Supporting information

Bis(dimethylchlorosilylvinyl)diphenylsilane (**3**) crystallizes in the monoclinic space group *C*2/*c*, with four molecules per unit cell.

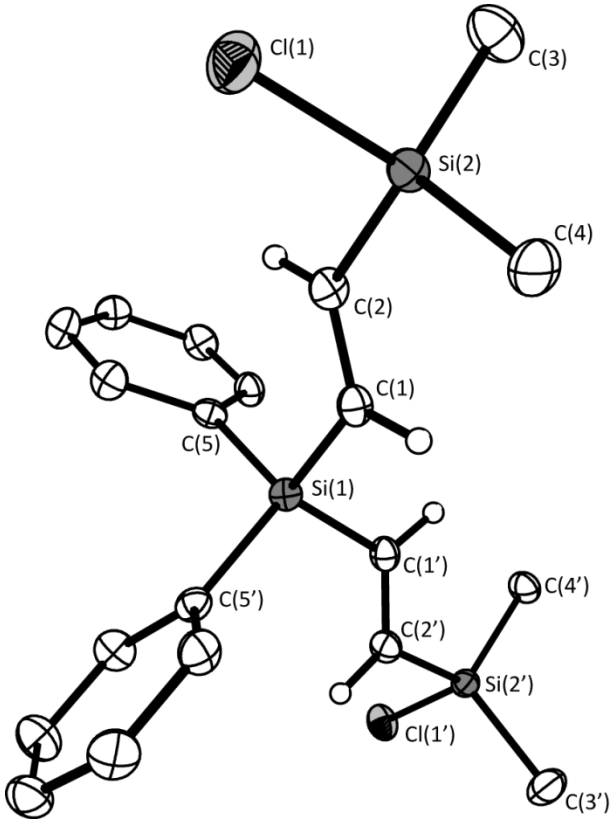

Figure S1: Molecular structure of **3** in the crystalline state. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms of methyl and phenyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl(1)–Si(1) 2.086(1), Si(1)–C(1) 1.869(2), Si(1)–C(5) 1.869(2), Si(2)–C(2) 1.857(2), Si(2)–C(3) 1.845(2), Si(2)–C(4) 1.848(2), C(1)–C(2) 1.334(2); C(1)–Si(1)–C(1') 110.3(1), C(5)–Si(1)–C(1') 107.2(1), C(5)–Si(1)–C(5') 110.4(1), C(2)–C(1)–Si(1) 125.7(1), C(1)–C(2)–Si(2) 123.3(1), C(3)–Si(2)–Cl(1) 107.2(1), C(4)–Si(2)–Cl(1) 107.4(1), C(3)–Si(2)–C(4) 112.9(1), C(2)–Si(2)–Cl(1) 105.4(1), C(3)–Si(2)–C(2) 112.4(1). Symmetric atoms are generated by symmetry $1 - x, y, ½ - z$.

Table S1: Selected NMR shifts [ppm] of compounds **14**, **17**, and **18** in $CDCl_3$ at 298 K (n.o. = not observable).

compound	*Si*F	Si*F*	Ph_2SiCH_2	CH_2SiF
14 (SiF_3)	–59.8	–139.6 (t)	1.23	0.88
17 (monosilicate)	n.o.	–131.4 (br)	1.27	0.83
18 (bissilicate)	–112.0	–119.2 (br)	1.27	0.74

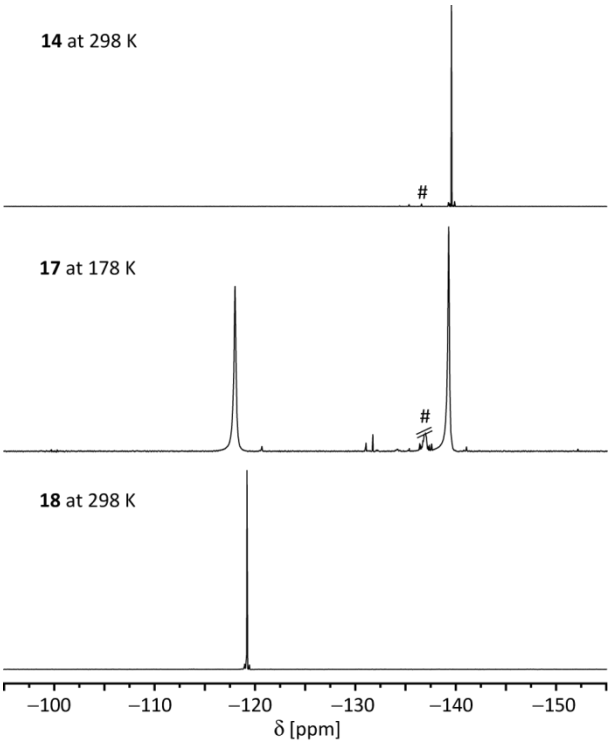

Figure S2: ^{19}F NMR spectra of **14**, **17** (1 eq. $[K{\cdot}18\text{-crown-6}]^+F^-$) and **18** (2 eq. $[K{\cdot}18\text{-crown-6}]^+F^-$) at declared temperatures in dichloromethane-d_2 (564 MHz); # denotes an impurity of **14** (ca. 1% at rt.).

Potassium 18-crown-6 silicate **17** crystallizes in the monoclinic space group $P2_1$, with two molecules per unit cell.

