Electronic Supplementary Information

On molecular architectures of siloxane coordination compounds: (Re-)investigating the coordination of the cyclodimethylsiloxanes D_n (n=5-8) towards alkali metal ions

F. Dankert,[a] L. Erlemeier[a], C. Ritter[a] and C. von Hänisch[a]*

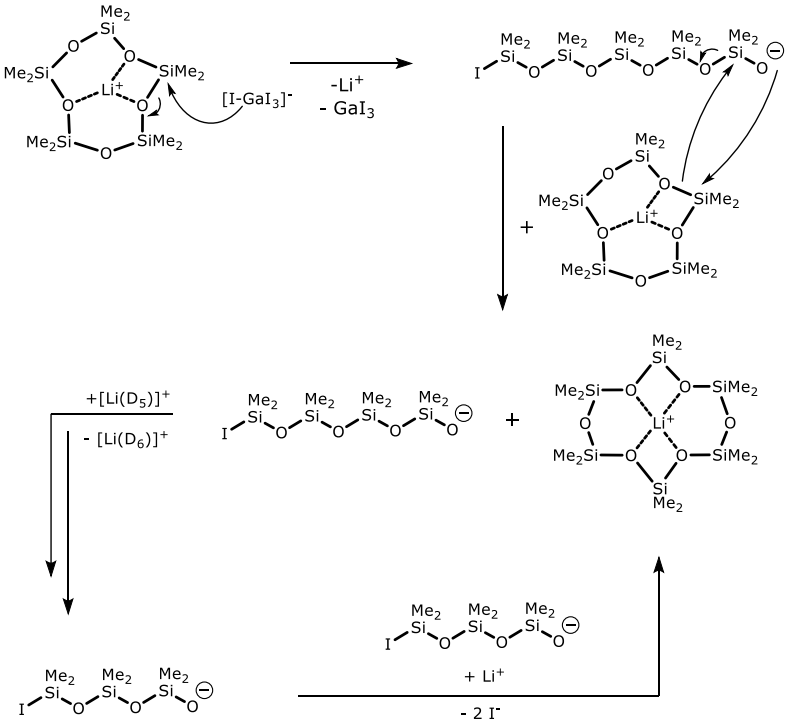
*Email: haenisch@staff.uni-marburg.de

[a] Department of Chemistry and Material Sciences Center, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany.

Content

1. Notes on template-driven ring-opening polymerizations

The depicted mechanism in Scheme S1 gives a proposal for the ring expansion from D_5 to D_6 in the presence of $[GaI_4]^-$ and a Li^+ template. Due to coordination it is most likely that the Li^+ ion will polarize the Si atoms. This makes the Lewis-acidic Si-centres vulnerable for nucleophilic attack of I^-. The ring is eventually cleaved to form an iodosilanolate which is itself nucleophilic. Another equivalent of $[Li(D_5)]^+$ is attacked and the ring is expanded under Li^+ templation. As depicted here, the $ISiMe_2(OSiMe_2)_nOSiMe_2O^-$ anions are the $SiMe_2O$-source for ring expansion. The ring expansion for the formation of larger ring (e.g. using K^+ or Cs^+ as a template) proceeds in seemingly similar manner.



Scheme S1: Tentative Li^+ directed ring transformation process referring to *Passmore* and co-workers.[1]

2. Single crystal X-Ray diffraction analysis

2.1 General Information

Single crystal X-ray diffraction experiments were carried out on a Bruker D8 Quest diffractometer at 100(2)K with MoKα radiation and respective X-ray optics (λ = 0.71073). For compound **10** the experiment was carried out on a STOE STADIVARI diffractometer with CuKα radiation (λ = 1.54186) at 130K. All structures were solved by direct methods and refinement with full-matrix-least-squares against F^2 using SHELXT- and SHELXL-2015 on OLEX2 platform.[2-4] To fix the disordered anions in compound **10, 11** as well as **12** we also used DSR[5] (=disordered model refinement) and placed an OLEX2 implemented initial, rigid $[Al_F]^-$ restraint. In case of **12**, we also refined the residual electron density more precisely using implemented $OCCF_3$ restraints. As a cause, the atom labelling is sometimes quite unconventional around the anions. The intrinsically disorder of these anions, legitimates these high numbers of restraints and it should be noted that the siloxane moieties aren't disordered and thus restraints had only been used for the anion. It should be further noted that due to twisting and tilting of the respective anions, more atom positions of the refined atom positions are possible. However, without the restraints we could not refine the anions properly. It should at this point also be noted that we improved the disorder behaviour of these anions as we placed the crystal at a higher temperature of -20°C to the diffractometer and then cooled down slowly to 100K/130K at a rate of 250K/h. The diffraction experiment for compound **10** had to be performed at a higher temperature due to phase transition at temperatures below this value and/or cracking of the crystal.

The crystallographic data for the compounds **1-12** and K[AlF_4] are denoted as follows: CCDC Nos. 1979351 (**1**), 1979352 (**2**), 1979354 (**2a**), 1979358 (**3**), 1979356 (**4**), 1979353 (**5**), 1979357 (**6**), 1979355 (**7**), 1979359 (**8**), 1979361 (**9**), 1979360 (**10**), 1979363 (**11**), 1979364 (**12**), 1979362 ($KAlF_4$). Crystallographic information files (CIF) can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) (link: www.ccdc.cam.ac.uk/data_request/cif). The respective crystal data and selected experimental parameters of the structure determinations are summarized in table S1-S4. Visualization of all structures was performed with the Diamond software package Version 4.6.0.

