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Hydride transfer reactions between penta- and tetra-coordinate silicon derivatives

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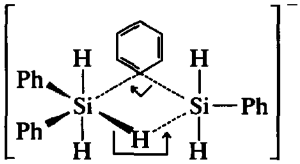
Abstract

$K[HSi(OR)_4]$ has been found to reduce Ph_3SiF and Ph_3SiCl and to induce H/D exchange with Ph_3SiD and Ph_2SiD_2. The mechanism of this exchange seems to be a one-step concerted mechanism through an intermediate with bridging hydrogen and deuterium atoms.

Potassium hydridosilicates have been suggested as intermediates in reactions in solution. For instance, the fast racemization of the optically active 1-NpPhMeSiH(D) (1-Np = 1-naphthyl) catalyzed by hydrides (KH, $LiAlH_4$, $LiAlD_4$) in THF or DME (dimethoxyethane) as solvent at room temperature has been rationalized in terms of coordination of H^- (or D^-) to silicon, leading to a pentacoordinate dihydridosilicate anion [1]. Likewise, the redistribution of Ph_2SiH_2 and $PhSiH_3$ in presence of hydrides ($LiAlH_4$, KH, or NaH) as catalysts has been shown to involve intermediates such as $[Ph_2SiH_3]^-$ and $[PhSiH_4]^-$, respectively [2]. Attack of these pentacoordinate silicates on to their tetracoordinate counterparts (eq. 1) was assumed to result in a phenyl-hydrogen exchange through an anionic intermediate (**1**).

$$Ph_2SiH_2 + [Ph_2SiH_3]^- \longrightarrow [Ph_3SiH_2]^- + PhSiH_3 \quad (1)$$



(**1**)

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Table 1

Reduction of halosilanes with $K[HSi(OEt)_4]$ (2) or [K, 18-crown-6] $[HSi(O^iPr)_4]$ (3) [a]

Hydridosilane	Halosilane	Product	Yield (%)
2	Ph_3SiCl	Ph_3SiH	84
2	Ph_3SiF	Ph_3SiH	92
3	Ph_3SiCl	Ph_3SiH	85
3	Ph_3SiF	Ph_3SiH	90

[a] $Si(O^iPr)_4$ was characterized in these reactions.

Recently, reactions of alkoxide and hydride ions with a trialkoxysilane were found to provide a unique and facile entry into stable hydridosilicates $[H_nSi(OR)_{5-n}]^-$ [3].

These have been shown to have a wide range of reactivities and considerable hydridic character. Thus, they are good vehicles for studying hydride transfer reactions between penta- and tetra-coordinate silicon species. In this context, we wish to report our studies on the chemical behaviour of $K[HSi(OEt)_4]$ towards functional silanes.

The reaction of $K[HSi(OR)_4]$ with halosilanes gave the corresponding silane in good yield (eq. 2). Table 1 summarizes the results.

$$K[HSi(OR)_4] + Ph_3SiX \xrightarrow{THF} Ph_3SiH + Si(OR)_4 + KX \qquad (2)$$

$R = Et$ or ^iPr

The overall reaction corresponds to a halide-hydride exchange. In order to understand the mechanism of the reaction, we studied H–D exchange between penta- and tetra-coordinate silicon derivatives.

When potassium hydridotetraethoxosilicate was mixed with triphenyldeuteriosilane, a mixture of Ph_3SiH and Ph_3SiD, $[HSi(OR)_4]^-$ and $[DSi(OR)_4]^-$, (characterized by ^{29}Si NMR) spectroscopy, was obtained rapidly (eq. 3).

$$K[HSi(OR)_4] + Ph_3SiD \overset{THF}{\rightleftharpoons} Ph_3SiH + K[DSi(OR)_4] \quad . \qquad (3)$$

$(R = Et$ or $^iPr)$

In the case of $[HSi(OEt)_4]^-$, a 50/50 mixture of Ph_3SiD/Ph_3SiH (as determined by ^1H NMR spectroscopy) was obtained after 5 min. This exchange reaction was sensitive to the steric hindrance by the reagent. Indeed, when the ethoxy groups were replaced by iso-propoxy groups, the exchange process of eq. 3 was much slower: a 50/50 Ph_3SiH/Ph_3SiD mixture was obtained after 90 min.

