Pentacoordinate Dihydridosilicates: Synthesis, Structure, and Aspects of Their Reactivity

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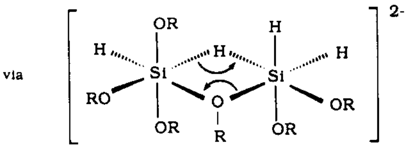
The reactions of H^- with trialkoxysilanes provide a unique and facile entry to anionic pentacoordinate dihydridosilicates $[H_2Si(OR)_3]^-$, isolated as stable crystalline products in the case of bulky R groups (R = *i*-Pr, *s*-Bu, *c*-C_6H_{11}). Their dynamic behavior (R = i-Pr and s-Bu) has been investigated by ^{29}Si and variable-temperature ^1H NMR. Intramolecular exchange of H atoms between axial and equatorial sites is indicated and was found to be significantly dependant on the nature of the solvent. Compared to $HSi(OR)_3$, $K[H_2Si(OR)_3]$ are versatile reagents: (1) the silicon atom is an electrophilic center and this leads to nucleophilic displacements of the alkoxy groups with Grignard reagents and organolithiums; (2) they are able to reduce very easily carbonyl derivatives to alcohols without any catalyst; (3) they react with primary halides through an ionic mechanism leading to the alkane; (4) the reaction with benzylic halides is more complex and affords the dimer as the major product, the formation of which can be explained by a SET process; (5) the ability to donate one electron is confirmed in the reaction with $Cp(CO)_2FeI$ and by direct ESR observation of stable radical intermediates.

In recent years, numerous pentacoordinate anionic derivatives have been reported and structurally characterized.[1,2] They provide useful models for intermediates in nucleophilic displacement reactions[3] at silicon. In the meantime, a number of synthetic methods that involve pentacoordinate derivatives or the intermediacy of such species have been reported.[1b,4,5] Recent work has also focused attention on the chemical behavior of pentacoordinate anionic silicates. For instance, enhanced reactivity toward nucleophiles was observed[6] and some reports suggested that these derivatives may have unusual properties compared with those of their tetracoordinated analogues.[2c,7]

Scheme I. Redistribution of $K[H_2Si(OR)_3]$ (R = Me, Et, *n*-Bu)

$$4\ K[H_2Si(OR)_3] \longrightarrow 3\ K[HSi(OR)_4] + SiH_4 + KH$$



As a part of our investigation of the reactions of such hypervalent organosilicon species,[1b,8] we became interested in pentacoordinate silicon hydrides.[7b,9] These species have been observed in the gas phase from the reaction of H^- with alkylsilanes.[10] They 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.[11] Likewise the re-

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Table I

$$HSi(OR)_3 \xrightarrow[S]{KH} \underset{1}{K[H_2Si(OR)_3]} + \underset{2}{K[HSi(OR)_4]}$$

run	$HSi(OR)_3$	S	reactn time, h	products,[b] %	
				1[a]	2[a]
1	$HSi(OMe)_3$	THF	2	0	100 (63)
2	$HSi(OEt)_3$	THF	6	40	60
3	$HSi(OEt)_3$	THF	24	0	100 (quant)
4	$HSi(OEt)_3$	THF (18-crown-6)	26	55	45
5	$HSi(OEt)_3$	DME	2	0	100 (quant)
6	$HSi(On\text{-}Bu)_3$	THF	4	50	50
7	$HSi(Oi\text{-}Pr)_3$	THF	6	100 (quant)	0
8	$HSi(OPh)_3$	THF	2	0	100 (quant)
9	$HSi(OPh)_3$	THF (18-crown-6)	2	15	85

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

distribution reaction of di- and trihydrosilanes, $RR'SiH_2$ and $RSiH_3$, in the presence of hydrides ($LiAlH_4$, KH, and NaH) as catalysts[12] has been shown to involve such intermediates. However, whereas fluoride and alkoxide anions are well-known to coordinate readily to a silicon atom to give stable derivatives,[1] hydridosilicates resulting from the addition of H^- at silicon have never been observed in solution before this work.[9]

We now have established the formation of several $[H_2Si(OR)_3]^-$ species (where R = Et, *n*-Bu, *i*-Pr, *s*-Bu, $c\text{-}C_6H_{11}$). In the present paper, we shall describe their synthesis and physical characterization. Also reported are some aspects of their chemistry.

Results and Discussion

1. The $[H_2Si(OR)_3]^-$ Anions. Synthesis and Spectroscopic Data. Reaction of potassium hydride with various trialkoxy- (or triaryloxy) silanes was found to yield the pentavalent ions $[H_2Si(OR)_3]^-$ (1) and $[HSi(OR)_4]^-$ (2), isolated as white powders that are very moisture sensitive. The results are summarized in Table I.

The ease of formation and the stability of the dihydridosilicates 1 depend greatly on the nature of the OR group attached at silicon and that of the solvent or on the use of a complexing agent such as 18-crown-6.

Influence of the OR Group. $HSi(OMe)_3$ in THF readily gave $K[HSi(OMe)_4]$ (Table I, run 1). Under the same conditions, the reactions of $HSi(OEt)_3$ and $HSi(OBu\text{-}n)_3$ with KH (Table I, runs 2,6) afforded respectively 60/40 and 50/50 mixtures of $K[HSi(OR)_4]$ and $K[H_2Si(OR)_3]$ (R = Et and *n*-Bu). $[HSi(OEt)_4]^-$ was exclusively obtained when the reaction was carried out for 24 h (Table I, run 3). In all of the above reactions, evolution of SiH_4 was detected. In sharp contrast, $HSi(OPr\text{-}i)_3$ gave only $K[H_2Si(OPr\text{-}i)_3]$ in 94% yield (Table I, run 7), and even after 7 days at room temperature less than 5% of $K[HSi(OPr\text{-}i)_4]$ was detected. In a similar manner, $[H_2Si(OBu\text{-}s)_3]^-$ was obtained as white crystals in 60% yield after recrystallization. The fast redistribution of a labile OR group (R = Ph, Table I, run 8) also occurs and, after 2 h, only $[HSi(OPh)_4]^-$ was recovered. These results suggest the occurrence of a fast redistribution reaction of the dihydridosilicate 1 (R = Me, Et, *n*-Bu, or Ph) (Scheme I), the rate of which is strongly decreased by steric effects (R = *i*-Pr, *s*-Bu). Such a reaction is typical of pentavalent species and no catalyst is required. As we suggested in the case of the exchange reactions of di- and trihydrosilanes catalyzed by hydrides, the migration of the OR and H groups could occur between pentacoordinated species through a concerted process involving a dimeric intermediate, formulated as 3 with a bridging H atom and OR group (Scheme I). The steric hindrance of bulky groups (R = *i*-Pr, *s*-Bu, *t*-Bu) prevents the formation of such an intermediate. Moreover, in the case of the bulky OBu-*t* group, no addition of H^- to silicon was detected after 24 h at room temperature; $HSi(OBu\text{-}t)_3$ remained unaffected.

