\text{Fax-Feq}}$  using the A-part, if not the optimization of such variable can be done with the B-part. The optimized parameters are kept constant for the whole simulation.

A first series of spectra is obtained with the following procedure: Vary the rate constant and obtain a new simulated spectrum. Zoom in the A-part (choose again a window  $\approx 3$  times as broad as the A-part in the “spectrum window” with the signal in the center of it) and vary the rate constant until experimental and simulated signal are visually matched as best as possible (no least-square analysis is performed due to the non-lorentzian type signals). Zoom in the B<sub>4</sub>-part and compare the two spectra. Most probably the rate constant will have to be modified again. Repeat this procedure until experimental and simulated spectra of both parts visually match as good as possible. Generating a simulated spectrum that matches the experimental one as good as possible might take some 30 min.



Load into the program the next experimental spectrum to be simulated. Change the chemical shift of the A- and B<sub>4</sub>-parts of the simulated signals until they matched exactly the experimental ones (due to the intrinsic chemical shift of the signals experienced at a higher temperature). Vary the rate constant until the shape of both signals is matched as good as possible. Repeat this procedure until the best simulated spectrum is obtained. Do the same with the next temperatures that need to be simulated.

At some point, experimental and simulated spectra might not match as good as possible for a specific rate constant due to the fact that simulated spectra are a combination of optimized rate constants ( $k$ ) and line widths (which indeed vary and are not constant with the temperature). The following procedure was used to optimize these 2 variables: At this temperature where varying  $k$  does not produce the best possible match, vary the line width of the part(s) that is(are) not matched and  $k$  until experimental and simulated spectra have the highest similarity. Go back to the previous temperature and introduce the “new” value(s) of the line width(s) and do not vary the rate constant, simulate the spectra. If the visual match improved, repeat this procedure for all other lower temperatures. If not, vary the rate constant again until the spectra are similar, and then go back to the lower temperatures.

Compare all sets of simulated spectra and choose the best one of all of them. A linear regression of  $\ln\left(\frac{k}{T}\right)$  versus  $\frac{1}{T}$  at this point will not give the best fit. Still, do a linear regression and interpolate a new rate constant for each temperature. With these new values of  $k$  go back to gNMR and repeat the simulation for each temperature with a  $k$  value similar or close to the “new” one obtained from the linear regression. This is done because the simulated spectra are compared only visually to the experimental ones, therefore a wide range of  $k$  values can be used for a specific temperature (especially at high temperatures) which will produce simulated spectra that to the human eye appear almost the same. As an example, the rate constant determined for F<sub>5</sub>W(OC<sub>6</sub>F<sub>5</sub>) (at 51 °C) had a  $\pm 2 \text{ sec}^{-1}$  uncertainty, but at 130 °C it was  $\pm 100 \text{ sec}^{-1}$ .

Doing this procedure several times will improve in general the simulated spectra. At the end, a series of  $k$  values which are very close to the “theoretical”  $k$  values of the best

linear regression will produce the best series of simulated spectra.

### 3.4 $^{19}\text{F}$ NMR input parameters for the simulations in gNMR<sup>[67]</sup>

#### 3.4.1 $\text{F}_5\text{W}(\text{OCH}_2\text{CF}_3)$

Sample concentration: 1.52 M (in  $\text{C}_2\text{D}_2\text{Cl}_4$ ).  $^2J_{\text{Fax-Feq}} = 65.80$  Hz.  $^1J_{\text{W-Fa}} = 44.20$  Hz.

$^1J_{\text{W-Feq}} = 39.57$  Hz. Line width A part/B<sub>4</sub> part (Hz): 14/16.

Temperature (K)/  $\delta$  A-part (ppm)/  $\delta$  B<sub>4</sub>-part (ppm):

313/108.982/129.777; 323/109.671/130.12; 333/111.226/131.123; 343/111.900/131.365;  
353/112.458/131.438; 373/113.770/131.928; 393/115.275/470.

