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Hypervalent silicon hydrides: evidence for their intermediacy in the exchange reactions of di- and tri-hydrogenosilanes catalysed by hydrides (NaH, KH and $LiAlH_4$)

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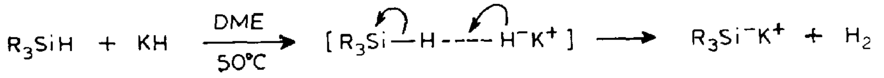
Abstract

Di- and tri-hydrogenosilanes, $RR'SiH_2$ and $RSiH_3$ (R = aryl, allyl or benzyl; R' = aryl or alkyl), readily undergo exchange reactions, involving silicon–carbon bonds and silicon–hydrogen bonds, in the presence of hydrides ($LiAlH_4$, KH and NaH) as catalysts. These results are discussed in terms of five-coordinate silicon hydrides as intermediates in the reaction.

We previously reported the synthesis of organosilylanions by the cleavage of the Si–H bond with an equimolecular amount of potassium hydride (KH) in dimethoxyethane (DME) (eq. 1) [1].

From a mechanistic point of view, this reaction could at first be considered to involve proton abstraction at silicon (eq. 1).



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

Tri- and di-hydrogenosilanes, $RSiH_3$ and R_2SiH_2, are of interest, since abstraction of a proton should lead to the corresponding organosilyl anions, $[RSiH_2]^+$ and $[R_2SiH]^-$ (Scheme 1); an example of the latter (as the diphenylsilyllithium) has been reported by Gilman et al. [2]. Subsequent formation of a dimer and (or) decomposition of $[R_2SiH]^-$ by α-elimination could be expected (Scheme 1).

Such a process could be, in principle, a possible catalytic route to functional polysilanes. We therefore decided to investigate this reaction, since functional polysilanes can only be prepared from R_2SiH_2 and $RSiH_3$ via transition-metal-catalyzed polymerisations [3,4]; classical routes using chlorosilanes and alkali metals lead mainly to non-functionalised polysilanes [5].

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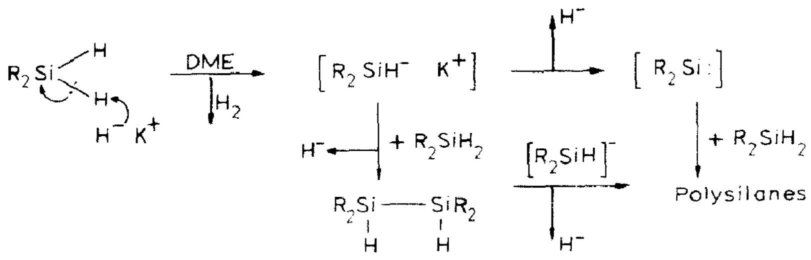

Scheme 1

I. Results

1. Reactions of dihydrogenosilanes with hydrides

Reaction of equimolecular amounts of Ph_2SiH_2 and KH in dimethoxyethane under mild conditions (Table 1, run 1) gave Ph_3SiH as the major product. This unexpected result suggests that an exchange reaction involving silicon–carbon and silicon–hydrogen bonds occurs [6*], instead of the expected deprotonation reaction observed with Ph_3SiH [1]. We have therefore extensively examined this reaction, varying the nature of the substituents attached at silicon, the nature of the solvent, and the reaction conditions. Our data are summarized in Table 1.

The implications can be summarized as follow:

(i) Diphenylsilane, Ph_2SiH_2, undergoes rapid phenyl–hydrogen exchange (Table 1, run 1). Replacing one phenyl groups in the starting material by a methyl group leads to a slower reaction (runs 8, 9), giving Ph_2MeSiH (Table 1, run 9); the methyl–silicon bond remaining unaffected. This behavior of an alkyl group has been confirmed in the case of $(n\text{-}C_5H_{11})_2SiH_2$ (Table 1, run 14): after 63 h at 70 °C, no redistribution reaction was detected. Thus it is possible to preserve a methylsilicon moiety or an alkylsilicon moiety while phenyl groups are readily undergoing redistribution.