Table II. ^{29}Si NMR Data[a] for 1 (R = Et, *n*-Bu, *i*-Pr) (S = THF): A Comparison with Those of $HSi(OR)_3$

$HSi(OEt)_3$	δ -59.6 ppm	[d, $J(^1H-^{29}Si)$ = 285 Hz]
$K[H_2Si(OEt)_3]$	δ -81.8 ppm	[t, $J(^1H-^{29}Si)$ = 218 Hz]
$HSi(OBu\text{-}n)$	δ -59.2 ppm	[d, $J(^1H-^{29}Si)$ = 286 Hz]
$K[H_2Si(OBu\text{-}n)_4]$	δ -80.8 ppm	[t, $J(^1H-^{29}Si)$ = 215 Hz]
$HSi(OPr\text{-}i)_3$	δ -63.4 ppm	[d, $J(^1H-^{29}Si)$ = 285 Hz]
$K[H_2Si(OPr\text{-}i)_3]$	δ -87.1 ppm	[t, $J(^1H-^{29}Si)$ = 213 Hz]
$HSi(OBu\text{-}s)$	δ -62.6 ppm	[d, $J(^1H-^{29}Si)$ = 282 Hz]
$K[H_2Si(OBu\text{-}s)_3]$	δ -85.6 ppm	[dd, $J(^1H-^{29}Si)$ = 222 and 194 Hz]

[a] The spectra were recorded in THF as solvent with external C_6D_6 as lock and TMS as reference.

Influence of the Solvent and a Complexing Agent (18-Crown-6). An increase of the basicity of the solvent, on going to DME from THF, was found to accelerate the formation of $K[HSi(OR)_4]$ (R = Et, Table I, run 5). In contrast, the presence of 18-crown-6 seems to stabilize greatly the dihydridosilicate anionic species (Table I, runs 4, 9). For instance a 55/45 mixture of $[H_2Si(OEt)_3]^-$ and $[HSi(OEt)_4]^-$ was observed after 24 h instead of pure $[HSi(OEt)_4]^-$ in the absence of 18-crown-6 (Table I, run 3). Similar observations were made in the case of $HSi(OPh)_3$ (Table I, runs 8 and 9). Finally, only [K, 18-crown-6] $[H_2Si(OC_6H_{11}\text{-}c)_3]$ was isolated in pure form (53% yield) when 1 equiv of 18-crown-6 was added.

The ready hydrolysis of these salts made both their analysis and subsequent NMR study difficult. Nevertheless, the dihydridosilicates 1 gave satisfactory spectroscopic data (see Experimental Section for details). In particular, the ^{29}Si NMR chemical shifts were in the usual range for anionic pentacoordinate silicates,[2,13] as summarized in Table II. Similar values were observed in the case of $[HSi(OR)_4]^{-7b}$ and anionic pentoxysilicates, $[Si(OR)_5]^-$ and $[R'_nSi(OR)_{5-n}]^-$.[2e,6d]

As expected, upfield shifts of ^{29}Si NMR resonances relative to those of the corresponding alkoxy- or phenoxysilanes were observed. Moreover, in the case of most of the dihydridosilicates 1 (R = Et, *n*-Bu, *i*-Pr), the spectra (solvent, THF) exhibit a triplet, consistent with two equivalent hydrogen atoms. The $^1H-^{29}Si$ coupling constant is smaller for the pentacoordinated dihydridosilicates than for the corresponding neutral species (Table II), as expected from the decrease in the proportion of s character

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Table III. ^{29}Si NMR Data: Influence of the Solvent (S)

run	$K[H_2Si(OR)_3]$	S	δ, ppm	$J(^1H-^{29}Si)$, Hz
1	$K[H_2Si(OEt)_3]$	THF (18-crown-6)	-77.7	225 (t)
2	$K[H_2Si(OPr\text{-}i)_3]$	C_6D_6	-87.3	224, 193 (dd)
3	$K[H_2Si(OPr\text{-}i)_3]$	C_6D_6(18-crown-6)	-81.3	222 (t)
4	$K[H_2Si(OPr\text{-}i)_3]$	THF (18-crown-6)	-82.0	223 (t)
5	$K[H_2Si(OPr\text{-}i)_3]$	DME	-86.4	212 (t)
6	$K[H_2Si(OBu\text{-}s)_3]$	C_6D_6^{a}	-85.2; -85.6	224–227, 192–195 (dd); 227, 195 (dd)
7	$K[H_2Si(OBu\text{-}s)_3]$	C_6D_6 (18-crown-6)	-80.2	223 (t)
8	$K[H_2Si(OBu\text{-}s)_3]$	THF (18-crown-6)	-81.0	224 (t)
9	$K[H_2Si(OC_6H_{11}\text{-}c)_3]$	C_6D_6 (18-crown-6)	-81.7	223 (t)
10	$K[H_2Si(OC_6H_{11}\text{-}c)_3]$	THF (18-crown-6)	-82.5	222 (t)

^{a} Two ^{29}Si NMR signals.

