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## RESEARCH ARTICLE

# Stabilisation of the [SiH6]2− Anion within a Supramolecular Assembly

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**Abstract:** The hypercoordinate [SiH6]2− anion is not stable in solution. Here, we report the room temperature, solution stable molecular [SiH6]2− complex, [{KCa(**NON**)(OEt2)}2][SiH6] (**NON** = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethyl-xanthene)), where the [SiH6]2− anion is stabilised within a supramolecular assembly that mimics the solid-state environment of the anion in the lattice of K2SiH6. Solution-state reactivity of the complex towards carbon monoxide, benzaldehyde, azobenzene and acetonitrile is reported, yielding a range of reduction and C–C coupled products.

## Results and Discussion

Hypercoordination ("hypervalency") is a well-recognised concept in main group chemistry, where in an electron-deficient species with multicentre σ-bonding, the bonding power of a pair of electrons is spread over more than two atoms.[1] The effect is most often observed in group 15-17 compounds, such as in commonly used reagents $PCl_5$, $SF_6$ and $[I_3]^-$,[1,2] but has also been reported in group 14 elements,[3] with hypercoordinate silicon intermediates being proposed in numerous reaction mechanisms.[4] A number of hypercoordinate silicon compounds have also been isolated, such as $SiF_4\cdot2NH_3$, the first reported hypercoordinate silicon compound by Gay-Lussac in 1809,[5] and the commonly used hexafluorosilicate $[SiF_6]^{2-}$ anion.[2] The scope of soluble hypercoordinate main group compounds is however limited. This is because hypercoordinate compounds typically require the use of highly electronegative substituents (such as F, Cl and/or O) to be stable out of the solid state.[2-5] As hydrogen is not highly electronegative,[6] binary hypercoordinate compounds bearing only hydrogen substituents that are stable in solution are rare.[2]

In 2012, Häussermann and co-workers reported the first structurally determined all hydrido silicates, $M_2SiH_6$ (M = K, Rb).[7] The hexahydridosilicates were synthesised in the solid state using a mixture of MH, Si and $BH_3NH_3$ at high temperatures (>450 °C)

and high pressures (>4 GPa). Under these conditions, $K_2SiH_6$ crystallises in the cubic $K_2PtCl_6$ structure type ($Fm\bar{3}m$), with each face of the $[SiH_6]^{2-}$ octahedron capped by a potassium cation. Kohlmann, Spektor and co-workers have recently expanded on this study, reporting the compound can form different polymorphs at even higher pressures.[8]

