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The First Structurally Characterized Hypervalent Silicon Hydride: Unexpected Molecular Geometry and Si−H···K Interactions

Michael J. Bearpark, G. Sean McGrady,* Paul D. Prince, and Jonathan W. Steed*

Department of Chemistry, King's College London
Strand, London WC2R 2LS, UK

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In addition to their unique variety of primary bonding modes,[1] transition-metal hydrides indulge in a wide range of secondary interactions, spanning the extremes of M−H···X and M···H−X, and including the type M−H···H−X.[2] While the primary bonding modes available to E−H moieties of p-block elements are necessarily more limited, the range of secondary interactions open to them should be as varied as those for transition-metal hydrides. However, this aspect of their chemistry remains underexplored, with only a handful of reports having appeared to date.[3,4] Here we describe the preparation and full structural characterization of a hypervalent silicon hydride that engages in Si−H···K interactions in the solid state, conserved across two very different structures. This work also breaks new ground in the chemistry of a class of compounds hitherto regarded solely as reactive intermediates.[5]

Reaction of H_2SiPh_2 with potassium metal in DME in the presence of 18-crown-6 leads to the formation of an off-white crystalline material characterized as $[K(18\text{-crown-}6)]^+[H_2SiPh_3]^-$ (**1**).[6] Compound **1** exists in two polymorphs with trigonal and monoclinic symmetry.[7] The monoclinic form is apparently a kinetic product and deposits first from DME solution. The trigonal form deposits slowly over a period of days. In each case the structure reveals the $[H_2SiPh_3]^-$ anion to be trigonal bipyramidal (tbp) with D_{3h} symmetry, that is, with both hydride substituents axial. The hypervalent nature of silicon is demonstrated by the reduced bond order in the H−Si−H unit, with Si−H bond distances of 1.64 Å in the trigonal form and 1.55 Å in the monoclinic crystal (cf. 1.49(3) Å in Ph_3SiH).[8] In solution the $^1J_{Si,H}$ coupling constant of 130 Hz is significantly lower than the value of 195 Hz measured for Ph_2SiH_2.[9] Similarly, the Si−C distances, at 1.928 Å (trigonal) and 1.917−1.946 Å (monoclinic), are 0.7−0.8 Å longer than those observed for tetravalent silicon.[8] In the trigonal polymorph the complex exhibits crystallographic three-fold molecular symmetry with a linear K···H−Si−H vector, Figure 1. The K···H distance, based on the position of the hydride substituent located in the difference Fourier map, is 2.69 Å (K···Si = 4.327 Å); as with M−H···K interactions observed for transition-metal hydride anions such as $[H_5W(PPh_3)_3]^-$,[10] this distance is significantly less than the sum of the van der Waals radii,[11] and shorter than the cation−anion distance in the binary hydride (2.854 Å).[12] In the monoclinic form there are two crystallographically independent (half) $[K(18\text{-crown-}6)]^+$ cations and one unique $[H_2SiPh_3]^-$ anion. The interactions with the two K^+ ions are very different, with one metal involved in a cation−π interaction[13] to one of the phenyl substituents (shortest K−C distances 3.360 and 3.375 Å), while the other K^+ ion engages in a K···H−Si interaction similar to that in the trigonal polymorph (K···H distance 3.108 Å; Si···K distance 4.709 Å), Figure 2. This greater distance arises from the fact that the anion is no longer situated directly above the cation in order to facilitate K···π interactions.

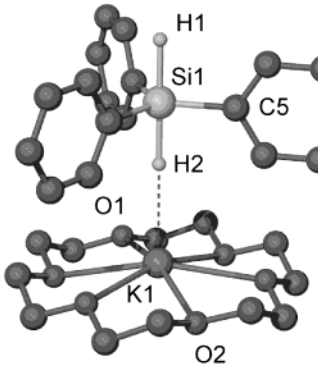

Figure 1. X-ray crystal structure of the trigonal form of $[K(18\text{-crown-}6)]^+[H_2SiPh_3]^-$ (**1**) showing the Si−H···K interaction. Selected bond lengths: K(1)−O(1) 2.791(2), K(1)−O(2) 2.795(2), Si(1)−C(5) 1.928(3), Si(1)−H(1) 1.64, Si(1)−H(2) 1.63, Si(1)···K(1) 4.327(1), K(1)−H(2) 2.69 Å.

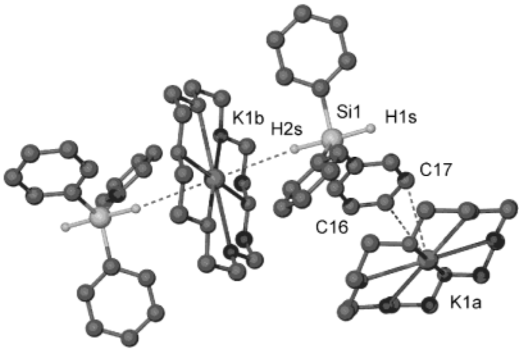

Figure 2. X-ray crystal structure of the monoclinic form of $[K(18\text{-crown-}6)]^+[H_2SiPh_3]^-$ (**1**) showing the two independent K^+ ions and K···π interaction. Selected bond lengths: K(1b)−H(2s) 3.21, K(1b)···Si(1) 4.717(1), K(1a)−C(16) 3.371(3), K(1a)−C(17) 3.358(3), Si(1)−C_{av} 1.927(2) Å.

