Inorganica Chimica Acta, *198–200* (1992) 705–713

Hydridosilicates: a new class of pentacoordinated silicon derivatives with unusual properties

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Abstract

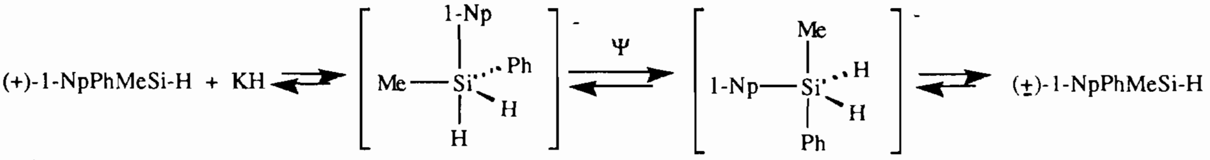
Reactions of RO^- and H^- with trialkoxy-(or triaryloxy)silanes have provided a unique and facile entry to a number of anionic pentacoordinated hydridosilicates, $[H_nSi(OR)_{5-n}]^-$ ($n=1$ and 2). $[H_2Si(OR)_3]^-$ anions have been only isolated as stable crystalline products in the case of bulky R groups (R = i-Pr, s-Bu and c-C_6H_{11}). From a mechanistic point of view, these species have been of particular interest and a wide range of reactivities has been observed. The silicon atom acts as an electrophilic center and undergoes fast nucleophilic displacement reactions. Hydridosilicates have been found to be good models in modeling the initial stages of the hydrolysis reactions of organic silicates in the sol–gel process. The high reactivity of the Si–H bond is illustrated both in the reactions where the hydridosilicates act as bases and as reducing reagents. The data also confirm unambiguously the intermediacy of such species in the reduction of aldehydes and ketones with hydrosilanes catalyzed by F^- and RO^-. More unusual is their good ability to act as one electron donors. This last feature seems at the present time characteristic of the anionic hydridosilicates. From a more general point of view, we may expect unique reactivity patterns from pentacoordinated anionic derivatives compared to their tetracoordinated counterparts. More studies will be necessary for a better understanding of the mechanistic features of these reactions. Use of these special properties will also be of interest.

Introduction

Over the last twenty years, considerable attention has been directed toward organosilicon compounds with coordination numbers greater than 4 [1]. Numerous penta- and hexacoordinated anionic derivatives have been reported and structurally characterized [1–3]. They provide useful models for intermediates in nucleophilic reactions at silicon [4]. A number of synthetic methods involving penta- or hexacoordinated intermediates has been reported [1b, c, 5, 6]. Furthermore, hypervalent anionic species have been shown of special interest in modeling hydrolysis reactions of organic silicates in the sol–gel process in the case of nucleophilic or basic catalysis [7].

Recent works have also focused attention on the chemical behavior of pentacoordinated neutral silicon species or anionic silicates. For instance, enhanced reactivity toward nucleophiles was observed and some reports suggested unique reactivity patterns of these derivatives compared with those of their tetracoordinated analogues [8, 3c].

As a part of our investigations of the reactions of such hypervalent organosilicon species [9, 10], we have been interested in the synthesis and chemistry of pentacoordinated silicon hydrides, $[H_nSi(OR)_{5-n}]^-$ [11]. Such derivatives have been observed in the gas phase from the reaction of H^- with SiH_4 and alkylsilanes [12]. They have been suggested as intermediates in reactions in solution. The fast racemization of the optically active 1-NpPhMeSiH(D) (1-Np = 1-naphthyl) is catalyzed by hydrides (KH, $LiAlH_4$, $LiAlD_4$) in THF or dimethoxyethane as solvent and occurs without chemical transformation. These latter data are interpretable in terms of coordination of H^- (or D^-) to silicon, leading to a pentacoordinated dihydridosilicate anion [13] (Scheme 1). Likewise, the redistribution reaction



Scheme 1.

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of $RR'SiH_2$ and $RSiH_3$ in the presence of hydrides as catalysts has been shown to involve such intermediates [14].

This account will summarize our studies in this field.

The $[H_nSi(OR)_{5-n}]^-$ anions. Synthesis and spectroscopic data

Direct treatment of an alkoxy-(or aryloxy)hydrosilane with the corresponding potassium alkoxide (or aryloxide) affords the anionic five-coordinate hydridosilicate $[HSi(OR)_4]^-$ (eqn. (1)) [11].

$$HSi(OR)_3 + KOR \xrightarrow[\text{r.t.}]{\text{THF or DME}} \underset{80\text{–}90\%}{[HSi(OR)_4]^-K^+} \qquad (1)$$

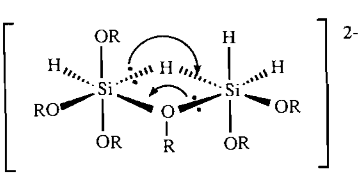
R = Me, Et, n-Bu, i-Pr, Ph

The reaction is quite general and has been carried out in either THF or dimethoxyethane (DME). In a similar manner, the hydridosilicate anions have been obtained as the sodium or [K, 18-crown-6] salts. In sharp contrast, the reaction of LiOR with $HSi(OR)_3$ leads to the competitive formation of $Si(OR)_4$ which corresponds to a nucleophilic displacement of the Si–H bond by RO^-. Elimination of LiH seems the driving force of the process [11d].