Whilst $K_2SiH_6$ is an air sensitive but thermodynamically stable solid at room temperature and ambient pressure, it rapidly decomposes upon dissolution.[7-8] That said, Lipke and Tilley reported that the $[SiH_6]^{2-}$ anion can be stabilised by coordination to ruthenium in the diruthenium Si–H σ-complex $[\{(PhB(CH_2PPh_2)_3Ru\}_2(\mu-\eta^3,\eta^3\text{-}H_6Si)]$ **I** (Figure 1).[9] Furthermore, Okuda and co-workers recently reported that using a macrocycle-supported strontium cation, the complex $[(Me_4TACD)_2Sr_2(THF)_4(\mu-\kappa^3,\kappa^3\text{-}SiH_6)]^{2+}$ **II** (Figure 1) is stable in THF below 0 °C.[10] In recent years, we have deployed the bulky xanthene-based diamido ligand $[NON]^{2-}$ (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethyl-xanthene)) for the isolation of a range of reactive main group complexes.[11] Here
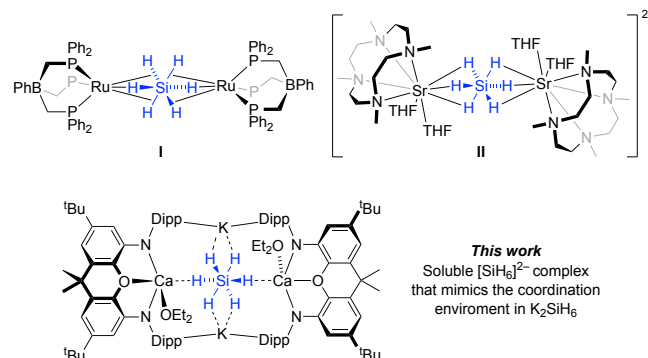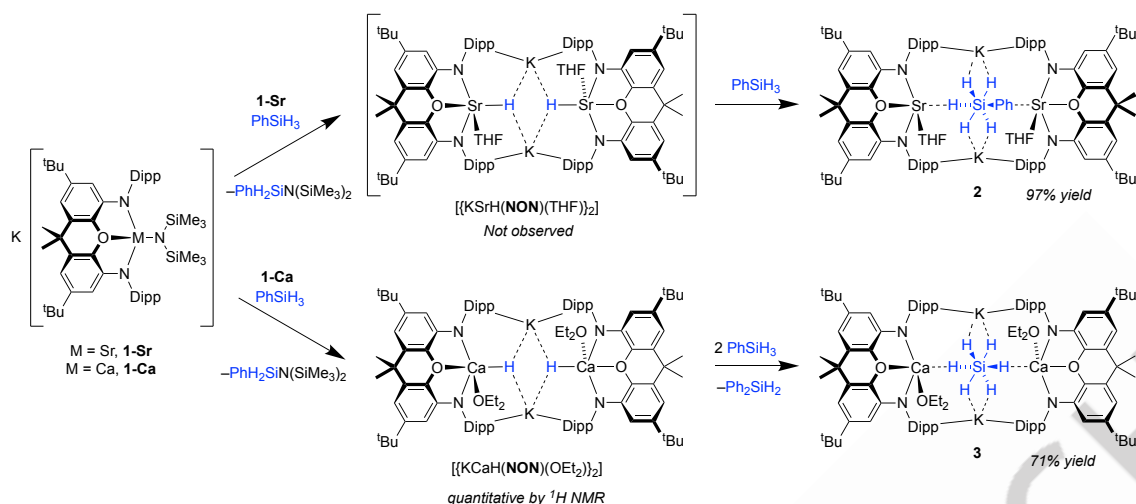


**Figure 1.** Molecular structures of previously reported hexahydridosilicate complexes (top) and the [{KCa(**NON**)(OEt2)}2][SiH6] assembly reported in this work (bottom).

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**Scheme 1.** Synthesis of hypercoordinate silicon complexes [{KSr(**NON**)(THF)}₂][PhSiH₅] (**2**) and [{KCa(**NON**)(OEt₂)}₂][SiH₆] (**3**).

we report that a bimetallic K/Ca salt of the ligand forms a dimeric supramolecular assembly that stabilises [SiH₆]²⁻ in solution through interactions that mimic those in the lattice of K₂SiH₆.[7-8]

At the outset of this work, we were initially targeting the anionic strontium hydride [{KSrH(**NON**)(THF)}₂], through the well reported route of σ-bond metathesis between the [(Me₃Si)₂N]⁻ ligated group 2 complex and phenylsilane.[12] Addition of 1.5 equivalents of phenylsilane to a benzene/THF solution of K[Sr(**NON**){N(SiMe₃)₂}] (**1-Sr**) saw the formation of the expected σ-bond metathesis by-product H₂PhSi–N(SiMe₃)₂ and a single **NON**-containing product by ¹H NMR spectroscopy (Scheme 1). Unexpected however, was that a signal corresponding to a Sr-*H* was not observed, but a 4H doublet at 5.13 ppm coupled to a 1H quintet at 5.39 ppm were instead present. Crystallisation of the reaction mixture followed by crystallographic analysis revealed the major product to be [{KSr(**NON**)(THF)}₂][PhSiH₅] **2** (Figure 2, top).[13] Compound **2** has the hypercoordinate silicon anion [PhSiH₅]²⁻ stabilised within a [{KSr(**NON**)(THF)}₂]²⁺ supramolecular assembly. The assembly is reminiscent of the "inverse crown ethers" pioneered by Mulvey, decorated on the interior with four Lewis acidic *s*-block metals.[14] From the solid-state structure, three of the all-hydride faces of the silicon octahedron are capped by the two potassium cations and one of the strontium centres, while the second strontium centre caps a face consisting of two hydrides and the *ipso*-phenyl carbon. The hypercoordinate anion is similar to the alkylpentahydridosilicate in [(Me₄TACD)₃Sr₃(μ-H)₃(μ³-SiH₅ⁿOct)]⁺, recently reported by Okuda,[10] however, to the best of our knowledge, **2** is the first example of an isolated arylpentahydridosilicate.