(ii) The redistribution of phenyl groups and hydrogen atoms on silicon occurs even when potassium hydride is used as a catalyst (silane/KH, 10/1; Table 1, runs 5, 11). KH is more efficient than NaH (Table 1, run 2); with the latter, a temperature of 70 °C (Table 1, run 3), or the use of the co-catalyst tris(3,6-dioxaheptyl)amine (TDA) [7] (Table 1, run 4), is necessary.

(iii) The reaction needs coordinating solvents. It can be performed in DME, whereas no redistribution occurs in THF (Table 1, run 6). In THF, addition of TDA as a co-catalyst is necessary for formation of Ph_3SiH.

(iv) Redistribution of allyl and benzyl groups also occurs; these reactions proceed at room temperature in presence of a catalytic amount of potassium hydride (Table 1, runs 12 and 13).

(v) In all of the above reactions, evolution of SiH_4 was detected.

2. Reaction of trihydrogenosilanes with potassium hydride

Table 2 lists the $RSiH_3/KH$ systems in which exchange reactions involving silicon–carbon and silicon–hydrogen bonds have been examined.

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* Reference number with asterisk indicates a note in the list of references.

Table 1. Reactions of dihydrogenosilanes with hydrides

Run	Silane	Hydride	Silane/H^- ratio	Solvent	Temperature (°C) [a]	Reaction time (h)	Products [b] (yields)
1	Ph_2SiH_2	KH	1/1	DME	r.t.	1	Ph_3SiH (40)
2	Ph_2SiH_2	NaH	1/1	DME	r.t.	2	no reaction
3	Ph_2SiH_2	NaH	1/1	DME	65–70	70	Ph_3SiH (30)
4	Ph_2SiH_2	NaH-TDA [c]	1/1	DME	65–70	70	Ph_3SiH (47)
5	Ph_2SiH_2	KH	10/1	DME	r.t.	24	Ph_3SiH (35) Ph_4Si (12)
6	Ph_2SiH_2	KH	10/1	THF	r.t.	14	no reaction
7	Ph_2SiH_2	KH-TDA [c]	10/1	THF	r.t.	24	Ph_3SiH (26)
8	$PhMeSiH_2$	KH	1/1	DME	r.t.	1	no reaction
9	$PhMeSiH_2$	KH	1/1	DME	r.t.	64	Ph_2MeSiH (41)
10	$PhMeSiH_2$	KH	1/1	DME	65–70	15	Ph_2MeSiH (11) Ph_3MeSi (21)
11	$PhMeSiH_2$	KH	10/1	DME	65–70	24	Ph_2MeSiH (21) Ph_3MeSi (17)
12	n-C_7H_{15}-allyl-SiH_2	KH	10/1	DME	r.t.	64	n-$C_7H_{15}SiH_3$ (20) n-$C_7H_{15}SiH(allyl)_2$ (20)
13	$PhCH_2CH_2SiH_2(PhCH_2)$	KH	10/1	DME	r.t.	24	$PhCH_2CH_2SiH_3$ (32) $PhCH_2CH_2SiH(PhCH_2)_2$ (32)
14	(n-$C_5H_{11})_2SiH_2$	KH	1/1	DME	70	63	no reaction

[a] r.t. = room temperature.
[b] The quantity of SiH_4 evolved was not determined; the yields are based on the total silicon recovered in the products.
[c] TDA [7] = $N(CH_2CH_2OCH_2CH_2OCH_3)_3$.

Table 2. Reactions of trihydrogenosilanes with hydrides [a]

Run	silane	Hydride	Silane/H^- ratio	Solvent	reaction time (h)	Products [b] (yields)
1	$PhSiH_3$	KH	1/1	DME	14	Ph_2SiH_2 (5) Ph_3SiH (24) Ph_4Si (5)
2	$PhSiH_3$	KH	10/1	DME	15	Ph_2SiH_2 (7) Ph_3SiH (20) Ph_4Si (7)
3	$PhSiH_3$	KH	10/1	THF	17	Ph_2SiH_2 (24) Ph_3SiH (17)
4	$PhSiH_3$	KH	10/1	Et_2O	17	no reaction
5	$PhSiH_3$	KH-TDA [c]	1/1	Et_2O	24	Ph_2SiH_2 (31) Ph_3SiH (10)
6	1-$NpSiH_3$	KH	10/1	DME	24	(1-$Np)_2SiH_2$ (8)
7	$PhCH_2SiH_3$	KH	10/1	DME	63	$(PhCH_2)_2SiH_2$ (5) $(PhCH_2)_3SiH$ (21)
8	$PhCH_2SiH_3$	KH	10/1	THF	63	$(PhCH_2)_2SiH_2$ (5) $(PhCH_2)_3SiH$ (21)
9	n-$C_7H_{15}SiH_3$	KH	1/1	DME	15	no reaction
10	$PhSiH_3$	$LiAlH_4$	10/1	DME	15	Ph_2SiH_2 (44) Ph_3SiH (traces)
11	$PhSiH_3$	$LiAlH_4$-TDA	10/1	Et_2O	26	Ph_2SiH_2 (22)

