Supplementary material

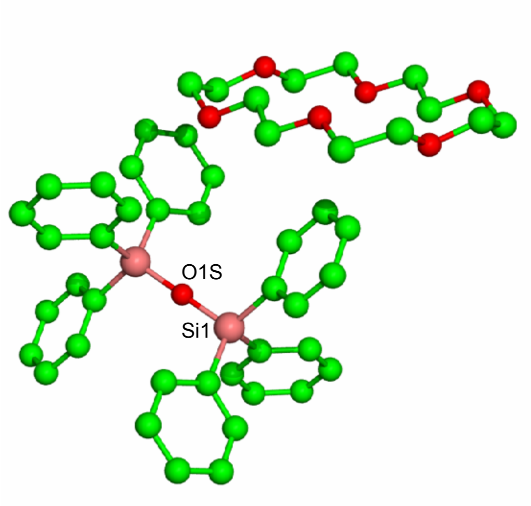

Figure S1 *The crystal structure of (Ph$_3$Si)$_2$O.18-c-6 isolated from the reaction of Ph$_3$SiH and KH in the presence of 18-c-6. Hydrogen atoms have been omitted for clarity.*

Synthesis of Bis(triphenylsilyl)ether·[18]crown-6 (**2**)

Potassium hydride (0.35 g, 8.8 mmol) was suspended in dry THF (5 ml). [18]crown-6 (1.1 g, 4.2 mmol) was dissolved in THF (10 ml) and added to the KH slurry. Triphenylsilane (0.99 g, 3.8 mmol) dissolved in THF (10 ml) was added to the crown/KH mixture dropwise by cannula over a period of 10 – 15 min whilst stirring. The mixture was left to stir for 5 h at room temperature, after which time it was allowed to settle, allowing the excess KH to separate from the solution. The solution was decanted into a separate Schlenk flask and the solvent evaporated to give a thick yellow/brown oil. A needle was inserted to scratch the glass and induce crystallisation. The very small seeded crystals were then redissolved in warm DME and placed in the refrigerator where overnight colourless crystalline cubes were deposited. Melting point = 141 - 144 °C. Recovered approximately 50 % yield, total yield not possible to determine – attempts to isolate and purify bulk sample were unsuccessful. ^{1}H NMR δ(CDCl$_3$): 3.69 (s, 24H), 7.2–7.5 (m, 18H), 7.98 (d, 12H). ^{13}C{^{1}H} NMR δ (CDCl$_3$): 70.70 (CH_2), 127.70 (CH), 129.78 (CH), 135.20 (CH), 136.41 (*ipso*).

Crystal data for **2**: $C_{48}H_{54}O_7Si_2$, M = 799.09, colourless cuboid, 0.40 × 0.40 × 0.40 mm^3, triclinic, space group $P\overline{1}$ (No. 2), a = 9.6423(11), b = 9.7626(12), c = 12.278(2) Å, α = 79.564(8), β = 72.247(7), γ = 86.267(10)°, V = 1082.5(3) Å^3, Z = 1, D_c = 1.226 g/cm^3, F_{000} = 426, KappaCCD, MoKα radiation, λ =

0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 55.0º, 7371 reflections collected, 4925 unique (R_{int} = 0.0389). Final *GooF* = 1.044, *R1* = 0.0566, *wR2* = 0.1071, *R* indices based on 3507 reflections with I > 2σ(I) (refinement on F^2) 367 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.132 mm^{-1}.