Formation of potassium dihydridosilicates, $K[H_2Si(OR)_3]$, occurs also in THF or DME, even in the absence of crown ether, from the reaction of alkoxy-(or aryloxy)silanes with potassium hydride (eqn. (2)) [11].

$$HSi(OR)_3 + KH \xrightarrow[\text{r.t.}]{\text{THF or DME}} K[H_2Si(OR)_3] + K[HSi(OR)_4] \qquad (2)$$

The dihydridosilicates may undergo a redistribution reaction leading to $K[HSi(OR)_4]$ with evolution of SiH_4 [11e]. The latter occurs more readily with decreasing steric hindrance at silicon, Me > Et, n-Bu > i-Pr, s-Bu, c-C_6H_{11}. For instance, $HSi(OMe)_3$ in THF gave $K[HSi(OMe)_4]$ in less than 2 h. In sharp contrast, $HSi(Oi\text{-}Pr)_3$ gave only $K[H_2Si(Oi\text{-}Pr)_3]$ in 94% yield, and even after 7 days at room temperature less than 5% of $K[HSi(Oi\text{-}Pr)_4]$ was detected. The fast redistribution of a labile OR group (R = Ph) also occurs readily and again, after 2 h, only $K[HSi(OPh)_4]$ was recovered. Such a reaction is typical of pentavalent species and no catalyst is required. The migration of the OR and H groups could occur between pentacoordinated species through a concerted process involving a dimeric intermediate like 1.



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The steric hindrance of bulky groups (R = i-Pr, s-Bu, c-C_6H_{11}) prevents the formation of such an intermediate. Increasing solvating power of the solvent, DME > THF, was found to accelerate the formation of $K[HSi(OR)_4]$.

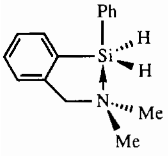
In Table 1 the ^{29}Si NMR data for $K[HSi(OR)_4]$ and $K[H_2Si(OR)_3]$ silicates are summarized and a comparison with $HSi(OR)_3$ (solvent: THF) is given [11]. The ^{29}Si NMR chemical are in the usual range of neutral and anionic pentacoordinated silicon compounds [1, 2, 15]. Similar values were recently reported for the anionic pentaoxysilicates $[Si(OR)_5]^-$ and $[R'_nSi(OR)_{5-n}]^-$ [2a, 8d]. As expected, upfield shifts of the ^{29}Si NMR resonances relative to those of the corresponding alkoxy- or phenoxysilanes were observed. The ^{29}Si signal of $K[HSi(OR)_4]$ appears as a doublet. In the case of most of the dihydridosilicates (R = Et, n-Bu, i-Pr), the spectra (solvent, THF) exhibit a triplet, consistent with two equivalent hydrogen atoms. The ^{29}Si–^1H coupling constants are smaller for the five-coordinate silicates than for the corresponding neutral species, as expected from the decrease of the proportions of s character of the orbital of the Si–H bond. Sodium or [potassium, 18-crown-6] salts gave quite similar ^{29}Si NMR spectra [11].

^{29}Si NMR studies have also been carried out changing the nature of the solvent, using either benzene-d_6 and toluene-d_8 or a complexing agent [18-crown-6] [11e]. As outlined above, in THF or DME which are good solvating agents, the ^{29}Si signal of $K[H_2Si(Oi\text{-}Pr)_3]$ appears as a triplet, indicating that in the trigonal-bipyramid geometry both hydrogens exchange quickly or are equatorial. The latter case was found for a neutral pentacoordinated silicon 2, resulting from intramolecular coordination of o-Me_2N–CH_2–C_6H_4 ligand

TABLE 1. ^{29}Si NMR data: $[H_2Si(OR)_3]^-$ and $[HSi(OR)_4]^-$ compared to $HSi(OR)_3$ (solvent: THF)

Silicate	δ (ppm) ($J(^1H$–$^{29}Si)$ Hz)
$HSi(OEt)_3$	−59.6 (d, 285)
$K^+[HSi(OEt)_4]^-$	−86.2 (d, 218)
$K^+[H_2Si(OEt)_3]^-$	−81.8 (t, 217)
$HSi(Oi\text{-}Pr)_3$	−63.4 (d, 285)
$K^+[HSi(Oi\text{-}Pr)_4]^-$	−90.5 (d, 215)
$K^+[H_2Si(Oi\text{-}Pr)_3]^-$	−87.1 (t, 213)
$[K^+$, 18-crown-6$][H_2Si(Oi\text{-}Pr)_3]^-$	−82.0 (t, 223)
$HSi(O\ s\text{-}Bu)_3$	−62.6 (d, 282)
$K^+[H_2Si(O\ s\text{-}Bu)_3]^-$	−85.6 (dd, 222 and 194)

to silicon, which shows the Si–H bonds in equatorial positions [16].



