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Hypervalent silicon hydrides: evidence of their intermediacy in the reaction of optically active 1-NpPhMeSiH(D) with hydrides

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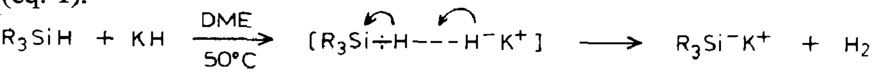
Abstract

Racemisation of optically active 1-NpPhMeSi*H(D) takes place rapidly in the presence of hydrides (KH, $LiAlH_4$, or $LiAlD_4$) in THF at room temperature. Under more drastic conditions, i.e. 50 °C for 24 h, (+)-1-NpPhMeSiH gave the racemic (±)-1-NpPhMeSi$^-$ anion. The results are discussed in terms of initial addition of H^- to silicon to generate a pentavalent organosilicon anion.

We previously reported that cleavage of the Si–H bond by an equimolecular amount of potassium hydride in dimethoxyethane (DME) gives organosilyl anions (eq. 1).



$$R_3SiH + KH \xrightarrow[50°C]{DME} [R_3Si\text{---}H\text{---}H^-K^+] \longrightarrow R_3Si^-K^+ + H_2 \qquad (1)$$

The reaction was considered to involve proton abstraction from silicon [1].

More recently, we found that in the presence of a catalytic amount of potassium hydride or lithium aluminium hydride, di- and tri-hydrogenosilanes undergo a fast redistribution reaction at room temperature involving Si–carbon and Si–hydrogen bonds [2] some SiH_4 being generated (eq. 2).

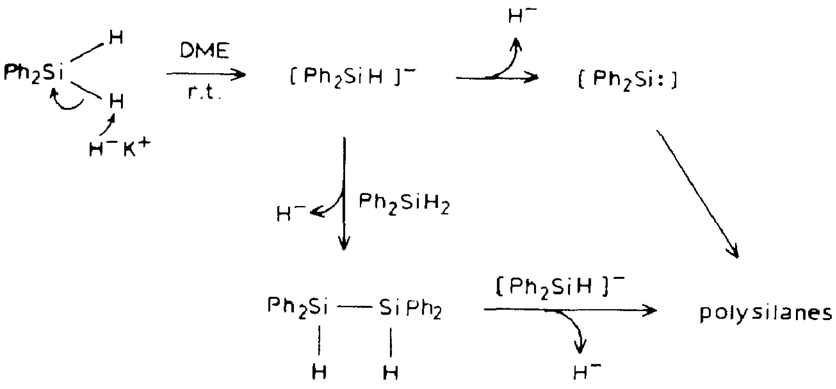
$$\underset{}{Ph_2SiH_2} \xrightarrow[\text{room temp.}]{\text{cat. KH, DME,}} \underset{(35\%)}{Ph_3SiH} + \underset{(12\%)}{Ph_4Si} + SiH_4 \qquad (2)$$

These observations cannot be accounted for in terms of a proton abstraction process, which should lead either to a dimer or to polysilanes (Scheme 1). On the contrary they strongly suggest that the reaction may occur through a hydride addition to silicon as observed in the gas phase [3], followed by an exchange reaction involving the formed hypervalent species (eq. 3–5).