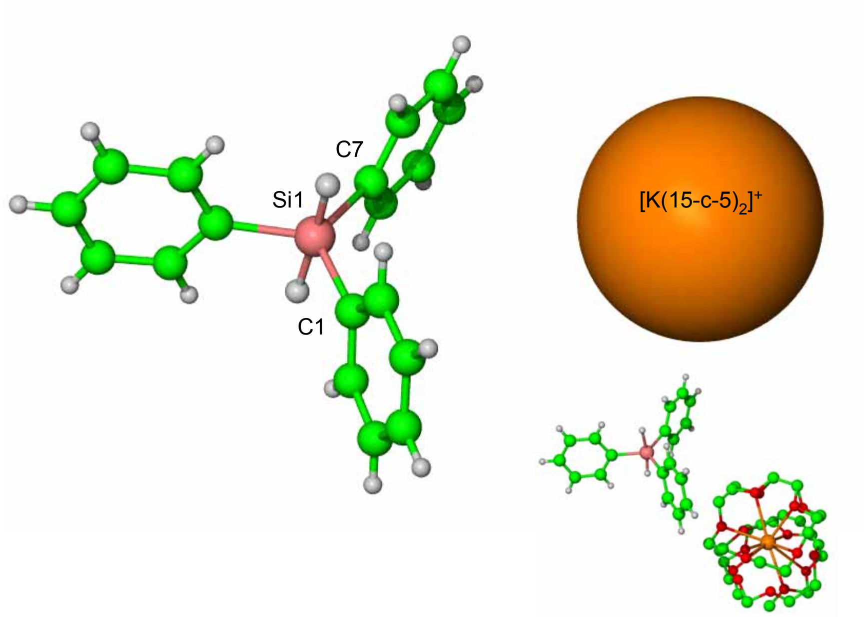

Figure S2. *Single-crystal X-ray structure of [K([15]crown-5)$_2$][Ph$_3$SiH$_2$] (**5**). The TBP geometry of the hypervalent silicon is consistent with the structural results for [K([18]crown-6)][Ph$_3$SiH$_2$](**1**). The [K([15]crown-5)$_2$]$^+$ cations stack upon each other inside pseudo-hexagonal channels resulting from the anion arrangement. The cation, consisting of a potassium ion sandwiched between two disordered crown ethers, are shown as a large sphere based on the potassium ion position for clarity. A disordered molecule of DME has also been omitted.*

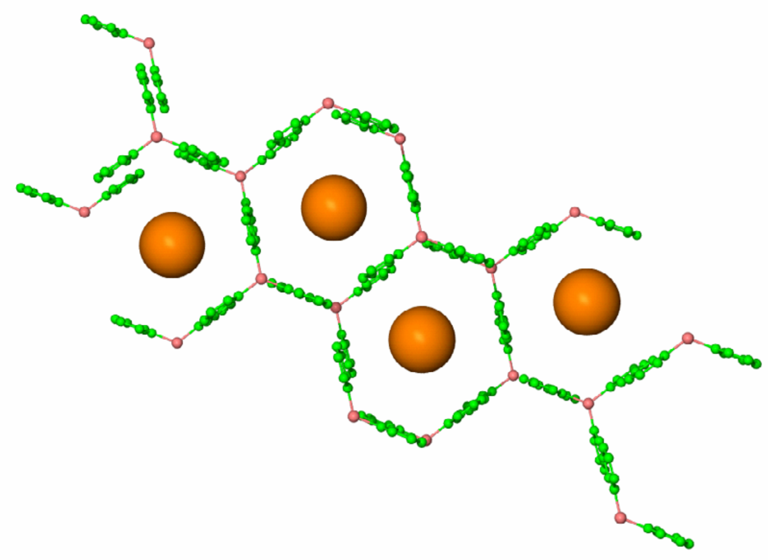

Figure S3. *The pseudo-hexagonal channels produced from the arrangement of the anions. The* $[K([15]crown\text{-}5)_2]^+$ *crown ether units are disordered and are represented as large orange spheres for clarity.*

Lineshape analysis

Kinetic data were analysed using the MEXICO program using the Arrhenius equation: $\ln(k) = \ln(A) - \exp(E_a/RT)$ and using also the Eyring equation: $\ln(k/T) = 23.76 - (\Delta H^‡/RT)+(\Delta S^‡/R)$. From the relevant plots we can extract enthalpy and entropy of activation, and a value for the Gibbs free energy of activation can be deduced using the relationship $\Delta G^‡ = \Delta H^‡ - T\Delta S^‡$. The calculated rates from the MEXICO program were used to produce Eyring and Arrhenius plots: the calculated rates are presented in Table S1 and the plots are shown in Figures S4 and S5, respectively.