#### 3.4.2 $\text{F}_5\text{W}(\text{OC}_6\text{F}_5)$

Sample concentration: 1.035 M (in  $\text{C}_2\text{D}_2\text{Cl}_4$ ).  $^2J_{\text{Fax-Feq}} = 66.00$  Hz.  $^1J_{\text{W-Fa}} = 61.20$  Hz.

$^1J_{\text{W-Feq}} = 35.90$  Hz. Line width A part/B<sub>4</sub> part (Hz): 15/12.

Temperature (K)/  $\delta$  A-part (ppm)/  $\delta$  B<sub>4</sub>-part (ppm):

303/143.948/147.229; 324/144.925/147.588; 344/145.755/147.926;  
363/146.380/148.222; 383/147.135/148.535; 403/147.939/148.794.

#### 3.4.3 $\text{F}_5\text{W}(\text{OC}(\text{CF}_3)_3)$

Sample concentration: 0.526 M (in  $\text{C}_2\text{D}_2\text{Cl}_4$ ).  $^2J_{\text{Fax-Feq}} = 65.30$  Hz.  $^1J_{\text{W-Fa}} = 65.18$  Hz.

$^1J_{\text{W-Feq}} = 34.90$  Hz. Line width A part/B<sub>4</sub> part (Hz): 3.6/6.2.

Temperature (K)/  $\delta$  A-part (ppm)/  $\delta$  B<sub>4</sub>-part (ppm):

293/158.073/150.332; 303/158.327/150.441; 313/158.576/150.552;  
333/159.059/150.778; 353/159.528/151.014; 363/159.750/151.130;  
373/159.946/151.252.

**3.4.4 F<sub>5</sub>Mo(OCH<sub>2</sub>CF<sub>3</sub>)**

Sample concentration 1.249 M (in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  ${}^2J_{\text{Fax-Feq}} = 89.68$  Hz. Line width A part/B<sub>4</sub> part (Hz): 38/30.

Temperature (K)/  $\delta$  A-part (ppm)/  $\delta$  B<sub>4</sub>-part (ppm):

303/215.947/233.646; 313/217.053/233.934; 323/218.110/234.200;

333/219.200/234.472; 343/220.150/234.750; 353/221.100/235.030;

363/222.800/235.280.

**3.4.5 F<sub>5</sub>Mo(OC<sub>6</sub>F<sub>5</sub>)**

Sample concentration 0.259 M (in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  ${}^2J_{\text{Fax-Feq}} = 91.50$  Hz. Line width A part/B<sub>4</sub> part (Hz): 25/29.

Temperature (K)/  $\delta$  A-part (ppm)/  $\delta$  B<sub>4</sub>-part (ppm):

273/243.251/249.189; 278/243.774/249.295; 283/244.290/249.405;

288/244.802/249.518; 293/245.305/249.629; 298/245.804/249.741;

303/246.290/249.858; 313/247.232/250.090; 323/248.328/250.328;

333/249.187/250.558.

**3.4.6 F<sub>5</sub>Mo(OC<sub>6</sub>F<sub>5</sub>) in CD<sub>2</sub>Cl<sub>2</sub>**

Sample concentration 0.036 M (in CD<sub>2</sub>Cl<sub>2</sub>):  ${}^2J_{\text{Fax-Feq}} = 91.30$  Hz. Line width A part/B<sub>4</sub> part (Hz): 31/33.

Temperature (K)/ $\delta$  A-part (ppm)/  $\delta$  B<sub>4</sub>-part (ppm)/[Rate constant (sec<sup>-1</sup>)]:

283/248.030/253.460/[189.3]; 288/248.455/253.573/[280.5];

293/248.70/253.686/[406.7]; 298/249.272/253.793/[603.1];

303/249.685/253.910/[869.6]; 323/250.050/254.065/[3282].