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[7] Crystal data for **1**: **(trigonal)** $C_{30}H_{41}KO_6Si$, M 564.82 g mol^{-1}, $R3$, $a = 9.4424(15)$ Å, $\beta = 97.930(10)°$, $U = 815.2(2)$ Å^3, $T = 120(2)$ K, $Z = 1$, unique data 2257 ($2\theta \leq 55°$), parameters 171, R_1 [$F^2 > 2\sigma(F^2)$] 0.0462, wR_2 (all data) 0.0933; **(monoclinic)** $C_{30}H_{41}KO_6Si$, M 564.82 g mol^{-1}, $P2_1/n$, $a = 9.3861(5)$ Å, $b = 20.2252(10)$ Å, $c = 16.5969(10)$ Å, $\beta = 130.540(3)$, $U = 3063.1(3)$ Å^3, $T = 125(2)$ K, $Z = 4$, unique data 6802 ($2\theta \leq 55°$), parameters 355, R_1 [$F^2 > 2\sigma(F^2)$] 0.0527, wR_2 (all data) 0.1232.

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^1H, ^{13}C and ^{29}Si NMR measurements in solution indicate equivalence of the hydride and phenyl ligands,[6] with the ^{29}Si NMR spectrum showing a triplet centered at δ −74.0, implying either that the solid-state structure is preserved or that pseudorotation is rapid.

The only comparable species characterized spectroscopically in the literature are silicate anions of the form $K^+[HSi(OR)_4]^-$ or $K^+[H_2Si(OR)_3]^-$.[14] The quite different electronic nature of the Si center in these complexes compared to **1** is reflected in their NMR spectra, with δ_H ca. 4.5, δ_{Si} ca. −85, and $^1J_{Si,H}$ ca. 215 Hz. No structural data are available for these systems, although their NMR properties were interpreted to show $[H_2Si(OPr^i)_3]^-$ and $[H_2Si(OBu^s)_3]^-$ each to possess either one Si−H_{ax} and one Si−H_{eq} bond, or two Si−H_{eq} bonds in a tbp array, depending on the counter-cation and solvent.[12,15] Hypervalent $[SiH_2R_3]^-$ anions have also been implicated as intermediates in the deprotonation of $SiHR_3$ by KH to give $KSiR_3$. Formation of $[SiH_2R_3]^-$, which is not isolated, is followed by irreversible loss of H_2 at 50 °C.[16] The relative thermal stability of compound **1**—albeit highly air- and moisture-sensitive—may well arise from the *trans* disposition of the two hydride ligands, which militates against intramolecular elimination of H_2.

Hypervalent hydrides of the post-transition elements which have been structurally characterized are otherwise limited to phosphoranes in which the hydride ligand occupies exclusively equatorial sites in a tbp structure.[17] Axial E−H moieties are clearly an exception in this area of chemistry, although silatrane presumably possesses an axial Si−H bond on account of the geometry restraints at the Si center,[18] and disilanes bound to a transition metal via an η^2-(Si−H) linkage display a *pseudo*-tbp arrangement in which the hydride ligands are disposed approximately *trans* to one another.[19] The electronegativities of hydrogen and silicon[1a] imply that in $[H_2SiPh_3]^-$ the H atoms should carry a substantial portion of the negative charge associated with the anion. Electrostatic attraction to the cationic potassium center may thus have a significant bearing on the solid-state structure deduced for **1**, with linear $Si{-}H^{\delta-}\cdots K^+$ contacts controlling the stereochemistry at the Si. Accordingly, we have carried out DFT calculations[20] to explore the relative apicophilicity[21] of H and C_6H_5 in the anion of **1**; viz. **1(a)**. These confirm that the D_{3h} geometry observed in the crystal is indeed the lowest-energy conformer of **1(a)**, and reproduce satisfactorily the experimental dimensions (expt: Si−H = 1.55 Si-C = 1.960 Å; calcd: Si−H = 1.584, Si−C = 1.962 Å). A second conformer **1(b)**, with one axial and one equatorial Si−H bond exists in a local minimum 8.6 kcal mol^{-1} higher than **1(a)**. All attempts to optimize the conformer with two equatorial Si−H bonds invariably converged to **1(a)**. A Mulliken analysis of **1(a)** ascribes the following partial charges: Si +0.34, H −0.27, C_6H_5 −0.27. In **1(b)** the corresponding values are Si +0.35; H_{ax} −0.24; H_{eq} −0.15. Hence, the negative charge on the anion is delocalized 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 nonbonded C···C contact in **1(a)** is 3.40 Å, twice the van der Waals radius of carbon;[9] in **1(b)** this is reduced to 3.08 Å. Repulsion between the three phenyl ligands thus appears to be the more important factor in determining the stereochemistry at Si. The relatively equal apportionment of negative charge between the H and C_6H_5 ligands is consistent with a weakening of the K···H−Si interaction to facilitate the cation−π interaction in the monoclinic polymorph.

The Si−H···K moieties observed in **1** invite comparison with the M−H···K bonds observed in transition-metal hydride complexes such as $[K(18\text{-crown-}6)]^+[H_5W(PPh_3)_3]^-$,[10] as well as with the Si−H···Li interactions found in main-group complexes such as $[Li\{Me_2Si(H)NBu^t\}]_3$.[3(b)] The Si−H···K interaction in **1** is certainly less covalent than either of these other types, and its uniquely linear geometry may reflect an essentially electrostatic interaction in this case.

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Supporting Information Available: Crystallographic data in CIF format for the two structures of compound **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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