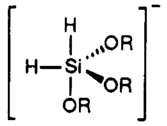
Table IV. ^{1}H NMR Data: $[H_2Si(OR)_3]^-$ (R = *i*-Pr, *s*-Bu)^a

run	$K[H_2Si(OR)_3]$	S	δ (Si–H), ppm
1	$K[H_2Si(OPr\text{-}i)_3]$	THF-d_8	3.47 (s)
2		toluene-d_8	4.38 (s) 3.72 (s)
3		toluene-d_8 + 18-crown-6	4.57 (s)
4	$K[H_2Si(OBu\text{-}s)_2]$	THF-d_8	3.86 (s); 3.54 (s)
5		toluene-d_8	4.38 (s); 4.35 (s); 3.90 (s); 3.86 (s)
6		toluene-d_8 + 18-crown-6	4.65 (s)

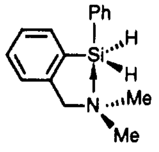
^{a} Room temperature.

in the Si–H bond and as observed in the case of monohydridosilicates.[13d]

An interesting feature in Table II is the somewhat different behavior of $[H_2Si(OBu\text{-}s)_3]^-$. In THF as solvent the silicon resonance appears as a doublet of doublets, clearly indicating the presence of two different hydrogen atoms bonded to silicon. The magnitude of the coupling constants ($J(^1H-^{29}Si)$ = 222 Hz and 194 Hz) and the comparison to that measured in the case of the hydridosilicate $[HSi(OR)_4]^-$ ($J(^1H-^{29}Si)$ = 218 Hz, R = Et and $J(^1H-^{29}Si)$ = 214 Hz, R = *i*-Pr) are consistent with a trigonal-bipyramidal structure in which a hydrogen atom occupies an equatorial position, the other one an axial position, as represented in 1.



1, R = *s*-Bu



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To gain more information, we undertook ^{29}Si NMR studies, changing the nature of the solvent, using either benzene-d_6 and toluene-d_8 or a complexing agent (18-crown-6) in the case of 1 with R = *i*-Pr and *s*-Bu (Table III).

The case of $K[H_2Si(OPr\text{-}i)_3]$ (Tables II and III, run 2–5), may be taken as an example. In THF and DME, which are known to be good solvating agents, the silicon resonance appears as a triplet, indicating that in the trigonal-bipyramid geometry both hydrogens exchange quickly or are equatorial. The latter case was observed in the neutral pentacoordinate silicon dihydride 4, resulting from intermolecular coordination of a *o*-$Me_2NCH_2C_6H_4$ ligand to silicon, which shows the SiH bonds in equatorial position.[14] A decrease of the solvating power on going to deuteriobenzene or toluene-d_8 gave a ^{29}Si signal of $K[H_2Si(OPr\text{-}i)_3]$ (Table III, run 2), which appears as a doublet of doublets at -87.3 ppm ($J(^1H-^{29}Si)$ = 224 and 193 Hz), clearly indicating the presence of two different hydrogen atoms bonded to silicon. The addition of 18-crown-6 (Table III, run 3) resulted in a ^{29}Si resonance attributable to a silicon atom bonded to two equivalent hydrogen atoms.

The above data are in agreement with an exchange process of the two hydrogen atoms. The rate of this process depends on the steric hindrance of the R group (the exchange is faster in the case of R = *i*-Pr than with R = *s*-Bu, in THF as solvent) but also on the coordination ability of the solvent or of 18-crown-6 toward the potassium cation.

Compared to $[H_2Si(OPr\text{-}i)_3]^-$, parallel observations have been made in the case of $[H_2Si(OBu\text{-}s)_3]^-$ (Table III, runs 6–8). The ^{29}Si spectrum of this anion in THF at ambient temperature exhibits a single resonance (dd, -85.6 ppm, $J(^1H-^{29}Si)$ = 222 Hz and $J(^1H-^{29}Si)$ = 194 Hz; Table II), in agreement with a reduced rate of exchange compared to that of $[H_2Si(OPr\text{-}i)_3]^-$ under similar conditions. When THF is replaced by deuteriobenzene (Table III, run 6), the room temperature spectrum contains two ^{29}Si resonances (dd, -85.2 ppm, $J(^1H-^{29}Si)$ = 224–227 Hz and $J(^1H-^{29}Si)$ = 192–195 Hz; dd, -85.6 ppm, $J(^1H-^{29}Si)$ = 227 Hz and $J(^1H-^{29}Si)$ = 195 Hz), indicating the presence of two types of silicon with different environments. This more complex behavior of $K[H_2Si(OBu\text{-}s)_3]$ in toluene-d_8 can be attributed to the presence of the tertiary asymmetric carbon centers of the *s*-Bu groups (-O*C*H$(CH_3)CH_2CH_3$). Likewise, lithium trisiamyl- and tri-*sec*-butylborohydride exhibit ^{1}B NMR spectra with a pair of doublets due to diastereoisomers.[15] At last, the addition of 18-crown-6 either in THF or benzene-d_6 resulted in both cases in the appearance of a single resonance (THF: t, -81.0 ppm, $J(^1H-^{29}Si)$ = 224 Hz. C_6D_6: t, -80.2 ppm, $J(^1H-^{29}Si)$ = 223 Hz), consistent with two equivalent hydrogen atoms bonded to silicon and a fast exchange process, as observed

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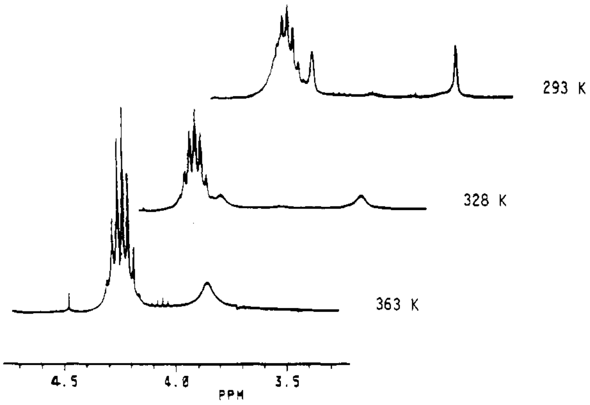


Figure 1. Variable-temperature ^1H NMR spectra (4.7–3.3 ppm region) of $K[H_2Si(OPr\text{-}i)_3]$ in toluene-d_8.

also for $[H_2Si(OR)_3]^-$ (R = Et, i-Pr, c-C_6H_{11}; Table III).

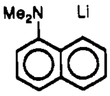
Further evidences of the dependence of the intramolecular exchange of the hydrogen atoms on the nature of the solvent were found in the ^1H NMR spectra of 1 (R = i-Pr and s-Bu; Table IV) and clearly confirm ^{29}Si NMR data.