**3.5 Unsuccessful Reactions****3.5.1 Molybdenum hexafluoride with (Perfluoro) *tert*-butoxy-trimethyl-silane**

- Attempts to synthesize molecules of the type F<sub>6-n</sub>Mo(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>n</sub> n ≥ 1 using the same procedures used to prepared all other F<sub>5</sub>MOR (M = W or Mo, R = -CH<sub>2</sub>CF<sub>3</sub> or -C<sub>6</sub>F<sub>5</sub>) molecules were all unsuccessful. Even a sample which was heated at 50 °C for 3 days

showed no reaction between MoF<sub>6</sub> and (CF<sub>3</sub>)<sub>3</sub>CO–Si(CH<sub>3</sub>)<sub>3</sub> as seen in the <sup>19</sup>F NMR.

### 3.5.2 Molybdenum hexafluoride with Lithium-*tert*-(perfluoro)-butoxide

- MoF<sub>6</sub> was reacted with LiOC(CF<sub>3</sub>)<sub>3</sub> in the same manner as WF<sub>6</sub> was reacted in 3.2.15. After pumping off volatile materials a dark brown solid remained always in the PFA tube. Neither <sup>19</sup>F NMR of the solid in different solvents, nor the volatile part showed signals corresponding to molecules of the form F<sub>6-n</sub>Mo(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>n</sub> n ≥ 1. Various attempts were carried out; in none of them the desired complexes could be isolated.

### 3.5.3 Tungsten hexafluoride with Diphenyl Zinc

- WF<sub>6</sub> and CH<sub>2</sub>Cl<sub>2</sub> were condensed inside a 4 mm PFA tube, into which Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> had been previously added. The tube was sealed and kept at –80 °C. The reaction mixture was monitored with NMR spectroscopy while the sample was warmed up from –80 °C up to room temperature. No reaction or new signals were observed in the <sup>19</sup>F NMR.

- The same reactants as before but in bigger quantities were given to a 15 mm PFA. The reaction mixture was stirred at room temperature for 8 h. Volatile materials were pumped off at room temperature. A dark brown solid material remained in the PFA tube. <sup>19</sup>F and <sup>13</sup>C NMRs from the –196 °C trap showed signals corresponding to WF<sub>6</sub>, and CH<sub>2</sub>Cl<sub>2</sub> respectively. A new <sup>13</sup>C signal was seen (128.5 ppm) and assigned to C<sub>6</sub>H<sub>6</sub>.<sup>[71]</sup> <sup>19</sup>F NMR of the solid part in various solvents showed signals which were assigned to hydrolysis byproduct (F<sub>4</sub>WO).<sup>[71]</sup>

- Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and WF<sub>6</sub> in Et<sub>2</sub>O as solvent were reacted at low temperature (–50 °C). The solid material which remained after working up the sample was dissolved in a series of solvents for <sup>19</sup>F NMR. No signals showing a ring substitution on tungsten were seen. Some crystals were obtained in Et<sub>2</sub>O. X-ray diffraction and analysis from the crystals gave [Zn(Et<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> ([F<sub>5</sub>WO]<sup>–</sup>)<sub>2</sub>. <sup>19</sup>F NMR of the crystals in acetone showed a doublet (56.0 ppm, 55 Hz) and a multiplet (29.9 ppm).

- WF<sub>6</sub>, freshly sublimed Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and freshly distilled CH<sub>2</sub>Cl<sub>2</sub> were reacted at low temperature (–40 °C) for 12 hours. A <sup>19</sup>F NMR of the dark colored reaction mixture showed no reaction. No signals from hydrolysis byproducts were observed. The solvent

was evacuated and Et<sub>2</sub>O was added to the remaining solid. Immediately a <sup>19</sup>F NMR signal was seen (62 ppm). Using acetone as solvent two <sup>19</sup>F NMR signals appeared (56 and 29 ppm). Signals are assigned again most probably to a hydrolysis byproduct [F<sub>5</sub>WO]<sup>-</sup> (the corresponding quintet was not seen in Et<sub>2</sub>O) due to residual water in the solvents which were kept over long period of time over molecular sieve.