$$PhSiH_3 + H^- \rightleftharpoons [PhSiH_4]^- \qquad (3)$$

$$[PhSiH_4]^- + PhSiH_3 \rightleftharpoons [Ph_2SiH_3]^- + SiH_4 \qquad (4)$$

$$[Ph_2SiH_3]^- \rightleftharpoons Ph_2SiH_2 + H^- \qquad (5)$$

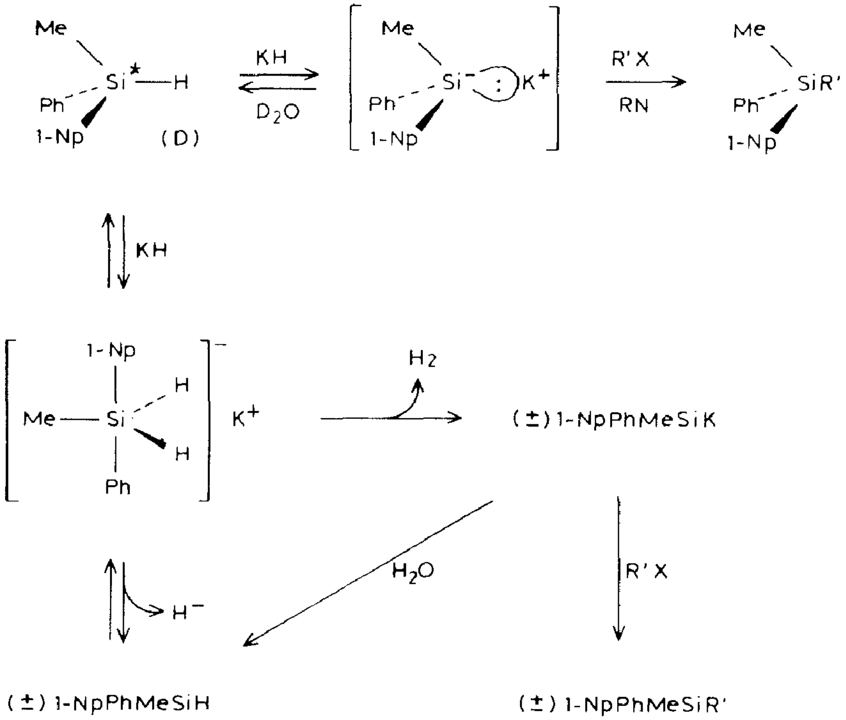


Scheme 1

The formation of the organosilyl anion from R_3SiH and KH could likewise be accounted for in terms of the intermediacy of a pentavalent organosilicon compound (eq. 6).

$$R_3SiH + KH \rightleftharpoons [R_3SiH_2^- \; K^+] \rightarrow R_3Si^- \; K^+ + H_2 \qquad (6)$$

In order to decide between these two possibilities, i.e., (i) proton abstraction from silicon and (ii) formation of a pentavalent intermediate by hydride addition to silicon, we have examined the reactions in the case of an optically active organosilane. Proton abstraction at silicon should lead to the anion with retention of configuration because of the optical stability of organosilyl anions [4] (Scheme 2). In



Scheme 2

Table 1

Racemisation of $R^1R^2R^3Si^*H(D)$ in the presence of metal hydrides (solvent = THF)

Run	Silane	Hydride	Ratio $SiH(D)/H^-(D^-)$	Half-racemisation [b] time (min) (H–D exchange%)
1	(+)-1-NpPhMeSiH [a]	$LiAlH_4$	0.75/1	1.5
2	(+)-1-NpPhMeSiH	$LiAlH_4$	1.25/1	3
3	(+)-1-NpPhMeSiH	$LiAlH_4$	2.5/1	4
4	(+)-1-NpPhMeSiH	$LiAlH_4$	5/1	2.75
5	(+)-1-NpPhMeSiH	$LiAlH_4$	10/1	1.5
6	(+)-1-NpPhMeSiH	$LiAlH_4$	20/1	2.25
7	(+)-1-NpPhMeSiH	KH	0.15/1	2.5
8	(−)-1-NpPhMeSiD	$LiAlH_4$	0.25/1	30 (25% H–D exchange after 3 h)
9	(−)-1-NpPhMeSiD	$LiAlH_4$	0.5/1	40
10	(−)-1-NpPhMeSiD	$LiAlD_4$	0.25/1	34
11	(−)-1-NpPhMeSiD	$LiAlD_4$	0.7/1	29
12	(−)-1-NpPhMeSiD	KH	0.6/1	7