In THF-d_8 the two hydrogens of $[H_2Si(OPr\text{-}i)_3]^-$ are equivalent and the ^1H NMR signal is a singlet at 3.47 ppm (Table IV, run 1). 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 (Table IV, run 2). One axial (s, 4.38 ppm) and one equatorial (s, 3.72 ppm) hydrogen atom can be discerned. In this case no $^2J(^1H-^1H)$ coupling was observed, but this is not unusual as axial–equatorial coupling constants are very small.[8f] Likewise, $K[H_2Si(OBu\text{-}s)_3]$ showed different behavior according to the nature of the solvent. In toluene-d_8, the resonances of the two hydrogens appear as four separate singlets, δ 4.38, 4.35, 3.90, and 3.86 ppm, respectively (Table IV, run 5). Such a pattern is indicative of the presence of two types of silicon (vide supra; ^{29}Si NMR data, Table III) and of two different hydrogen atoms bonded to each of them. In this case also no $^2J(^1H-^1H)$ coupling constant was observed. In THF-d_8, two singlets of nearly equal intensity are seen at δ 3.86 and 3.54 ppm (Table IV, run 4). Finally, the addition of 18-crown-6 in THF-d_8 gave a single resonance at 4.65 ppm (Table IV, run 6).

Variable ^1H NMR studies in deuteriotoluene (see under Experimental Section for details) also were carried out. At ambient temperature, as expected from ^{29}Si results, $K[H_2Si(OPr\text{-}i)_3]$ 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 (Figure 1), and reappeared as a broad singlet at still higher temperature (363 K, Figure 1). When the same 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}.

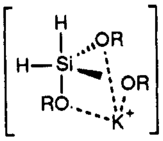
Table V

$$K[H_2Si(OR)_3] \xrightarrow[\text{or } 2R'Li,\ THF]{2R'MgX} R'_2SiH_2 + R'_3SiH$$

run	$K[H_2Si(OR)_3]$	R'MgX	T,[c] °C	t, h	products,[a] %	
					R'_2SiH_2	R'_3SiH
1	$K[H_2Si(OEt)_3]$	$PhCH_2MgCl$	−30 → 0	2	80	
2		n-BuMgBr	−30 → 0	2	60	10
3		PhMgBr	−30 → 0	0.5	60	20
4		$CH_2{=}CHMgBr$[b]	−30 → 0	2	55	
5		$CH_2{=}CHCH_2MgBr$[b]	0 → rt	2	31	
6			0 → rt	4	59	
7	$K[H_2Si(OPr\text{-}i)_3]$	PhMgBr	rt	3	77	10
8		$PhCH_2MgCl$	40	2	63	20
9		n-BuMgBr	rt	3	50	15
10		PhLi	−20	0.75	14	46

[a] Yields of isolated products. [b] Yields were not optimized. [c] rt = room temperature.

In summary, the above data, i.e., either ^{29}Si and ^1H NMR, clearly establish the presence of an intramolecular process in which the hydrogen atoms bonded to silicon interchanges apical–equatorial positions. Besides steric hindrance (R = s-Bu), this process is mainly controlled by the nature of 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 5 in which the potassium cation is strongly coordinated to the oxygen atoms could be invoked and this would prevent the intramolecular hydrogen exchange in solvents such as benzene-d_6 or toluene-d_8. When going to DME, THF/18-crown-6, or C_6D_6/18-crown-6 and increasing the solvating power, the structure of $K[H_2Si(OR)_3]$ consists of isolated K^+ and $[H_2Si(OR)_3]^-$ ions. As a consequence, an enhanced rate of exchange is observed.



5

2. Chemical Reactivity. Recent work clearly indicated that pentacoordinate silicon species have varied chemistry, significantly different from that of their tetravalent counterparts.[1b] From this point of view, the dihydridosilicates $K[H_2Si(OR)_3]$ reported here exhibit a wide range of reactivities. They can undergo facile nucleophilic attack at silicon by nucleophiles such as Grignard reagents and organolithiums. The high reactivity of the SiH bond will be illustrated in reactions with carbonyl derivatives. Finally, evidence will be given on the possibility for these species to transfer one electron to suitable substrates.

Reactions with Grignard Reagents and Organolithiums. We have recently reported the high reactivity of pentacoordinate anionic o-arenediolato-[16], fluoro-, and alkoxosilicates[6a,d] toward strong nucleophiles, such as Grignard reagents or organolithiums, relative to that of the tetracoordinated species.

As we have observed previously with monohydridosilicates,[7b] 1 (R = Et and i-Pr) reacted with a slight excess of a Grignard reagent R'MgBr, and R'_2SiH_2 was obtained in good yield (Table V). The formation in high yield of the dihydrosilanes provides good chemical evidence for the structure of the dihydrosilicates 1 and for the presence of a high proportion of $K[H_2Si(OEt)_3]$ in solution (Table V, runs 1–6). The reaction took place readily under mild conditions in the case of $K[H_2Si(OEt)_3]$ but a higher tem-

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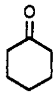
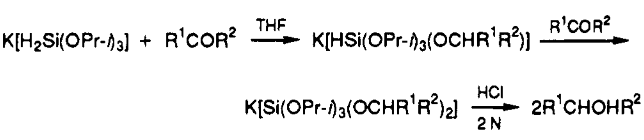
Table VI

$$\underset{1}{K[H_2Si(OPr\text{-}i)_3]} + \underset{7}{R^1COR^2} \xrightarrow[4\ h]{THF} \xrightarrow{HCl\ (2N)} R^1CHOHR^2$$

run	7	7/1 ratio	R^1CHOHR^2,[a] (recovered R^1COR^2) %
1	PhCHO	2	74
2	$CH_3(CH_2)_6CHO$	2	62
3	PhCOPh	2	50 (26)
4		2	73 (24)
5	$PhCOCH_3$	2	36 (40)

[a] Yields of the isolated alcohols are based upon the amount of carbonyl compound introduced. As the ratio $R^1COR^2/K[H_2Si(OPr\text{-}i)_3]$ is 2 and the yields greater than 50% (except with $PhCOCH_3$ because of partial enolisation), the data show that $[H_2Si(OPr\text{-}i)_3]^-$ transfers both of the hydrogens bonded to silicon.

