Hypervalent hydridosilicates: synthesis, structure and hydride bridging†‡§¶

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A range of hydridosilicate anions has been prepared and characterised by spectroscopic, structural and computational methods. The general approach involved reaction of KH with a neutral silane precursor in the presence of [18]crown-6. In this manner, [K([18]crown-6)]$^+$ salts of $[Ph_3SiH_2]^-$ (**1**), $[Ph_3SiF_2]^-$ (**9**), and $[(p\text{-}FC_6H_4)_3SiHF]^-/[(p\text{-}FC_6H_4)_3SiH_2]^-$ (**12**) were stabilised and characterized by NMR spectroscopy and X-ray diffraction. In each case, the anion adopts a trigonal bipyramidal (TBP) geometry with three equatorial phenyl groups eclipsing the axial Si–H/Si–F bonds. The Si–H · · · K distances, along with DFT calculations on **1**, indicate an electrostatic interaction that does not dictate the geometry adopted by the anion. A $[H_2SiO^iPr_3]^-$ salt (**7**) has also been crystallised in the same way; X-ray diffraction shows in this case a distorted TBP array with axial hydride ligands, and both Si–H · · · K and Si–O · · · K interactions. ^{1}H NMR exchange experiments show **1** to undergo facile hydride exchange with Ph_3SiH. Compound **1** acts as a good hydride transfer reagent to a variety of substrates, but its high reactivity often results in redistribution and other side reactions.

Introduction

Hypervalent silicon compounds continue to generate a great deal of interest.[1] This activity stems from a desire to understand the intermediacy of pentacoordinate silicon in nucleophilic substitutions, and pentacoordination in general.[2–7] Hypervalent silanes are particularly topical in the context of intramolecular hypervalent interactions in hypervalent silane transition metal complexes.[8–16] While many pentacoordinate hypervalent fluorosilicates have been studied and characterised, hydridosilicates are more reactive and challenging experimentally, and reports have been limited largely to descriptions of their preparation and reactivity. Few structural studies have been reported, and those species that have been characterised generally consist of zwitterionic systems, rather than a discrete $[X_5Si]^-$ (X = any atom) anion. Within the realm of silane chemistry the Si–H · · · M hydride bridging interaction is also of interest. Some reports have classed Si–H · · · M interactions as agostic; Sekiguchi *et al.* have characterised a series of di(alkali metal), complexes $[M(ligand)_n]_2[(HMe_2Si)_2C{=}C(SiMe_2H)_2]$ (M = Li, Na, K, Rb, Cs), which exhibit such so-called Si–H · · · M agostic interactions.[17,18] Si–H · · · Li interactions have been established by Goldfuss and co-workers in $[M(Me_2Si(H)N^tBu)]$ (M = Li, $Mg_{0.5}$) systems.[19] Further examples of similar Si–H · · · Li interactions are also known.[20–22] An example of an Si–H · · · Na interaction is found in the crystal structure of a sodium alcoholate, $[Na_8(O_3C_5H_{11})_6][SiH_3]_2$.[23] Alkali metal silyls of the form $M[SiH(Si^tBu_3)_2]$ (M = Li, Na, K) have also been prepared. The X-ray structure analysis of the benzene solvate of $K[SiH(Si^tBu_3)_2]$ shows a Si–H · · · K contact with an H · · · K distance of 3.01 Å. This, at the outset of our study, was the only example of an Si–H · · · K interaction in the Cambridge Structural Database (CSD).[24] We now report the synthesis, reactivity and structural characterisation of a range of crown-ether stabilised hypervalent silanes, which exhibit a range of interesting geometries and Si–H · · · K interactions. Part of this work has been published previously in preliminary form.[25]

Results and discussion

Synthesis and structure

We have undertaken the preparation and structural characterisation of a range of hypervalent dihydrido-, fluorohydrido- and difluorosilicates of the form $[R_3SiH_2]^-$, $[R_3SiHF]^-$ and $[R_3SiF_2]^-$, where R = an aryl or alkoxy group. The formation of these silicates can be achieved either by reaction of an alkali metal with Ph_2SiH_2, or by reaction of a triarylsilane with KH or KF. In each case, a crown ether is included to complex the alkali metal counter cation, affording greater solubility of the complex and stabilising the ionic product. Hypervalent hydridosilicates of the form $[(RO)_3SiH_2]^-$ and $[(RO)_4SiH]^-$ have previously been prepared by the reaction of $(RO)_3SiH$ with KH and KOR, respectively.[26–28] We carried out the reaction of KH with Ph_3SiH in the presence of [18]crown-6 in an attempt to produce $[K([18]crown\text{-}6)][Ph_3SiH_2]$ (**1**), in the manner used to synthesise the analogous alkoxyhydridosilicates; however the only isolated product was $(Ph_3Si)_2O\cdot[18]crown\text{-}6$ (**2**) (see ESI¶), with the oxygen source apparently being the THF solvent. However, reaction of Ph_2SiH_2 with potassium metal resulted instead in a redistribution of phenyl ligands to produce

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† Dedicated to Professor Ken Wade on occasion of his 75th birthday.

‡ The HTML version of this article has been enhanced with colour images.

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1 as the major product, in 84% yield based on Ph. The reaction of $PhSiH_3$ with potassium metal and [18]crown-6 also yielded **1**, in addition to other redistribution products.[29] However, reaction of $(p\text{-}MeC_6H_4)_2SiH_2$ (**3**) did not produce any hypervalent species under the conditions in which **1** is produced, and the reaction proceeded instead to give a silyl product.[29] The ^1H NMR spectrum of **1** shows a singlet at δ 5.95, with satellites from $^{29}Si–^1H$ coupling, which is assigned to the SiH_2 unit. The SiH resonance is shifted to high frequency compared to that of Ph_2SiH_2 (δ 3.9) and Ph_3SiH (δ 5.6) and has a much reduced coupling constant of 131 Hz (consistent with the hypercoordination at silicon) compared to the coupling constants of 197 and 199 Hz measured for Ph_2SiH_2 and Ph_3SiH, respectively, in the same solvent. The ^{29}Si NMR spectrum of **1** in THF-d_8 reveals a triplet with $^1J(^{29}Si–^1H)$ = 131 Hz, centred at δ −74 ppm, consistent with both protons being in equivalent environments or exchanging quickly on the NMR timescale. The reaction was repeated using Ph_2SiD_2 (**4**) in place of Ph_2SiH_2 to give $[K([18]crown\text{-}6)][Ph_3SiD_2]$ (**1D**). Altering the crown ether to [15]crown-5 gave $[K([15]crown\text{-}5)_2][Ph_3SiH_2]$ (**5**), which was also isolated as a main product of the reaction between $PhSiH_3$, potassium metal and two equivalents of [15]crown-5.

Increasing the quantity of the silane in the reaction between potassium metal, [18]crown-6 and Ph_2SiH_2, to greater than one equivalent led to the formation of a mixture of $[SiH_3]^-$, Ph_3SiH, and SiH_4, in addition to **1** in both THF and DME. Characterisation is based on the chemical shifts of silane species from ^1H NMR spectroscopic data. The broad nature of the resonances implies the existence of a dynamic exchange process. The only comparable species characterised by NMR spectroscopy in the literature are $Li[Ph_3SiH_2]$[30] and silicate anions of the form $K[(OR)_4SiH]$ or $K[(OR)_3SiH_2]$.[31] Our NMR results for **1** are consistent with the chemical shift observed for $Li[Ph_3SiH_2]$. The alkoxy-substituted silicate anions appear quite different to **1**, with δ_H *ca.* 4.5 and ^1J(Si–H) 190–220 Hz. Structural analyses of these systems have not been reported, although their NMR spectra have been interpreted in terms of $[(O^iPr)_3SiH_2]^-$ and $[(O^tBu)_3SiH_2]^-$ each possessing either one axial ($Si–H_{ax}$) and one equatorial Si–H bond ($Si–H_{eq}$) about the trigonal bipyramidal (TBP) silicon centre, or else two $Si–H_{eq}$ bonds in a TBP array, depending on the nature of the countercation and solvent.[31]

Highly air- and moisture-sensitive crystals of **1** and **5** were isolated from the reaction mixture by decanting the reaction solution, and were coated with a protective perfluoropolyalkyl ether oil. The less concentrated solution of **1** was retained and stored in a refrigerator, and after several days a further crop of crystals with distinctly different habit formed. The α form (mp 124 °C) deposited in far greater abundance from the concentrated solution when DME or THF was used as the solvent. Both forms (**1**α and **1**β, respectively) were subjected to single-crystal X-ray analysis. The geometry of the silane anion in both polymorphs is essentially the same: a TBP array with the hydrogen atoms occupying the axial positions, confirming the TBP geometry of $[Ph_3SiH_2]^-$ inferred by Rot *et al.*[30] The anion in the β polymorph exhibits crystallographic D_{3h} symmetry, whilst that in the monoclinic α form has approximate D_{3h} symmetry, owing to canting of the phenyl group planes with respect to the H–Si–H axis. The hypervalent nature of silicon is demonstrated by the reduced bond order in the H–Si–H unit, with Si–H bond lengths of 1.64 Å in the trigonal form and 1.55 Å in the monoclinic polymorph (*cf.* 1.49(3) Å in Ph_3SiH).[32] Similarly, the Si–C distances, at 1.928 Å (β) and 1.917–1.946 Å (α; two independent distances), are 0.07–0.08 Å longer than those observed for Ph_4Si.[33] In the trigonal β form the complex exhibits crystallographic threefold molecular symmetry with a linear H–Si–H vector; Fig. 1. The K···H distance, based on the position of the hydride substituent located in the difference Fourier map, is 2.82 Å (K···Si = 4.318 Å), remarkably less than the sum of the van der Waals radii[34] and shorter than the K···H distance in the binary hydride (2.854 Å).[35] In the monoclinic form there are two crystallographically independent half $[K([18]crown\text{-}6)]^+$ cations and a unique $[Ph_3SiH_2]^-$ anion. The interactions of the anion with the two K^+ centres are very different. One metal ion is involved in a cation–π interaction[36] to one of the phenyl substituents, with the shortest K···C distances measured at 3.360 and 3.375 Å, while the other K^+ ion engages in a K···H–Si interaction similar to that observed in the trigonal form (K···H distance = 3.108 Å; Si···K distance = 4.709 Å); Fig. 2. The

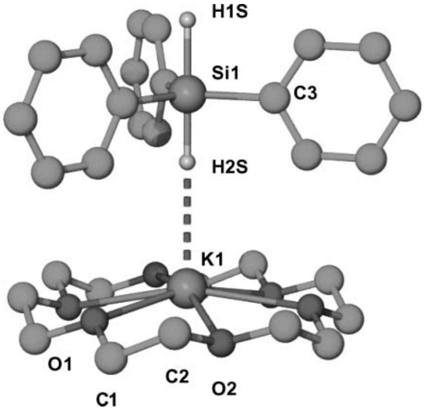


Fig. 1 Single-crystal X-ray structure of the trigonal (β) form of **1** showing the Si–H···K interaction as a dotted line. All C–H hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): K(1)–O(1) 2.794(2), K(1)–O(2) 2.799(2), Si(1)–C(3) 1.938(3), Si(1)–H(1S) 1.60, Si(1)–H(2S) 1.50, Si(1)–K(1) 4.32, K(1)–H(2) 2.82.