Table S1 *Temperature and rate data from* ***1*** *+* Ph_3SiH

Temperature/K	Calculated rate/s^{-1}
293	7.3

298	11.4
303	16.6
308	36.33
313	56.52
318	106.70
323	137.45
328	164.97

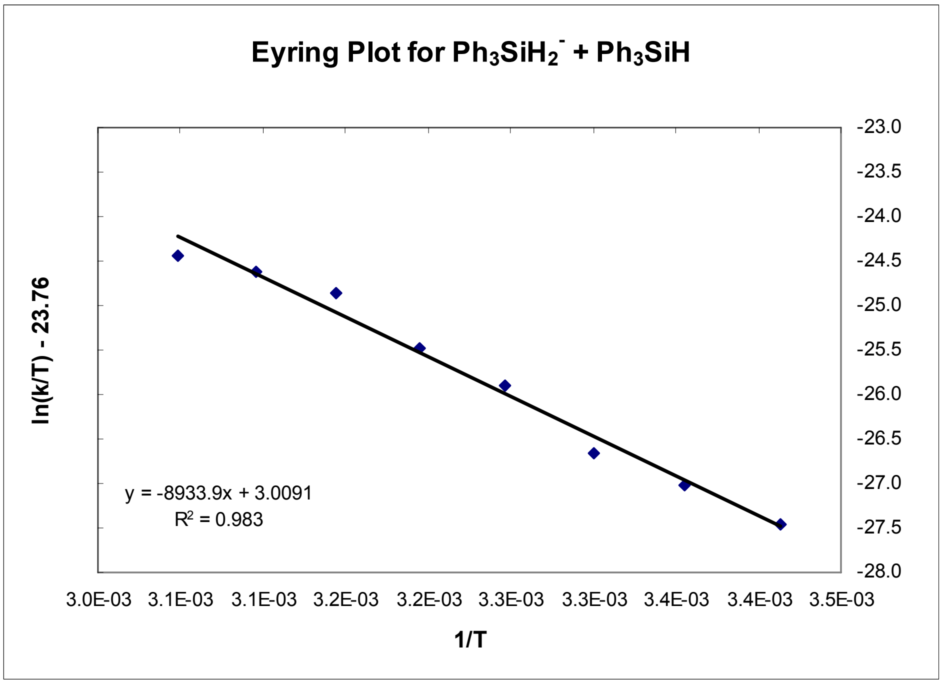

Figure S4 *Eyring plot from calculated rates for the reaction of **1**and Ph_3SiH.*