The formation of **2** is proposed to proceed through the anionic strontium hydride [{KSrH(**NON**)(THF)}₂] as an intermediate, which reacts with a further equivalent of phenylsilane to give **2** (Scheme 1). In an attempt to observe the hydride intermediate, multiple repeats of the reaction between **1-Sr** and phenylsilane were undertaken, varying the reaction conditions and stoichiometry of phenylsilane, however in every case, **2** was the only observed product. As the proposed anionic strontium hydride intermediate could not be observed, it was envisioned that the mechanism may be reproducible and studied using the lighter group 2 calcium

analogue, where the proposed anionic hydride [{KCaH(**NON**)(OEt₂)}₂] intermediate is already reported to be stable in solution.[15] One equivalent of phenylsilane was added to the anionic calcium bis(trimethylsilyl)amido complex K[Ca(**NON**){N(SiMe₃)₂}] (**1-Ca**) in benzene/Et₂O solution at room temperature (Scheme 1). Within minutes, this gave the previously reported anionic calcium hydride [{KCaH(**NON**)(OEt₂)}₂] in quantitative yield (as determined by ¹H NMR spectroscopy), demonstrating that the anionic strontium hydride is a viable intermediate in the formation of **2**. To investigate the second step, the formation of the [PhSiH₅]²⁻ anion, a further equivalent of phenylsilane was added to [{KCaH(**NON**)(OEt₂)}₂] at room
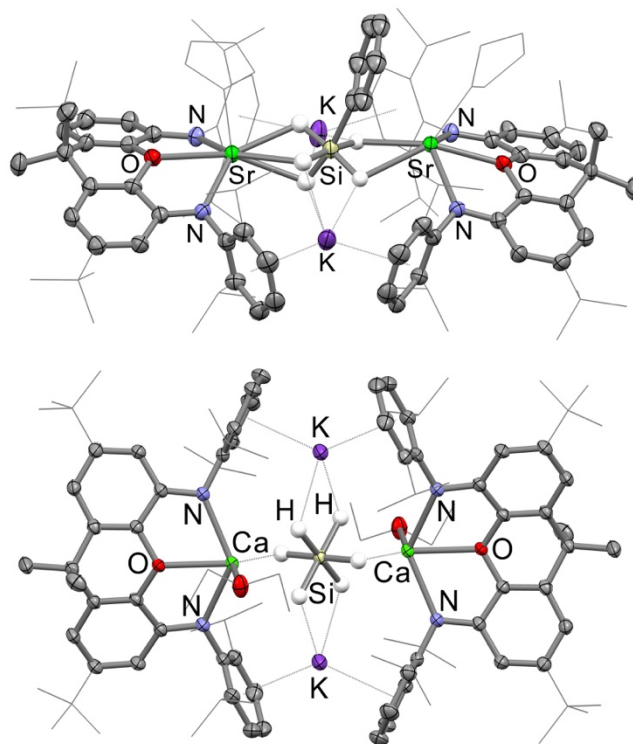


**Figure 2**. Molecular structures of **2** (top) and **3** (bottom) as determined by X-ray crystallography.[13] Displacement ellipsoids set at the 50% probability level. All non-Si hydrogen atoms omitted and select groups shown in wireframe for clarity.