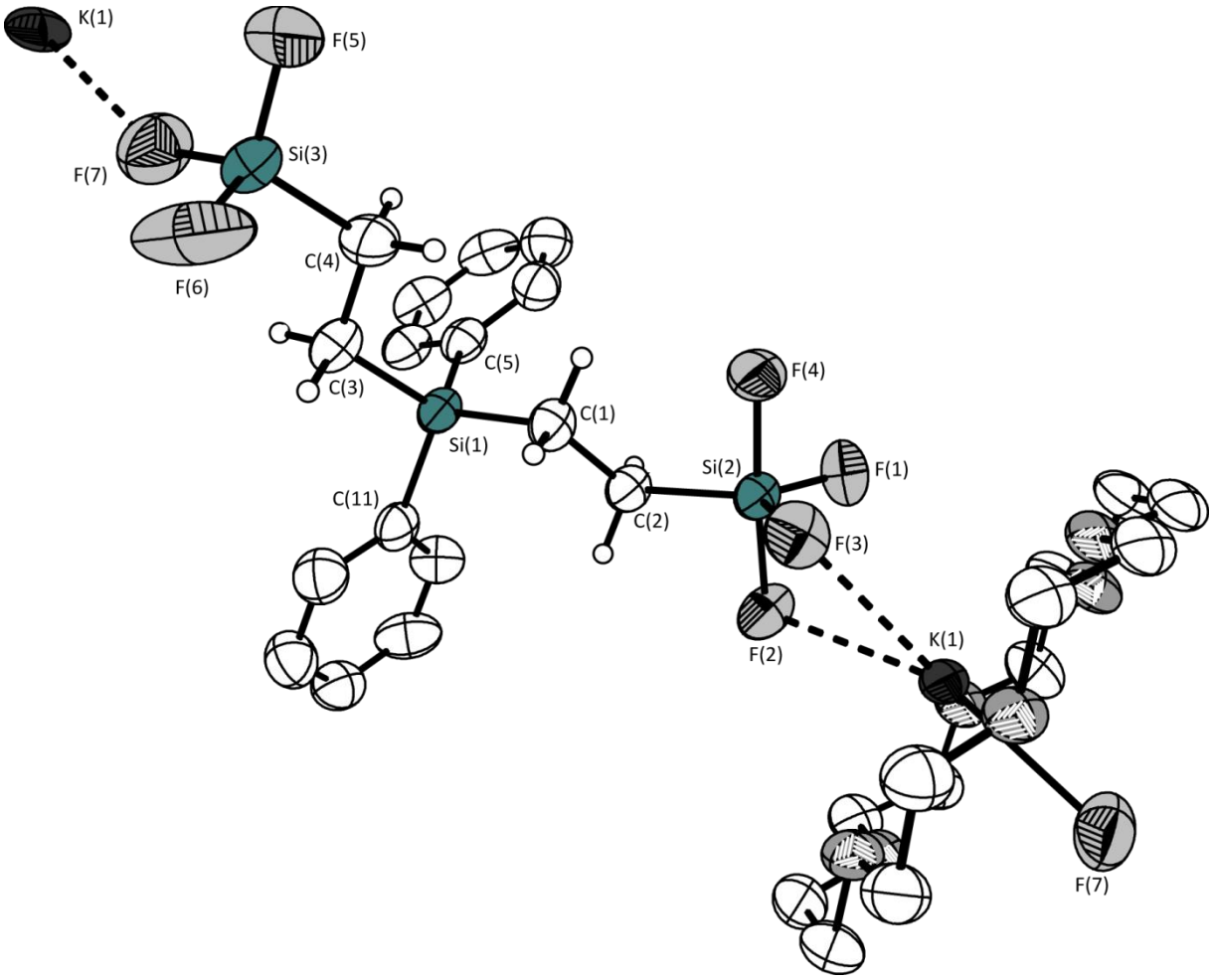

Figure S3: Molecular structure of **17** in the crystalline state. Thermal ellipsoids are drawn at 50% probability level. Only methylene hydrogen atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: K(1)–F(1) 3.298(4), K(1)–F(2) 2.611(4), K(1)–F(3) 3.006(7), K(1)–F(7) 2.677(5), Si(2)–F(1) 1.620(4), Si(2)–F(2) 1.705(4), Si(2)–F(3) 1.625(5), Si(2)–F(4) 1.670(4), Si(2)–C(2) 1.889(5), Si(3)–F(5) 1.568(4), Si(3)–F(6) 1.539(5), Si(3)–F(7) 1.536(5), C(1)–C(2) 1.526(6), C(3)–C(4) 1.534(8), F(2)–K(1)–F(7^2) 157.6(2), F(3)–K(1)–F(7^2) 141.2(2), Si(2)–F(2)–K(1) 105.2(2), Si(3)–F(7)–K(1^1) 152.0(3), F(1)–Si(2)–F(4) 89.7(2), F(1)–Si(2)–C(2) 91.3(2), F(1)–Si(2)–F(3) 113.0(3), F(1)–Si(2)–F(2) 86.4(2), C(2)–Si(2)–F(3) 125.4(3), C(2)–Si(2)–F(2) 91.3(2), F(2)–Si(2)–F(3) 89.3(2), C(4)–Si(3)–F(7) 110.3(3), F(5)–Si(3)–F(7) 108.4(3), C(1)–Si(1)–C(3) 106.7(3). Symmetric atoms are generated by symmetry $1 + x, y, 1 + z$ and $-1 + x, y, -1 + z$.