2.2 Crystallographic Data

Table S1. Selected crystal structure data of the structure determinations of the compounds **1·C$_6$D$_6$**, **2**, and **2a**

Compound	**1·C$_6$D$_6$**	**2**	**2a**
Empirical formula	$C_{28}H_{72}Ga_2I_8Li_2O_{11}Si_{11}$	$C_{12}H_{36}GaI_4LiO_6Si_6$	$C_{12}H_{38}GaI_4LiO_7Si_6$
Formula weight	2068.40	1029.21	1047.22
Crystal colour, habit	Colourless, needle	Colourless, platelet	Colourless, platelet
Temperature/K	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1	*C*2/*c*	*P*-1
a/Å	11.1168(4)	18.8841(7)	10.5200(4)
b/Å	16.9018(6)	10.4111(4)	11.1154(4)
c/Å	19.8102(8)	19.2669(8)	16.6027(7)
α/°	98.9980(10)	90	88.3260(10)
β/°	95.0500(10)	112.8520(10)	78.6540(10)
γ/°	102.9710(10)	90	69.4900(10)
Volume/Å^3	3553.2(2)	3490.6(2)	1781.15(12)
Z	2	4	2
ϱ_{calc}g/cm^3	1.933	1.958	1.953
μ/mm^{-1}	4.457	4.554	4.466
F(000)	1948.0	1944.0	992.0
Crystal size/mm^3	0.262 × 0.193 × 0.121	0.133 × 0.129 × 0.071	0.177 × 0.125 × 0.089
Radiation	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)
2Θ range for data collection/°	4.486 to 52.84	4.56 to 53.594	4.456 to 56.7
Reflections collected	14525	29905	33652
Independent reflections	14525 [*]	3736 [R_{int} = 0.0423, R_{sigma} = 0.0237]	8849 [R_{int} = 0.0325, R_{sigma} = 0.0334]
Data/restraints/parameters	14525/0/582	3736/0/153	8849/2/301
Goodness-of-fit on F^2	1.099	1.069	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.0800	R_1 = 0.0221, wR_2 = 0.0417	R_1 = 0.0250, wR_2 = 0.0374
Final R indexes [all data]	R_1 = 0.0651, wR_2 = 0.0873	R_1 = 0.0313, wR_2 = 0.0438	R_1 = 0.0381, wR_2 = 0.0400
Largest diff. peak/hole / e Å^{-3}	1.62/-1.11	0.54/-0.57	1.72/-1.38
Absolute structure parameter	-	-	-

* refined as a two-component twin

Table S2. Selected crystal structure data of the structure determinations of the compounds **3-5**

Compound	**3**	**4**	**5**
Empirical formula	$C_{12}H_{36}GaI_4NaO_6Si_6$	$C_{15}H_{44}Cl_2GaI_4NaO_7Si_7$	$C_{15}H_{44}Cl_2GaI_4KO_7Si_7$
Formula weight	1045.26	1204.34	1220.45
Crystal colour, habit	Colourless, platelet	Colourless, platelet	Colourless, platelet
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1
a/Å	19.4191(10)	11.6548(5)	10.8831(4)
b/Å	19.9922(10)	20.5389(9)	11.2425(5)
c/Å	19.9247(11)	21.1652(10)	18.6043(7)
α/°	90	114.0800(10)	89.9390(10)
β/°	113.151(2)	99.536(2)	81.6520(10)
γ/°	90	103.956(2)	74.7930(10)
Volume/Å^3	7112.5(7)	4285.0(3)	2171.68(15)
Z	8	4	2
ϱ_{calc}g/cm^3	1.952	1.867	1.866
μ/mm^{-1}	4.482	3.882	3.916
F(000)	3952.0	2304.0	1168.0
Crystal size/mm^3	0.281 × 0.256 × 0.184	0.257 × 0.161 × 0.089	0.301 × 0.172 × 0.132
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.276 to 53.63	4.276 to 50.998	4.206 to 56.702
Reflections collected	264211	103252	40306
Independent reflections	15192 [R_{int} = 0.0453, R_{sigma} = 0.0172]	15885 [R_{int} = 0.0398, R_{sigma} = 0.0264]	10795 [R_{int} = 0.0359, R_{sigma} = 0.0363]
Data/restraints/parameters	15192/0/565	15885/0/687	10795/0/348
Goodness-of-fit on F^2	1.144	1.147	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.0843	R_1 = 0.0575, wR_2 = 0.1553	R_1 = 0.0338, wR_2 = 0.0629
Final R indexes [all data]	R_1 = 0.0650, wR_2 = 0.0975	R_1 = 0.0665, wR_2 = 0.1582	R_1 = 0.0495, wR_2 = 0.0676
Largest diff. peak/hole / e Å^{-3}	2.63/-1.98	2.62/-1.27	3.33/-1.67
Absolute structure parameter	-	-	-

Table S3. Selected crystal structure data of the structure determinations of compounds **6-8**