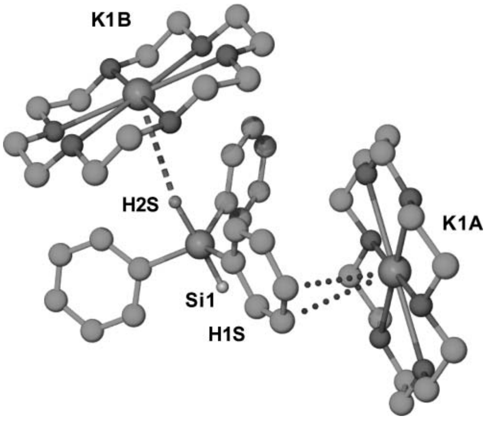


Fig. 2 Single-crystal X-ray structure of the monoclinic (α) form of **1** showing the Si–H···K interaction as a dotted line. All C–H hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): K(1A)–O(av) 2.796, K(1B)–O(av) 2.780, Si(1)–C(av) 1.927, Si(1)–H(1S) 1.55, Si(1)–H(2S) 1.55, Si(1)–K(1B) 4.717(1), K(1B)–H(2S) 3.21, K(1A)–C(16) 3.371(3), K(1A)–C(17) 3.358(3). Angle ∠H(1S)–Si(1)–H(2S) 177.8°.

greater distance in the monoclinic form arises from the fact that the anion is no longer situated directly above the cation, in order to facilitate the K$^+\cdots\pi$ interactions.

The structure of [K([15]crown-5)$_2$][Ph$_3$SiH$_2$] (**5**) exhibits considerable disorder in the [K([15]crown-5)$_2$]$^+$ cations and a molecule of DME solvent (see ESI¶). The silane anion in **5** is structurally very similar to its counterpart in **1**β, and exhibits a perfect TBP arrangement with all three phenyl groups in equatorial sites. There are however, no K···H–Si short contacts of the type observed in **1**. The potassium ion is sandwiched between two disordered [15]crown-5 moieties, which isolate the metal centre and prohibit interaction between the potassium ion and the silicon hydride ligands. The results suggests that the TBP geometry of the anion is not dictated by the K···H–Si interactions observed in **1**. The average Si–C bond length is 1.948 Å, and this is comparable with those of **1**. The plane of the phenyl rings is aligned with the H–Si–H moiety, akin to both polymorphs of **1**. The hypervalent anions in the crystal structure of **5** form 2-dimensional hexagonal channels within which the cations reside (see ESI¶). It is noteworthy that even in the absence of cation–anion interactions, the preferred geometry of the anion is TBP with axial hydride ligands.

In light of the novel Si–H···K interaction observed in the X-ray structure determined for **1**, a neutron diffraction study of **1D** was attempted. After exhaustive attempts, only crystals of the monoclinic α-form were obtained. Cooling to 20 K revealed diffuse lines, but sharper diffraction maxima were observed at 120 K, hence the data were collected at this higher temperature. Experimental problems meant that only a low precision data set was obtained. While the structure confirms the positions of the hydride substituents, the precision is low and the detailed structure is not presented. Both Si–D bond lengths measured from the neutron diffraction study are of the order of 1.6 Å (Si–H(1D) 1.598(15) and Si–H(2D) 1.597(15) Å); this gives a K(1B)–H(1D) distance of 3.17 Å. Assuming the trigonal form of [K([18]crown-6)][Ph$_3$SiH$_2$] (**1**) has the same Si–H bond length as that determined for the monoclinic form, the K···H distance for the trigonal form would be approximately 2.72 Å, very much shorter than the sum of the van der Waals radii of the two atoms.

Dynamic NMR spectroscopic studies

Attempts to prepare **1** using an excess of Ph$_2$SiH$_2$, with respect to potassium and [18]crown-6, resulted in a mixture of hydrosilane products. The ^{1}H NMR spectrum of this mixture shows, in addition to a broadened resonance at *ca.* δ 6 ppm associated with **1**, a broad signal at approximately δ 5.5 ppm with $^1J(^{29}\mathrm{Si}–^1\mathrm{H}) = 200$ Hz, assigned to Ph$_3$SiH. A resonance at *ca.* δ 1.2 ppm with $^1J(^{29}\mathrm{Si}–^1\mathrm{H}) = 82$ Hz was also evident. The breadth of the peaks associated with **1** and Ph$_3$SiH implies that a dynamic exchange process may be occurring. An EXSY experiment confirmed this, indicating proton exchange between **1** and Ph$_3$SiH, the species with a resonance at δ 1.2. ^{29}Si and ^{29}Si{^{1}H} NMR spectroscopy carried out on the sample gave results that were consistent with **1** and Ph$_3$SiH. The species responsible for the resonance in the ^{1}H NMR spectrum at δ 1.2 is consistent with the known NMR data for a [SiH$_3$]$^-$ with $^1J(^{29}\mathrm{Si}–^1\mathrm{H})$ *ca.* 80 Hz.[37] Deliberate addition of Ph$_3$SiH (1 equivalent) to a solution of **1** and examination of the mixture by EXSY (Fig. 3) confirmed SiH proton exchange between these species. This exchange could arise from simple hydride transfer from **1** to Ph$_3$SiH; alternatively it may involve "[K([18]crown-6)]$^+$H$^-$" as an intermediate. Another possible exchange mechanism is that previously proposed by Corriu *et al.*, in which an anionic intermediate in the form of a bridged dimer was assumed to mediate exchange in reactions observed between K[HSi(OR)$_4$] and phenylsilanes.[38]

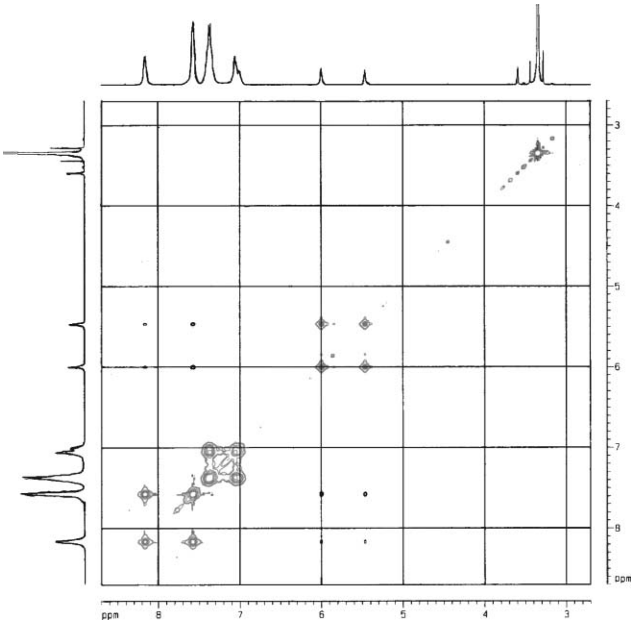


Fig. 3 EXSY spectrum of a sample containing **1** and Ph$_3$SiH in THF-d_8. The features on and near-diagonal correspond to exchange, and the eight off-diagonal features intersecting at 5.5 and 6.0 with 7.5 and 8.2 ppm correspond to through-space coupling.

The exchange process was further investigated by variable temperature ^{1}H NMR spectroscopy in THF-d_8. The resonances corresponding to the Si–H protons of **1** and Ph$_3$SiH broadened upon heating, but the low boiling point of the solvent (56 °C) prevented the observation of coalescence and the extraction of thermodynamic parameters for the process. In addition, the relatively high temperatures had a deleterious effect on the mixture, with the ^{1}H NMR spectrum after heating showing a significant number of new, unassignable resonances. On leaving the sample to stand over 14 d, crystals were isolated and characterised by single crystal X-ray diffraction as the known Ph$_4$Si.[33] Lineshape analysis for the hydride exchange process between [K([18]crown-6)][Ph$_3$SiH$_2$] (**1**) and Ph$_3$SiH with the aid of the MEXICO[39] program permitted calculation of the activation energy (E_a) for the exchange process (see ESI¶). Analysis of the data using the Arrhenius equation yielded an E_a of 81.5(5) kJ mol^{-1}; using the Eyring equation gave average values of $\Delta H^\ddagger = 74.3(5)$ kJ mol^{-1} and $\Delta S^\ddagger = 25(2)$ J K^{-1} mol^{-1}, and an activation free energy barrier of 67 kJ mol^{-1}. The positive value of the entropy of activation deduced from this experiment suggests that a dissociative mechanism is in operation. The bridging (associative) model suggested by Corriu *et al.*[31] for redistribution of OR ligands would presumably correspond to a negative $\Delta S^\ddagger$; accordingly we propose an exchange process involving simple hydride transfer from **1** to Ph$_3$SiH. However the entropy values presented here must be treated with some caution, as upon completion of the experiment the sample had degraded, with many small, unassignable peaks appearing along with a broad feature at *ca.* δ 5 ppm. This could correspond to the formation of some Ph_2SiH_2, which implies that our proposed exchange process is not necessarily the only one occurring. There are a few studies of intermolecular hydride exchange reported for this type of system,[38,40,41] but the thermodynamics of these processes have not been explored. However, similar studies have been carried out for intramolecular fluoride site exchange based on a pseudorotation mechanism in pentacoordinate fluorosilicates. Typical activation energy values for such processes are around 40 kJ mol^{-1}.[42]

If the proposed mechanism involving hydride exchange is correct, the reaction of KH and Ph_3SiH in the presence of 18-crown-6 should produce **1**, although difficulties have been noted previously with this procedure.[40] The reaction was attempted in an NMR tube, using 1.25 to 1.5 equivalents of hydride with respect to the silane and crown ether, and was followed by ^1H NMR spectroscopy at various time intervals (see ESI Fig. S6¶). It is clear from the spectra that **1** is indeed formed from the reaction between KH and Ph_3SiH, but that this reaction is very slow (days). The rate of this reaction, then, is likely to be affected by the exchange process discussed above: as soon as **1** is formed, it is free to exchange hydrides with the parent silane, decreasing the number of sites available for nucleophilic attack of H^- (by KH). The overall effect will be to decrease the rate of formation of **1**. When a preparative scale reaction was conducted without stirring, **1** was isolated by quenching the reaction with toluene after 24 h. This appears to be the effect of disturbing the exchange process, as **1** is relatively insoluble in the toluene–THF solvent system, whereas Ph_3SiH remains in solution.