Scheme II. Reduction of Carbonyl Derivatives with $K[H_2Si(OPr\text{-}i)_3]$



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

$$K[Si(OPr\text{-}i)_3(OCHR^1R^2)_2] \xrightarrow[2\ N]{HCl} 2R^1CHOHR^2$$

Table VII. Reduction of Organic Halides

$$RX \xrightarrow[THF]{K[H_2Si(OPr\text{-}i)_3]} RH + RR$$

run	RX	T,[d] °C	reactn time, h	RH,[a] %	RR,[a] %
1	$C_{12}H_{25}Br$	rt	15	81	
2	$C_{12}H_{25}Cl$	45	24	25	
3	$PhCH_2Br$	rt	4	29	44
4	$PhCH_2Cl$	rt	18	49	24
5	Ph_2CHCl	rt	10	30	50
6	Ph_3CBr	rt	3	60	15
7	$CH_2{=}CH(CH_2)_4Br$	rt	15	89[c]	

[a] Yields refer to the percentages of the R group recovered in RH and RR. The only other product is the unreacted starting material. [b] RR = (4-tritylphenyl)diphenylmethane.[26] [c] Less than 5% yield of methylcyclopentane was observed. [d] rt = room temperature.

perature was required to produce R'_2SiH_2 from $K[H_2Si(OPr\text{-}i)_3]$. As a consequence, a higher ratio of R'_3SiH resulting from the displacement of a Si–H bond was obtained. Finally, this reaction represents a convenient way of making R'_2SiH_2, especially when R′ is a vinyl or allyl group (Table V, runs 4 and 5). 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.

Reaction of $[H_2Si(OPr\text{-}i)_3]^-$ with 2 equiv of PhLi at low temperature (Table V, run 10) afforded a mixture of Ph_3SiH (46%) and Ph_2SiH_2 (14%). Reaction of $K[H_2Si(OEt)_3]$ with [8-(dimethylamino)-1-naphthyl]lithium also led to the ready displacement of the ethoxy groups bonded to silicon and bis[8-(dimethylamino)-1-naphthyl]silane was isolated in moderate yield (59%) (Table V, run 6).

Reduction of Carbonyl Derivatives. The reduction of aldehydes and ketones with hydrosilanes catalyzed by fluoride and alkoxide ions has been recognized as a useful synthetic method for a number of years.[5a,17,19] Recent reports focused also on the use of hypervalent silicon hydrides as reducing agents.[1b,13b,20] Solutions most probably containing the ion $[\overline{HSi(OC_6H_4O}_2)]^-$ and the corresponding complex of 2,2′-dihydroxybiphenyl were found to reduce both ketones and aldehydes directly in excellent yield.[21] Similar reagents prepared from aliphatic 1,2-diols, especially pinacol, also were effective. Intramolecularly coordinated hydrosilanes have also been shown to be powerful hydride donors.[22] Also, the reduction of carbonyl compounds, including esters, with pentacoordinate $[HSi(OR)_4]^-$ anions was found to proceed in high yield.[7b]

In a similar manner, the isolated $K[H_2Si(OPr\text{-}i)_3]$ also was effective and either aldehydes or ketones were reduced in the absence of a catalyst under mild conditions (Table VI). In sharp contrast, under similar experimental conditions, $HSi(OR)_3$ is unreactive.

The yields of primary and secondary alcohols generally are high (50–80% yield). As outlined in Table VI, $K[H_2Si(OPr\text{-}i)_3]$ is able to give up both of the hydrogens to silicon. This suggests that the reactions go through a pentavalent hydridosilicate intermediate such as $[HSi(OR)_3(OR')]^-$, which can reduce a second molecule of carbonyl derivative[7b] (Scheme II).

The lower yield in the case of $PhCOCH_3$ as observed previously with $[HSi(OR)_4]^-$[7b], can be attributed to a partial enolization of the ketone by the alkoxide ions liberated during the reaction or by $K[H_2Si(OPr\text{-}i)_3]$ itself. From this point of view, the basic properties of $K[H_2Si(OPr\text{-}i)_3]$ are well illustrated by the reaction with phenylacetylene. Fast deprotonation was observed and the potassium acetylide could be trapped with Me_3SiCl (82%).

Finally, the reduction of benzophenone gave only benzhydrol. No trace of the blue ketyl radical anion was detected during the reaction, and no benzopinacol was isolated. Furthermore, a dilute mixture of $K[H_2Si(OPr\text{-}i)_3]$ and benzophenone was found to be ESR inactive.

Reactivity toward Organic Halides. Alkyl halides were reduced to the corresponding alkanes by $K[H_2Si(OPr\text{-}i)_3]$ in THF (Table VII, runs 1, 2).

The bromide was rapidly reduced, showing a 81% reduction in 15 h at room temperature. In contrast, the chloride reacted sluggishly, giving only 25% reduction in 24 h at 40–45 °C. Under similar conditions, $HSi(OPr\text{-}i)_3$ was found to be unreactive.

The occurrence of a single electron transfer pathway (SET) in the reaction of organic halides with metal hydrides has been discussed in detail.[23] Thus, the reaction of $K[H_2Si(OPr\text{-}i)_3]$ with 6-bromo-1-hexene, which can serve

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[17] (a) Boyer, J.; Corriu, R. J. P.; Perz, R.; Reyé, C. *Tetrahedron* **1981**, *37*, 2165. (b) Boyer, J.; Corriu, R. J. P.; Perz, R.; Poirier, M.; Reyé, C. *Synthesis* **1981**, 555. (c) Chuit, C.; Corriu, R. J. P.; Perz, R.; Reyé, C. *Synthesis* **1982**, 981.

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[19] (a) Fujita, M.; Hiyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 4629. (b) Hosomi, A.; Hayashida, H.; Kohra, S.; Tominaga, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1411. (c) Kohra, S.; Hayashida, H.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 89.