Compound	**6·DCM**	**7**	**8·DCM**
Empirical formula	$C_{15}H_{48}Cl_2Ga_2I_7NO_7Si_7$	$C_{17}H_{50}Cl_2GaI_4O_8RbSi_8$	$C_{33}H_{50}AlCl_2F_{36}O_{12}RbSi_8$
Formula weight	1649.81	1340.98	1730.80
Crystal colour, habit	Colourless, platelet	Colourless, platelet	Colourless, platelet
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$Pbcn$	P-1
a/Å	11.2628(5)	18.0474(7)	14.1058(8)
b/Å	20.6445(18)	13.5623(6)	19.3758(11)
c/Å	22.3771(11)	19.3971(8)	26.4291(15)
α/°	90	90	89.960(2)
β/°	98.338(2)	90	75.318(2)
γ/°	90	90	89.615(2)
Volume/Å^3	5148.0(6)	4747.7(3)	6987.3(7)
Z	4	4	4
ϱ_{calc}g/cm^3	2.129	1.876	1.645
μ/mm^{-1}	5.539	4.545	1.077
F(000)	3064.0	2568.0	3456.0
Crystal size/mm^3	0.400 × 0.132 × 0.106	0.251 × 0.176 × 0.13	0.315 × 0.218 × 0.194
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.174 to 52.844	4.304 to 56.702	4.264 to 52.998
Reflections collected	198653	78935	210484
Independent reflections	10511 [R_{int} = 0.0475, R_{sigma} = 0.0166]	5924 [R_{int} = 0.0465, R_{sigma} = 0.0209]	28938 [R_{int} = 0.0421, R_{sigma} = 0.0286]
Data/restraints/parameters	10511/6/483	5924/0/196	28938/6/1691
Goodness-of-fit on F^2	1.155	1.074	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0834	R_1 = 0.0244, wR_2 = 0.0498	R_1 = 0.0469, wR_2 = 0.1237
Final R indexes [all data]	R_1 = 0.0390, wR_2 = 0.0860	R_1 = 0.0341, wR_2 = 0.0528	R_1 = 0.0537, wR_2 = 0.1263
Largest diff. peak/hole / e Å^{-3}	1.58/-1.20	1.31/-0.86	1.05/-0.69
Absolute structure parameter	-	-	-

Table S4. Selected crystal structure data of the structure determinations of compounds **9**, **10 and 11**

Compound	**9·DCM**	**10**	**11·DCM**
Empirical formula	$C_{33}H_{50}AlCl_2CsF_{36}O_{12}Si_8$	$C_{36}H_{60}AlF_{36}KO_{14}Si_{10}$	$C_{31}H_{44}AlCl_2F_{36}KO_{11}Si_7$
Formula weight	1778.24	1747.82	1610.27
Crystal colour, habit	Colourless, platelet	Colourless, block	Colourless, platelet
Temperature/K	100(2)	130(2)	100(2)
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	*P*-1	*Pbcm*	$P2_1/c$
a/Å	14.1058(8)	11.097(2)	26.8104(18)
b/Å	19.3758(11)	23.519(5)	23.8671(16)
c/Å	26.4291(15)	28.345(6)	30.129(2)
α/°	89.960(2)	90	90
β/°	75.318(2)	90	95.933(2)
γ/°	89.615(2)	90	90
Volume/Å^3	6987.3(7)	7398(3)	19176(2)
Z	4	4	12
ϱ_{calc}g/cm^3	1.690	1.569	1.673
μ/mm^{-1}	0.899	3.611	0.463
F(000)	3528.0	3536.0	9672.0
Crystal size/mm^3	0.315 × 0.218 × 0.194	0.241 × 0.23 × 0.222	0.540 × 0.462 × 0.192
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54186)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.312 to 56.792	7.518 to 129.994	4.42 to 50.62
Reflections collected	277295	141479	202464
Independent reflections	34913 [R_{int} = 0.0367, R_{sigma} = 0.0239]	6429 [R_{int} = 0.0225, R_{sigma} = 0.0075]	34849 [R_{int} = 0.0271, R_{sigma} = 0.0190]
Data/restraints/parameters	34913/0/1812	6429/1522/683	34849/1638/2446
Goodness-of-fit on F^2	1.096	1.113	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = 0.0844	R_1 = 0.0706, wR_2 = 0.1954	R_1 = 0.0760, wR_2 = 0.1922
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.0879	R_1 = 0.0752, wR_2 = 0.1996	R_1 = 0.0901, wR_2 = 0.2060
Largest diff. peak/hole / e Å^{-3}	0.65/-0.82	1.12/-0.80	2.34/-1.53
Absolute structure parameter	-	-	-

Table S5. Selected crystal structure data of the structure determinations of compounds **12** and **KAl$_F$**

Compound	**12**	**KAl$_F$**
Empirical formula	$C_{40}H_{72}AlCsF_{36}O_{16}Si_{12}$	$C_{32}Al_2F_{72}K_2O_8$
Formula weight	1989.94	2012.48
Crystal colour, habit	Colourless, block	Colourless, block
Temperature/K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$
a/Å	11.1101(9)	23.8518(16)
b/Å	27.2474(18)	12.9216(8)
c/Å	27.564(2)	20.6513(11)
α/°	90	90
β/°	94.171(3)	115.296(2)
γ/°	90	90
Volume/Å^3	8322.1(11)	5754.5(6)
Z	4	4
ϱ_{calc}g/cm^3	1.588	2.323
μ/mm^{-1}	0.760	0.479
F(000)	4000.0	3872.0
Crystal size/mm^3	0.249 × 0.228 × 0.188	0.381 × 0.203 × 0.107
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.328 to 50.612	4.364 to 50.154
Reflections collected	337172	88440
Independent reflections	30281 [R_{int} = 0.0419, R_{sigma} = 0.0193]	10202 [R_{int} = 0.0869, R_{sigma} = 0.0386]
Data/restraints/parameters	30281/1557/1911	10202/0/1034
Goodness-of-fit on F^2	1.028	1.165
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1566	R_1 = 0.0986, wR_2 = 0.2133
Final R indexes [all data]	R_1 = 0.0628, wR_2 = 0.1590	R_1 = 0.1173, wR_2 = 0.2207
Largest diff. peak/hole / e Å^{-3}	1.55/-1.44	1.22/-0.64
Absolute structure parameter	0.179(16)	-

2.3 Representation of additional X-ray structures

2.3.1 [Li(D$_6$)(H$_2$O)]GaI$_4$ (2a)