With a view to exploring the structure of **1** in solution, we carried out a series of NOESY and COSY experiments. The results show that the *ortho* protons couple through space to the Si–H protons on the phenyl groups; there is also some evidence of through-space coupling to the methylene protons on the crown ether, indicating preservation of the solid-state structure in solution. Low temperature ^1H NMR experiments did not show any broadening of the Si–H resonance down to 180 K, the lowest temperature achievable with the solvent.

Influence of the crown ether on $[Ph_3SiH_2]^-$

An analogous procedure to that employed in the synthesis of **1** from the reaction between potassium metal and Ph_2SiH_2, was carried out using 2 equivalents of [15]crown-5 in place of [18]crown-6 in order to produce **5**. The ^1H NMR spectrum of the product in THF-d_8 is similar to that of **1**, with a $^1J(^{29}Si–^1H)$ of 132 Hz. Crystals of **5** were easily obtained from the reaction solution, using a similar procedure to that described for **1**, as noted above. Changing the crown ether in this case does not appear to have an effect on the formation of the hypervalent anion. However, the nature of the crown ether does have a significant influence on the exchange process observed for **1** and Ph_3SiH. An ^1H NMR study of the exchange between **5** and Ph_3SiH revealed no significant broadening of either of the Si–H resonances up to 325 K. A lineshape analysis of the spectrum was not possible on account of the very slow exchange, and it appears a different mechanism is in operation; this manifests itself in a reduction of the intensity of the resonance from the $[Ph_3SiH_2]^-$ species with respect to Ph_3SiH as the temperature increases. A ^1H NMR spectrum recorded after heating and subsequent cooling to room temperature showed an *increase* in the ratio of the $[Ph_3SiH_2]^-$: Ph_3SiH intensities. We conclude from this study that the counter-cation of **1** must be involved in the exchange mechanism. Sequestering the K^+ ion between a pair of [15]crown-5 ligands dramatically decreases the exchange rate.

Reactivity of $[K([18]crown\text{-}6)][Ph_3SiH_2]$

Several elementary reactions were carried out to assess the reactivity of **1** as a hydride transfer reagent. In each case, these were carried out in NMR tubes, and the conclusions are based on subsequent ^1H NMR analysis.

A recrystallised sample of **1**, produces a colourless solution in THF. Addition of 1 equivalent of Ph_3GeH in THF to the solution results in immediate effervescence and the formation of a bright yellow solution. The same colour and effects are obtained when Ph_3GeH is reacted with potassium metal in the presence of [18]crown-6. Subsequent ^1H NMR analysis of this reaction mixture reveals the disappearance of resonances for both the Ge–H and the Si–H moieties from **1**, and the appearance of a resonance associated with the Si–H proton of Ph_3SiH. Upon addition of HCl to this mixture the Ge–H resonance reappears. These observations are consistent with Ph_3GeH being deprotonated by **1** to produce the anion $[Ph_3Ge]^-$, on account of the higher electronegativity of Ge with respect to Si.[34] From a consideration of the relative electronegativities of C and Si, the reaction of Ph_3CH with **1** would be expected to deprotonate the tertiary carbon in an analogous manner to that inferred from the reaction of **1** with Ph_3GeH. However, addition of Ph_3CH in THF to a solution of **1** in THF causes no such reaction. No effervescence is observed, and the reaction mixture takes on a blood-red colour. The ^1H-NMR spectrum of this mixture is not easy to interpret, and addition of HCl to the reaction does not regenerate the starting material. Similar results are obtained for the reaction between PhCCH and **1**—the resulting ^1H NMR spectrum contains a multitude of unidentifiable resonances, and addition of HCl to the reaction does not regenerate the starting material.

A mixture of Ph_3SiF and **1** appears to undergo a redistribution reaction, producing $[Ph_3SiF_2]^-$ and $[Ph_3SiFH]^-$. Although no products were isolated, the details of the reaction are based on ^1H and ^{19}F NMR spectroscopic evidence. The ^1H NMR spectrum of the reaction products clearly shows the presence of Si–H with both a chemical shift (δ 5.4) and coupling constant ($^1J(^{29}Si–^1H) = 196$ Hz) consistent with Ph_3SiH, but there is no evidence of **1**. The ^{19}F NMR spectrum shows only a trace of Ph_3SiF, and the major peak (δ −101.7, $^1J(^{29}Si–^{19}F) = 255$ Hz) is consistent with $[Ph_3SiF_2]^-$ as reported for the complex $[K([2.2.2]cryptand)][Ph_3SiF_2]$ (δ −102.26 and $^1J(^{29}Si–^{19}F) = 259$ Hz) by Yamaguchi *et al.*[43]

Studies of $[H_2SiO(iPr)_3]^-$

The only isolated dihydridosilicates reported in the literature prior to this research are of the form $M[H_2Si(OR)_3]$.[26,31,44,45] In order to compare the structures of **1** and the silicate anions $[H_2Si(OR)_3]^-$ we repeated the synthesis of $[H_2Si(O^iPr)_3]^-$ by reaction of KH with $HSi(O^iPr)_3$, both in the presence and absence of [18]crown-6. Despite many attempts with crystals that appeared visually to be diffraction quality, we could not solve the structure of K[$H_2Si(O^iPr)_3$] (**6**). However, more success was enjoyed when $[K([18]crown\text{-}6)]^+$ was used as the counter-ion. Although, obtaining good quality crystals proved difficult using THF as the solvent, its replacement with Et_2O produced high quality crystals, which were used for an X-ray diffraction study. The structure of [K([18]crown-6][$H_2Si(OR)_3$] (**7**) shows the anion to adopt a distorted TBP array, with both hydride substituents in axial positions (Fig. 4) The isopropoxy groups occupy equatorial positions in a stereochemistry that appears to be at odds with Bent's Rule and known "apicophilicity",[46,47] *i.e.*, that the most electronegative atoms should be in the axial positions. The geometry determined by our study is also contrary to that predicted by Corriu and co-workers based on NMR spectroscopic data.[31] The anion exhibits short contacts from both an isopropoxy oxygen atom and one of the axial hydride ligands to the K^+ cation, in contrast to the single Si–H · · · K^+ interaction seen in **1**. This bidentate cation–anion arrangement is similar to those seen for hypervalent fluorosilicates. The H–Si–H moiety shows significant distortion from a true TBP arrangement, with a substantial deviation from linearity (<HSiH angle 160.3°). This appears to be brought about by the very short $K^+ \cdots H$ contact at 2.49 Å. The Si–H2S unit shows a similarly short interaction with the tertiary C–H on the isopropoxy group, with H · · · H distances of 2.27 and 1.91 Å, respectively; these are significantly shorter than the sum of the van der Waals radii (2.4 Å).

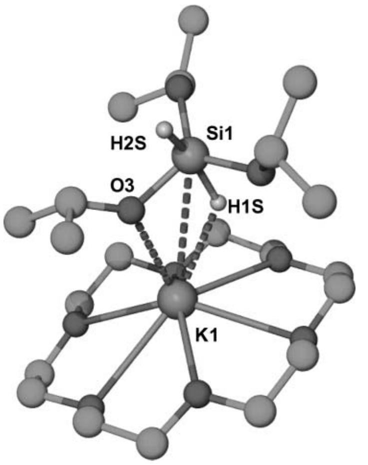
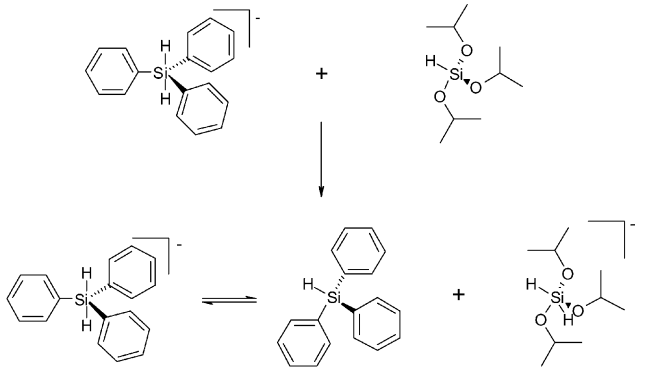


Fig. 4 X-Ray structure of K([18]crown-6)[$H_2Si(O^iPr)_3$] (**7**). Selected bond lengths: K(1)–Si(1) 3.653(2), K(1)–O(3) 2.799(4), K(1)–H(1S) 2.83, Si(1)–O(1) 1.697(4), Si(1)–O(2) 1.751(4), Si(1)–O(3) 1.716(4), Si(1)–H(1S) 1.52, Si(1)–H(2S) 1.49 Å.

To explore the similarities and differences between **1** and **7**, we carried out some simple studies involving mixing **1** and $HSi(OiPr)_3$, and in a separate experiment mixing [K([18]crown-6)][$H_2Si(OiPr)_3$] and Ph_3SiH. The results are summarised in Scheme 1, and indicate that **7** is formed upon combination of $HSi(OiPr)_3$ and **1**, presumably through hydride attack on the trialkoxysilane, which also produces Ph_3SiH. The Ph_3SiH thus formed goes on to exchange with unreacted **1**, *vide supra.* In contrast, when **7** is combined with Ph_3SiH, there is no evidence for the formation of **1**. Corriu *et al.*[38] have previously reported hydride exchange between K[$HSi(OEt)_4$], Ph_2SiH_2 and Ph_3SiH.



