

### Preliminary communication

## A general route to five-coordinate hydridosilicates

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### Abstract

Five-coordinate potassium hydridosilicates,  $[\text{HSi}(\text{OR})_4]^- \text{K}^+$  (R = Et, i-Pr, Ph), have been obtained in good yield from the reaction of a trialkoxy- or triaryloxy-silane with the corresponding potassium alkoxide or aryloxy, and characterized spectroscopically. Reaction of the hydrosilicates with an excess of Grignard reagent gives the corresponding triorganosilanes.

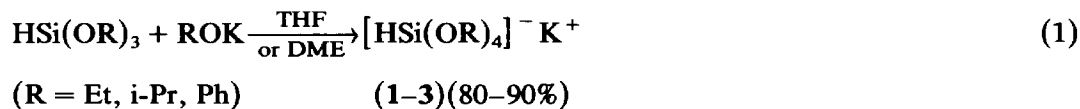
### Introduction

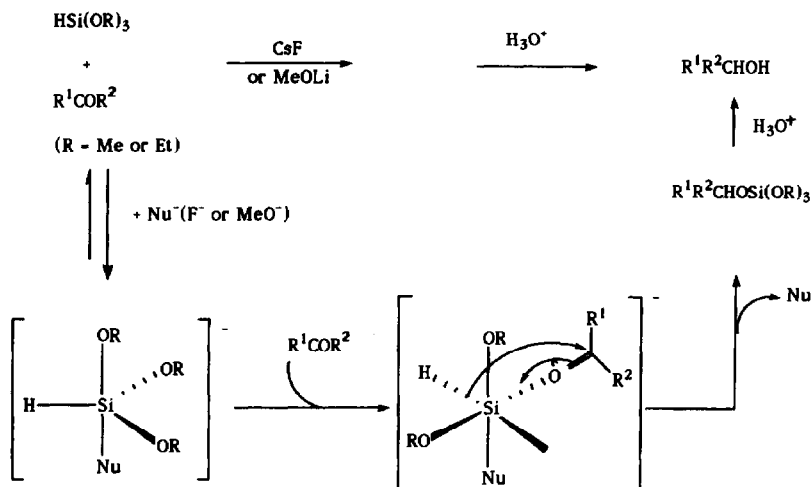
As a part of our systematic investigation of the reactions of hypervalent organo-silicon species [1], we became interested in pentacoordinate anionic hydridosilicates for two main reasons:

- (1) Numerous pentacoordinated silicon compounds have been reported [2] and their structures discussed [3], but no general synthetic route to hydridosilicates has been developed.
- (2) Pentacoordinated hydridosilicates have been suggested to be reactive intermediates in the reduction of aldehydes and ketones with hydrosilanes catalyzed by fluoride [4] or alkoxide [5] ions (Scheme 1).

We have now found that these pentacoordinated hydridosilicates may be obtained directly from the reaction of an alkoxy- or aryloxy-hydrosilane with the corresponding potassium alkoxide or aryloxy.

Treatment of triethoxysilane  $\text{HSi}(\text{OEt})_3$  with one equivalent of potassium ethoxide as a suspension in a large excess of THF or DME at room temperature yielded the corresponding hydridosilicate 1 (eq. 1) which was isolated as a white powder by removal of the solvent.





Scheme 1

This reaction, which is general for other potassium alkoxides or aryloxides, can be optimized to give yields of up to 80–90%. In sharp contrast, sodium or lithium alkoxides failed to give the hydrosilicates. The use of a crown-ether specific for potassium is not necessary to stabilize the products [6].

The hydrosilicates, 1–3 (eq. 1), gave satisfactory spectroscopic data. In particular, the  $^{29}\text{Si}$  NMR chemical shifts were in the usual range for anionic pentacoordinated silicates [7]; as expected, upfield shifts of the  $^{29}\text{Si}$  NMR resonances relative to those of the corresponding alkoxy- or aryloxy-silanes were observed. The  $^{29}\text{Si}$ –H coupling constants are consistent with a five-coordinate structure [6]. The value of the  $^1\text{H}$ – $^{29}\text{Si}$  coupling constant is smaller for the five-coordinated silicates than for the neutral corresponding species (Table 1), as expected from the decrease in the proportions of *s* character of the orbital of the Si–H bond.

As observed previously for *o*-arenediolato- and fluoro-organosilicates [1], 1 reacts readily with an excess of a Grignard reagent  $\text{RMgBr}$ , at low temperature; whatever the nature of the nucleophile ( $\text{R} = n\text{-Bu}$ ,  $\text{Ph}$  or  $\text{PhCH}_2$ ), the triorganosilane  $\text{R}_3\text{SiH}$  was obtained in high yield (eq. 2), and the formation of such compounds provides sound chemical evidence for the nature of compound 1.

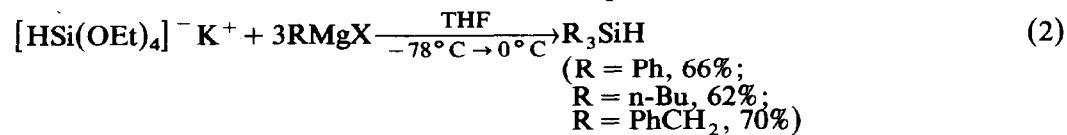


Table 1

 $^{29}\text{Si}$  NMR spectral data for 1–3 (S = THF)

$\text{HSi}(\text{OEt})_3$	$\delta - 58.8$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 285 Hz)
$[\text{HSi}(\text{OEt})_4]^-$ 1	$\delta - 88.1$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 223 Hz)
$\text{HSi}(\text{O-}i\text{-Pr})_3$	$\delta - 62.7$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 285 Hz)
$[\text{HSi}(\text{O-}i\text{-Pr})_4]^-$ 2	$\delta - 90.7$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 214 Hz)
$\text{HSi}(\text{OPh})_3$	$\delta - 70.5$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 320 Hz)
$[\text{HSi}(\text{OPh})_4]^-$ 3	$\delta - 111.9$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 296 Hz)

It is evident that we devised a general method for the preparation of potassium hydridosilicates. These compounds should be excellent models for examining of the mechanism of reduction of carbonyl derivatives by hydrosilanes. Further studies aimed at elucidation of the special features of the reactions of these five-coordinate species are in progress.

## References

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