#### 3.5.4 Molybdenum hexafluoride with Diphenyl Zinc

- MoF<sub>6</sub> and freshly sublimed Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> were reacted without any solvent at -30 °C in a PFA tube. After pumping off volatile materials at -30 °C a gray powder remained. Acetone was added and a sample was taken for NMR. No <sup>19</sup>F NMR signals were seen and <sup>13</sup>C NMR signals were assigned most probably to diphenyl zinc. In CH<sub>2</sub>Cl<sub>2</sub> the same results were observed.

- The same reactants like before and CH<sub>2</sub>Cl<sub>2</sub> were reacted at room temperature. No reaction was detected between the two species (as seen in the <sup>19</sup>F NMR). The same reactants and using Et<sub>2</sub>O (kept over molecular sieve) as a solvent produced the same results like in the WF<sub>6</sub> reaction; only one <sup>19</sup>F NMR signal (≈ 62 ppm) was seen. Evacuating the solvent and recondensing acetone into the tube showed in the <sup>19</sup>F NMR spectroscopy the same signal (one doublet ≈ 56 ppm).

#### 3.5.5 Tungsten hexafluoride with Phenyl lithium

- Li(C<sub>6</sub>H<sub>5</sub>) and hexane (which was stored over molecular sieve over a long period of time) were added into a 4 mm PFA tube. WF<sub>6</sub> was condensed inside. The tube was sealed and kept at -90 °C. The reaction mixture was monitored with NMR spectroscopy while the sample was warmed up from -90 °C up to -10 °C. No reaction or new signals for an aromatic substitution on the tungsten were observed in the <sup>19</sup>F NMR. One new signal (59 ppm) was seen and assigned most probably to a hydrolysis byproduct do to residual water in the solvent. Pumping off the volatile materials and adding CH<sub>2</sub>Cl<sub>2</sub> produced again the same signal (64 ppm, <sup>19</sup>F NMR).

- Li(C<sub>6</sub>H<sub>5</sub>) and freshly distilled hexane were added into a PFA tube. WF<sub>6</sub> was condensed inside. The sample was stirred and reacted at room temperature. A

fter pumping off all volatile materials a  $^{19}\text{F}$  NMR of the  $-196\text{ }^\circ\text{C}$  trap showed only  $\text{WF}_6$ . The remaining solid in  $\text{CH}_2\text{Cl}_2$  gave in the  $^{19}\text{F}$  NMR only one signal (64.6 ppm) again most probably assigned to a hydrolysis byproduct coming from impurities like  $\text{LiOH}$  in  $\text{Li}(\text{C}_6\text{H}_5)$ .

- Freshly sublimed  $\text{Li}(\text{C}_6\text{H}_5)$  and  $\text{WF}_6$  were reacted in freshly distilled  $\text{CH}_2\text{Cl}_2$  like described before. Neither a reaction was detected nor were hydrolysis byproducts seen in the  $^{19}\text{F}$  NMR.

### 3.5.6 Molybdenum hexafluoride with Phenyl lithium

- Freshly sublimed  $\text{Li}(\text{C}_6\text{H}_5)$  and freshly distilled  $\text{Et}_2\text{O}$  were put into a PFA tube equipped with a magnetic stirrer. The mixture was stirred at room temperature for a couple of minutes and then cooled down to  $-196\text{ }^\circ\text{C}$ .  $\text{MoF}_6$  was condensed inside the tube and the sample was stirred at  $-78\text{ }^\circ\text{C}$ . The temperature of the bath was raised gradually to  $-40\text{ }^\circ\text{C}$  at which some intense coloration (red, orange) was seen. The reaction mixture was stirred and kept at this temperature for the whole night. A  $^{19}\text{F}$  NMR of the sample gave one signal at 144 ppm and one at  $-186$  ppm. Signals are due to a decomposition product between  $\text{MoF}_6$  and diethyl ether (see next paragraph).