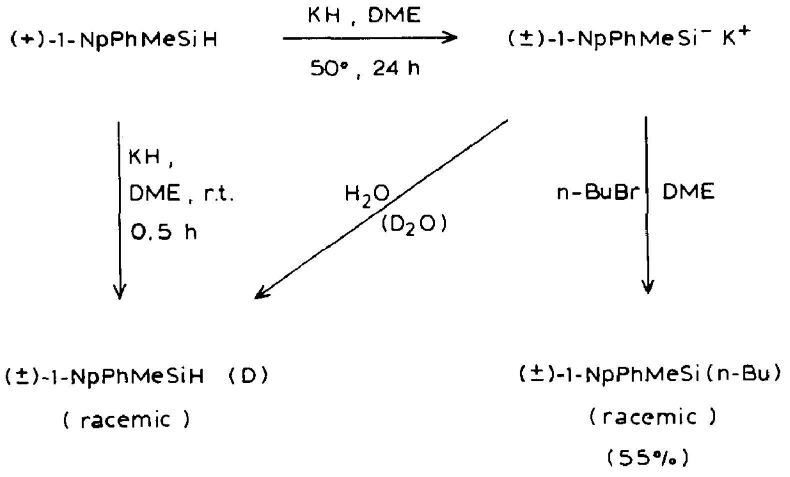
[a] 1-Np = 1-naphthyl. [b] Details are given in the experimental section.

contrast, formation of a pentavalent intermediate should lead to racemisation taking place more rapidly than formation of the organosilyl anion (Scheme 2).

Previous work has shown the strong tendency of the Si–H bond to be in he equatorial position of pentacoordinated structures [5]. Thus, a fast racemisation could be expected to take place through the formation of a symmetric pentacoordinated silicon hydride, whatever the process leading to this species [4].

We report there the chemical and stereochemical behaviour of an optically active hydrogeno- or deutero-silane in the presence of $LiAlH_4$ (or $LiAlD_4$) and potassium hydride in THF as a solvent. Relevant results are summarized in Table 1 and Scheme 3.

Treatment of (+)-1-NpPhMeSiH with KH at 50 °C in dimethoxyethane for 24 h and subsequent addition of n-BuBr was found to give racemic (±)-1-NpPhMeSi(n-