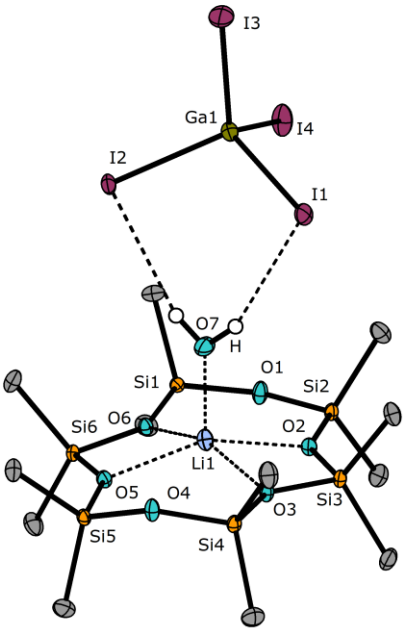


Figure S1. Molecular structure of **2a** in the crystal. Thermal displacement ellipsoids are drawn at 50% probability. Hydrogen atoms were crystallographically localized and fixed with DFIX [0.84] commands. Selected bond lengths [pm]: O1···Li1 326.4(4), O2-Li1 215.4(5), O3-Li1 213.1(5), O4···Li1 321.8(5), O5-Li1 213.7(4), O6-Li1 210.1(4), O7-Li1 192.3(5). Selected bond angles [°]: O2-Li1-O3 71.1(1), O2-Li1-O6 103.6(1), O3-Li1-O5 103.0(1), O5-Li1-O6 71.7(1), Si1-O1-Si2 154.1(1), Si1-O6-Si6 142.1(1), Si2-O2-Si3 143.4(1), Si3-O3-Si4 142.7(1), Si4-O4-Si5 145.7(1), Si5-O5-Si6 143.7(1).

2.3.2 K[AlF]

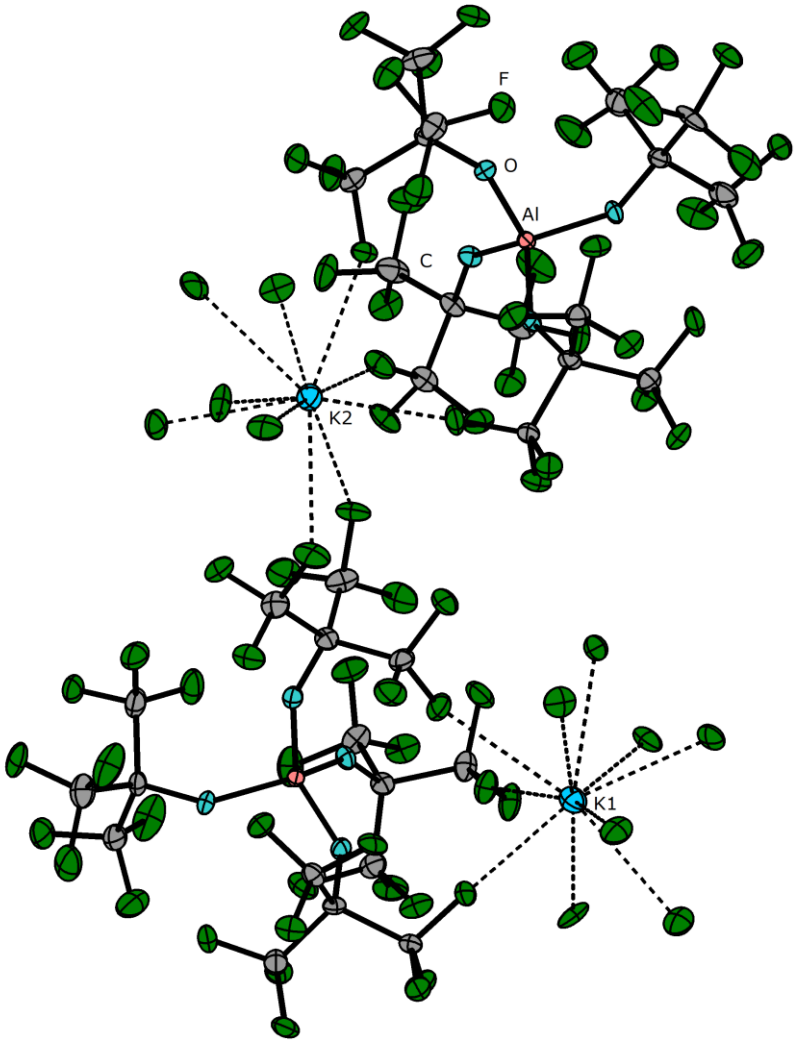


Figure S2. Molecular structure of **K[ALF]** in the crystal and additional fluorine atoms representing the coordination sphere of K1 and K2. Additional fluorine atoms are symmetry generated over x, 1/2-y, 1/2+z; x, 3/2-y, 1/2+z or 1-x, 1-y, 1-z (attached to K1) and x, -1+y, z or 2-x, -1/2+y, 3/2-z (attached to K2). Thermal displacement ellipsoids are drawn at 50% probability. The potassium ions are tenfold coordinated by the anions (CN = 10). The coordination of the CF_3 groups towards K1 have atom distance values of 267.5(4)-302.0(7). The coordination of the CF_3 groups towards K2 have atom distance values of 270.9(6)-294.0(6).