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temperature. In contrast to the strontium reaction, a $^1$H NMR spectrum taken of the reaction mixture was extremely broad, even after allowing to stand at room temperature overnight. However, upon addition of a second equivalent of phenylsilane, the $^1$H NMR spectrum sharpened to reveal a single **NON**-containing product and interestingly, one equivalent of $Ph_2SiH_2$ identifiable by a 2H singlet at 5.08 ppm. Moreover, the doublet and quintet previously assigned to the $[PhSiH_5]^{2-}$ anion in **2** were notably absent and replaced with a sharp 6H singlet at 5.38 ppm with $^{29}$Si satellites ($J_{SiH}$ = 114 Hz).

Single crystal X-ray analysis revealed the major product as $[\{KCa(\textbf{NON})(OEt_2)\}_2][SiH_6]$ **3** (Figure 2, bottom).[13] The compound consists of a hypercoordinate $[SiH_6]^{2-}$ anion stabilised within a dicationic $[\{KCa(\textbf{NON})(OEt_2)\}_2]^{2+}$ assembly. From the solid-state structure, the four Lewis acidic metals of the assembly (2xK, 2xCa) surround the anion in a fashion that resembles the solid state lattice of $K_2SiH_6$, but with only half the number of Lewis acids surrounding the anion (four instead of eight).[9-10] The two potassium cations in **3** sandwiching the $[SiH_6]^{2-}$ anion are 6.7729(6) Å apart. This is almost identical to the equivalent K···K separation in $K_2SiH_6$ (6.791(1) Å).[9] The two calcium centres are notably closer at 5.9109(5) Å, explained by the smaller ionic radius of $Ca^{2+}$.

As X-ray diffraction is inherently unreliable at accurately determining the position of hydrogen atoms, **3** was additionally characterised by single crystal neutron diffraction (Figure 3 and SI).[13] Large single crystals of **3** (approx. 2x1x1 mm) were grown from a benzene solution over several days, ultimately yielding a neutron diffraction structural model in which the locations of the $[SiH_6]^{2-}$ hydrides can be accurately determined. The $[SiH_6]^{2-}$ was found to be a slightly distorted octahedron, with all adjacent H–Si–H angles in the range of 86.1(10)-93.9(10)°. Furthermore, the three unique Si–H bond lengths were found to be 1.588(17), 1.596(17) and 1.624(18) Å, which are approximately 0.1 Å longer than those in typical silanes (e.g. Si–H = 1.494(6) Å in the neutron structure of $Ph_3SiH$).[16] The three crystallographically unique hydrides occupy slightly different chemical environments within the cavity, with one of the hydrides lying perfectly in line with the two calcium centres, interacting with only one calcium centre, while the other two each lie between a calcium and potassium
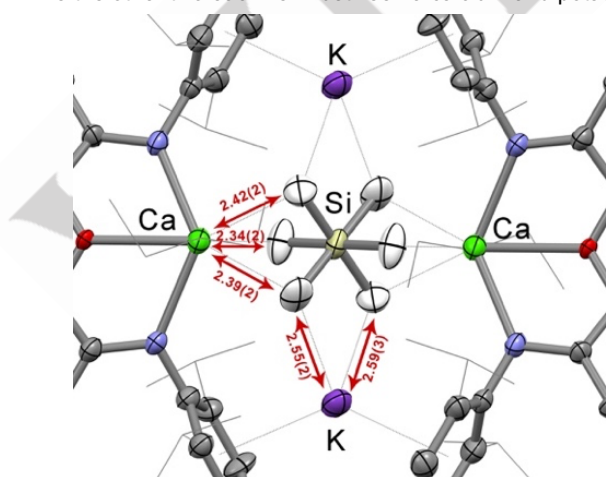
centre. This contrasts with what is observed by $^1$H NMR spectroscopy, where all hydrides are equivalent, suggesting that the $[SiH_6]^{2-}$ anion is tumbling within the cavity in solution on the $^1$H NMR timescale.