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A decrease of the solvating power on going to benzene-d_6 resulted in a ^{29}Si signal which appears as a doublet of doublets (Table 2, run 3), clearly indicating the presence of two different hydrogen atoms bonded to silicon. The addition of 18-crown-6 (Table 2, run 4) resulted again in a ^{29}Si resonance attributable to a silicon atom bonded to two equivalent hydrogen atoms.

Further evidence was found in the ^{1}H NMR spectra [11e]. For instance, in THF-d_8, the two hydrogens of $[H_2Si(Oi\text{-}Pr)_3]^-$ are equivalent and the ^{1}H NMR signal is a singlet at 3.41 ppm. In contrast, when changing from THF-d_8 to toluene-d_8, as expected from ^{29}Si results, the spectrum shows two singlets at 4.38 and 3.72 ppm. One axial (s, 4.38 ppm) and one equatorial (s, 3.72 ppm) hydrogen can be discerned. In this case, no $^2J(^1H\text{–}^1H)$ coupling was observed, but this is not unusual as axial-equatorial coupling constants are very small.

Variable temperature ^{1}H NMR studies in toluene-d_8 are also quite clear [11e]. At ambient temperature, as expected, $K[H_2Si(Oi\text{-}Pr)_3]$ exhibits two singlets at 4.38 and 3.72 ppm and the relative intensities are consistent with the presence of one of the two hydrogen atoms occupying an equatorial site, the other one being axial. As the temperature is raised, the two signals broadened, essentially disappeared at about 328 K (Fig. 1), reappeared as a broad singlet at still higher temperature (363 K, Fig. 1). When the sample is cooled to room temperature, the two initial signals returned. The free energy of activation of this intramolecular isomerization of the H atoms bonded to silicon was found to be 16.3 kcal mol^{-1}.

Parallel observations have been made in the case of $[H_2Si(O\ s\text{-}Bu)_3]^-$. The only difference is a reduced rate of exchange compared to that of $[H_2Si(Oi\text{-}Pr)_3]^-$ under similar conditions. For instance, the ^{29}Si spectrum of $[H_2Si(O\ s\text{-}Bu)_3]^-$ exhibits a single resonance (dd, −85.6 ppm, $J(^1H\text{–}^{29}Si) = 222$ Hz and $J(^1H\text{–}^{29}Si) = 194$ Hz, Table 1).

TABLE 2. ^{29}Si NMR data: $K[H_2Si(Oi\text{-}Pr)_3]$

Run no.	Solvent	δ (ppm)	$J(^1H\text{–}^{29}Si)$ (Hz)
1	THF	−87.1	213(t)
2	DME	−86.4	212(t)
3	C_6D_6	−87.3	224, 193(dd)
4	C_6D_6 + 18-crown-6	−81.3	222(t)

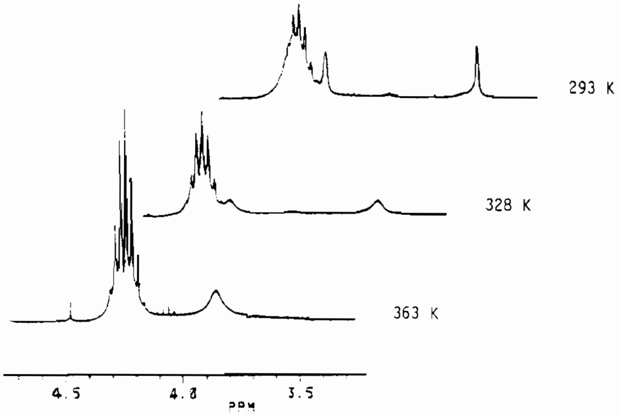
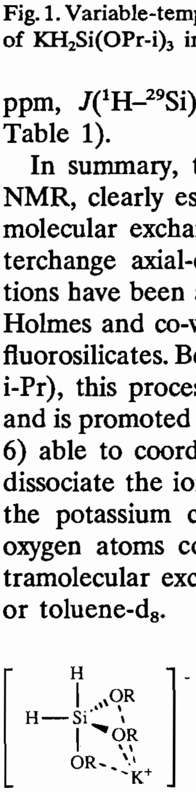


Fig. 1. Variable-temperature ^{1}H NMR spectra (4.7–3.3 ppm region) of $KH_2Si(OPr\text{-}i)_3$ in toluene-d_8.

In summary, the above data, i.e. either ^{29}Si or ^{1}H NMR, clearly establish the presence of a rapid intramolecular exchange in which the hydrogen atoms interchange axial-equatorial positions. Similar observations have been also made by Damrauer *et al.* [17] and Holmes and co-workers [4d, 18] in the case of anionic fluorosilicates. Besides steric hindrance (R = s-Bu versus i-Pr), this process is mainly controlled by the solvent and is promoted by any species (THF, DME, 18-crown-6) able to coordinate to the potassium cation and to dissociate the ion pair. Aggregates such as 3 in which the potassium cation is strongly coordinated to the oxygen atoms could be invoked and prevent the intramolecular exchange in solvents such as benzene-d_6 or toluene-d_8.