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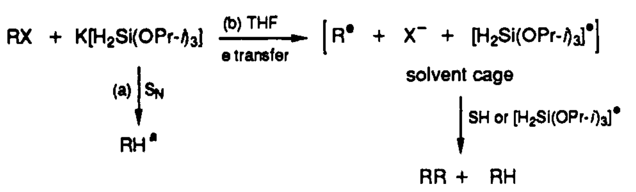
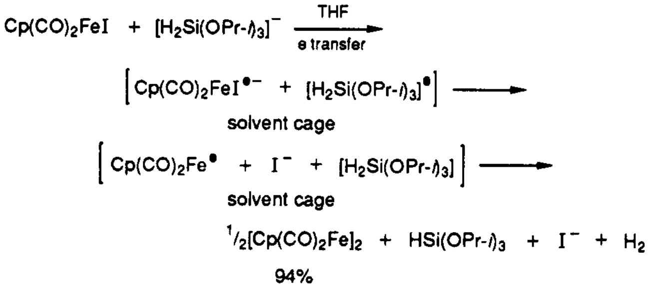
Scheme III. Reduction of Organic Halides



^{a}R = alkyl; RH results from path a. R = $PhCH_2$, Ph_2CH, Ph_3C; RH results from path a or/and b.

Scheme IV. Reaction of $K[H_2Si(OPr\text{-}i)_3]$ with $Cp(CO)_2FeI$



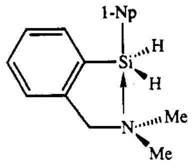
as a probe for the detection of a SET process,[24] was examined. The rearranged cyclic product, which should be indicative of the formation of the transient 5-hexen-1-yl radical,[24] was obtained in less than 5% yield besides 1-hexene (Table VII, run 7), as we observed previously in the case of $[HSi(OEt)_4]^-$.[7b]

Reaction of $K[H_2Si(OPr\text{-}i)_3]$ with 1 equiv of $PhCH_2X$ (X = Cl, Br) or Ph_2CHCl gave the "dimer", as well as the expected toluene and diphenylmethane (Table VII, runs 3, 5). Moreover, $PhCH_2Br$, which is known to have a higher ability to add an extra electron, reacted to give the dimer as the major product (Table VII, run 3). Finally, in the case of Ph_3CBr, Ph_3CH (60%) and *p*-$[(C_6H_5)_2CH]C_6H_4C(C_6H_5)_3$[25] (15%) were isolated as the main organic products (Table VII, run 6). The reaction solution was found to be ESR active and showed a spectrum consistent with the resonance of the trityl radical[23a,28] generated by one electron transfer from $K[H_2Si(OPr\text{-}i)_3]$ to Ph_3CBr. Thus the following features, (i) detection of the dimers, i.e., $(PhCH_2)_2$ and $(Ph_2CH)_2$ respectively in the case of $PhCH_2X$ (X = Cl or Br) and Ph_2CHCl, resulting from radical coupling; (ii) the higher yield of $(PhCH_2)_2$ when going from $PhCH_2Cl$ to $PhCH_2Br$; and (iii) the radical $Ph_3C.$ observed by ESR, all indicate that a SET process can be invoked in the reduction of benzylic halides. 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 III).

$K[H_2Si(OPr\text{-}i)_3]$ as Single Electron Transfer Reagent. The aptitude of the pentacoordinate dihydridosilicates to transfer one electron also was evidenced by the reaction with $Cp(CO)_2FeI$, which afforded exclusively the iron dimer $[Cp(CO)_2Fe]_2$ in 94% yield (Scheme IV).

In addition, a THF solution of $K[H_2Si(OPr\text{-}i)_3]$, when p-dinitrobenzene (DNB) was added, turned green, indicating the formation of the radical anion. A diluted aliquot of this solution showed an ESR spectrum that was identified as that of the radical anion of *p*-dinitrobenzene (g = 2.002).[17a,29] $HSi(OEt)_3$ itself did not produce the radical anion when treated with *p*-dinitrobenzene. Thus, it is apparent that the electron transfer was due to the interaction of the pentavalent silicate anion with DNB.

$K[H_2Si(OPr\text{-}i)_3]$ was also added to 2,6-di-*tert*-butylbenzoquinone. The solution was found again to be ESR active and showed a three-line spectrum (a = 1.256, g = 1.999), assigned to the radical anion of the benzoquinone.[30] In contrast, a mixture of a neutral penta- or hexacoordinate compounds such as 8 and 9 with 2,6-di-*tert*-butylbenzoquinone was found ESR inactive. Furthermore, under similar conditions, [K, 18-crown-6]$[Ph_3SiF_2]$ did not give an ESR signal.



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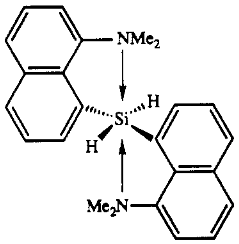

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Conclusion

Like fluoride and alkoxide ions, H^- is able to coordinate readily to silicon in solution. Reactions with a trialkoxysilane provide a unique and facile entry to the anionic pentacoordinate dihydridosilicates $[H_2Si(OR)_3]^-$, isolated as stable crystalline products in the case of bulky R groups (R = *i*-Pr, *s*-Bu, or *c*-C_6H_{11}).

From a mechanistic point of view, our data illustrate clearly the versatile chemical behavior of the hydridosilicates. Besides a high reactivity as electrophilic center toward nucleophiles (RMgX, RLi), these species can act as efficient hydride transfer reagents (carbonyl derivatives, primary organic halides). Concomitant basic properties are illustrated by the reaction with $PhC{\equiv}CH$. They have also a good ability to act as electron donors. This latter feature seems at the present time characteristic of the anionic hydridosilicates as shown by comparison with $[Ph_3SiF_2]^-$ and neutral penta- or hexacoordinate silicon hydrides, which do not exhibit such a property.

Experimental Section

All reactions were carried out under argon, using a vacuum line and Schlenck tubes. Solvents were dried and distilled before use. Tetrahydrofuran (THF) was first distilled over calcium hydride and then over sodium benzophenone. All carbonyl compounds and organic halides used are commercial products. Triethoxysilane (Fluka) and trimethoxysilane (Aldrich) were used as received. Other alkoxy- and phenoxysilanes were prepared from trichlorosilanes and the corresponding alcohols (or phenol).[31] R_2SiH_2

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[24] Review: Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206.