2.3.3 $^{1}_{\infty}[M(D_8)Al_F]$ (M = Rb^+: 8, M = Cs^+: 9)

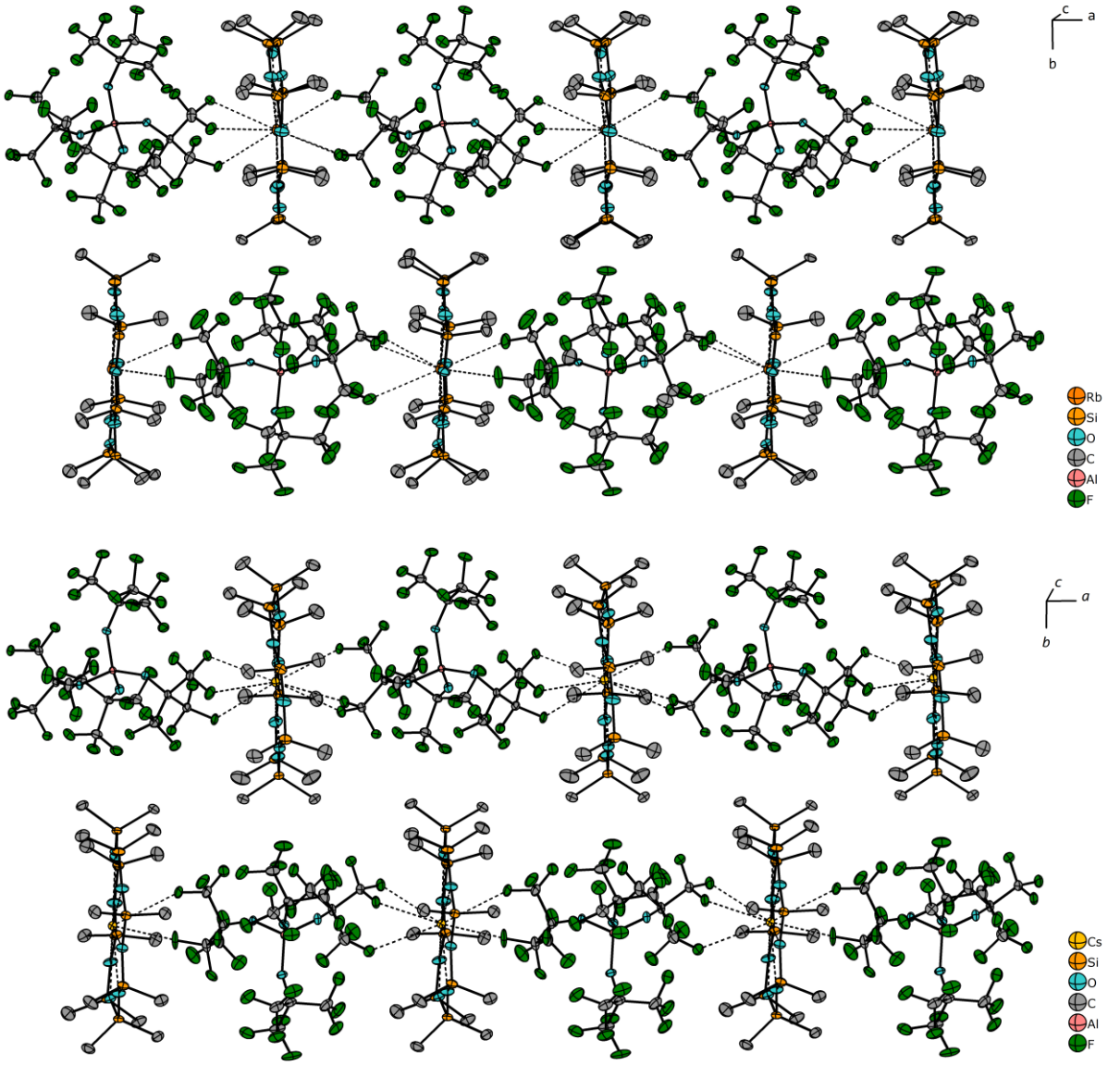


Figure S3. Infinite chains of **8** (top) and **9** (bottom) along [100] in the crystal. Thermal displacement ellipsoids are drawn at 50% probability. DCM molecules are omitted for clarity.

2.3.4 [K(D5)2AlF] (10)

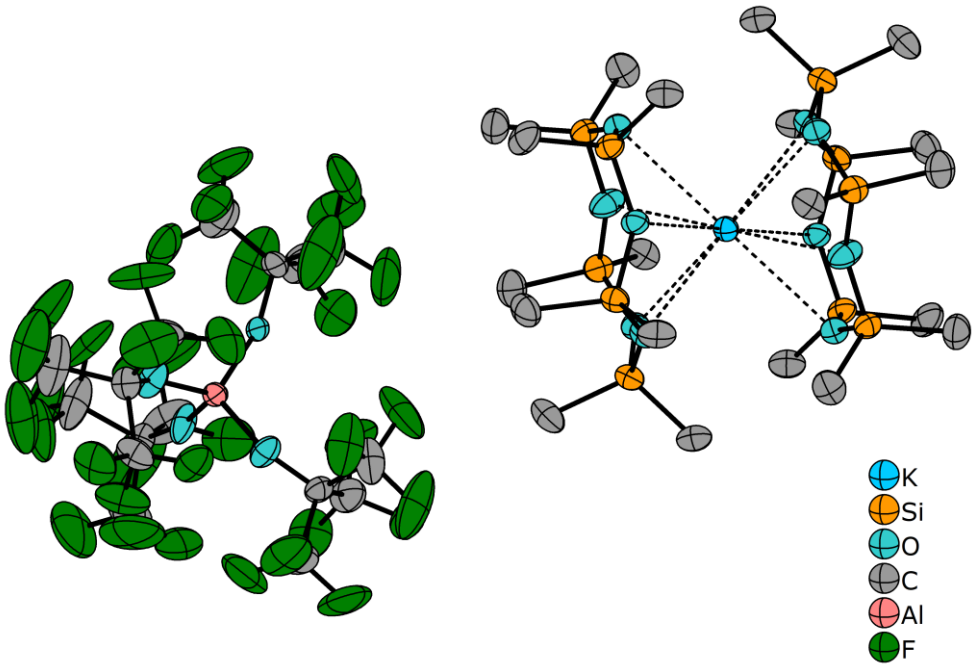


Figure S4. Molecular structure of **10** in the crystal showing the siloxane complex as well as the restraint of the WCA. The disordered part of the anion (x, y, 3/2-z) has not been displayed for clarity. Thermal displacement ellipsoids are drawn at the 30% probability level.