Compound **3** is stable in toluene or benzene for weeks at room temperature, making it the first (non-transitional metal stabilised) $[SiH_6]^{2-}$ complex to be stable in solution at room temperature. The dimeric structure seen in the solid state is retained in solution, as confirmed by Diffusion Ordered Spectroscopy (DOSY) NMR, with a diffusion coefficient of 6.35 x $10^{10}$ $m^2s^{-1}$ corresponding to a hydrodynamic radius of 9.8 Å for **3** (see SI for further details). This is slightly larger than that reported for the dimeric anionic calcium hydride $[\{KCaH(\textbf{NON})(OEt_2)\}_2]$ (9.6 Å). The encapsulation of the $[SiH_6]^{2-}$ anion within the $[\{KCa(\textbf{NON})(OEt_2)\}_2]^{2+}$ supramolecular assembly is critical for the stabilisation of the anion. This can be demonstrated by disrupting the assembly in solution by the addition of 18-crown-6 (a potassium sequestering reagent). This leads to immediate decomposition of the $[SiH_6]^{2-}$ anion to $H_2$ and various Si-containing products (by NMR spectroscopy).

To probe the electronic structure of **3**, the compound was additionally investigated by Density Functional Theory (DFT). The geometry of **3** was optimised at the PBE0-D3BJ/BS1 level of theory, which is in excellent agreement with the single-crystal X-ray and neutron diffraction data.[13] Each Si–H distance is reproduced to within crystallographic error (1.601-1.625 Å *in silico*, 1.598(17)-1.628(18) Å experimentally). Furthermore, the slightly distorted octahedral $[SiH_6]^{2-}$ anion was found to interact with the $[\{KCa(\textbf{NON})(OEt_2)\}_2]^{2+}$ assembly through principally coulombic means. Natural bonding orbital (NBO) analysis of the complex gives the natural charge of the central silicon atom as +0.13 and the associated hydrides in the range of −0.30 to −0.34, indicating relatively covalent interactions between the silicon and the hydrides. Summing the natural charges leads to a net −1.71 charge, which is close to −2 as expected for the dianion. Harmonic frequencies found two ($T_{1u}$-like) sets of IR-active principally Si–H modes,[9] with three bending modes (1052, 1036, 967 $cm^{-1}$) and three stretching modes (1603, 1539, 1497 $cm^{-1}$). The bending modes are clearly identifiable in the experimental ATR-FTIR spectrum of **3** at 1053, 1013, and 976 $cm^{-1}$, which are in good agreement with the calculated values. The stretching modes are also visible in the IR spectrum at 1620, 1558, and 1503 $cm^{-1}$, albeit at significantly lower intensities than those calculated. This is suggested to be due to facile conformational change within the cavity and consequent broadening of peaks (see SI).

As **3** is a soluble model of $K_2SiH_6$, we were keen to investigate its solution-state reactivity, particularly towards unsaturated substrates. When a $C_6D_6$ solution of **3** was exposed to 1 atm. of CO an immediate reaction occurred, evident by the fast release of a colourless gas. A $^1$H NMR spectrum taken of the reaction mixture 10 mins after exposure showed essentially quantitative conversion to the previously reported ethylenediolate complex $[\{KCa(\textbf{NON})(OEt_2)\}_2(C_2H_2O_2)]$ **4**, formed by the reduction and C–C coupling of two molecules of CO (Scheme 2).[15] As **4** was previously synthesised *via* the reaction between the anionic calcium hydride $[\{KCaH(\textbf{NON})(OEt_2)\}_2]$ and CO, the reaction shows that **4** can act as a hydride source. The colourless gas released was found to silane ($SiH_4$), identifiable in the $^1$H NMR spectrum as a singlet at 3.10 ppm.