Scheme 1 Addition of $HSi(O^iPr)_3$ to [K([18]crown-6)][H_2SiPh_3] results in formation of an alkoxysilicate anion, and a proton exchange involving [K([18]crown-6)][H_2SiPh_3] and Ph_3SiH.

DFT Calculations on hypervalent anions $[Ph_3SiH_2]^-$ and $[H_2Si(O^iPr)_3]^-$

DFT calculations were carried out on the anions $[Ph_3SiH_2]^-$ and $[(^iPrO)_3SiH_2]^-$ to assess the relative stability of the three available stereoisomers; *i.e.*, with Si–H bonds in axial–axial (*aa*), axial–equatorial (*ae*) and equatorial–equatorial (*ee*) positions. The results for calculated energy differences in the stereoisomers of the two anions are summarised in Tables 1 and 2, respectively.

A Mulliken charge analysis of *aa*-$[Ph_3SiH_2]^-$ ascribes the following partial charges: Si +0.34, H −0.27, Ph −0.27. In *ae*-$[Ph_3SiH_2]^-$ the corresponding values are Si +0.35, H_{ax} −0.24, H_{eq} −0.15. Hence the negative charge in $[Ph_3SiH_2]^-$ is delocalised over all five ligands, and there are no grounds for assuming that the axial location of the Si–H bonds is a consequence of electrostatic repulsion between the hydride ligands. The closest non-bonded C · · · C contact in *aa*-$[Ph_3SiH_2]^-$ is 3.40 Å, twice the van der Waals radius of carbon.[34] In *ae*-$[Ph_3SiH_2]^-$, this is reduced to 3.08 Å. The results show repulsion between the three phenyl ligands to be a more important factor in determining the stereochemistry at Si than charge repulsion. The relatively equal apportionment of negative charge between the H and Ph ligands is consistent with the lengthening of the K · · · H–Si interaction to facilitate the $K^+ \cdots \pi$ interaction in the monoclinic α-form of **1**, in contrast to the shorter, linear K · · · H–Si interaction in the trigonal polymorph (β). These results accord with a recent bond energy analysis of $[Ph_3SiH_2]^-$ and related hypervalent silicate species,[2] in which the axial hydride

Table 1 Relative energies of stereoisomers of $[Ph_3SiH_2]^-$, calculated by DFT[25]

Geometry	Energy/hartrees	ΔE/kJ mol^{-1}
aa (D_{3h})	−985.65324	0
ae (C_s)	−985.63951	+36
ee	Converged to *aa* isomer	

Table 2 Relative energies of stereoisomers of $[(^iPrO)_3SiH_2]^-$, calculated by DFT

Geometry	Energy/hartrees	ΔE/kJ mol^{-1}
aa (D_{3h})	−872.12488	0
ae (C_s)	−872.11702	+21
ee (C_{2v})	−872.11902	+15

ligands were shown to be stabilized considerably by the presence of three electron-withdrawing phenyl groups.

An extensive conformational analysis for $[(^{i}PrO)_3SiH_2]^-$ to include the isopropoxy groups was not attempted due to excessive demands on computer time, and the calculations were constrained on the crystal structure conformations for the isopropoxy groups. The results give a good indication of the preferred isomer with respect to substituents directly bonded to the silicon centre and this certainly agrees with the observed *aa* geometry in the crystal structure.

In conclusion, the DFT and X-ray results show that the preferred sites of the hydride substituents in the TBP geometry for both anions are axial. The axial/equatorial arrangement suggested by NMR spectroscopic data may be attributed to the formation of cation–anion pairs in solution, with the inequivalence of the two Si–H substituents arising from the interaction of one hydride with the K⁺ ion.

Further studies of hypervalent hydrido- and fluorosilicates

The reaction of KH with Ph_3SiH in the presence of crown ethers led us to study the reactions of KH with other triarylsilanes and to alter the alkali metal. The combination of Na metal and [15]crown-5 with Ph_2SiH_2 or $PhSiH_3$ gives $[Na([15]crown\text{-}5)][SiH_3]$, which will be reported separately along with other $[SiH_3]^-$ species.[29] An inseparable mixture of both $[Na([18]crown\text{-}6)][Ph_3SiH_2]$ (**8**) and $[Na([18]crown\text{-}6)][SiH_3]$ was recovered from the reaction of Na and [18]crown-6 with both $PhSiH_3$ and Ph_2SiH_2. The NMR spectroscopic data for **8** are in good agreement with those obtained for **1** with the SiH resonance at δ 5.93 ppm and $^1J(^{29}Si\text{–}^1H) =$ 131 Hz (*cf.* 5.95 and 130 Hz, respectively, for **1**). The ^{29}Si NMR signal, at δ −73.9 (*cf.* −74.0 for **1**) appears as a triplet that collapses to a singlet upon proton decoupling.

The reaction of KH with Ph_3SiF and [18]crown-6 in THF produced $[K([18]crown\text{-}6)][Ph_3SiF_2]$ (**9**) as the main product. The mixed $[Ph_3SiHF]^-$ was not isolated. The same product was obtained from reaction of Ph_3SiF and KF in the presence of [18]crown-6, and has been previously reported.[42] The crystal structure has not previously been determined,[43] although in our hands the compound appeared to be reasonably stable in air. The structure of a single-crystal of **9** was determined by X-ray diffraction, and is shown in Fig. 5. The fluorosilicate **9** may be compared with **1** and also with $[K([2.2.2]cryptand)][Ph_3SiF_2]$[43] (CSD code[48] WOFJAC). The anions all adopt a trigonal bipyramidal geometry with approximately linear X–Si–X units (X = H, F). The Si–C distances in the hydrides (α- and β-**1**) are slightly longer than in the fluorides, which may be correlated with the fact that the Si–F distances are longer than Si–H.

The reaction between KH, [18]crown-6 and $(p\text{-}FC_6H_4)_3SiH$ (**10**) was also investigated using ^1H NMR spectroscopy, and the structure of the isolated product was determined by single-crystal X-ray diffraction. The initial product of the reaction is the hypervalent dihydridosilicate $[K([18]crown\text{-}6)][(p\text{-}FC_6H_4)_3SiH_2]$ (**11**), which was characterised by ^1H, ^{19}F and ^{29}Si NMR spectroscopy. However, upon crystallisation the compound undergoes some decomposition to release fluoride, resulting in the formation of mixed crystals of the hydride $[(p\text{-}FC_6H_4)_3SiH_2]^-$ and the fluoro/hydrido anion $[(p\text{-}FC_6H_4)_3Si(F)H]^-$, *i.e.* $[K([18]crown\text{-}6)]_2[(p\text{-}FC_6H_4)_3SiH_2][(p\text{-}FC_6H_4)_3Si(F)H]$ (**12**); Fig. 6. The two cations in the asymmetric unit occupy very different environments: one has a silicate anion on either side, with one anion interacting with the potassium ion through a H–Si–H/F···K interaction, whilst the other anion interacts with potassium through a π···K contact. The remaining cation is complexed with two molecules of THF through an O···K contact (one per face of the crown), and the whole cation complex is disordered over two sites. The fluoride in the axial site was modelled with a site occupancy factor of 0.5.

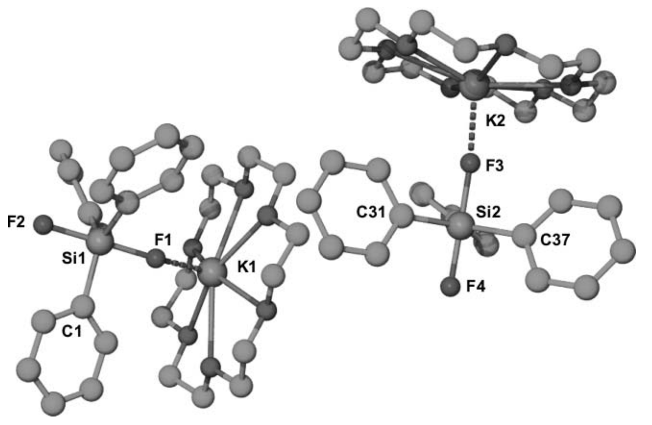


Fig. 5 The crystal structure of $[K([18]crown\text{-}6)][Ph_3SiF_2]$ (**9**) obtained from the reaction of Ph_3SiF and KH in the presence of [18]crown-6.

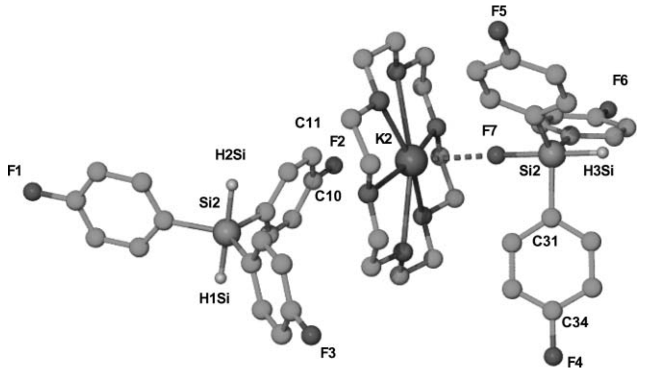


Fig. 6 X-Ray crystal structure of $[K([18]crown\text{-}6)]_2[(p\text{-}FC_6H_4)_3SiH_2]\cdot[K([18]crown\text{-}6)][(p\text{-}FC_6H_4)_3Si(F)H]$ (**12**).

The reaction between KH and **10** was studied by ^1H NMR spectroscopy, in order to investigate the fluoride redistribution reaction. The reaction was followed as a function of time (see ESI Fig. S7¶), the results clearly show that the first species to form is the dihydridosilicate $[K([18]crown\text{-}6)][(p\text{-}FC_6H_4)_3SiH_2]$, **11** followed by the fluorohydridosilicate $[K([18]crown\text{-}6)][(p\text{-}FC_6H_4)_3Si(F)H]$ (**13**). The resonances of both species in the aromatic region are broad, implying that an exchange similar to that found between **1** and Ph_3SiH is occurring. Also evident in the ^1H NMR spectrum are sharp resonances in the aromatic region, whose appearance coincides with the formation of the fluorohydrido species **13**; these then must arise through fluoride abstraction from the aryl substituents.