[25] The (4-tritylphenyl)diphenylmethane results from the rearrangement of the 1-(diphenylmethylene)-4-tritylcyclohexa-2,5-diene, i.e., the dimer of the triphenylmethyl radical,[26,27] under our experimental conditions.

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and R_3SiH (R = *n*-Bu, Ph, $PhCH_2$) are well-known derivatives and were identified by their melting or boiling point and their ^1H NMR spectra. Potassium hydride was purchased from Aldrich. The amount of potassium hydride as a suspension in mineral oil was washed three times with dried hexane, removing the liquid phase with a syringe; the white solid obtained was dried under vacuum and weighted. [8-(Dimethylamino)-1-naphthyl]lithium was prepared by using a 1:1 reaction of 1-(dimethylamino)naphthalene and *n*-BuLi in diethyl ether as solvent. 18-Crown-6 (Aldrich) was dried with molecular sieves and recrystallized from hexane before use.

^1H NMR spectra were obtained on a AW-60, AW-80, or AC-250 Bruker instrument, ^{29}Si NMR spectra on a AC-200 or AC-250 Bruker spectrometer; chemical shifts, δ, are relative to TMS. IR spectra were recorded on a Perkin-Elmer 298 or Perkin-Elmer 1600 spectrometer. ESR spectra were obtained on a Bruker ER 200 D instrument. Melting points were taken under vacuum using a Gallenkamp melting point apparatus and are uncorrected. Gas chromatography analyses were performed on a Delsi 30 instrument using a 1.40 m, Chromosorb W, DMCS, 10% SE 30 column and using nonadecane as internal standard.

1. Preparation of Dihydridosilicates $K[H_2Si(OR)_3]$. The general procedure (A) is given in the following example. **$K[H_2Si(OPr\text{-}i)_3]$.** A solution of triisopropoxysilane (5.46 g, 26.5 mmol) in THF (30 ml) was added dropwise to a slurry of potassium hydride (1.06 g, 26.5 mmol) in THF (50 mL) stirred at room temperature. After 6 h of stirring, the reaction mixture was filtered to remove traces of potassium hydride and the solvents were removed under vacuum, without heating, leading to a white powder of the title compound (6.1 g, 25 mmol), 94% yield. Recrystallization from ether at −20 °C gave the title compound as white crystals (5.3 g, 21.5 mmol), 82% yield: mp 180–185 °C (dec); ^1H NMR (C_6D_6, 20 °C), δ, 4.50 (m, 3 H, CH), 4.38 (s, 1 H, SiH), 3.72 (s, 1 H, SiH), 1.2 (d, J = 6 Hz, 18 H, CH_3). ^{29}Si NMR, see Tables II and III. Anal. Calcd for $C_9H_{23}KO_3Si$: C, 43.85; H, 9.39; Si, 11.39. Found: C, 43.21; H, 9.20; Si, 11.73.

[K, 18-crown-6][$H_2Si(OPr\text{-}i)_3$]. Procedure A was used with triisopropoxysilane (5.46 g, 26.5 mmol) and potassium hydride (1.06 g, 26.5 mmol). A solution of 18-crown-6 (7.0 g, 26.5 mmol) in THF (20 mL) was added first to the potassium hydride slurry followed by addition of the triisopropoxysilane. Recrystallization from a mixture of hexane and THF (10:1) at −20 °C gave the title compound as white crystals (10.7 g, 20.7 mol), 78% yield: mp 70–80 °C (dec); ^1H NMR (C_6D_6) δ 4.7 (br m, 3 H, CH), 4.5 (s, 2 H, SiH), 3.4 (s, 24 H, 18-crown-6), 1.4 (d, J = 6 Hz, 18 H, CH_3); ^{29}Si NMR, see Table III. Anal. Calcd for $C_{21}H_{47}KO_9Si$: C, 49.38; H, 9.27; O, 28.19; Si, 5.50. Found: C, 48.71; H, 8.69; O, 28.41; Si, 5.42.

$K[H_2Si(OBu\text{-}s)_3]$. Procedure A with tri-*sec*-butoxysilane (5.15 g, 20.8 mmol) and potassium hydride (0.83 g, 20.8 mmol) in THF (60 mL) gave the title compound as white crystals (3.5 g, 12.2 mmol), 60% yield, after recrystallization from ether: mp 170 °C (dec); ^1H NMR (C_6D_6) δ 4.4–4.0 (m, 4 H, CH + SiH), 3.7 (s, 1 H, SiH) 3.90 and 3.86 (2 pics, ratio 1/3, 1 H, SiH), 1.7–0.9 (m, 24 H, CH_3CH_2); ^{29}Si NMR, see Tables II and III. Anal. Calcd for $C_{12}H_{29}KO_3Si$: C, 49.95; H, 10.13; O, 9.37; Si, 16.63. Found: C, 50.13; H, 10.20; O, 9.15; Si, 15.96.

[K, 18-crown-6][$H_2Si(OBu\text{-}s)_3$]. Procedure A, using tri-*sec*-butoxysilane (3.76 g, 15 mmol), 18-crown-6 (4.0 g, 15 mmol), and potassium hydride (0.60 g, 15 mmol) in 50 mL of THF, gave the title compound as white crystals (5.1 g, 9.2 mmol), 62% yield: mp 65–80 °C (dec); ^1H NMR 4.7–4.6 (m, 5 H, CH and SiH), 3.5 (s, 24 H, 18-crown-6), 1.8–1.1 (m, 24 H, CH_3 and CH_2CH_3); ^{29}Si NMR, see Table III. Anal. Calcd for $C_{24}H_{53}KO_9Si$: C, 52.14; H, 9.66. Found: C, 52.74; H, 9.66.

[K, 18-crown-6][$H_2Si(OC_6H_{11}\text{-}c)_3$]. Procedure A, using tricyclohexyloxysilane (3.26 g, 10.0 mmol), 18-crown-6 (3.2 g, 12.0 mmol), and potassium hydride (0.50 g, 12.5 mmol) in 50 mL of THF, gave the title compound as white crystals (3.35 g, 5.3 mmol), 53% yield; mp 104–110 °C; ^1H NMR (C_6D_6) δ 3.6 (br s, 28 H, SiH, CH and 18-crown-6), 2.2–1.2 (m, 30 H, CH_2); ^{29}Si NMR, see Table III. Anal. Calcd for $C_{30}H_{59}KO_9Si$: C, 57.11; H, 9.42; O, 22.82; Si, 4.45. Found: C, 56.85; H, 9.51; O, 22.49; Si, 4.09. This compound was not isolated without crown ether.