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When going to DME, THF/18-crown-6 or benzene-d_6/18-crown-6 and, thus, increasing the solvating power, the structure of $K[H_2Si(Oi\text{-}Pr)_3]$ consists of isolated K^+ and $[H_2Si(Oi\text{-}Pr)_3]^-$ ions. As a consequence, an enhanced rate of exchange is observed.

The $[H_nSi(OR)_{5-n}]^-$ anions. The chemical reactivity

Many of the reactions of organosilicon compounds which are catalyzed by nucleophiles, including those commonly used in organic synthesis, involve hypervalent silicon intermediates [1b, c, 9b]. However, in spite of the considerable amount of structural investigations devoted to them, relatively little of their chemistry has been explored. Some recent work indicated that pentacoordinated species may have varied chemistry, significantly different from that of their tetravalent counterparts [1b, c, 8, 9].

Recent calculations on tetracoordinated silicon derivatives SiH_nF_{4-n} have been compared with those on the anionic species $[SiH_nF_{5-n}]^-$, formed by addition of a fluoride anion [4d, 19]. The pentavalent silicon atom is still electropositive and an increase of the negative charge is observed on all substituents. Moreover, the lengthening of the bonds on going from a tetrahedron to a trigonal-bipyramid geometry allows a higher reactivity of such pentacoordinated compounds to be expected.

Hydridosilicates, $[H_nSi(OR)_{5-n}]^-$, are simple molecules and, as shown above, a number of them can be readily prepared in a pure form by coordination of RO^- and H^- to silicon [11]. Thus, these species are of particular interest for mechanistic studies and, as will be discussed, a wide range of reactivities has been observed. They can undergo facile nucleophilic attack at silicon by nucleophiles (RMgX, RLi, ROH, H_2O). The high reactivity of the Si–H bond will be illustrated both in reactions where the hydridosilicates will act as a base or as a hydride transfer reagent toward carbonyl derivatives. Finally, evidence will be given of the possibility for the hydridosilicate anions to donate one electron to suitable substrates.

In the course of the discussion, much of the material will be related to $[HSi(OR)_4]^-$ (R = Et). In most cases, dihydridosilicates, $[H_2Si(OR)_3]^-$, show similar chemical behavior [11].

Reactivity toward nucleophiles

Reactions with Grignard reagents and organolithiums
Pentacoordinated anionic *o*-arenediolato- [8a, 20], fluoro- and alkoxosilicates [8d] were found to be more reactive toward strong nucleophiles, such as Grignard reagents or organolithiums, than the corresponding tetracoordinated compounds. A 10–10^2 fold rate acceleration has been observed in the case of $[MePhSiF_3]^-$ or $[Ph_3SiF_2]^-$ with the most hindered nucleophiles (i-PrMgBr, t-BuMgBr) [8b, d].

Analogous reactions were performed in the case of $[HSi(OEt)_4]^-$ as the potassium salt. Treatment with a slight excess of a Grignard reagent R'MgX (R' = n-Bu, Ph, $PhCH_2$) led to the formation of the triorganosilane $R'_3Si\text{-}H$ (Scheme 2) [11d].

$$K[HSi(OEt)_4] + 3\,R'MgX \xrightarrow{\text{THF, - 78 °C to 0°C, 8 h.}} R'_3SiH$$

R' = Ph, 66 % ; R' = n- Bu, 62 % ; R' = $PhCH_2$, 70 % .

Scheme 2. Reactivity of $[HSi(OEt)_4]^-$ toward Grignard reagents.

The reaction with 4 molar equiv. of phenyllithium in THF or ether at 0 °C for 2 h afforded the tetrasubstituted silane, Ph_4Si (85% yield). At −78 °C for 1 h with only 3 equiv. of the organolithium reagent, a mixture of Ph_4Si (35%) and Ph_3SiH (42%) as major products was obtained.

Dihydridosilicates, $[H_2Si(OR)_3]^-$ (R = Et and i-Pr) have been also readily converted into diorganosilanes R'_2SiH_2 with Grignard reagents, R'MgX (Table 3) [11e]. The reaction took place under mild conditions in the case of $K[H_2Si(OEt)_3]$. Higher temperature is required to produce R'_2SiH_2 from $K[H_2Si(Oi\text{-}Pr)_3]$ and a higher ratio of R'_3SiH resulting from the displacement of a Si–H bond was obtained. This reaction represents a convenient and alternative way of making R'_2SiH_2, especially when R' is a vinyl or allyl group (Table 3). These two compounds are not easily accessible by conventional reactions and our method would avoid the use of H_2SiCl_2 as a starting material.

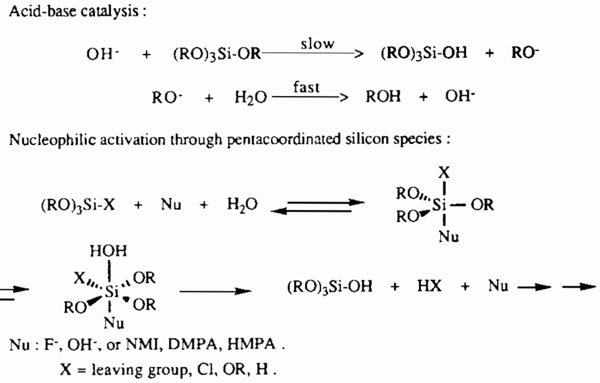
Alcoholysis and hydrolysis reactions
The hydrolysis of organic silicates, mainly $Si(OMe)_4$ and $Si(OEt)_4$, is the key reaction in the sol–gel process for the preparation of silica. The mechanism depends greatly on the reaction conditions (neutral or catalyzed with acids, bases or nucleophiles) and has been studied by several groups [21–24].