The reaction of KH and [18]crown-6 with a number of other silanes was attempted; namely $(p\text{-}CF_3C_6H_4)_3SiH$ (**14**),[49] $(p\text{-}MeOC_6H_4)_3SiH$ (**15**), $(p\text{-}MeC_6H_4)_3SiH$ (**16**) and $(m\text{-}F_2C_6H_3)_3SiH$ (**17**); either by the direct reaction of KH with the silane in the presence of the crown ether, or by reaction with **1**. In all cases it proved impossible to isolate analytically pure samples because of the highly reactive nature of the compounds and complications arising from side reactions; hence characterisation is based solely upon NMR spectroscopic data. The reaction between KH and **14** in the presence of [18]crown-6 gave a hypervalent fluorohydridosilicate product, [K([18]crown-6)][(p-$CF_3C_6H_4)_3SiHF$] (**18**), presumably by fluoride abstraction from the -CF_3 group. The hypervalent nature of **18** is demonstrated in the ^{1}H NMR spectrum by a doublet assigned to SiH centred at δ 5.74 with $^1J(^{29}\text{Si}–^1\text{H}) =$ 125 Hz, comparable to **1** but smaller than for Ph_2SiFH (**19**)[50] $^1J(^{29}\text{Si}–^1\text{H}) = 231$ Hz or the parent silane **14**. The $^1\text{H}\{^{19}\text{F}\}$, ^{19}F and $^{19}\text{F}\{^1\text{H}\}$ spectra show that the doublet arises from coupling with fluorine, with $^1J(^{19}\text{F}–^1\text{H}) = 38$ Hz. This is certainly smaller than the coupling constant measured for **19** ($^1J(^{19}\text{F}–^1\text{H}) = 54$ Hz; see ESI Fig. S8¶). The ^{1}H and ^{19}F and NMR spectra contain other resonances which cannot be assigned to **18**. Since there are no other SiH resonances, this species may tentatively be assigned as [p-$CF_3C_6H_4)_3SiF_2]^-$. The ^{19}F NMR spectrum supports this assignment, with a peak at δ −101.7 and satellites corresponding to $^1J(^{29}\text{Si}–^{19}\text{F}) = 260$ Hz.

The reaction of KH with (p-$MeOC_6H_4)_3SiH$ (**15**) was carried out in THF-d_8 and followed by ^{1}H NMR spectroscopy. The reaction produced a hypervalent product tentatively assigned as [K([18]crown-6)][(p-$MeOC_6H_4)_3SiH_2$] (**20**) in very small amounts. This assignment is based on the characteristic splitting of the phenyl protons, resulting in the *ortho* resonances being shifted to higher frequency and the observation of a signal at approximately δ 6 ppm with $^1J(^1\text{H}–^{29}\text{Si}) = 127$ Hz assigned to the hypervalent H–Si–H unit. On standing for 72 h, the amount of hypervalent product had increased and a further product had appeared, which is possibly of the form $(R_3Si)_2O$ or $(R_3Si)_2$ (where R = (p-MeC_6H_4)).

^{1}H NMR spectroscopic studies of the combination of (p-$MeC_6H_4)_3SiH$ (**16**) with KH/[18]crown-6 in THF showed no evidence of reaction after 48 h. Reaction of the silane **16** with **1** in THF showed evidence of both **16** and Ph_3SiH in solution, along with some resonances consistent with a hypervalent $[R_3SiH_2]^-$ species. However, it is not clear if this is **1** or [K([18]crown-6)][(p-$MeC_6H_4)_3SiH_2$]. This reaction requires further study.

Combination of (m-$F_2C_6H_3)_3SiH$ (**17**) with KH/[18]crown-6 as with the other fluoroarylsilanes apparently resulted in fluoride abstraction from the aryl ligand to give [K([18]crown-6)][(m-$F_2C_6H_3)_3SiHF$] (**21**). This assignment is based on low coupling constants of $^1J(^1\text{H}–^{29}\text{Si}) = 130$ Hz and $^1J(^1\text{H}–^{19}\text{F}) = 33.2$ Hz; comparable to those found for **13** and **18**.

Experimental

Materials and methods

Molecular sieves purchased from either Lancaster or Aldrich and were stored in an oven at 80 °C. Prior to use they were baked *in vacuo* at 250 °C for a minimum of 3 h. The solvents Et_2O, THF, toluene, DME and Bu_2O were dried by distillation from sodium, using benzophenone as an indicator, and degassed by bubbling argon *via* a cannula through the solvent for 15–20 min. For NMR spectroscopy the solvents THF-d_8 and toluene-d_8, purchased from Goss, were stored over sodium for a period of approximately 2–3 d and were then degassed by a freeze–pump–thaw method. The deuteriated solvents were then decanted from the sodium and stored over fresh sodium or pre-dried 4Å sieves; both methods produced dry solvents. KH purchased from Aldrich as a 60% suspension in mineral oil was transferred into a flask fitted with Young's valves, and under an argon atmosphere the mineral oil was removed *via* cannula. The hydride was then washed, typically with 6 portions of pentane, removing each aliquot in turn by cannula to remove all the mineral oil. The hydride was then dried *in vacuo* and stored in a glove box. KH was always used in conjunction with all-glass equipment. Crown ethers were dissolved in a minimum quantity of dry degassed Et_2O and stored over pre-dried 4Å sieves for at least 24 h. The solution was decanted from the sieves and the solvent removed under reduced pressure. The crown ethers were stored in a glove box. Potassium was cut into small chunks in a glove box (after removal of the oxidised metal surface) and used immediately. DME was dried over Na/benzophenone and stored in ampoules over 4Å molecular sieves. All other operations were carried out in Schlenk tubes baked in an oven then treated with Me_3SiCl followed by three pump–purge steps. THF-d_8 was dried over Na and stored in ampoules over 4Å molecular sieves. [18]crown-6 was dried by dissolving in dry diethyl ether over 4Å molecular sieves. Microanalyses for C, H and N were carried out at the University of North London. NMR tubes used were standard 5 mm diameter borosilicate glass fitted with a Young's NMR valve, and treated by exactly the same process as the reaction glassware. Samples were loaded into the NMR tube inside a glove box. Care was taken to avoid contact with the PTFE valve of the NMR tube to prevent reaction of the sample with the valve surface. THF-d_8 used for the NMR was dried over sodium metal for 14 d then stored over baked 4Å molecular sieves, and degassed using freeze–pump–thaw cycles. The solvent was injected into the NMR tube *via* a rubber septum using a dried glass syringe.

X-Ray crystallography

Suitable single crystals were mounted using silicon grease on a thin glass fibre. Crystallographic measurements were carried out using a Nonius KappaCCD equipped with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). The standard data collection temperature was 120 K, maintained using an open flow N_2 Oxford Cryostream device. Integration was carried out using the Denzo-SMN[51] package. Data sets were corrected for Lorentz and polarisation effects and for the effects of absorption. Structures were solved using direct methods in SHELXS-97[52] and developed using conventional alternating cycles of least-squares refinement with SHELXL-97[53] and difference Fourier synthesis with the aid of the graphical interface program XSeed.[54] In all cases non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. Si–H hydrogen atoms were located experimentally and their positional and displacement parameters refined wherever possible. Molecular graphics were produced using the program POV-Ray.[55]

DFT Calculations

Geometry optimisations for the anions $[Ph_3SiH_2]^-$ and $[(^i\text{PrO})_3SiH_2]^-$ were performed at the B3LYP level for

$[(^{i}PrO)_3SiH_2]^-$, using a 6-31+G* basis set on Si and O and 6-31G* on C and H atoms to allow for charge redistribution. Frequency calculations were carried out to confirm the structures obtained were minima. RMS Forces were converged, but not the displacements, which is expected as the lowest vibrational frequencies are between 10 and 15 cm^{-1}. All calculations were carried out using Gaussian.[56] For $[Ph_3SiH_2]^-$[25] the optimisations were carried out at the B3LYP/6-31G* level.

Syntheses

$[K([18]crown\text{-}6)][Ph_3SiH_2]$ (1). [18]crown-6 (1.7 g, 6.4 mmol) dissolved in DME (30 ml) was transferred into a Schlenk tube containing chopped potassium metal (0.35 g, 6.4 mmol) whilst stirring to produce a deep blue solution. To this solution Ph_2SiH_2 (1.7 g, 6.4 mmol) was added dropwise by syringe over a period of 5 min; the solution took on a yellow/green tinge, eventually turning deep amber. After addition of Ph_2SiH_2 was complete, the volume was reduced to 20 mL by evaporation under reduced pressure, and the solution placed in a refrigerator at 5 °C for a period of 2 d, whereupon colourless crystals had formed. The solution was transferred to a freezer at −20 °C, where more crystals were obtained. The pale yellow solution was decanted, and the colourless crystals were isolated. Stored under nitrogen the crystals developed a brown coating that was removed by washing with benzene. ^1H NMR δ(THF-d_8): 3.14 (s, 24H), 5.81 (s, 2H $^1J(^{29}Si–^1H)$ = 131 Hz), 6.8–6.9 (m, 9H), 7.98 (d, 6H). $^{13}C\{^1H\}$ NMR δ(THF-d_8): 68.48 (CH_2), 123.79 (*meta*), 124.31 (*ortho*), 135.25 (*para*), 156.24 (*ipso*). $^{29}Si\{^1H\}$ NMR δ(THF-d_8): −74.01 (s). ^{29}Si NMR δ(THF-d_8): −73.99 (t, $J(^{29}Si–^1H)$ = 131 Hz). IR ν/cm^{-1} (neat): ν(Si–H) 1524(m). Mp 122–124 °C. Anal. calc. for $C_{30}H_{41}O_6SiK$: C, 63.89; H, 7.32. Found: C, 61.34; H, 7.32%. Several samples were tested all giving low readings for carbon possibly due to decomposition.

*Crystal data for **1**α.* $C_{30}H_{41}O_6SiK$, M = 564.82, colourless block, 0.8 × 0.8 × 0.5 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 9.3861(5), b = 20.2252(10), c = 16.5969(10) Å, β = 103.540(3)°, V = 3063.1(3) $Å^3$, Z = 4, D_c = 1.225 g cm^{-3}, F_{000} = 1208, KappaCCD, Mo-Kα radiation, λ = 0.71073 Å, T = 125(2) K, $2\theta_{max}$ = 55.0°, 16817 reflections collected, 6802 unique (R_{int} = 0.0810). Final GooF = 1.018, $R1$ = 0.0527, $wR2$ = 0.1039, R indices based on 4249 reflections with $I > 2\sigma(I)$ (refinement on F^2), 355 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.251 mm^{-1}.