[a] All reactions were performed at room temperature except run 5, which was at reflux temperature.
[b] The quantity of SiH_4 evolved was not determined; yields are based on the total silicon recovered in the products.
[c] TDA [7] = $N(CH_2CH_2OCH_2CH_2OCH_3)_3$.

As with dihydrogenosilanes, phenyl and benzyl groups migrate under mild conditions (room temperature; Table 2) in the presence of catalytic amounts of potassium hydride. The 1-naphthyl group [1-Np] also undergoes redistribution under similar conditions, although with a markedly lower yield. As observed with $(n\text{-}C_5H_{11})_2SiH_2$, no reaction occurs between $n\text{-}C_7H_{15}SiH_3$ and potassium hydride.

These reactions can be carried out in either DME or THF. No reaction product could be isolated from analogous reactions with Ph_2SiH_2 in THF. (see Table 1, run 6 and table 2, run 3), suggesting a higher reactivity for the $RSiH_3$ derivatives.

This higher reactivity is confirmed with $LiAlH_4$, which is efficient towards $PhSiH_3$ either in DME or in ether in presence of an equimolecular amount of TDA (Table 2, run 10 and 11).

II. Discussion and conclusion

Clearly, the above data rule out a mechanism in which the reaction of hydrides with either R_2SiH_2 or $RSiH_3$ involves a proton abstraction at silicon (Scheme 1) as this would lead neither to the formation of SiH_4 nor the redistribution of the aryl groups.

Two different mechanisms may be proposed to account for the experimental observations:

(i) nucleophilic attack of the hydride at silicon, leading to cleavage of a Si–C bond and generation of a carbanion, R^- (Scheme 2). R^- can react with R_2SiH_2, to give R_3SiH and H^-, which will act as a catalyst. Attack of H^- on $RSiH_3$ would explain the formation of SiH_4.

$$R_2SiH_2 + H^- \longrightarrow R^- + RSiH_3$$
$$R^- + R_2SiH_2 \longrightarrow R_3SiH + H^-$$
$$RSiH_3 + H^- \longrightarrow R^- + SiH_4$$

Scheme 2

(ii) The fast reversible formation of a pentavalent hydridoorganosilyl anion in the initial step, involving the addition of H^- at silicon (Scheme 3).

$$PhSiH_3 + H^- \rightleftharpoons [PhSiH_4]^-$$
$$[PhSiH_4]^- + PhSiH_3 \rightleftharpoons [Ph_2SiH_3]^- + SiH_4$$
$$[Ph_2SiH_3]^- \rightleftharpoons Ph_2SiH_2 + H^-$$

Scheme 3

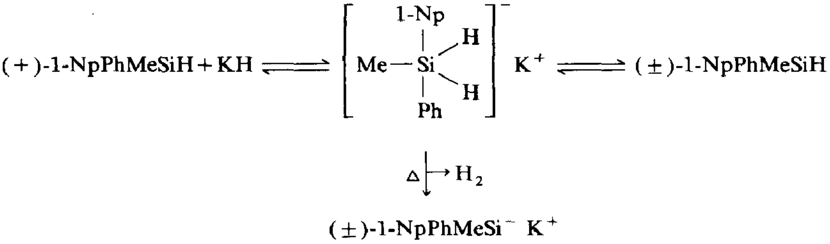
The redistribution could take place between these hypervalent species and the neutral R_2SiH_2 or $RSiH_3$ molecules.