TABLE 3. $K[H_2Si(OR)_3] + 2R'MgX \xrightarrow{THF} R'_2SiH_2 + R'_3SiH$

$K[H_2Si(OR)_3]$	R'MgX	*t* (°C)	*t* (h)	Products (%)	
				R'_2SiH_2	R'_3SiH
$K[H_2Si(OEt)_3]$	$PhCH_2MgCl$	−30→0	2	80	
	n-BuMgBr	−30→0	2	60	10
	PhMgBr	−30→0	0.5	60	20
	$CH_2{=}CHMgBr$	−30→0	2	55	
	$CH_2{=}CHCH_2MgBr$	0→r.t.	2	31	
$K[H_2Si(Oi\text{-}Pr)_3]$	PhMgBr	r.t.	3	77	10
	$PhCH_2MgCl$	40	2	63	20
	n-BuMgBr	r.t.	3	50	15

Under basic conditions, the more common mechanism is considered to be a pure nucleophilic displacement at silicon. The increase of rate due to the catalyst corresponds to an increase of the nucleophilicity of the reagent, OH^- instead of H_2O (Scheme 3), i.e. a normal acid–base catalysis.

Another possible mechanism would be the coordination of the base, i.e. an ionic agent like F^- or a neutral good coordinating agent like *N*-methylimidazole (NMI), dimethylaminopyridine (DMPA) and hexamethylphosphortriamide (HMPA), affording first a pentacoordinated silicon intermediate [25]. The next step would be the attack of water, giving a hexacoordinated intermediate that leads to the products (Scheme 3).



Scheme 3. Hydrolysis of organic silicates.

As a support of such an assumption, calculations by Burggraf *et al.* have shown that the formation of hypervalent siliconates in solutions of silicic acid is a quite favorable process [19b, 26]. Attack of OH^- onto silicic acid produces a stable siliconate $[Si(OH)_5]^-$. No energy barrier exists to its formation and the enthalpy of the reaction is predicted to be -37.7 kcal mol^{-1}. Similar conclusions have been done in the case of fluoride anions [27].

The above mechanism implies that the pentacoordinated intermediate is more reactive toward the substituting nucleophile (H_2O in this case) than the related tetracoordinated neutral derivative. In order to check this hypothesis, the alcoholysis and hydrolysis of the $[Si(OR)_5]^-$ and $[H_nSi(OR)_{5-n}]^-$ anions has been investigated [10f].

Pentaalkoxosilicates [K, 18-crown-6][$Si(OR)_5$] [2a, 8d] are easily obtained according to the Damrauer procedure (eqn. (3)) [17].

$$Si(OR)_4 + KOR \xrightarrow{\text{18-crown-6}} [K, \text{18-crown-6}][Si(OR)_5] \quad (3)$$

R = Me, Et, n-Bu, Ph

The pentacoordinated species itself (R = Et, as an example) was easily hydrolyzed. The early stage of gelification was observed after 2–3 h of reaction. In sharp contrast, hydrolysis of $Si(OEt)_4$ was slow and no transformation was observed after 7 days at room temperature. Similar sets of data were obtained with $Si(OR)_4$ (R = Me, n-Bu or Ph) [23].

To get more information about the mechanism, these studies have been extended to the hydridosilicates, $[H_nSi(OR)_{5-n}]^-$, which contain two different substituents at silicon, i.e. H and OR groups. These two potential leaving groups are expected to react differently with ROH or H_2O and, thus, to provide some new insights into the mechanism of the reaction.

Alcoholysis of the hydridosilicates, $[HSi(OR)_4]^-$, leads to the only displacement of the Si–H bond. They are exclusively converted into the corresponding pentacoordinated oxysilicates in the presence of 18-crown-6 (eqn. (4)). This suggests that the reaction might involve the formation of a hexacoordinated intermediate resulting from the attack of ROH at a pentavalent silicon atom.

$$K[HSi(OR)_4] + ROH \xrightarrow{\text{18-crown-6}} [K, \text{18-crown-6}][Si(OR)_5] + H_2 \quad (4)$$

R = Me, Et, n-Bu, Ph

On the contrary, $HSi(OR)_3$ itself does not react with alcohols.