2.3.5 [K(D$_7$)Al$_F$] (11)

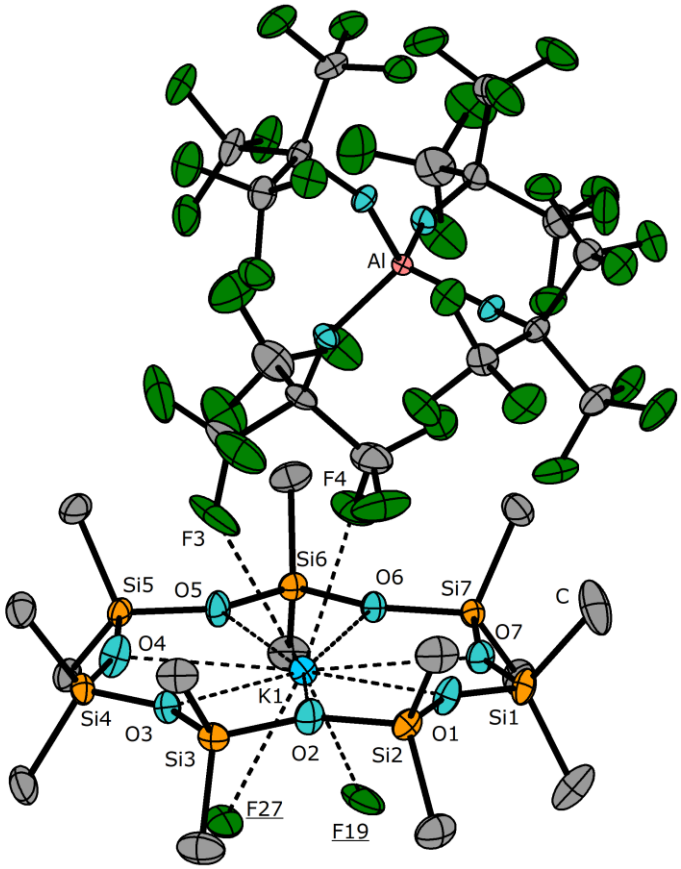


Figure S5. Molecular structure of **11** in the crystal. Only one out of three independent molecules is shown and solvent molecules are omitted for clarity. Thermal displacement ellipsoids are drawn at 50% probability. Underlined atom labels indicate symmetry generation over 1-x, -1/2+y, -1/2z. O1-K1 291.0(3), O2-K1 288.0(3), O3-K1 286.7(3), O4-K1 311.6(3), O5-K1 285.9(3), O6-K1 287.1(3), O7-K1 299.7(3), F3-K1 336.4(4), F4-K1 278.5(3), F27-K1 283.8(3), F19-K1 307.8(3). Selected bond angles [°]: O1-K1-O2 51.9(1), O1-K1-O7 51.2(1), O2-K1-O3 52.5(9), O3-K1-O4 50.0(1), O4-K1-O5 50.4(1), O5-K1-O6 52.7(1), O6-K1-O7 51.2(1), Si1-O1-Si2 152.3(2), Si1-O7-Si7 157.7(2), Si2-O2-Si3 157.7(2), Si3-O3-Si4 149.6(2), Si4-O4-Si5 162.9(3), Si5-O5-Si6 149.6(2), Si6-O6-Si7 152.4(2).

2.3.6 [Cs(D6)2AlF] (12)