In favor of the second mechanism are the following features:

(i) Numerous pentavalent silicon anions have been isolated and structurally characterized [8–11] and they are frequently invoked as intermediates in reactions of organosilanes in solution [12].

(ii) Squires et al. found that H^- reacts with alkylsilanes in the gas phase to give pentavalent adduct ions as the exclusive products [13]. Both experimental and computational works have also been recently reported by Damrauer et al. [14]. Moreover we have found that stable five-coordinate potassium hydridosilicates $[HSi(OR)_4]^- K^+$ and $[H_2Si(OR)_3]^- K^+$ [15] can be obtained in good yield and characterised spectroscopically.

(iii) We have observed that a fast racemisation of the optically active 1-NpPhMeSi-H(D), catalysed by hydrides (KH, $LiAlD_4$, and $LiAlH_4$), occurs in THF or DME at room temperature [16]. Under drastic conditions, (+)-1-NpPhMeSiH gave the racemic (±)-1-NpPhMeSi$^-$ anion. These results were rationalized in terms of the formation of a five-coordinate hydridoorganosilyl anion; the competitive cleavage of either of the Si–H bonds would explain the fast racemisation of (+)-1-NpPhMeSiH (Scheme 4).

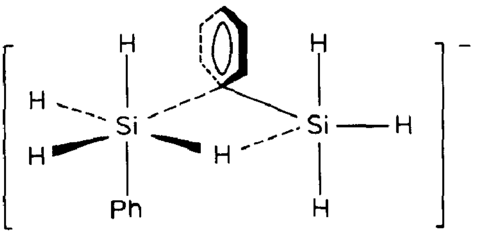


Scheme 4

(iv) Very ready hydrogen–chlorine exchange reactions, using chlorosilanes, acid chlorides [17] and PCl_5 [18], have been observed with pentacoordinated hydrogenosilanes.

(v) When carrying out the reaction between $PhSiH_3$ and KH in the presence of an excess of allyl bromide, we never detected allylbenzene which would arise from the coupling reaction with $Ph^- K^+$ (Scheme 2). Moreover, in nucleophilic displacements at silicon, the cleavage of a Si–C bond with $LiAlH_4$ was never observed.

In conclusion, the above considerations strongly suggest that the observed exchange of silicon–carbon bonds with silicon–hydrogen bonds (R = phenyl, 1-naphthyl, allyl and benzyl) occurs through an anionic activation. The first step would be the addition of H^- to silicon, leading to a pentacoordinated intermediate (as described in Scheme 3 in the case of $PhSiH_3$) followed by an exchange reaction. The migration of the phenyl group between $[PhSiH_4]^-$ and $PhSiH_3$ could possibly occur through a concerted process involving a dimeric intermediate, formulated as **1**, with a bridging H atom and phenyl group [19*].



(1)

Experimental

Materials

Lithium aluminium hydride was supplied by Janssen Chimica, sodium hydride by Merck (60 wt% dispersion in mineral oil) and potassium hydride by Aldrich (35 wt% dispersion in mineral oil). Sodium hydride and potassium hydride were cautiously washed, before use, by shaking them three times with anhydrous hexane. The resulting solid residue was subjected to pumping under vacuum to remove any residual solvent. Lithium aluminium hydride solutions were prepared as follows: the hydride was added portionwise to degassed THF or DME, stirred at room temperature for 30 min, and filtered to give a clear solution. These solutions were titrated using a calibrated iodine solution [20].

Allyltrimethoxysilane and tris(3,6-dioxaheptyl)amine (TDA) were kindly provided by Rhône–Poulenc Spécialités Chimiques. TDA was freshly distilled from calcium hydride before use.

The following materials have been described: Ph_2SiH_2 [21], Ph_3SiH [22], Ph_4Si [23], $PhMeSiH_2$ [24], Ph_2MeSiH [25], $PhSiMe_3$ [23], $(n\text{-}C_5H_{11})_2SiH_2$ [26], $n\text{-}C_7H_{15}SiH_3$ [27], 1-naphthylSiH_3 [20], (1-naphthyl)$_2SiH_2$ [29], $PhCH_2SiH_3$ [30], $(PhCH_2)_2SiH_2$ [30], $(PhCH_2)_3SiH$ [25], $PhCH_2CH_2SiH_3$ [32].