The mechanism of the above reaction was demonstrated in the case of $K[H_2Si(Oi\text{-}Pr)_3]$, which reacts with one equiv. of i-PrOH to give the substitution of one Si–H bond only. $K[HSi(Oi\text{-}Pr)_4]$ is obtained in near quantitative yield (eqn. (5)).

$$K[H_2Si(Oi\text{-}Pr)_3] + i\text{-}PrOH \xrightarrow{\text{18-crown-6}} [K, \text{18-crown-6}][HSi(Oi\text{-}Pr)_4] + H_2 \quad (5)$$

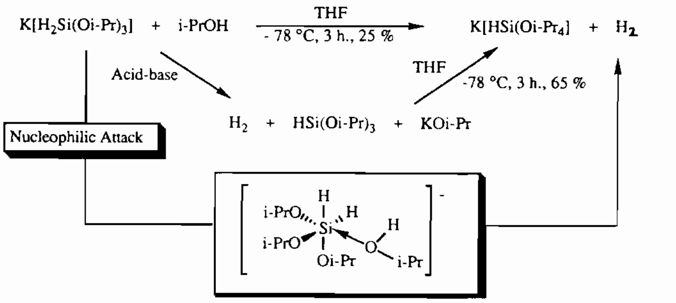
The reaction proceeds slowly at −78 °C. Under similar conditions, reaction of $HSi(Oi\text{-}Pr)_3$ with KOi-Pr is fast even at −78 °C compared to the alcoholysis of $K[H_2Si(Oi\text{-}Pr)_3]$ (Scheme 4). This fact demonstrates that the alcoholysis does not correspond to an acid–base reaction which would be relatively temperature independent, followed by a recombination of KOi-Pr and $HSi(Oi\text{-}Pr)_3$ (Scheme 4). The most convincing mechanism corresponds to the formation of a hexacoordinated intermediate resulting from the attack of ROH at a pentavalent silicon (Scheme 4).

The above observations, i.e.

(i) the alcoholysis reaction is faster in the case of pentacoordinated hydridosilicates compared to the corresponding $HSi(OR)_3$,

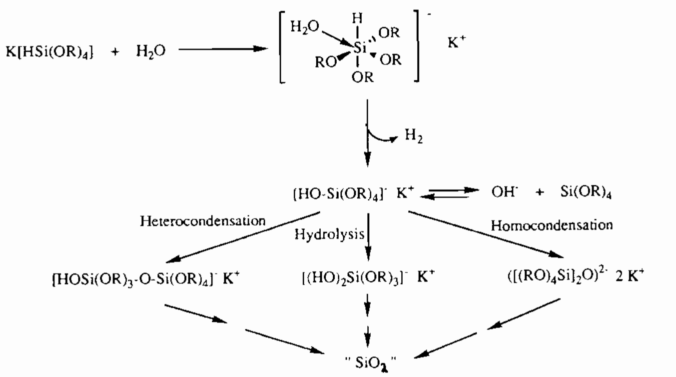
(ii) the reaction is a direct nucleophilic substitution at a pentavalent silicon atom rather than a base-catalyzed process,

can be extended to the hydrolysis reaction. In the case of $HSi(Oi\text{-}Pr)_3$, no hydrolysis was observed after 5 days. In contrast, immediate evolution of hydrogen occurred



Scheme 4. Alcoholysis of $K[H_2Si(Oi\text{-}Pr)_3]$.

in the reaction of $K[HSi(Oi\text{-}Pr)_4]$ and H_2O. A monolithic gel is slowly formed (gelification time: 30 h), indicating a slow hydrolysis of the Si–Oi–Pr bonds due to steric hindrance. Thus, we can assume that the first step is the nucleophilic attack of H_2O at silicon through a hexacoordinated intermediate (Scheme 5). A pentacoordinated hydroxysilicate is formed with evolution of H_2. This hydroxysilicate can undergo homo- and heterocondensation or hydrolysis with progressive cleavage of the Si–O bonds and formation of a gel (Scheme 5).



Scheme 5. Hydrolysis of organic silicates.

Hydridosilicates as hydride transfer reagents

Reactions with Ph–C≡C–H and Ph_3CH: $K[HSi(OEt)_4]$ as a base

When phenylacetylene reacted with one equiv. of $K[HSi(OEt)_4]$ in THF, deprotonation was observed. The metalation was complete within 4 h at room temperature and led to potassium acetylide, which was trapped with Me_3SiCl (eqn (6)).

$$\mathrm{Ph{-}C{\equiv}C{-}H} \xrightarrow[\text{THF, r.t.}]{\mathrm{K[HSi(OEt)_4]}}$$

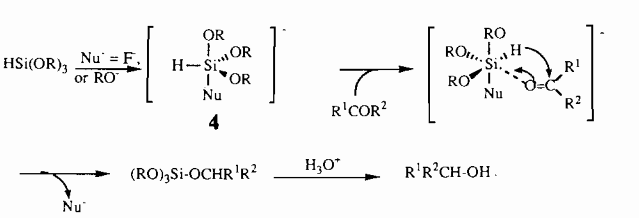
$$\mathrm{Ph{-}C{\equiv}C^{-}K^{+}} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{Ph{-}C{\equiv}C{-}SiMe_3} \qquad (6)$$

87%

In a similar manner, the reaction of Ph_3CH with $K[HSi(OEt)_4]$ resulted in the formation of Ph_3CK. Upon deuterolysis, Ph_3CD was obtained in 35% yield.

Reduction of carbonyl derivatives

The reduction of aldehydes and ketones with hydrosilanes catalyzed by fluoride and alkoxide ions [28–30] has been recognized as a useful synthetic method for a number of years [6b]. Pentacoordinated hydridosilicates like **4** have been suggested to be the reactive intermediates (Scheme 6).