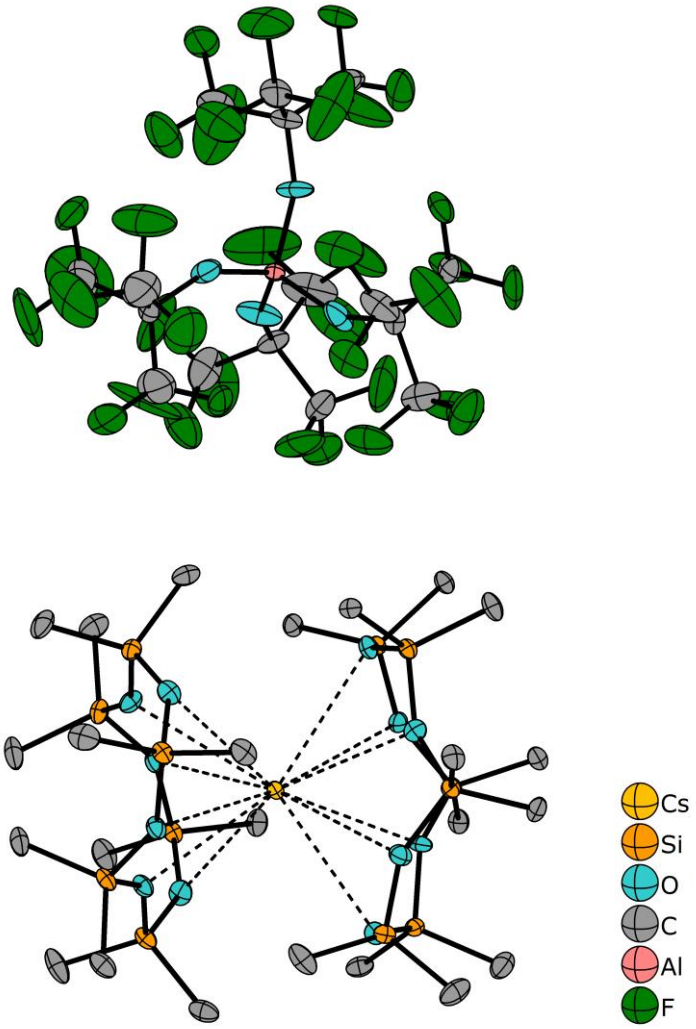


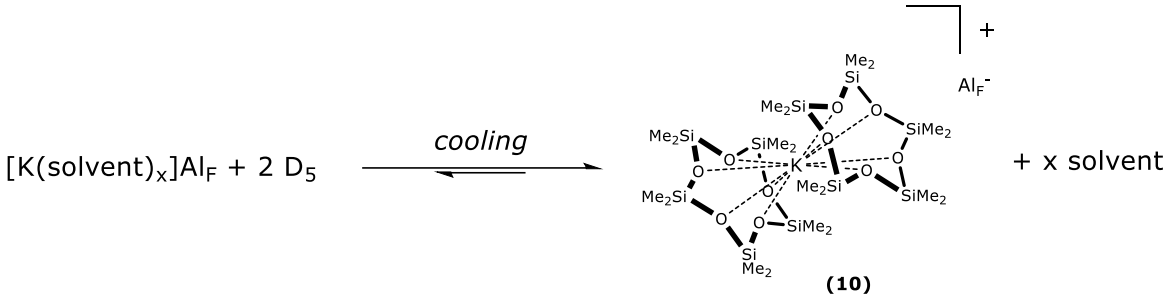
Figure S6. Molecular structure of **12** in the crystal showing the siloxane complex as well as the restraint of the WCA. Only one out of two independent molecules is shown for clarity. Thermal displacement ellipsoids are drawn at the 30% probability level.

3. NMR spectroscopy

3.1 General Information

NMR spectra were recorded on different Bruker Spectrometer types e.g. AV III HD 300 MHz or AV III HD 500 MHz. For the VT NMR we have performed a measurement on the 500 MHz spectrometer. For this purpose, a freshly prepared sample of D5 and KAl_F in the stoichiometric ratio 2:1 was filled into a *J. Young* NMR tube. We started the ^{29}Si NMR (dept) measurement at ambient temperature (300K) and cooled down slowly in 10K steps. All spectra have been visualized with the MestReNove software package 9.0.1.

3.2 Behavior in solution of compound 10



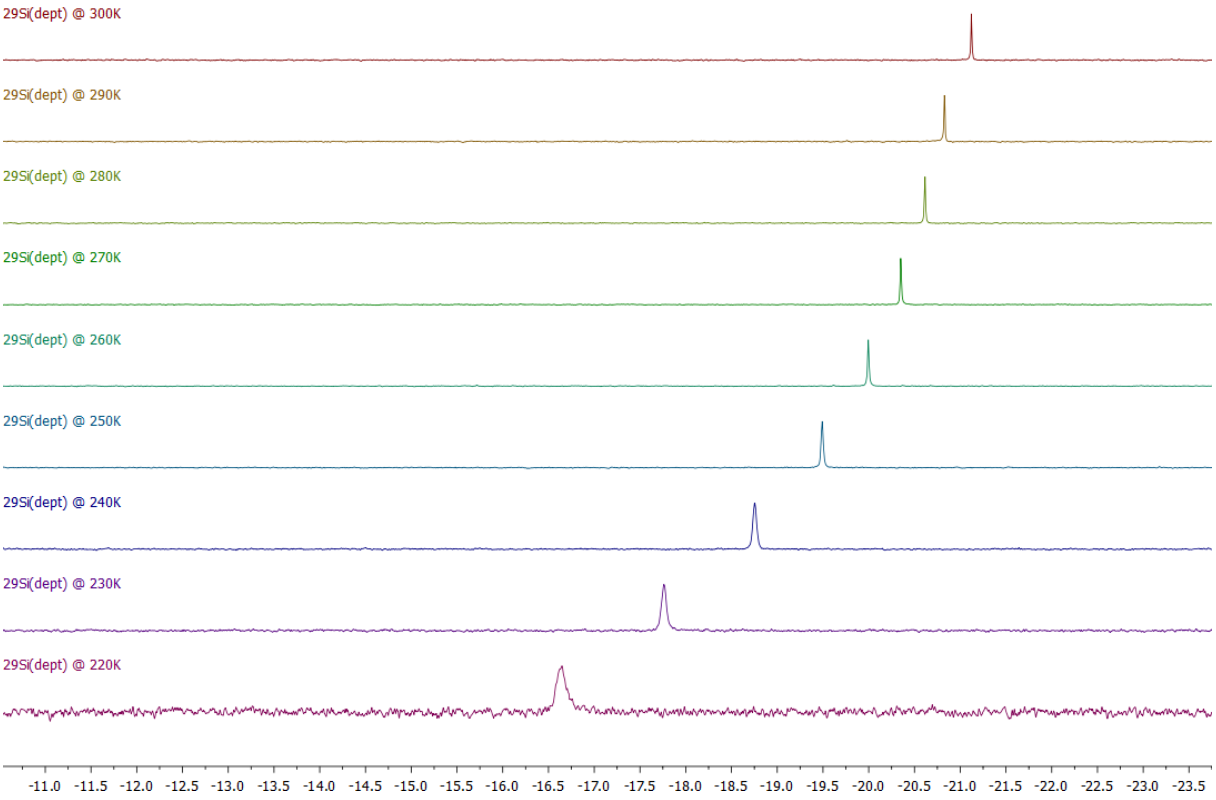
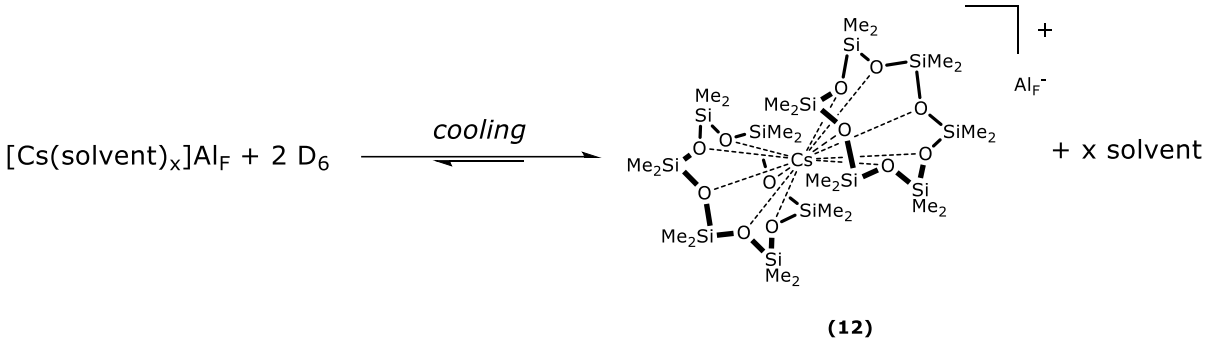


