Preliminary communication

Five-coordinate potassium dihydridosilicates: synthesis and some aspects of their reactivity

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(Received February 15th, 1989)

Abstract

Five-coordinate potassium dihydridosilicates, $K^+[H_2Si(OR)_3]^-$ (R = Et, i-Pr) have been obtained by reaction of a trialkoxysilane with potassium hydride. Reaction of the dihydridosilicate with an excess of a Grignard reagent gives the corresponding diorganosilane. The ease of reduction of carbonyl compounds by the dihydridosilicate in the absence of a catalyst is indicative of the high reactivity of the Si–H bond in such species.

There is much interest in the existence [1,2], structures [3], reactivity [4], and isomerisations [2,5] of pentacoordinate silicon derivatives that have been proposed as intermediates in reactions of organosilanes in solution [5].
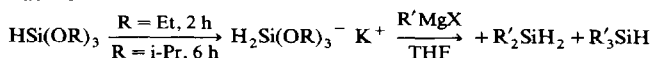
As a part of our investigation of the reactions of such hypervalent organosilicon species [6] we became interested in pentacoordinated silicon hydrides. These species have been observed in the gas phase from the reaction of H^- with alkylsilanes [7], and suggested as intermediates in reactions in solution. For instance, the fast racemisation of the optically active 1-NpPhMeSiH(D) (1-Np = 1-naphthyl) catalysed by hydrides (KH, LiAlH$_4$, LiAlD$_4$) in THF or DME as solvent at room temperature has been rationalized in terms of coordination of H^- (or D^-) to silicon, leading to a five-coordinate dihydridosilyl anion [8]. Likewise the redistribution reaction of di- and tri-hydrogenosilanes, $RR'SiH_2$ and $RSiH_3$ in the presence of hydrides (LiAlH$_4$, KH and NaH) as catalysts [9] has been shown to involve such intermediates. However, whereas fluoride or alkoxide anions are well known to coordinate readily to a silicon atom to give stable derivatives [1,4], hydridosilicates resulting from the addition of H^- at silicon have never been observed in solution.

We have found that potassium hydride reacts with trialkoxy- or triaryloxy-silanes to yield the pentavalent ions, $H_2Si(OR)_3^-$ or $HSi(OR)_4^-$ depending on the reaction conditions, as summarized in Table 1.

It can be seen that the ease of formation and the stability of the dihydridosilicate

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Table 1

$$\text{HSi(OR)}_3 + \text{KH} \xrightarrow[\text{or DME}]{\text{THF, r.t.}} \underset{\textbf{(1)}}{\text{HSi(OR)}_4^-\ \text{K}^+} + \underset{\textbf{(2)}}{\text{H}_2\text{Si(OR)}_3^-\ \text{K}^+}$$

Run	HSi(OR)$_3$ (solvent)	reaction time (h)	Products (%) [b]	
			1 [a]	**2** [a]
1	HSi(OEt)$_3$ (THF)	6	60	40
2	HSi(OEt)$_3$ (THF)	24	100(80)	–
3	HSi(OEt)$_3$ (DME)	1.5	100(75)	–
4	HSi(O-i-Pr)$_3$ (THF)	6	–	100(94)
5	HSi(O-i-Pr)$_3$ (THF)	168	< 5	> 95
6	HSi(OPh)$_3$ (THF)	2	100(84)	–

[a] Relative ratio of **1** and **2** determined by ^{29}Si NMR. [b] Chemical yields of **1** or **2** obtained after removal of the solvent.

2 depends greatly on the nature of the OR group attached at silicon and on that of the solvent (Table 1). Thus:

(i) HSi(OPh)$_3$ in THF readily gave HSi(OPh)$_4^-$ K$^+$ (Table 1, run 6). Under the same conditions, the reaction of HSi(OEt)$_3$ with KH in THF (Table 1, run 1) afforded a 60/40 mixture of HSi(OEt)$_4^-$ K$^+$ (**1**) [10], and H$_2$Si(OEt)$_3^-$ K$^+$ (**2**). HSi(OEt)$_4^-$ was exclusively obtained when the reaction was carried on for 24 h (Table 1, run 2). In sharp contrast, HSi(O-i-Pr)$_3$ gave only H$_2$Si(O-i-Pr)$_3^-$ K$^+$ in 94% yield (Table 1, run 4), and even after 7 days at room temperature less than 5% of HSi(O-i-Pr)$_4^-$ K$^+$ was detected. These results suggest the occurrence of a fast redistribution reaction of the dihydridosilicate **2** (R = Ph or Et), the rate of which is strongly lowered by steric effects (R = i-Pr).