Scheme 6. Reduction of aldehydes or ketones by $HSi(OEt)_3$ catalyzed by F^- or RO^-.

Recent reports focused also on the use of hypervalent silicon hydrides as reducing agents. Solutions most probably containing the ion $[H\text{–}Si\text{–}(\text{–}OC_6H_4O)_2]^-$ and the corresponding complex of 2,2′-dihydroxyphenyl were shown to reduce both ketones and aldehydes in excellent yields [31]. Similar reagents prepared from aliphatic 1,2-diols were also effective [32]. The bis[α,α-bis(trifluoromethyl)benzenemethanolato(2 –)-C^2,O]hydridosilicate(1 –) anion was recognized as a reducing agent [32]. Intramolecularly coordinated hydrosilanes have been shown to be powerful hydride donors [9b, 33].

$K[HSi(OEt)_4]$ was found to reduce ketones and aldehydes effectively in the absence of a catalyst at room temperature (Table 4) [11d]. Under similar conditions, $HSi(OEt)_3$ is unreactive. Yields are generally high (up to 90%). The lower yield in the case of acetophenone has been attributed to partial enolization of the starting material due to ethoxide anions liberated during the reaction or the hydridosilicate itself, the basic behavior of which was outlined above. The presence of the enolate derived from $PhCOCH_3$ was demonstrated with Me_3SiCl as a trapping agent. Reduction of benzophenone gave only benzhydrol. Formation of the ketyl radical anions was not detected during the reaction.

In a similar case, $K[H_2Si(Oi\text{-}Pr)_3]$ was also effective [11e]. Aldehydes and ketones were converted into primary and secondary alcohols, respectively, in good yields

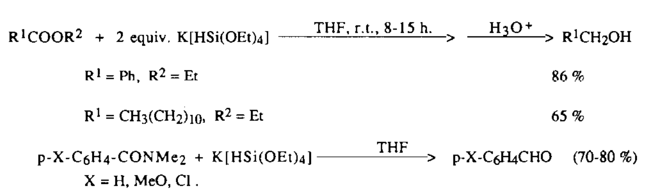
TABLE 4. Reduction of carbonyl derivatives

$$K[HSi(OEt)_4] + R^1COR^2 \xrightarrow{THF} \xrightarrow{H_3O^+} R^1R^2CHOH$$

R^1COR^2	*t* (°C)	Reaction time (h)	R^1R^2CHOH (%)
PhCHO	0	3	90
p-BrC_6H_4CHO	0	4	84
$CH_3(CH_2)_6CHO$	0	4	80
PhCOPh	r.t.	15	73
PhCOMe	r.t.	15	53

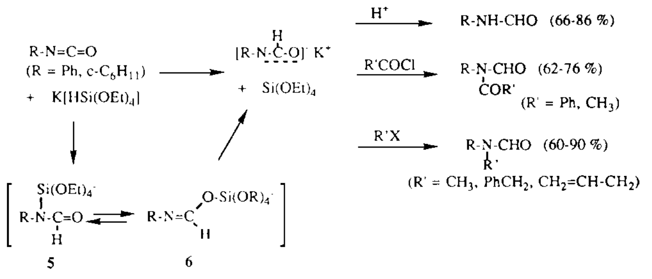
(50–80%). Moreover, $[H_2Si(Oi\text{-}Pr)_3]^-$ is able to give up both of the hydrogens bonded to silicon.

The efficiency of $K[HSi(OEt)_4]$ as a hydride transfer agent is also illustrated by its reactions with esters. Whereas no reduction was observed with dilithium bis(benzenediolato)hydridosilicate, ethylbenzoate and ethyldodecanoate are converted to the alcohols with $[HSi(OEt)_4]^-$ (Scheme 7). Non-enolizable amides are reduced into the corresponding aldehydes.



Scheme 7. Reduction of esters and amides by $K[HSi(OEt)_4]$.

Reaction of $K[HSi(OEt)_4]$ with one equiv. of R–NCO (R = Ph, c-C_6H_{11}) in THF or ether led quantitatively to the potassium imidates with concomitant formation of $Si(OEt)_4$ as shown in Scheme 8. Under similar conditions, $HSi(OEt)_3$ was found unreactive. Hydrosilylation of isocyanates requires the presence of a transition metal catalyst such as Pt–C, $PdCl_2$ or $(PPh_3)_3RhCl$ [34]. From a mechanistic point of view, the reaction goes through the formation of pentacoordinated adducts resulting from the hydrosilylation of the isocyanates (Scheme 8). Related *N*-silylamide **5** and *O*-silylimidate **6** structures have been observed and characterized in the reaction of Ph–NCO with neutral pentavalent hydrosilanes [35]. Because of the leaving group ability of N-substituted formamidyl ligand, the pentacoordinated intermediates **5** and **6** would readily evolve to the potassium imidates. Evidence for the formation of the imidate anions was found by ^1H and ^{13}C NMR and by reactions with electrophiles (Scheme 8). Treatment with formic acid resulted in *N*-phenyl(or cyclohexyl)formamide. As expected, the anion was selectively alkylated on nitrogen, even though the negative charge resides chiefly on oxygen. *N*-Acylformamides were also obtained in high yields.