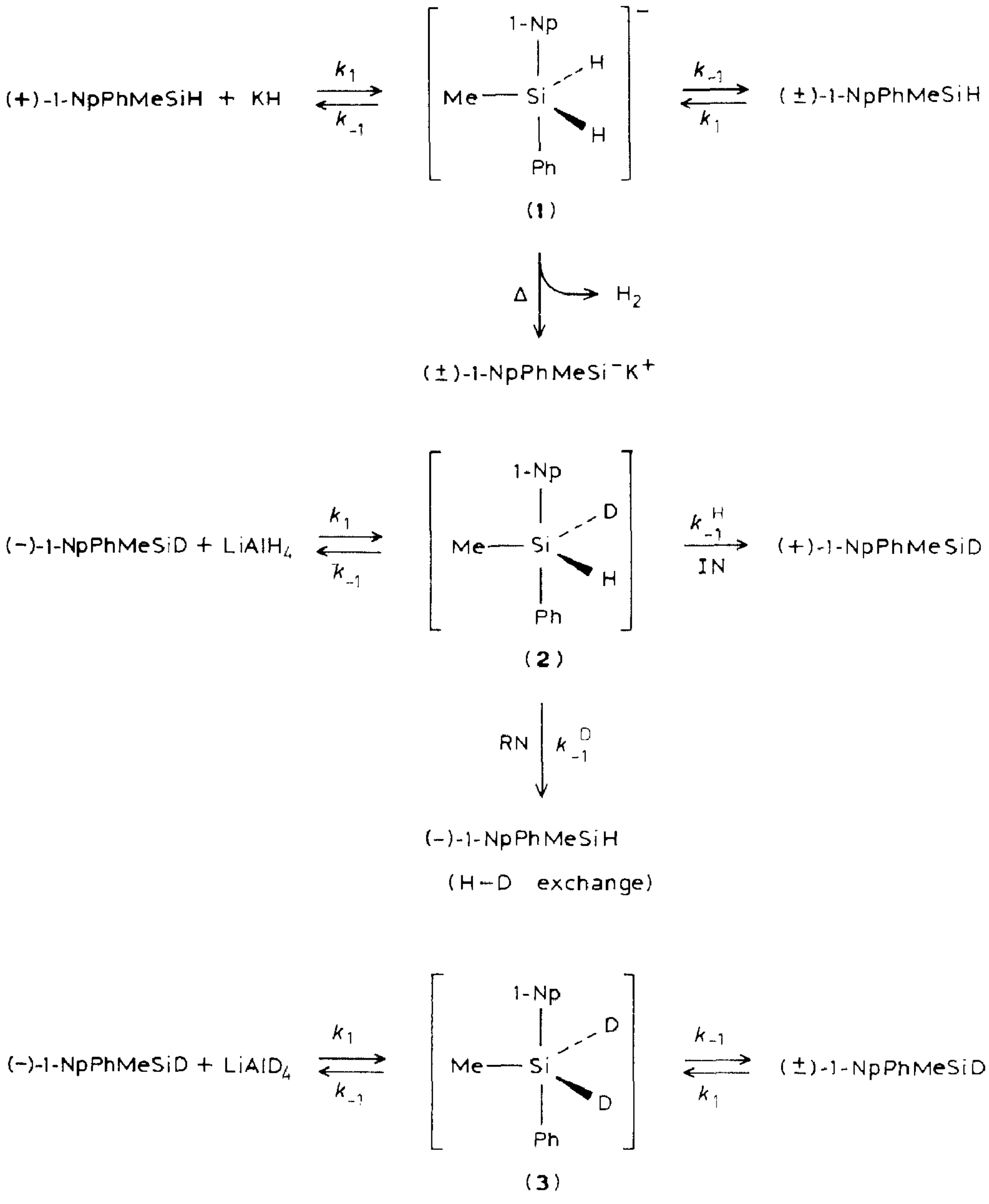


Scheme 3

Bu) in 55% yield, via the formation of the corresponding organosilyl anion with loss of the optical activity (Scheme 3). Hydrolysis or deuterolysis after the initial reaction with KH also gave racemic product.

The most important findings are as follows:

(i) A fast racemisation of (+)-1-NpPhMeSiH occurs in the presence of potassium hydride either in THF or DME. Similar behaviour is observed with lithium aluminium hydride in THF, as briefly reported by Peddle et al. [6].



Scheme 4

(ii) The formation of the organosilyl anion, $[\text{1-NpPhMeSi}]^-$ is slower (24 h instead of a few minutes for racemisation), and the reaction has to be carried out at higher temperatures (Scheme 2).

(iii) Half-racemisation times are not very sensitive to the ratio SiH/H^- (Table 1, runs 1–7). KH, the solubility of which is quite low in THF, is also an efficient catalyst.

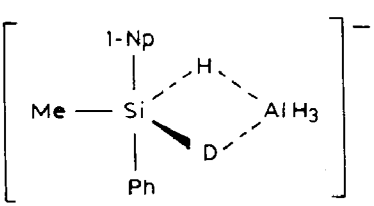
(iv) Hydrogen-deuterium exchange is slow (Table 1, runs 8 and 9), only 25% of 1-NpPhMeSiD undergoing exchange in 3 h.

(v) There are large isotope effects; i.e., k_H/k_D having a value of ca. 3 (Table 1, runs 7 and 12) or ca. 10 (Table 1, runs 1–6 and 8, 9).

These observations clearly rule out a mechanism in which the organosilyl anion results from proton abstraction at silicon (Scheme 2); retention of configuration would be expected, and the hydrogen–deuterium exchange would not occur. They are, however, consistent with an initial fast reversible formation of a pentavalent hydride organosilicon anion in the initial step of the process as a result of coordination of H^- with silicon (Scheme 4). As previously mentioned, because of the strong tendency of the Si–H bond to be in the equatorial position of pentacoordinated structures [5] the most reasonable intermediate will have a symmetric geometry such as **1** (Scheme 4). The formation of this intermediate may involve either equatorial attack of H^- or apical attack followed by pseudorotation of the initially formed five-coordinated intermediate [4]. This would lead to competitive cleavage of either of the Si–H bonds, and would account for the fast racemisation of the optically active (+)-1-NpPhMeSiH observed in the presence of LiAlH_4 or KH (Table 1).