*Crystal data for **1**β.* $C_{30}H_{41}O_6SiK$, M = 564.82, very pale green cubic blocks, 0.25 × 0.25 × 0.25 mm, trigonal, space group $R3m{:}R$ (No. 160), $a = b = c$ = 9.4377(12), $\alpha = \beta = \gamma$ = 97.956(6) Å, V = 813.80(18) $Å^3$, Z = 1, D_c = 1.152 g cm^{-3}, F_{000} = 302, KappaCCD, Mo-Kα radiation, λ = 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 49.9°, 4637 reflections collected, 1043 unique (R_{int} = 0.0506). Final GooF = 1.132, $R1$ = 0.0330, $wR2$ = 0.0697, R indices based on 1000 reflections with $I > 2\sigma(I)$ (refinement on F^2 77 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.237 mm^{-1}. Absolute structure parameter[57] = 0.54(7).

$[K([18]crown\text{-}6)][Ph_3SiD_2]$ (1D). Complex **1D** was prepared in a similar procedure to **1**. 18-crown-6 (0.68 g, 2.6 mmol) dissolved in 1,2-DME (20 mL) was transferred into a Schlenk tube containing chopped potassium metal (0.1 g, 2.6 mmol) whilst stirring to produce a deep blue solution. To this solution Ph_2SiD_2 (0.48 g, 2.6 mmol) was added dropwise by syringe over a period of 5 min and the solution took on a yellow/green tinge eventually turning deep amber. After addition of Ph_2SiH_2 was complete the volume was reduced to 20 mL by evaporation and placed in a refrigerator at 5 °C for a period of 2 d where colourless crystals formed. ^1H NMR δ(THF-d_8): 3.4 (s, 24H), 6.9–7.1 (m, 9H), 8.1 (dd, 6H),. $^{13}C\{^1H\}$ NMR δ(THF-d_8): 70.42 (CH_2), 125.6 (*meta*), 126.1 (*ortho*), 135.3 (*para*), 158.3 (*ipso*). $^{29}Si\{^1H\}$ NMR δ(THF-d_8): −74.9 (quintet, $^1J(^{29}Si–^2H)$ = 20.5 Hz. ^2H NMR δ(THF-d_8): 5.98 (s, $^1J(^{29}Si–^2H)$ = 20.5 Hz). MS (FAB), m/z (relative intensity): 303 (1), 259 (0.06), 184 (0.08), 39 (0.5).

$(p\text{-}MeC_6H_4)_2SiH_2$ (3). $(p\text{-}MeC_6H_4)_2SiCl_2$ (10 g, 36 mmol) dissolved in Bu_2O (60 mL) was placed in a pressure equalised dropping funnel and added dropwise over a period of approximately 1 h to a slurry of $LiAlH_4$ (1.4 g, 36 mmol) in Bu_2O (20 mL) stirred over an ice bath. The reaction mixture was allowed to warm to room temperature and stirred for 24 h after which the solvent was evaporated under reduced pressure. $CHCl_3$ (40 mL) was added whilst stirring the mixture over a ice bath, followed by dropwise addition of HCl (approx. 1–2 M) (care!) until no more effervescence was observed. The mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous layer was washed with 2 × 20 mL portions of $CHCl_3$. The ethereal washings were combined dried over $MgSO_4$ and filtered. The final product was obtained by distillation 70–80 °C/approx. 0.25 mbar. Yield: 6.2 g (83%). ^1H NMR $\delta(CDCl_3)$: 2.34 (s, 3H), 4.89 (s, $^1J(^{29}Si–^1H)$ = 198 Hz, 2H), 7.17 (d, $^3J(^1H–^1H)$ = 8 Hz, 4H), 7.48 (d, $^3J(^1H–^1H)$ = 8 Hz, 4H). $^{13}C\{^1H\}$ NMR $\delta(CDCl_3)$: 21.5 (*Me*), 128.0 (*para*), 128.9 (*meta*), 135.4 (*ortho*), 139.8 (*ipso*). ^{29}Si NMR $\delta(CDCl_3)$: −34 (tt, $^1J(^{29}Si–^1H)$ = 198 Hz, $^3J(^{29}Si–^1H)$ = 5.5 Hz. $^{29}Si\{^1H\}$ NMR $\delta(CDCl_3)$: −34 (s). MS (EI), m/z (relative intensity): 212 (M^+, 0.89), 197 ($M - CH_3$), 120 (C_7H_7SiH, 1), 105 (C_6H_4SiH, 0.021). IR ν/cm^{-1} (neat): 2135 ν(Si–H).

Ph_2SiD_2 (4). Ph_2SiCl_2 (24 g, 95 mmol) was added dropwise to a slurry of $LiAlD_4$ (2 g, 50 mmol) in Et_2O (100 mL). After addition was complete, the mixture was refluxed for 24 h allowed to cool to room temperature and filtered through a glass sinter, to remove $LiAlCl_4$, and the solvent reduced to half volume where more $LiAlCl_4$ precipitated. The remaining liquor was decanted from the $LiAlCl_4$ and distilled. One fraction was collected at 68–72 °C at 0.6 mbar. The ^1H NMR spectrum revealed that Et_2O was also present in a silane : ether ratio of 3 : 1, this may be due to the formation of a complex, with silicon acting as a Lewis acid and the ether oxygen as the Lewis base. The crude product was dissolved in Et_2O (50 mL) and HCl (2 M) added dropwise until effervescence ceased, this was followed by addition of distilled water (10 mL). The ethereal layer was separated and the aqueous layer was washed with 3 × 30 mL portions of Et_2O. All the organic extracts were combined, dried over $MgSO_4$ and filtered. After the ether had been evaporated under reduced pressure the product was obtained by reduced pressure distillation 68–72 °C/approx 0.6 mbar. Yield: 13.1 g (74%). ^1H NMR $\delta(CDCl_3)$: 7.57 (m, 6H), 7.59 (d, 4H). $^{13}C\{^1H\}$NMR $\delta(CDCl_3)$: 128.1 (*para*), 129.9 (*meta*), 131.42 (*ipso*), 135.7 (*ortho*). ^{29}Si NMR $\delta(CDCl_3)$: −33.9 (quintet of multiplets, $^1J(^{29}Si–^2H)$ = 30.5 Hz). $^{29}Si\{^1H\}$ NMR $\delta(CDCl_3)$: −33.9 (quin, $^1J(^{29}Si–^2H)$ = 30.5 Hz).

^{2}H NMR δ(CHCl$_3$): 5.1 (s, $^1J(^{29}\mathrm{Si}–^2\mathrm{H}) = 30.5$ Hz) MS (EI), *m*/*z* (relative intensity): 186 (1.00), 107 (0.97), 105 (0.24), 79 (0.08). IR ν/cm^{-1} (neat): ν(Si–D) 1549(s).

[K([15]crown-5)$_2$][Ph$_3$SiH$_2$] (5). [15]crown-5 (1.7 g, 6.4 mmol) dissolved in DME (30 mL) was transferred into a Schlenk tube containing freshly chopped potassium metal (0.35 g, 6.4 mmol) whilst stirring to produce a deep blue solution. To this solution Ph$_2$SiH$_2$ (1.7 g, 6.4 mmol) was added dropwise by syringe over a period of 5 min and the solution took on a yellow/green tinge eventually turning deep amber. After addition of Ph$_2$SiH$_2$ was complete the volume was reduced to 20mL by evaporation and placed in a refrigerator at 5 °C for a period of 2 d, whereupon colourless crystals formed. The solution was transferred to a freezer at −20 °C where more crystals were obtained. The solution (now pale yellow) was decanted and the colourless crystals were isolated. Stored under nitrogen the crystals developed a brown coating that was removed by washing with benzene. ^{1}H NMR δ(THF-*d*$_8$): 3.44 (s, 40H), 5.96 (s, 2H $^1J(^{29}\mathrm{Si}–^1\mathrm{H}) = 131$ Hz), 6.9–7.1 (m, 9H), 8.11–8.14 (m, 6H). ^{13}C{^{1}H} NMR δ(THF-*d*$_8$): 68.79 (*C*H$_2$), 125.57 (*meta*), 126.05 (*para*), 137.09 (*ortho*), 158.20 (*ipso*). ^{29}Si{^{1}H} NMR δ(THF-*d*$_8$): −74.01 (s). ^{29}Si NMR δ(THF-*d*$_8$): −73.99 (t, $J(^{29}\mathrm{Si}–^1\mathrm{H}) = 131$ Hz). Anal. calc. for C$_{38}$H$_{57}$O$_{10}$SiK: C, 61.59; H, 7.75. Found: C, 61.44; H, 7.39%.

Crystal data for 5. C$_{38}$H$_{57}$O$_{10}$SiK, $M = 741.049$, colourless block, 0.70 × 0.50 × 0.40 mm, orthorhombic, space group *Pnma* (No. 62), $a = 37.820(8)$, $b = 12.712(3)$, $c = 17.536(4)$ Å, $V = 8431(3)$ Å^3, $Z = 8$, $D_c = 1.167$ g cm^{-3}, $F_{000} = 2960$, KappaCCD, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{\max} = 50.0°$, 35476 reflections collected, 7703 unique ($R_{\mathrm{int}} = 0.1724$). Final GooF = 1.262, $R1 = 0.1319$, $wR2 = 0.3374$, R indices based on 4149 reflections with $I > 2\sigma(I)$ (refinement on F^2), 541 parameters, 2 restraints. Lp and absorption corrections applied, $\mu = 0.205$ mm^{-1}.