(ii) An increase in the solvating power of the solvent, on going to DME from THF, led to formation of HSi(OR)$_4^-$ K$^+$ (R = Et, Table 1, run 3).

The dihydridosilicates **2** (R = Et and i-Pr) gave satisfactory NMR data. In particular, the ^{29}Si NMR chemical shifts were in the usual range for anionic pentacoordinated silicates [4e–f,9,10]; as expected, upfield shifts of the ^{29}Si NMR resonances relative to those of the corresponding alkoxysilanes were observed (Table 2). The ^{1}H–^{29}Si coupling constants are also consistent with a five-coordinate structure [4e,10,11]. The value of the ^{1}H–^{29}Si coupling constant is smaller for the five-coordinated silicates than for the corresponding neutral species (Table 2), as expected from the decrease in the proportion of s character in the Si–H bond.

Table 2

^{29}Si NMR data [a] for **2** (R = Et, i-Pr) (S = THF): a comparison with those of HSi(OR)$_3$ and HSi(OR)$_4^-$

HSi(OEt)$_3$	δ −58.8 ppm (d, J^1H—^{29}Si) 285 Hz
HSi(OEt)$_4^-$	δ −88.1 ppm [10] (d, $J(^1$H—^{29}Si) 223 Hz
H$_2$Si(OEt)$_3^-$	δ −80.6 ppm (t, $J(^1$H—^{29}Si) 218 Hz
HSi(O-i-Pr)$_3$	δ −62.7 ppm (d, $J(^1$H—^{29}Si) 285 Hz
HSi(O-i-Pr)$_4^-$	δ −90.7 ppm [10] (d, $J(^1$H—^{29}Si) 214 Hz
H$_2$Si(O-i-Pr)$_3^-$	δ −86.9 ppm (t, $J(^1$H—^{29}Si) 210 Hz

[a] The spectra were recorded in THF as solvent with external C$_6$D$_6$ as lock and TMS as reference.

Table 3

$$\text{HSi(OR)}_3 \xrightarrow[R = \text{i-Pr, 6 h}]{R = \text{Et, 2 h}} \text{H}_2\text{Si(OR)}_3{}^-\ \text{K}^+ \xrightarrow[\text{THF}]{R'\text{MgX}} + R'_2\text{SiH}_2 + R'_3\text{SiH}$$

$\text{H}_2\text{Si(OR)}_3{}^-\ \text{K}^+$	$R'\text{MgX}$	$T(^\circ\text{C})$	t (h)	Products (%) [a]	
				$R'_2\text{SiH}_2$	$R'_3\text{SiH}$
$\text{H}_2\text{Si(OEt)}_3{}^-\ \text{K}^+$	PhCH_2MgCl	$-30 \rightarrow 0$	2	80	–
	n-BuMgBr	$-30 \rightarrow 0$	2	60	10
	PhMgBr	$-30 \rightarrow 0$	0.5	60	20
$\text{H}_2\text{Si(OiPr)}_3{}^-\ \text{K}^+$	PhMgBr	r.t.	3	77	10
	PhCH_2MgCl	40	2	63	20
	n-BuMgBr	r.t.	2	50	15

[a] Yields of isolated products.