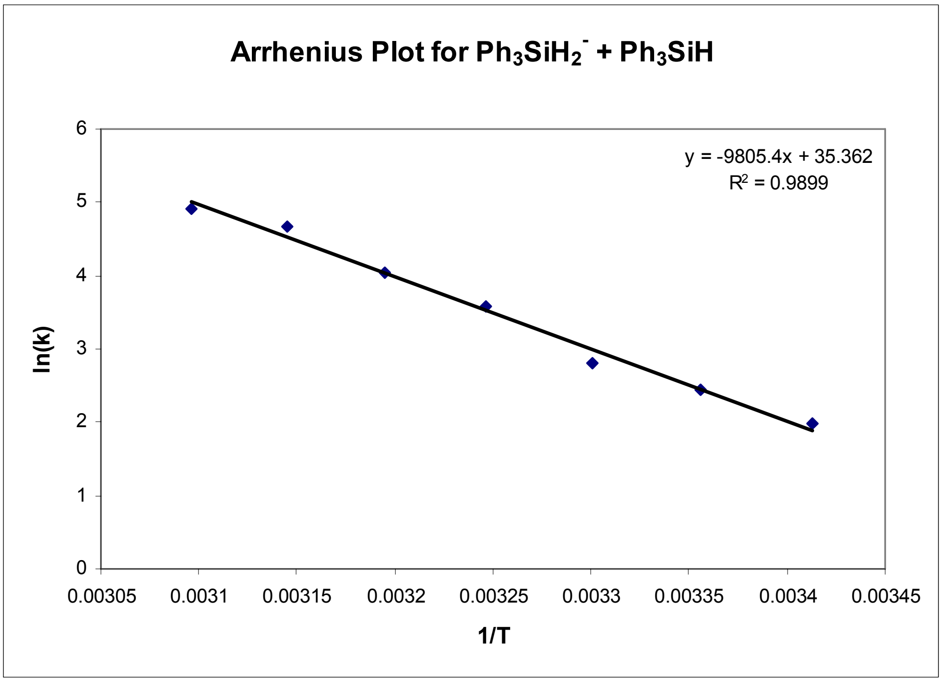

Figure S5 *Arrhenius plot from calculated rates for the reaction of **1** and Ph_3SiH.*

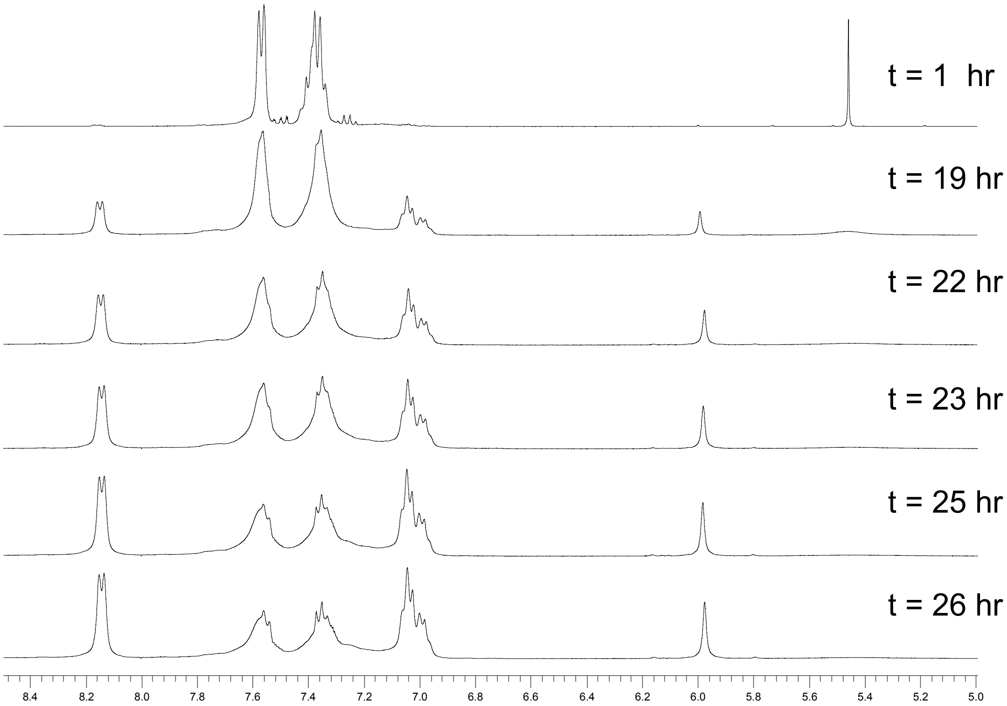

Figure S6 *^1H NMR spectrum showing formation of **1** over time from the reaction between Ph_3SiH + KH in the presence of 18-crown-6. The initial spectrum at 1 h after mixing shows only a trace of **1**.*