Under more drastic conditions, decomposition of the pentavalent intermediate, **1**; takes place, with the formation of the racemic organosilyl anion by loss of hydrogen.

In the absence of a kinetic isotope effect, it might be expected that the racemisation would be twice as fast as the hydrogen–deuterium exchange (V_{rac} 2 k^{H}_{-1}, intermediate **2**, Scheme 4). Surprisingly, marked isotope effects are observed, and depend on the nature of the hydride reagent: $k_H/k_D = 3$ for KH/SiH/SiD (runs 7 and 12) and $k_H/k_D \geqslant 10$ for LiAlH_4/SiH/SiD (runs 1 to 6 and 8, 9) and for $\text{LiAlH}_4/\text{LiAlD}_4$/SiD (runs 1 to 6 and 10, 11). These values are consistent with cleavage of the Si–H or Si–D bonds in the rate-determining step of the process (intermediate **2** and **3**, Scheme 4). The large effect of the presence of the aluminium atom ($k_H/k_D \geqslant 10$ instead of 3) is consistent with a process involving a pentavalent transition state such as **4**.



(**4**)

Experimental

All reactions were carried out under dry nitrogen. The THF and DME were freshly distilled from lithium aluminium hydride before use. The lithium aluminium hydride and deuteride were supplied by Janssen Chimica, and potassium hydride by Aldrich. A dispersion of potassium hydride, in mineral oil, was washed three times with dry hexane to remove the oil. Specific rotations were measured with a Perkin–Elmer 241 polarimeter and ^1H NMR spectra were recorded with a Bruker WP60 spectrometer. Lithium aluminium hydride (deuteride) solutions were prepared by adding the hydride (deuteride) in portions to a stirred degassed solution of THF, stirring the mixture at room temperature, for 30 min, then filtering it to give a clear solution. These solutions were titrated against iodine [7].

(−)-MePh-1-NpSiD, $[\alpha]_D$ −30 °C (*c* 10, hexane) was prepared by chlorination of (+)-MePh-1-NpSiH, $[\alpha]_D$ +34.3° (*c* 10, hexane) [8] followed by reduction with $LiAlD_4$ [9]. All reactions were performed with the same concentration of silane, viz., 0.15 mole l^{-1}. The ratio of deuterated to undeuterated compound was estimated from the ^1H NMR spectrum of the mixture.

General procedure

This is illustrated by the following example. To a stirred solution of (+)-MePh-1-NpSiH (0.477 g, 1.92 mmol) $[\alpha]_D$ 33.5° (*c* 10, hexane) in 12 ml of THF was added 0.3 ml (2 mmol) of a 0.69 mole l^{-1} solution of $LiAlH_4$. A 2 ml aliquot was hydrolysed with a solution of 4 molar HCl and the mixture extracted twice with Et_2O. The ethereal layer was washed with water, dried over $MgSO_4$, and evaporated. The residue was weighed then dissolved in hexane. A plot of $[\alpha]_D$ against time gave the half-racemisation time.

Time (min)	*c*	α (°)	$[\alpha]_D$ (°)
2	15.14	0.283	18.69
4	17.0	0.206	12.1
8	21.4	0.095	4.4

Formation of 1-naphthylphenylmethylsilyl potassium, and its reaction with n-BuBr

To a stirred suspension of potassium hydride (10 mmol) in 10 ml of 1,2-dimethoxyethane was added dropwise a solution of 2.48 g (10 mmol) of (+)-1-Np-PhMeSiH $[\alpha]_D$ +34°, (*c* 10, hexane) in 15 ml of 1,2-dimethoxyethane. The mixture stirred for 24 h at 50 °C and monitored either by IR or ^1H NMR spectroscopic examination of deuterolyzed aliquots. When reaction was complete, the 1-naphthylphenylmethylsilylpotassium was treated at 25 °C with n-BuBr (2.74 g, 20 mmol) and the reaction stirred for 1 h at room temperature. After hydrolysis and the usual work up, 1.7 g of (±)-1-NpPhMeSi(n-Bu) was recovered as an oil, which gave IR and ^1H NMR data identical with those for an authentic sample [10].

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