A fast exchange reaction was also observed in the case of Ph_2SiD_2 (eq. 4).

$$Ph_2SiD_2 + 2K[HSi(OEt)_4] \rightleftharpoons Ph_2SiH_2 + Ph_2SiHD + K[DSi(OEt)_4] \qquad (4)$$

After 10 min, the ^1H NMR spectrum showed the presence of Ph_2SiH_2 (or Ph_2SiHD); comparison of integrated intensities of phenyl groups and SiH_2 (or SiHD) gave a 10:1 ratio, indicating that in the diphenylsilanes the D:H ratio is 50:50. After removal of the pentacoordinate species, ^{29}Si and ^2H NMR spectroscopy of the mixture of diphenylsilanes showed peaks corresponding to Ph_2SiH_2, Ph_2SiHD and Ph_2SiD_2. Moreover, the ratio of the pentacoordinate species in eq. 4 was demonstrated chemically by reaction with benzaldehyde. We have shown previously that pentacoordinate silicon hydride compounds, $[HSi(OR)_4]^-$, are good reducing agents toward carbonyl compounds [3]. After evaporation of the solvent, the solid residue from the reaction shown in eq. 4 was washed twice with dry, deoxygenated pentane and evaporated to dryness to leave a mixture of $[HSi(OEt)_4]^-$ and $[DSi(OEt)_4]^-$ in 48% yield. This solid residue was dissolved in THF and treatment with benzaldehyde (eq. 5) gave, after hydrolysis, a 1:1 mixture (determined using ^1H NMR spectroscopy) of deuterated and undeuterated benzyl alcohols in 84% yield.

$$[HSi(OEt)_4]^- + [DSi(OEt)_4]^- \xrightarrow[2)\,H_3O^+]{1)\,PhCHO} PhCH_2OH + PhCHDOH \qquad (5)$$

This D/H exchange reaction was faster than the phenyl redistribution (eq. 1) since only traces of Ph_3SiH were observed after 15 h at room temperature (eq. 6).

$$Ph_2SiH_2 + K[HSi(OEt)_4] \xrightarrow[15\text{ h, r.t.}]{THF} Ph_3SiH\ (\text{traces}) \qquad (6)$$

We have also studied the ability of tetraethoxysilane to react with hydrides to give pentacoordinate species. No reaction was observed between tetraethoxysilane and KH or NaH (eq. 7), or even with KH in the presence of 18-crown-6.

$$KH + Si(OEt)_4 \xrightarrow[15\text{ h}]{THF} \text{no reaction} \qquad (7)$$

However, a pentacoordinate species can be obtained when Ph_3SiH is added to KH and $Si(OEt)_4$ (eq. 8).

$$Ph_3SiH + KH + Si(OEt)_4 \xrightarrow{THF} [HSi(OEt)_4]^- + Ph_3SiH \qquad (8)$$

After 20 h at room temperature, ^{29}Si NMR spectroscopy of the reaction indicated two major components, $K[HSi(OEt)_4]$ and Ph_3SiH; only small amounts of $Si(OEt)_4$ were observed. Since KH did not react with $Si(OEt)_4$ (eq. 7), the formation of $[HSi(OEt)_4]^-$ proves the intermediacy of $[Ph_3SiH_2]^-$. It is formed *in situ* by reaction of KH with Ph_3SiH, as demonstrated previously [2], and illustrated by the fast racemization of optical active MePh(1-Np)SiH (1-Np = 1-naphthyl) in the presence of KH [1]. Ph_3SiH plays the role of a transfer agent for the hydride from KH to $Si(OEt)_4$. In order to check this, we used catalytic amounts of Ph_3SiH. After 60 h of reaction of Ph_3SiH/KH, 1:10, two principal resonances were observed in ^{29}Si NMR spectra: one corresponds to $K[HSi(OEt)_4]$, the other to $Si(OEt)_4$. The process is effectively catalytic but slower than if the reactants are in stoichiometric proportions.