n-Heptylallylsilane

A solution of (n-heptyl)MgBr, prepared from 35.8 g (0.2 mol) of $n\text{-}C_7H_{15}Br$ and 5.28 g (0.22 mol) of magnesium in 250 ml of diethyl-ether, was added dropwise to a solution of 32.4 g (0.2 mol) of allyltrimethoxysilane in 100 ml of diethyl-ether, and the mixture stirred at room temperature for 12 h. The solution was filtered, added to a slurry of 7.6 g (0.2 mol) of $LiAlH_4$ in 250 ml of diethyl-ether, and stirred at room temperature for 15 h. Hydrolysis was carried out with a cold saturated NH_4Cl solution. After standard workup, distillation of the solvent left a liquid that was distilled, to give 20.41 g (60% yield) of $n\text{-}C_7H_{15}(CH_2{=}CHCH_2)SiH_2$ b.p. 190–191°C; IR (CCl_4) ν(Si–H) 2131 cm^{-1}. ^{1}H NMR (CCl4): δ 4.95–5.8(m, 1H, $CH_2{=}\mathit{CH}$), 4.35–4.75(m, 2H, $\mathit{CH_2}{=}CH$), 3.45 (q, 2H, SiH_2, $J = 3$ Hz), 1.2–1.5(m, 2H, $CH_2{=}CH\mathit{CH_2}$), 0.3–1.3(m, 15H, $n\text{-}C_7H_{15}$); mass spectrum, *m/e* (assignment) 170 (molecular peak).

Benzylphenethylsilane

The reduction of the corresponding dimethoxysilane [35] was performed with $LiAlH_4$ in diethyl-ether, at room temperature by the same procedure as for n-heptylallylsilane. After standard work-up, distillation of the solvent left a liquid that was distilled to give 13.85 g(64% yield) of $PhCH_2(PhCH_2CH_2)SiH_2$ b.p. 171–173°C (16 mmHg); IR (CCl_4): ν(Si-H) 2135 cm^{-1}. ^{1}H NMR (CCl_4): δ 6.85 (m, 10H, aromatic), 3.70 (q, 2H, SiH_2, $J = 3$ Hz), 2.45 (t, 2H, $Ph\mathit{CH_2}CH_2$, $J = 9$ Hz), 1.93 (t, 2H, $Ph\mathit{CH_2}Si$, $J = 3$ Hz), 0.80 (t.t., 2H, $PhCH_2\mathit{CH_2}$, $J = 9$ and 3 Hz); mass spectrum, *m/e* (assignment) 226 (molecular peak).

Reactions with the hydrides (KH, NaH, $LiAlH_4$)

General procedure. All reactions were carried out under nitrogen using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. The reaction conditions are given in Table 1 and 2. The mixture was stirred at room temperature, except for runs 3, 4, 10, 11, 14 (Table 1) and run 5 (Table 2), and then hydrolysed with acid (2*N* HCl) at 0 °C. The silanes were usually identified by GLC analysis (Girdel 75FH1 equipped with a column (1,4 m) packed with SE-30 (10%) silicones on Chromosorb WHMDS 80/100) by comparison with authentic samples. If authentic samples were not available, the silanes were purified by TLC (silica gel 60 PF254 Merck) using hexane or hexane/benzene, 4/1 as eluants, and identified by their IR and ^{1}H NMR spectra. The yields quoted are based on the percentage of the total silicon recovered in the products of the reaction.

Typical reaction: $PhSiH_3$, KH (Table 2, run 3). A suspension of 24 mg (0.6 mmol) of potassium hydride (cautiously washed with dry hexane) in 5 ml of THF was stirred magnetically at room temperature under a nitrogen atmosphere in a 50 ml Schlenck tube. A solution of 0.648 g (6 mmol) of $PhSiH_3$ in 5 ml of THF was then added dropwise. The mixture was stirred at room temperature for 17 h and then hydrolysed by dropwise addition of 2*N* HCl at 0 °C. The organic layer was extracted with diethyl ether, dried over magnesium sulfate, and freed of solvent under vacuum. The residue (538 mg) was analyzed by GLC and ^{1}H NMR using authentic samples, as a mixture of Ph_2SiH_2 (24% yield) and Ph_3SiH (17% yield).

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