Figure S7. VT ^{29}Si NMR (dept) of compound **10**: A characteristic low-field shift is observed at lower temperatures and thus silyl-ether coordination is present. The sample precipitates from the solvent at temperatures below 230K which results in broad resonances.

3.3 Behavior in solution of compound 12



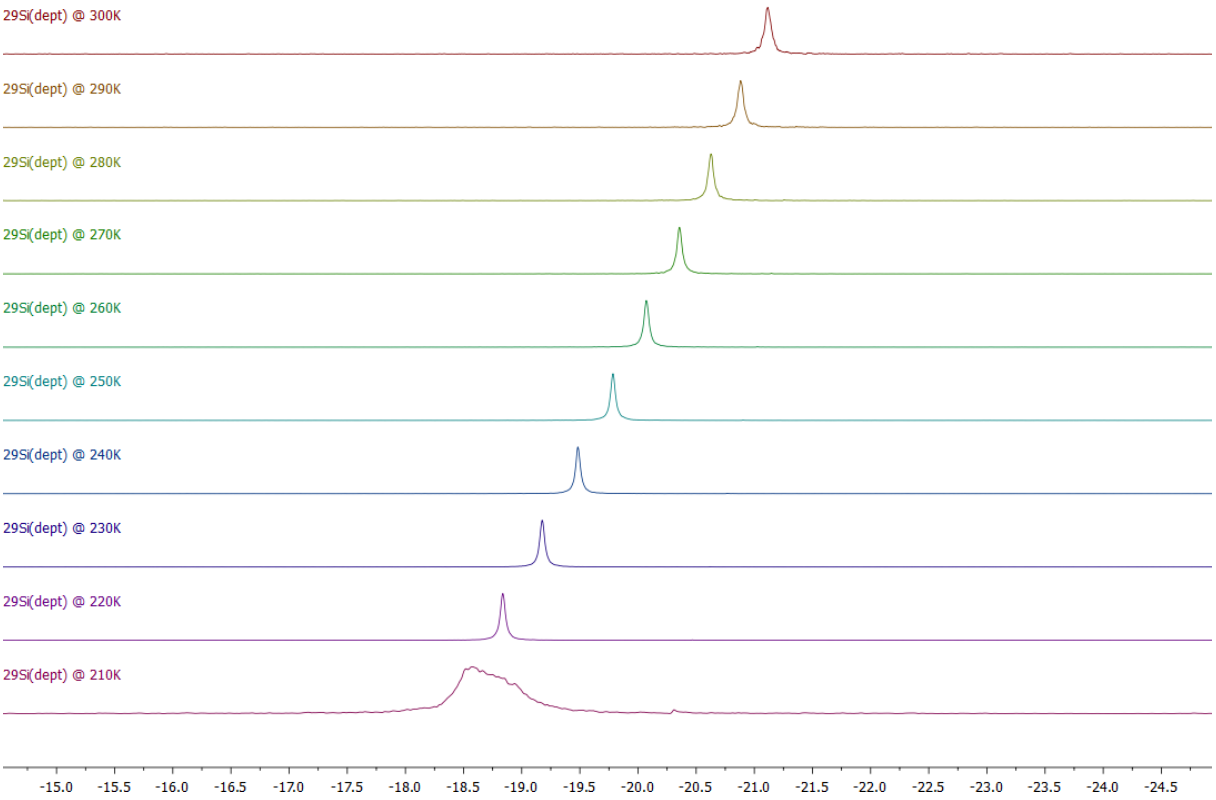


Figure S8. VT ^{29}Si NMR (dept) of compound **12**: A characteristic low-field shift is observed at lower temperatures and thus silyl-ether coordination is present. The sample precipitates from the solvent at temperatures below 220K which results in broad resonances.

4. References

[1] Decken, A.; LeBlanc, F. A.; Passmore, J.; Wang, X. Cyclodimethylsiloxane $(Me_2SiO)_m$ (m = 3–6) Ring Transformations on Reactions with $AgSbF_6$; Crystal Structure of $Ag(Me_2SiO)_7SbF_6$, *Eur. J. Inorg. Chem.* 2006, **2006**, 4033–4036

[2] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3–8.

[3] Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2015, **A71**, 3–8.

[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann H., *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

[5] Kratzert, D.; Holstein, J. J.; Krossing, I., DSR: enhanced modelling and refinement of disordered structures with SHELXL. *J. Appl. Crystallogr.*, 2015, **48**, 933–938.