**Figure 3.** Part of the molecular structure of **3** showing the environment of the $[SiH_6]^{2-}$ anion as determined by single-crystal neutron diffraction. All hydrogen atoms (apart from those associated with the $[SiH_6]^{2-}$ anion) have been omitted and selected groups shown in wireframe for clarity. Displacement ellipsoids set at the 50% probability level. Key distances displayed in red (Å).
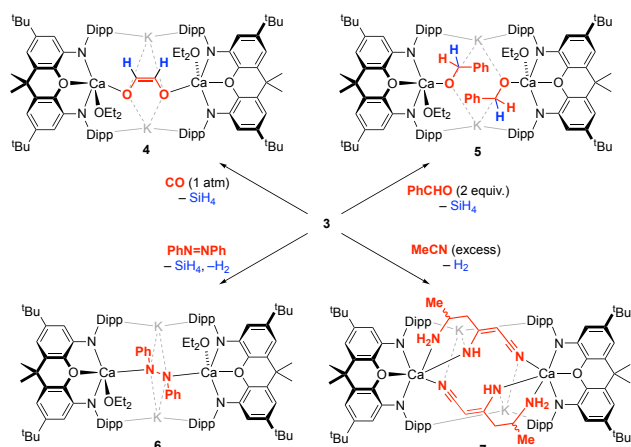
3

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**Scheme 2.** Reactivity of **3** towards carbon monoxide, benzaldehyde, azobenzene and acetonitrile. Potassium cations greyed out for clarity.

The reaction between **3** and benzaldehyde was also investigated. Room temperature addition of 2 equiv. of benzaldehyde to a benzene solution of **3** also saw the rapid evolution of silane. Upon workup, the hydrocalciated product [{KCa(**NON**)(OEt$_2$)(OCH$_2$Ph)}$_2$] **5** was obtained in a 76% crystalline yield (Scheme 2). The solid-state structure of **5** (Figure 3) shows the compound retains the [{Ca(**NON**)(OEt$_2$)}$_2$]$^{2+}$ dimeric architecture with one phenylmethanolate bound to each calcium. The hydrocalciation of aldehydes and ketones is a well reported reaction for calcium hydrides, once again showing synergy between **3** and group 2 hydrides.[17] Interestingly, the hexahydridosilicate was not found to exclusively act as a hydride source. In the reaction between **3** and azobenzene, the two-electron reduction of the substrate was observed, giving the diamide complex [{KCa(**NON**)}$_2$(Ph$_2$N$_2$)] **6** in a 43% crystalline yield (Scheme 3). From the solid state structure of **6** (Figure 3),[13] the [{Ca(**NON**)}$_2$]$^{2+}$ supramolecular assembly has once again been maintained, but with two calcium centres bridged by a [Ph$_2$N$_2$]$^{2-}$ anion. The N–N bond distance is 1.444(3) Å, which is in the typical range of an N–N single bond,[18] confirming the two-electron reduction of the substrate. Furthermore, performing the reaction in C$_6$D$_6$ in a sealed J. Young NMR tube, the presence of both SiH$_4$ and H$_2$ were clearly visible in the $^1$H NMR spectrum.