Several mechanisms may be proposed to explain the hydride transfer from a penta- to a tetra-coordinate silicon derivative. The dissociative mechanism (a) is rules out by the results of eq. 7: no reaction was observed between KH and $Si(OEt)_4$.

Mechanism (a)

$$[HSi(OR)_4]^- + Ph_3SiD \rightleftharpoons Si(OR)_4 + D^- + Ph_3SiH$$

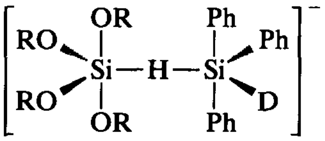
$$Si(OR)_4 + D^- \rightleftharpoons [DSi(OR)_4]^-$$

Another possible route is mechanism (b), which postulates the formation of a new pentacoordinate silane with both hydrogen and deuterium. This intermediate may be formed through a mono-bridged intermediate such as (4), analogous to the fluoro-compound $[Si_2F_7(OAc)_2]^-$ (5) identified by ^{19}F NMR spectroscopy [4].

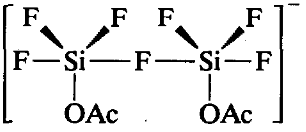
Mechanism (b)

$$[HSi(OR)_4]^- + Ph_3SiD \rightleftharpoons Si(OR)_4 + [Ph_3SiHD]^-$$

$$[Ph_3SiHD]^- + Si(OR)_4 \rightleftharpoons Ph_3SiH + [DSi(OR)_4]^-$$



(4)



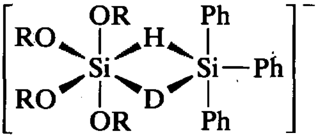
(5)

However the reaction of eq. 8 does not favour mechanism (b); indeed, traces of $Si(OEt)_4$ were observed in the reaction mixture, showing that the reaction was nearly complete.

A third mechanism (c) can explain all experimental facts; it corresponds to a one-step concerted process via intermediate **6** with bridging hydrogen and deuterium atoms.

Mechanism (c)

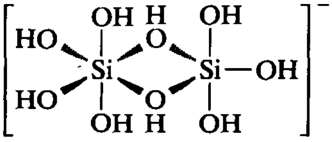
$$[HSi(OR)_4]^- + Ph_3SiD \rightleftharpoons Ph_3SiH + [DSi(OR)_4]^-$$



(6)

The driving force of this exchange is the formation of the penta-/hexa-coordinate disilicon intermediate which requires the existence of a preformed pentacoordinate silicon anion.

Intermediate **6** is consistent with the effect of the steric hindrance observed in the reaction of eq. 3. This intermediate is comparable to intermediate **1** postulated in the redistribution reaction of Ph_2SiH_2 (eq. 1). In addition, a structure with two bridging hydroxides, $Si_2(OH)_9^-$ (**7**), was calculated to be possible in the attack of $Si(OH)_5^-$ on $Si(OH)_4$, which occurs in silanol polymerization [5].



(7)

In conclusion, we have shown that pentacoordinate silicon hydrides or deuterides (isolated, or as intermediates) very easily transfer a hydride or a deuteride to a tetracoordinate silicon compound. This fast-transfer is best explained by the formation of an intermediate with bridging hydrogen and deuterium atoms.

Further examples of exchange reactions involving the ability of a pentacoordinate silicon compound or intermediate to transfer one group to a tetracoordinate silicon derivative is under progress.

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