[K([18]crown-6][H$_2$Si(OR)$_3$] (7). [18]crown-6 (1.02 g, 3.86 mmol) was dissolved in Et$_2$O (15 mL) and added to a slurry of KH (0.16 g, 4.0 mmol) in Et$_2$O (5 mL). (PriO)$_3$SiH[31] (0.76 g, 3.70 mmol) was added dropwise to the KH/[18]crown-6 mixture. Initially a very small amount of gas was evolved; possibly SiH$_4$. The reaction mixture was stirred for 2 h and placed in a refrigerator, whereupon colourless crystals appeared which were harvested by removing the supernatant liquor and washing with 2 (5 mL) portions of pentane. The remaining supernatant was saved and pentane added to yield more crystals. Total yield 1.25 g (66%). ^{1}H NMR δ(C$_6$D$_6$): 1.37 (d, 18H, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 6$ Hz), 3.16 (s, 24H), 4.42 (s, 2H, $^1J(^{29}\mathrm{Si}–^1\mathrm{H}) = 222$ Hz), 4.61 (septet, 3H, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 6$ Hz)). ^{13}C{^{1}H} NMR δ(C$_6$D$_6$): 27.84 (*C*H$_3$), 62.68 (*C*H), 70.41 (*C*H$_2$). ^{29}Si{^{1}H} NMR δ(C$_6$D$_6$): −81.1 (s). ^{29}Si NMR δ(THF-*d*$_8$): −81.1 (t, $J(^{29}\mathrm{Si}–^1\mathrm{H}) = 222$ Hz).

Crystal data for 7. C$_{21}$H$_{47}$KO$_9$Si, $M = 510.78$, colourless block, 0.30 × 0.20 × 0.20 mm, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 9.2574(9)$, $b = 15.1610(12)$, $c = 20.5984(17)$ Å, $V = 2891.0(4)$ Å^3, $Z = 4$, $D_c = 1.174$ g cm^{-3}, $F_{000} = 1112$, Mo-Kα radiation, $\lambda = 0.71070$ Å, $T = 145(2)$ K, $2\theta_{\max} = 50.0°$, 10561 reflections collected, 4928 unique ($R_{\mathrm{int}} = 0.0809$). Final GooF = 1.056, $R1 = 0.0677$, $wR2 = 0.1453$, R indices based on 3533 reflections with $I > 2\sigma(I)$ (refinement on F^2), 300 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.266$ mm^{-1}. Absolute structure parameter[57] = 0.00(8).

[Na([18]crown-6)][Ph$_3$SiH$_2$] (8) and [Na([18]crown-6)][SiH$_3$] (mixture). [18]crown-6 (1.93 g, 7.3 mmol) dissolved in THF (40 mL) was transferred into a Schlenk tube containing freshly chopped sodium metal (0.17 g, 7.4 mmol) whilst stirring to produce an intense blue solution. To this solution PhSiH$_3$ (0.85 g, 7.9 mmol) was added dropwise by syringe over a period of 5 min and the solution took on a gold colour, eventually obtaining a green tinge. The mixture began to turn cloudy after 1 h, and after stirring for 24 h it had separated into an off-white precipitate and an amber solution. The solution was removed and retained. The precipitate was washed with pentane (20 mL) followed by Et$_2$O (20 mL) and these washings were combined with the reaction solution, which produced a pale yellow crystalline product when placed in the freezer. Warm THF (200 mL) dissolved most of the precipitate: on cooling this too produced crystals. Both batches of crystals showed identical ^{1}H NMR spectra. Total yield of crystalline products = 1.8 g. ^{1}H NMR δ(THF-*d*$_8$): 1.27 (s, 4H*, $J(^{29}\mathrm{Si}–^1\mathrm{H}) = 78.5$ Hz), 3.51 (s, 38H), 5.93 (s, 2H $J(^{29}\mathrm{Si}–^1\mathrm{H}) = 131$ Hz), 6.9–7.2 (m, 9H), 8.1 (d, 6H). ^{13}C NMR δ(THF-*d*$_8$): 70.15 (s, *C*H$_2$), 125.59 (s, *C*H, *meta*), 126.11 (s, *C*H, *para*), 137.08 (s, *C*H, *ortho*), 156.24 (s, *C*Si, *ipso*). ^{29}Si{^{1}H} NMR δ(THF-d$_8$): −73.90 (s). ^{29}Si NMR δ(THF-d$_8$): −73.86 (t, $J(^{29}\mathrm{Si}–^1\mathrm{H}) = 131$ Hz). *Given as 4 as the ratio of [SiH$_3$]$^-$/[Ph$_3$SiH$_2$] protons.

[K([18]crown-6)][Ph$_3$SiF$_2$] (9). KF (0.15 g, 2.6 mmol) was placed along with [18]crown-6 (0.68 g, 2.6 mmol) in a Schlenk tube and suspended in THF (40 mL). To this was added Ph$_3$SiF (0.63 g, 2.3 mmol) in THF (30 mL) whilst stirring. The mixture was left to stir for 24 h after which hexane was carefully added to give a 3 : 1 THF–hexane layered system. Upon standing, white crystals appeared. Yield. 1.13 g, 77%. ^{1}H NMR δ(THF-*d*$_8$): 3.31 (s, 24H), 6.84–6.95 (m, 9H), 7.91–7.95 (m, 6H),. ^{13}C NMR δ(THF-*d*$_8$): 70.50 (s, *C*$_{12}$H$_{24}$O$_6$), 125.70 (s, broad, *meta*), 135.41 (s, *para*), 137.94 (t, $^3J(^{13}\mathrm{C}–^{19}\mathrm{F}) = 7.46$ Hz), 152.10 (t, $^2J(^{13}\mathrm{C}–^{19}\mathrm{F}) \approx 40$ Hz). ^{19}F NMR δ(THF-*d*$_8$): −100.3 (s, $^1J(^{29}\mathrm{Si}–^{19}\mathrm{F}) = 255$ Hz). ^{19}F{^{1}H} NMR δ(THF-*d*$_8$): −100.3 (s, $^1J(^{29}\mathrm{Si}–^{19}\mathrm{F}) = 255$ Hz). ^{29}Si{^{1}H} NMR δ(THF-*d*$_8$): −107.7 (t, $^1J(^{29}\mathrm{Si}–^{19}\mathrm{F}) = 253$ Hz). ^{29}Si NMR δ(THF-*d*$_8$): −107.7 (t, $^1J(^{29}\mathrm{Si}–^{19}\mathrm{F}) = 255$ Hz). Anal. calc. for C$_{30}$H$_{39}$F$_2$KO$_6$Si: C, 59.97; H, 6.54. Found: C, 59.69; H, 6.80%.

Crystal data for [K([18]crown-6)][Ph$_3$SiF$_2$]. C$_{30}$H$_{39}$F$_2$KO$_6$Si, $M = 600.80$, colourless block, 0.50 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.5474(3)$, $b = 37.429(3)$, $c = 17.6357(8)$ Å, $\beta = 103.016(16)°$, $V = 6140.2(6)$ Å^3, $Z = 8$, $D_c = 1.300$ g cm^{-3}, $F_{000} = 2544$, KappaCCD, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 115(2)$ K, $2\theta_{\max} = 55.0°$, 24097 reflections collected, 11948 unique ($R_{\mathrm{int}} = 0.1088$). Final GooF = 1.091, $R1 = 0.0816$, $wR2 = 0.1058$, R indices based on 7304 reflections with $I > 2\sigma(I)$ (refinement on F^2), 722 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.264$ mm^{-1}.

(*p*-FC$_6$H$_4$)$_3$SiH (10). Mg turnings (2.6 g, 107 mmol) were placed in a round-bottom flask and stirred under an Ar atmosphere until a reflective coating had been applied to the glass surface, when Et$_2$O (60 mLl) was introduced. To this was added 1,4-C$_6$H$_4$BrF (10.5 ml, 16.7 g, 95.4 mmol) dissolved in Et$_2$O (100 mL) dropwise at a rate to maintain steady reflux, the colour of the mixture changing from colourless to green to deep brown over this period. After addition the mixture was heated to maintain a gentle reflux for 1 h and allowed to cool to room temperature. HSiCl$_3$ (3.0 ml, 4.0 g, 30.0 mmol) was dissolved in Et$_2$O (100 mL) and added dropwise to the brown mixture over 1 h. After addition of the silane was complete, the mixture was stirred for 30 min and dilute HCl was added dropwise to neutralise excess Grignard. The ether layer was separated and washed with dilute HCl and dried over $MgSO_4$ to produce a green/yellow solution which when filtered through charcoal to give a pale yellow solution. The Et_2O was removed under reduced pressure to give a pale yellow oil. The final product was obtained by subliming at 300 °C at 0.6 mbar. The product was isolated as a colourless oil that crystallises over a period of 2–3 d at room temperature. Yield 6.97 g (75%). ^{1}H NMR δ(CDCl$_3$): 5.52 (s, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 201$ Hz, 1H), 6.85–6.95 (m, 6H), 7.30–7.35 (m, 6H). ^{13}C NMR δ(CD$_2$Cl$_2$): 115.8 (d, $^{2}J(^{19}\mathrm{F}–^{13}\mathrm{C}) = 19.9$ Hz, *meta*), 129.0 (d, $^{4}J(^{19}\mathrm{F}–^{13}\mathrm{C}) = 3.6$ Hz *ipso*), 138.1, (d, $^{3}J(^{19}\mathrm{F}–^{13}\mathrm{C}) = 7.7$ Hz, *ortho*), 164.7 (d, $^{1}J(^{19}\mathrm{F}–^{13}\mathrm{C}) = 249.5$ Hz, *para*). ^{19}F{^{1}H} NMR δ(CD$_2$Cl$_2$): −111.0 (s). ^{19}F NMR δ(CD$_2$Cl$_2$): −111.0 (m). ^{29}Si{^{1}H} NMR δ(CDCl$_3$): −19.1 (s). ^{29}Si NMR δ(CDCl$_3$): −19.1 (dt, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 201$ Hz, $^{3}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 5.5$ Hz. MS (EI), *m*/*z* (relative intensity): 123 (0.18), 218 (1), 219 (0.68), 313 (0.35), 314 (0.34). IR ν/cm^{-1} (HCBD mull): 2146 (s) ν(Si–H). Anal. calc. for $(FC_6H_4)_3SiH$ C, 68.77; H, 4.17. Found C, 68.67; H, 4.28%. Mp 42–44 °C.