Scheme 8. Reaction of $K[HSi(OEt)_4]$ with isocyanates.

Hydridosilicates as electron transfer reagents

Reactivity toward organic halides [11]

$K[HSi(OEt)_4]$ reacts smoothly with alkyl halides in THF to give the corresponding alkanes in 30–35% yields. The bromides are more reactive than the chlorides. Moreover concomitant formation of $Si(OEt)_4$ is observed (Table 5) [11d]. Under similar experimental conditions, $HSi(OEt)_3$ is found unreactive.

The occurrence of a single electron transfer pathway (SET) in the reaction of organic halides with metal hydrides has been discussed in details [36, 37]. Moreover, the pentacoordinated anion formed *in situ* from phenyldimethylsilane and fluoride anion has been reported previously to be a SET reagent [29a]. Thus, the reaction of the isolated $K[HSi(OEt)_4]$ with 6-bromo-1-hexene, which can serve as a probe for the detection of a SET process, was examined. The rearranged cyclic product, which should be indicative of the formation of the transient 5-hexen-1-yl radical, was formed in less than 5% besides 1-hexene.

Organic halides that might produce stable radical intermediates have been also treated. Reaction with one equiv. of $PhCH_2X$ (X = Cl, Br) or Ph_2CHCl gave the dimer in addition to the expected toluene and diphenylmethane, respectively. Finally, in the case of Ph_3CBr, Ph_3CH and *p*-$[(C_6H_5)_2CH]$–C_6H_4–$C(C_6H_5)_3$ (22%) were isolated as the main organic products (Table 5). The reaction solution was ESR active and showed a spectrum consistent with the resonance of the trityl radical generated by one electron transfer from $K[HSi(OEt)_4]$ to Ph_3CBr [36a, 38]. However, we cannot exclude that a part of RH ($PhCH_3$, Ph_2CH_2, or Ph_3CH) results from a direct nucleophilic substitution and we propose the following scheme for the above reactions (Scheme 9).

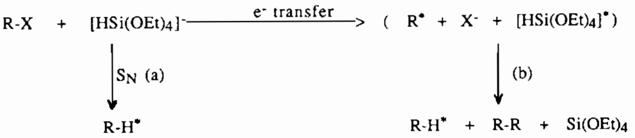
Miscellaneous reactions

The aptitude of the pentacoordinated hydridosilicates to donate one electron was confirmed with substrates such as Cu^+, Ag^+ cations and $Cp(CO)_2Fe$–I (Scheme 10). In both cases, $Si(OEt)_4$ was the major organosilicon product (up to 90%). In the case of the iron iodide

TABLE 5. Reduction of organic halides
$K[HSi(OEt)_4] + RX \xrightarrow{THF,\ r.t.} RH + RR + Si(OEt)_4$

RX	Reaction time (h)	RH (%)	RR^a (%)
$PhCH_2Cl$	40	16	14
$PhCH_2Br$	20	37	34
Ph_2CHCl	15	12	40
Ph_3CBr	15	47	22^a

^{a}RR = *p*-$[(C_6H_5)_2CH]$–C_6H_4–$C(C_6H_5)_3$.



•R = alkyl : R-H results from path (a) .
•R = $PhCH_2$, Ph_2CH, Ph_3C : R-H may result from path (a) or / and (b) .

Scheme 9. Reduction of organic halides with $K[HSi(OEt)_4]$.

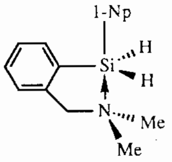
$$\mathrm{Cp(CO)_2Fe\text{-}I} + \mathrm{K[HSi(OEt)_4]} \xrightarrow{e^-\ \text{transfer}} \mathrm{Cp(CO)_2Fe^{\bullet}} + \mathrm{HSi(OEt)_4^{\bullet}} + \mathrm{KI}$$
$$\longrightarrow [\mathrm{Cp(CO)_2Fe}]_2 + \mathrm{Si(OEt)_4} + \mathrm{H_2}$$

Scheme 10.

complex, the reaction gave the iron dimer $[Cp(CO)_2Fe]_2$ quantitatively.

In addition, THF solutions of $K[HSi(OEt)_4]$ with *p*-dinitrobenzene (DNB) or 2,6-di-tert-butylbenzoquinone (DBQ) were found to be ESR active [39, 40]. $HSi(OEt)_3$ itself did not produce the corresponding radical anions. Thus, it is apparent that the electron transfer was due to the interaction of the pentavalent silyl anion with DBN or DBQ.

This latter feature seems at the present time characteristic of the anionic hydridosilicates. Mixtures of neutral penta- or hexacoordinated silicon hydrides such as **7** and **8** with DBQ were found to be ESR inactive. Furthermore, under similar conditions, [K, 18-crown-6][Ph_3SiF_2] did not give an ESR signal.



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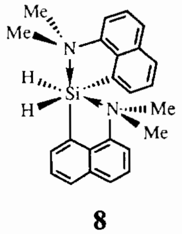

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