- A sample containing only  $\text{MoF}_6$  and  $\text{Et}_2\text{O}$  was prepared and stirred at room temperature for a couple of hours. The reaction mixture turned dark colored. A  $^{19}\text{F}$  NMR of the sample showed some new signals 160 ppm (very small), 145 ppm and  $-185$  ppm. The signals are exactly the same signals seen in the attempt mentioned before. Signals are assigned to a decomposition products between  $\text{MoF}_6$  and diethyl ether and not to any kind of reaction with phenyl lithium.

### 3.5.7 Tungsten hexachloride with Phenyl lithium

-  $\text{WCl}_6$  and freshly sublimed  $\text{Li}(\text{C}_6\text{H}_5)$  were reacted in freshly distilled  $\text{Et}_2\text{O}$  at room temperature for 24 h. No reaction was detected between the two species ( $^{13}\text{C}$  NMR). The PFA tube was sealed and heated at  $50\text{ }^\circ\text{C}$  for another 24 h. After opening the tube and performing a  $^{13}\text{C}$  NMR of the mixture no reaction was detected between the two species. No further attempts with  $\text{WCl}_6$  and  $\text{Li}(\text{C}_6\text{H}_5)$  were carried out.

### 3.5.8 Tungsten hexafluoride with Pentafluorophenyl-difluoro-borane

-  $(\text{C}_6\text{F}_5)\text{BF}_2$  was added into a previously dried 4 mm PFA tube. An excess of  $\text{WF}_6$  and  $\text{CH}_2\text{Cl}_2$  were condensed into the tube. The mixture was kept at  $-196\text{ }^\circ\text{C}$  and transferred into the NMR machine which was previously cooled down to  $-78\text{ }^\circ\text{C}$ . The temperature of the sample was raised gradually to room temperature while the  $^{19}\text{F}$  NMR spectra of the sample were recorded. No reaction was detected between the two species.

- The same reactants as before but in bigger quantities were given into a 15 mm PFA. The reaction mixture was stirred at room temperature for 1 h. A sample of the mixture was taken for  $^{19}\text{F}$  NMR. Only signals corresponding to the starting materials were seen.

- An attempt at room temperature with a-HF and the same reactants as before did not produce new  $^{19}\text{F}$  NMR signals. After heating and stirring the sample for 1 day at  $100\text{ }^\circ\text{C}$ , also no reaction between  $\text{WF}_6$  and  $(\text{C}_6\text{F}_5)\text{BF}_2$  had taken place. Neither a reaction was seen if an excess of pentafluorophenyl-difluoro-borane was used.

### 3.5.9 Tungsten hexachloride with Phenyl-trichloro-silane

-  $(\text{C}_6\text{H}_5)\text{SiCl}_3$ ,  $\text{WCl}_6$ , and a mixture of  $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$  were added into a PFA tube. The mixture was stirred at room temperature for 3 days. Evacuation of the solvents left a dark blue/green material which dissolved partially in  $\text{CH}_2\text{Cl}_2$ . Some yellow needles crystallized from the methylene chloride solution and were analyzed by X-ray diffraction. After a few scans a pre-analysis of the reflections gave a structure which contained a tungsten atom and no aromatic ring(s). The X-ray diffraction was stopped and the structure was not solved completely. The remaining solid material was partially soluble in EtCN (blue solution) and in  $\text{Et}_2\text{O}$  (green suspension). Crystallization of the dissolved material was attempted in both samples; no crystals were obtained.

### 3.5.10 Tungsten hexafluoride with Phenyl-trifluoro-silane

-  $\text{WF}_6$ ,  $(\text{C}_6\text{H}_5)\text{SiF}_3$ , and  $\text{CH}_2\text{Cl}_2$  were condensed into a PFA tube. The mixture was stirred at low temperature ( $-30\text{ }^\circ\text{C}$ ). A sample of the mixture was taken and placed into a 4 mm PFA tube. No reaction was detected, as seen by the low temperature  $^{19}\text{F}$  NMR.

- The same mixture as before was warmed to room temperature and stirred at this

temperature for a couple of days. Again no reaction was seen ( $^{19}\text{F}$  NMR).