[K([18]crown-6)]$_2$[(*p*-FC$_6$H$_4$)$_3$SiH$_2$]·[(FC$_6$H$_4$)$_3$Si(F)H] (12). KH (0.060 g, 1.5 mmol) was suspended in THF (15 mL) and stirred. [18]crown-6 (0.43 g, d 1.6 mmol) was dissolved in THF (15 ml) and added to the KH suspension; to this was then added (4-C$_6$H$_4$F)$_3$SiH (0.51 g, 1.6 mmol) dissolved in THF (5 mL). The mixture was stirred for 4 h, after which pentane was carefully added to give a 3 : 1 THF–pentane layered system. Upon standing for 72 h at approx. 5 °C the solution produced colourless crystals. Yield 0.54 g, 54%. ^{1}H NMR δ(THF-d_8): 3.46 (s, 24H), 5.92 (s, 2H $J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 132$ Hz), 6.74 (m, 6H), 8.07 (m, 6H). ^{13}C NMR δ(THF-d_8): 70.49 (s), 112.06 (d, $^{2}J(^{19}\mathrm{F}–^{13}\mathrm{C}) = 19.1$ Hz meta), 135.36 (d, $^{3}J(^{19}\mathrm{F}–^{13}\mathrm{C}) = 6.3$ Hz, *ortho*), 141.89 (d, $^{4}J(^{19}\mathrm{F}–^{13}\mathrm{C}) = 3.6$ Hz, *ipso*), 161.15 (d, $^{1}J(^{13}\mathrm{C}–^{19}\mathrm{F}) = 241$ Hz, *para*). ^{19}F{^{1}H} NMR δ(THF-d_8): −120.0 (s). ^{19}F NMR δ(THF-d_8): −120.0 (m). ^{29}Si{^{1}H} NMR δ(THF-d$_8$): −75.1 (s). ^{29}Si NMR δ(THF-d_8): −75.1 (t, broad, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 135$ Hz).

Crystal data for ***12*** *[K([18]crown-6)]$_2$[(FC$_6$H$_4$)$_3$SiH$_2$]·[(FC$_6$H$_4$)$_3$Si(F)H]·ca.2THF.* $C_{70.5}H_{91}F_{6.5}K_2O_{14}Si_2$, $M = 1420.32$, colourless block, 0.30 × 0.20 × 0.20 mm, monoclinic, space group $C2/c$ (No. 15), $a = 43.5927(18)$, $b = 9.6984(5)$, $c = 40.2731(18)$ Å, $\beta = 120.188(2)°$, $V = 14717.5(12)$ Å^3, $Z = 8$, $D_c = 1.282$ g cm^{-3}, $F_{000} = 6004$, KappaCCD, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 50.0°$, 27159 reflections collected, 12445 unique ($R_{int} = 0.0734$). Final GooF = 1.121, $R1 = 0.0935$, $wR2 = 0.1490$, R indices based on 8745 reflections with $I > 2\sigma(I)$ (refinement on F^2), 840 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.238$ mm^{-1}. The Si–F fluorine atom was modelled at 0.5 occupancy because of apparent H/F disorder.

(*p*-MeOC$_6$H$_4$)$_3$SiH (15). Mg turnings (3.8 g, 156 mmol) were placed in a round-bottom flask and stirred under an Ar atmosphere until a reflective coating had been applied to the glass surface. To this was added dropwise 1,4-MeOC$_6$H$_4$Br (28.04 g, 18.8 mL, 150 mmol) dissolved in Et$_2$O (80 mL) over a period of 1 h, the colour of the mixture changing from colourless to green to deep brown over this period. After the addition the mixture was heated to maintain a gentle reflux for 4 h and allowed to cool to room temperature. HSiCl$_3$ (6.4 g (6.4 ml), 47.2 mmol) was dissolved in Et$_2$O (80 ml) and added dropwise to the brown mixture over 1 h. After addition of the silane was complete, the mixture was stirred for 30 min before pouring over ice–HCl. The ether layer was separated, washed with dilute HCl and dried over MgSO$_4$ to produce a green/yellow solution. The Et$_2$O was removed under reduced pressure to give the crude product. The product was distilled at 295 °C at approx. 0.5 mbar. Yield 13.6 g (82%). ^{1}H NMR δ(CD$_2$Cl$_2$): 3.78 (s, 9H), 5.38 (s, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 196$ Hz, 1H), 6.91 (d, $^{3}J(^{1}\mathrm{H}–^{1}\mathrm{H}) = 8.6$ Hz, 6H), 7.46 (d, $^{3}J(^{1}\mathrm{H}–^{1}\mathrm{H}) = 8.6$ Hz, 6H). ^{13}C NMR δ(CDCl$_3$): 54.62 (s, *Me*), 113.41 (s, *meta*), 124.46 (s, *ipso*), 136.72 (s, *ortho*), 160.71 (s, *para*). ^{29}Si NMR δ(CDCl$_3$): −19.0 (dm, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 196$ Hz). ^{29}Si{^{1}H} NMR δ(CDCl$_3$): −19.0 (s). MS (EI), *m*/*z* (relative intensity): 350 (1), 242 (0.97). IR ν/cm^{-1} (HCBD mull): ν(Si–H) 2138(s). Anal. calc. for $(CH_3OC_6H_4)_3SiH$ C, 71.96: H, 6.33. Found C, 71.71; H, 6.46%.

(*p*-MeC$_6$H$_4$)$_3$SiH (16). HSiCl$_3$ (4.5 g, 33.2 mmol) was dissolved in Et$_2$O (10 mL) and added dropwise to a 4-MeC$_6$H$_4$MgBr/Et$_2$O solution (100 mL, 1 M (100 mmol of reagent)) at room temperature whilst stirring. Near to complete addition of the silane the formation of an off-white precipitate was evident, the quantity of which increased as the addition was completed. Excess Grignard reagent was neutralised by dropwise addition of HCl (1–2 M). The organic layer was separated and the aqueous layer was washed with 3 × 40 mL portions of Et$_2$O. The organic extracts were combined, dried over MgSO$_4$ and filtered. Et$_2$O was removed under reduced pressure and a yellow oily suspension resulted. The crude product was recrystallised from hot petroleum spirit (bp 60–80 °C), then placed in a freezer at −40 °C. Yield: 7.2 g (72%). ^{1}H NMR δ(CDCl$_3$): 2.35 (s, 9H), 5.41 (s, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 198$ Hz, 1H), 7.18 (d, $^{1}J(^{1}\mathrm{H}–^{1}\mathrm{H}) = 8$ Hz, 6H), 7.46 (d, $^{1}J(^{1}\mathrm{H}–^{1}\mathrm{H}) = 8$ Hz, 6H). ^{13}C NMR δ(CDCl$_3$): 21.55 (s), 128.8 (s), 130.1 (s), 135.8 (s), 139.6 (s). ^{29}Si{^{1}H} NMR δ(CDCl$_3$): −18.8 (s). ^{29}Si NMR δ(CDCl$_3$): −18.8 (dm, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 198$ Hz, $^{3}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 5$ Hz). MS (EI), *m*/*z* (relative intensity): 167 (1), 210 (0.25), 91 (0.15), 302 (0.06). IR ν/cm^{-1} (Nujol mull): 2116 ν(Si–H). Mp = 80–82 °C. Anal. calc. for $(CH_3C_6H_4)_3SiH$ C, 83.38: H, 7.33. Found C, 83.46; H, 7.39%.

(3,5-F$_2$C$_6$H$_3$)$_3$SiH (17). Mg turnings (1.26 g, 51.8 mmol) were placed in a round-bottom flask and stirred under an Ar atmosphere until a reflective coating had been applied to the glass surface, when Et$_2$O (40 mL) was slowly introduced. To this was added 1-Br, 3,5-C$_6$H$_2$F$_2$ (9.16 g, 47.5 mmol) dissolved in Et$_2$O (60 mL) dropwise at a rate to maintain steady reflux, the colour of the mixture changing from colourless to green to brown over this period. After the addition the mixture was heated to maintain a gentle reflux for 1 h and allowed to cool to room temperature. HSiCl$_3$ (0.76 mL, 2.12 g, 15.6 mmol) was dissolved in Et$_2$O (60 mL) and added dropwise to the brown mixture over 1 h. After addition of the silane was complete, the mixture was stirred for 30 min and dilute HCl was added dropwise to neutralise excess Grignard. The ether layer was separated, washed with dilute HCl and dried over MgSO$_4$ to produce a green/yellow solution which when filtered through charcoal gave a pale yellow solution. The Et$_2$O was removed under reduced pressure to give a pale yellow oil. The final product was obtained by distillation at 300 °C at approximately 0.6 mbar. Yield 2.2 g (73%). ^{1}H NMR δ(CDCl$_3$): 5.44 (s, $^{1}J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 213$ Hz, 1H), 6.92–6.98 (m, 3H), 7.03–7.1

(m, 6H). ^{13}C NMR δ(CDCl$_3$): 106.7 (t, $^2J(^{19}F–^{13}C) = 26$ Hz, *para*), 118.3 (m, *ortho*), 135.7, (t, $^3J(^{19}F–^{13}C) = 5.4$ Hz, *ipso*), 163.6 (dd, $^1J(^{19}F–^{13}C) = 252$ Hz, $^3J(^{19}F–^{13}C)$ 11 Hz, *meta*). $^{19}F\{^1H\}$ NMR δ(CDCl$_3$): −109.65 (s). ^{19}F NMR δ(CDCl$_3$): −109.65 (m). $^{29}Si\{^1H\}$ NMR δ(CDCl$_3$): −17.4 (m). ^{29}Si NMR δ(CDCl$_3$): −17.4 (d of multiplets, $^1J(^{29}Si–^1H) = 212$ Hz). $M_r = 368.348$ g mol^{-1}. MS (EI), m/z (relative intensity): 368 (0.58), 254 (1).

Conclusions

We have shown that although reactive, hypervalent hydridosilicates of the form $[R_3SiHX]^-$ (where X = H or F) are amenable to study and are isolable; hence they can no longer be thought to exist only as transitory intermediates in reactions. The hypervalent H–Si–H unit does not seem to engage in intermolecular hydrogen bonding, but prefers instead to interact in an electrostatic manner with a metal cation forming a hydride bridge; when a suitable cation is not available for this type of interaction a TBP arrangement with axial hydrides persists. Qualititative observations suggest that the sequestered cation of **5** leads to a more air- and moisture-stable compound. Accessibility of the cation also appears to enhance the proclivity of $[Ph_3SiH_2]^-$ to engage hydride exchange reactions. We have also shown that although silicon has a propensity to become hypervalent, this appears to be somewhat dependent on the substituents attached to the silicon centre. NMR spectroscopic data for the hypervalent hydridosilicates and fluorosilicates reported here are remarkably consistent across all of the systems, suggesting a similar TBP arrangement with axial H–Si–H and H–Si–F units in each case. In all of the systems ligand redistribution reactions of hydride, fluoride and phenyl groups are highly prevalent.

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