As observed previously for o-arenediolato- [4a] and fluoroorgano-silicates [4d], **2** (R = Et and i-Pr) reacts readily with a slight excess of a Grignard reagent RMgBr and $R_2\text{SiH}_2$ was obtained in good yield (Table 3). Formation in high yields of the dihydrogenosilanes provides good chemical evidence for the nature of the dihydridosilicates **2**, and for the presence of a high proportion of $\text{H}_2\text{Si(OEt)}_3{}^-\ \text{K}^+$ in solution (see Table 3). The reaction took place readily under mild conditions in the case of $\text{H}_2\text{Si(OEt)}_3{}^-\ \text{K}^+$ but a higher temperature was required to produce $R_2\text{SiH}_2$ from $\text{H}_2\text{Si(O-i-Pr)}_3{}^-\ \text{K}^+$.

The isolated $\text{H}_2\text{Si(O-i-Pr)}_3{}^-$ was also found to reduce carbonyl derivatives in the absence of a catalyst under mild conditions (Table 4).

The yields of primary and secondary alcohols are generally high (50–80% yield). The lower yield in the case of PhCOCH_3 can be attributed to a partial enolisation of the ketone by alkoxide ions liberated during the reaction. Complex **2** is also able to give up both of the hydrogens bonded to silicon (Table 4, run 1–4); this suggests that the reaction goes through a pentavalent hydridosilicate intermediate such as $[\text{HSi(OR)}_3(\text{OR}')]^-$, which can reduce a second molecule of the carbonyl derivative
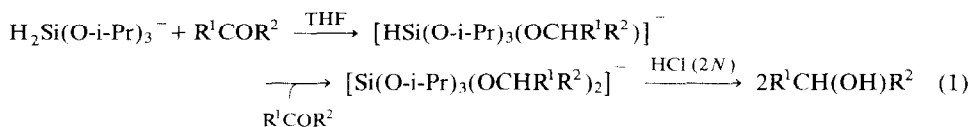
Table 4

$$\text{H}_2\text{Si(O-i-Pr)}_3{}^-\ \text{K}^+ + R^1\text{COR}^2 \xrightarrow[\text{r.t., 4 h}]{\text{THF}} \xrightarrow{\text{HCl (2}N\text{)}} R^1\text{CHR}^2$$
$$\underset{\textbf{(2)}}{} \quad \underset{\textbf{(3)}}{} \qquad\qquad\qquad \underset{\text{OH}}{|}$$
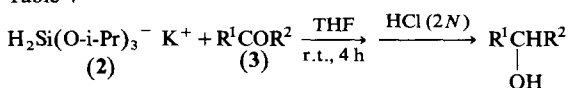
Run	3	3/2 ratio	$R^1\text{CH(OH)}R^2$ [a] (recovered $R^1\text{COR}^2$) (%)
1	PhCHO	2	74
2	PhCOPh	2	50 (26)
3	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	2	62
4	PhCOCH_3	2	36 (40)
5	PhCOCH_3	1	80 (14)

[a] Yields of the isolated alcohols are based on the amount of carbonyl compound $R^1\text{COR}^2$ introduced. As the ratio $R^1\text{COR}^2/\text{H}_2\text{Si(O-i-Pr)}_3{}^-\ \text{K}^+$ is 2 (run 1–4), and the yield is greater than 50% (except with PhCOCH_3 because of partial enolisation), the data show that $\text{H}_2\text{Si(O-i-Pr)}_3{}^-$ transfers both of the hydrogens bonded to silicon.

[10] (eq. 1).

$$H_2Si(O\text{-}i\text{-}Pr)_3^- + R^1COR^2 \xrightarrow{\text{THF}} [HSi(O\text{-}i\text{-}Pr)_3(OCHR^1R^2)]^-$$

$$\xrightarrow[R^1COR^2]{} [Si(O\text{-}i\text{-}Pr)_3(OCHR^1R^2)_2]^- \xrightarrow{\text{HCl}\,(2N)} 2R^1CH(OH)R^2 \quad (1)$$

In conclusion, we have found that like fluoride and alkoxide ions [1,4], H^- coordinate with silicon, and gives potassium dihydridosilicates, $H_2Si(OR)_3^-$ K^+. These pentavalent species react readily with Grignard reagents to give R_2SiH_2, and show a high reactivity as reducing agents for carbonyl compounds. Investigation of special features of the reactions of these five-coordinate derivatives is now in progress.

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