- The mixture was heated to 40 °C for 12 h, a  $^{19}\text{F}$  NMR revealed again no new signals.
- A PFA tube containing  $\text{WF}_6$ ,  $(\text{C}_6\text{H}_5)\text{SiF}_3$ ,  $\text{CH}_2\text{Cl}_2$  and a-HF was prepared.. The reaction mixture was stirred at room temperature. Again no reaction was seen ( $^{19}\text{F}$  NMR). No further attempts with phenyl-trifluoro-silane and tungsten hexafluoride were carried out.

### 3.5.11 Molybdenum hexafluoride with Phenyl-trifluoro-silane

- $\text{MoF}_6$  and  $(\text{C}_6\text{H}_5)\text{SiF}_3$  were condensed into a 4 mm PFA tube. The tube was sealed and kept at -40 °C. The reaction mixture was monitored by NMR spectroscopy while the sample was warmed up from -40 °C up to 10 °C. At 0 °C very small, almost non detectable,  $^{19}\text{F}$  signals corresponding to the W-F region were observed. The sample was kept at this temperature for 30 min. The signals did not grow in intensities. At 10 °C the PFA tube busted inside the NMR machine either due to an excess pressure of  $\text{MoF}_6$  or an extremely spontaneous reaction inside the tube.
- The reaction was repeated at low temperature (0 °C) using  $\text{CH}_2\text{Cl}_2$  as a solvent in a bigger PFA tube (15 mm). After stirring the sample for a couple of days at this temperature, none of the  $^{19}\text{F}$  NMR signals seen in the previous attempt were seen. No reaction was detected.
- $\text{MoF}_6$ ,  $(\text{C}_6\text{H}_5)\text{SiF}_3$ ,  $\text{CH}_3\text{CN}$  and F-11 were added into a PFA tube. The mixture was stirred at room temperature. A new signal, most probably from residual water in the solvent used, was seen at 148 ppm which is assigned to  $[\text{CH}_3\text{CN-MoF}_4\text{O}]^{[71]}$ . No other new signals were detected.

### 3.5.12 Tungsten hexafluoride with Pentafluorophenyl-trifluoro-silane

- $\text{WF}_6$ ,  $(\text{C}_6\text{F}_5)\text{SiF}_3$  and  $\text{CH}_3\text{CN}$  (which was stored over molecular sieve over a long period of time) were added into a PFA tube. The tube was heated up to 65 °C. No relevant reaction was detected by  $^{19}\text{F}$  NMR and only one new signal was seen at 66 ppm. The signal is tentatively assigned to  $\text{F}_5\text{WO}^{-[25]}$  (most probably due to hydrolysis from residual water present in the solvent).



- To test the “dryness” of the solvent,  $\text{WF}_6$  and  $\text{CH}_3\text{CN}$  were put into a PFA tube and stirred at room temperature. A  $^{19}\text{F}$  NMR of the sample showed clearly this signal (66 ppm) seen before in all previous attempts with  $\text{CH}_3\text{CN}$ .
- The same reactants as before,  $(\text{CH}_3)_4\text{NF}$  and freshly distilled  $\text{CH}_3\text{CN}$  were added into a PFA tube. After stirring the sample for a couple of days at room temperature, no new signals  $^{19}\text{F}$  were detected in the NMR spectroscopy.