Finally, the reaction between **3** and acetonitrile was investigated. Addition of 2 equiv. of acetonitrile to benzene solutions of **3** at room temperature repeatedly led to complex mixtures of products. However, upon addition of excess acetonitrile, a major product was observed in the $^1$H NMR spectrum (Scheme 3). After workup and crystallographic analysis, the major product was confirmed to be [{KCa(**NON**)(NH$_2$CH(Me)CH$_2$C(NH)=CHC≡N)}$_2$] **7** (Figure 3).[13] Complex **7** is a result of two trimerisations of acetonitrile, with 4 new C–C bonds being formed between 6 molecules of acetonitrile. The compound is isolated as a mixture of diastereomers, which is observable in both the NMR spectra and solid-state structure (see SI for further details).[13] Two related acetonitrile trimerisations have been reported using *f*-block metals,[19] but to the best of our knowledge this is the first example of such a reaction being achieved using main group elements. As all reported examples of this type of reaction occur using dimeric, bimetallic, Lewis acidic metal systems, it is postulated that the reaction is being templated by the [{Ca(**NON**)}$_2$]$^{2+}$ architecture.
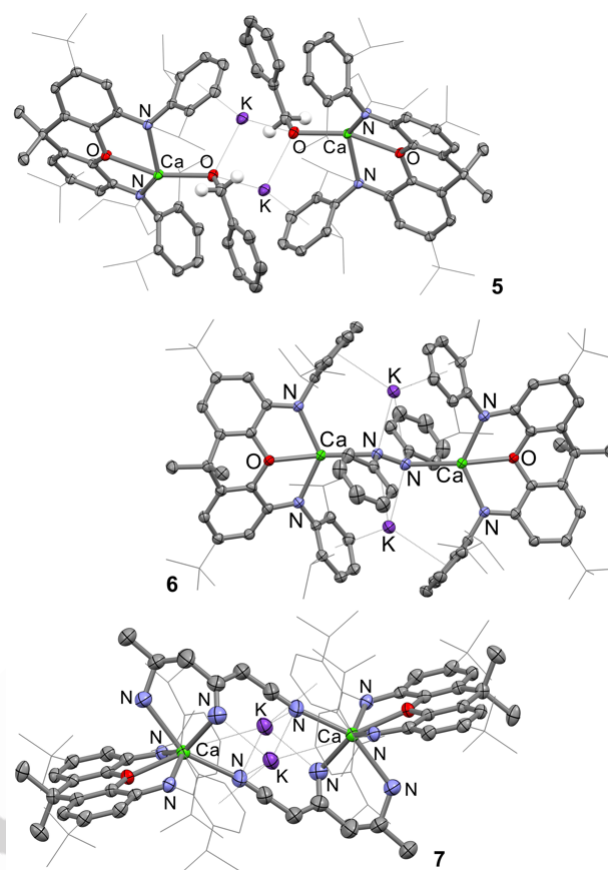


**Figure 3**. Molecular structures of **5** (top), **6** (centre) and **7** (bottom) as determined by X-ray crystallography.[13] Displacement ellipsoids set at the 50% probability level. Most hydrogen atoms have been omitted and select groups shown in wireframe for clarity.

## Conclusion

Here we report the first hypercoordinate [PhSiH$_5$]$^{2-}$ anion along with first room temperature stable molecular complex bearing the [SiH$_6$]$^{2-}$ anion. Both anions are stabilised within a hydrocarbon supramolecular assembly that mimics the solid-state environment of the anion in the lattice of K$_2$SiH$_6$.[7] The solution-state reactivity of the [SiH$_6$]$^{2-}$ complex **3** has been explored towards small unsaturated molecules. The reaction with carbon monoxide leads to the previously reported *cis*-ethylenediolate compound,[15] showing analogous reactivity of the anionic calcium hydride. The reaction with benzaldehyde yields the phenylmethanolate complex through hydrocalciation of the aldehyde. Reaction with azobenzene leads to the formal 2e-reduction of the starting material where reaction with excess acetonitrile leads to a remarkable trimerisation of acetonitrile forming four new C–C bonds. We are currently investigating the mechanism of this trimerisation; the results of which will be published in due course.

## Supporting Information

The authors have cited additional references within the Supporting Information.[11c][15][20-40]

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# RESEARCH ARTICLE

## Entry for the Table of Contents
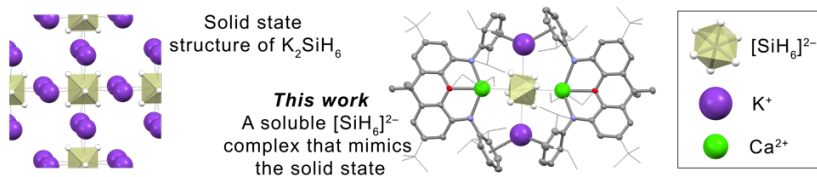


**Bring solid state chemistry into solution.** Using a supramolecular assembly to mimic the coordination environment of $[SiH_6]^{2-}$ in the solid-state, a molecular $[SiH_6]^{2-}$ complex that is stable in solution is reported.

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