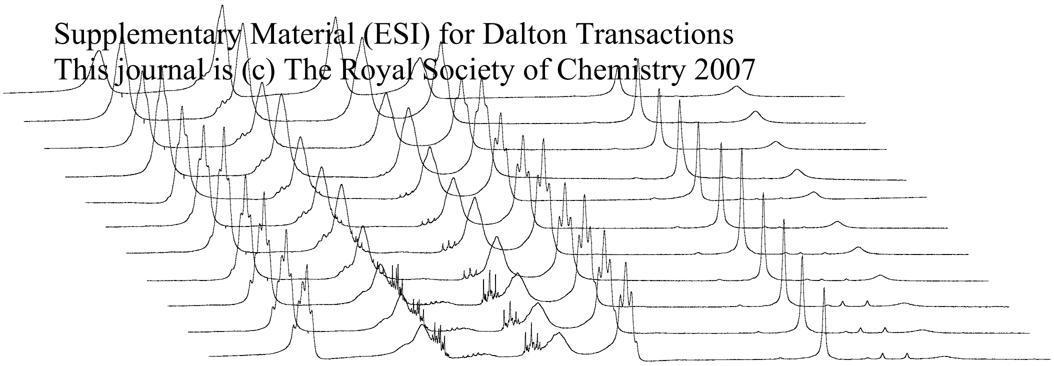

Figure S7 *The reaction of KH and (4-fluorophenyl)$_3$SiH in the presence of 18-crown-6 in THF-d8 over time monitored by ^{1}H NMR. Initially the reaction produces the dihydrido species, which from the broadening of the resonances indicates hydride exchange with the neutral starting material. This is followed by formation of a hydrido-fluoro hypervalent species. The fluorine source can only be the starting material and in conjunction with the observed formation of this species the appearance of sharp resonances in the phenyl region can clearly be seen and must be the by product of the fluorine abstraction.*

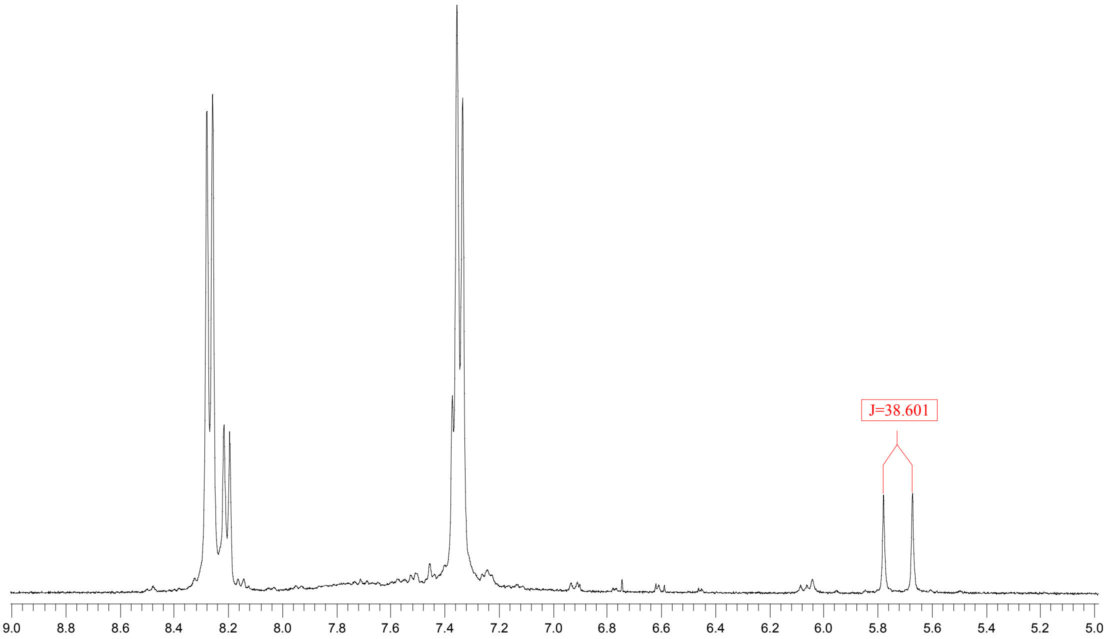

Figure S8 *^{1}H NMR spectrum of* ***18*** *The doublet with $^1J(^1H-^{19}F) = 38$ Hz corresponding to the hypervalent F—Si—H hypervalent unit has been highlighted in red. An $^{19}F\{^1H\}$ experiment confirms that the doublet arises from coupling with fluorine. Clearly, there is at least one other species contributing to the aromatic region: this is tentatively assigned as $[(CF_3C_6H_4)_3SiF_2]^-$.*