### 3.5.13 Molybdenum hexafluoride with Pentafluorophenyl-trifluoro-silane

- Some attempts with  $\text{MoF}_6$  and Pentafluorophenyl-trifluoro-silane were carried out in different solvents and at different temperatures. None of them showed new  $^{19}\text{F}$  NMR signals corresponding to  $\text{F}_{6-n}\text{Mo}(\text{C}_6\text{F}_5)_n$  species. The reactions tried are summarized as follow:
- $\text{MoF}_6$  and  $(\text{C}_6\text{F}_5)\text{SiF}_3$  in  $\text{CH}_2\text{Cl}_2$  at room temperature. No reaction was seen. The same sample was heated at  $40\text{ }^\circ\text{C}$  for 30 min and the same results were obtained no reaction takes place.
- $\text{MoF}_6$  and  $(\text{C}_6\text{F}_5)\text{SiF}_3$  in  $\text{CH}_3\text{CN}$  at room temperature. No reaction was seen.
- $\text{MoF}_6$ ,  $(\text{C}_6\text{F}_5)\text{SiF}_3$ , and  $(\text{CH}_3)_4\text{NF}$  in  $\text{CH}_3\text{CN}$ , at room temperature. No reaction was seen.
- $\text{MoF}_6$  and  $(\text{C}_6\text{F}_5)\text{SiF}_3$  in a-HF at room temperature. No reaction was detected.
- $\text{MoF}_6$  and  $(\text{C}_6\text{F}_5)\text{SiF}_3$  in  $\text{CH}_2\text{Cl}_2$  at  $40\text{ }^\circ\text{C}$ . No reaction was seen; no  $^{19}\text{F}$  NMR signal for hydrolysis byproducts was detected
- $\text{MoF}_6$  and  $(\text{C}_6\text{F}_5)\text{SiF}_3$  in a mixture of  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  at room temperature. No reaction was seen.

### 3.5.14 Tungsten hexafluoride with Trimethyl-pentafluorophenyl-tin

- $\text{WF}_6$ ,  $(\text{C}_6\text{F}_5)\text{Sn}(\text{CH}_3)_3$  and methylene chloride were reacted in a PFA tube first at low temperatures.  $^{19}\text{F}$  NMR of the sample revealed no reaction between the two species. The sample was reacted at room temperature and after 3 days of being stirred a  $^{19}\text{F}$  NMR of

the reaction mixture showed new, very small signals (doublet 118.4 ppm, 64 Hz; quintet 88.5 ppm, 64 Hz; aromatic region -140.1, -155.6, -163.8 ppm). Attempts to crystallize anything out of this sample were unsuccessful.

- The reaction was repeated using larger amounts of  $(\text{C}_6\text{F}_5)\text{Sn}(\text{CH}_3)_3$ . After stirring the sample at room temperature for 3 days, a  $^{19}\text{F}$  NMR of the sample showed again this time only the doublet at  $\approx 118$  ppm. The corresponding quintet was not seen. Heating up the reaction mixture (45 °C) for a couple of hours did not produce any mayor changes in the new signal seen. Attempts to crystallize anything out of this sample were unsuccessful.

### 3.5.15 Tungsten hexafluoride with $\text{Hg}(\text{SCF}_3)_2$

$\text{WF}_6$ ,  $\text{Hg}(\text{SCF}_3)_2$  and methylene chloride were reacted in a PFA tube at room temperature for 4 h.  $^{19}\text{F}$  NMR of the sample showed only the two reactants and no other new signal was detected. The reaction mixture was stirred at room temperature for 3 more days and the  $^{19}\text{F}$  NMR results were the same as before. The sample was heated at 40 °C for one more day and no reaction between the two reactants is seen in the  $^{19}\text{F}$  NMR. No further attempts using these reactants were carried out.

### 3.5.16 Molybdenum hexafluoride with $\text{Hg}(\text{SCF}_3)_2$

$\text{MoF}_6$  and  $\text{Hg}(\text{SCF}_3)_2$  were reacted without solvent in a PFA tube at room temperature. After a few minutes a red/brown coloration for the mixture was seen. A  $^{19}\text{F}$  NMR of the mixture in F-11 showed, besides  $\text{MoF}_6$  and traces of  $\text{Hg}(\text{SCF}_3)_2$ , no new signals corresponding to the F-Mo region and only one new signal ( $\approx -46$  ppm) was detected. The signal is assigned unequivocally to  $\text{F}_3\text{CS}-\text{SCF}_3$ .<sup>[71]</sup> No further attempts using this reactants were carried out.