$K[H_2Si(OR)_3]$, R = Et, *n*-Bu. A solution of trialkoxysilane (10.0 mmol) in THF (5 mL) was added dropwise to a slurry of potassium hydride (10.0 mmol) in THF (5 mL) and the mixture was stirred at room temperature and analyzed by ^{29}Si NMR. A mixture of $K[H_2Si(OR)_3]$ and $K[HSi(OR)_4]$ was obtained (see Table I).

R = Et: $K[H_2Si(OEt)_3]$ (THF) δ −81.85 ppm (t, $J(^1H-^{29}Si)$ = 217 Hz); $K[HSi(OEt)_4]$ (THF) δ −88.1 ppm ($J(^1H-^{29}Si)$ = 223 Hz).[13d]

R = *n*-Bu: $K[H_2Si(OBu\text{-}n)_3]$ (THF) δ −80.80 ppm (t, $J(^1H-^{29}Si)$ = 215 Hz); $K[HSi(OBu\text{-}n)_4]$ (THF) δ −86.1 ppm ($J(^1H-^{29}Si)$ = 219 Hz).[13d]

[K, 18-crown-6][$H_2Si(OPh)_3$]. A solution of triphenoxysilane (10.0 mmol) in THF (5 mL) was added dropwise to a slurry of potassium hydride (10.0 mmol) and 18-crown-6 (10.0 mmol) in 5 mL of THF. The solution was analyzed by ^{29}Si NMR. A mixture of two compounds was observed (see Table I). [K, 18-crown-6][$H_2Si(OPh)_3$] (THF) δ = −98.1 ppm (t, $J(^1H-^{29}Si)$ = 284 Hz); [K, 18-crown-6][$HSi(OPh)_4$] (THF) δ = −118.9 ppm (d, $J(^1H-^{29}Si)$ = 304 Hz).[13d]

2. Nucleophilic Substitution Reactions. $K[H_2Si(OEt)_3]$ with $PhCH_2MgCl$. The following example is given as general procedure B. The dihydrosilanes obtained are known and were characterized by ^1H NMR. A solution of $HSi(OEt)_3$ (1.66 g, 10.25 mmol) in 10 mL of THF was added at room temperature to a slurry of potassium hydride (0.41 g, 10.25 mmol) in 20 mL of THF and the mixture was stirred for 2 h; the reaction mixture was cooled to −78 °C and a solution of $PhCH_2MgCl$ (21 mmol) in Et_2O was added. The mixture was stirred for 2 h at 0 °C then hydrolyzed by using a saturated solution of ammonium chloride. After standard workup followed by distillation, $(PhCH_2)_2SiH_2$ was obtained (1.76 g, 8.1 mmol), 80% yield: bp 150–160 °C (12 mmHg).

$K[H_2Si(OEt)_3]$ with PhMgBr. Procedure B using triethoxysilane (1.73 g, 10.5 mmol), potassium hydride (0.42 g, 10.5 mmol), and PhMgBr (21 mmol) gave Ph_2SiH_2 (1.1 g, 6.0 mmol), 60% yield, bp 50–60 °C (1 mmHg), and Ph_3SiH (0.5 g, 2 mmol), 20% yield, bp 105–110 °C (0.1 mmHg).

$K[H_2Si(OEt)_3]$ with *n*-BuMgBr. Procedure B using triethoxysilane (2.17 g, 13.25 mmol), potassium hydride (0.53 g, 13.25 mmol), and *n*-BuMgBr (26.5 mmol) gave *n*-Bu_2SiH_2 (1.15 g, 8.0 mmol), 60% yield, bp 55–60 °C (12 mmHg), and *n*-Bu_3SiH (0.27 g, 1.35 mmol), 10% yield, bp 95–100 °C (12 mmHg).

$K[H_2Si(OEt)_3]$ with allylMgBr. General procedure B was used but $K[H_2Si(OEt)_3]$ was prepared in diethyl ether as solvent (40 mL) instead of THF from triethoxysilane (2.3 g, 14.0 mmol) and potassium hydride (0.56 g, 14.0 mmol) and a reaction time of 14 h. AllylMgBr (28 mmol) in diethyl ether was added at −78 °C and the reaction mixture allowed to warm up to room temperature and stirred for 2 h. Standard workup followed by distillation gave $(allyl)_2SiH_2$ (0.87 g, 7.8 mmol), bp 102–105 °C [lit.[32] 103 °C (740.3 mmHg)]. ^1H NMR (CCl_4, TMS) δ 5.75 (m, 2 H, CH=), 4.90 (m, 4 H, CH_2=), 3.75 (m, 2 H, SiH), 1.7 (m, 4H, CH_2).

$K[H_2Si(OEt)_3]$ with vinylMgBr. VinylMgBr was prepared in THF as solvent and procedure B was used without hydrolysis. Instead of hydrolysis, the volatiles were evaporated under vacuum and trapped at −196 °C before distillation. Using triethoxysilane (4.35 g, 26.5 mmol), potassium hydride (1.06 g, 26.5 mmol), and vinylMgBr (52 mmol) in THF gave $(vinyl)_2SiH_2$ (0.70 g, 8.3 mmol), 31% yield after distillation with a 25-cm-long packed column, bp 37–42 °C (traces of THF are present). The reaction was not optimized. IR (CCl_4) $\nu_{C=C}$ 3055 cm^{-1}, ν_{Si-H} 2145 cm^{-1}; ^1H NMR (CCl_4, TMS) δ 6.0 (one pic, 6 H, CH=CH_2), 4.13 (one pic, 2 H, SiH).

$K[H_2Si(OEt)_3]$ with [8-(dimethylamino)-1-naphthyl]lithium. General procedure B using triethoxysilane (1.56 g, 9.5 mmol), potassium hydride (0.38 g, 9.5 mmol), and [8-(dimethylamino)-1-naphthyl]lithium gave, after recrystallization from hexane–THF (5:1), the bis[8-(dimethylamino)-1-naphthyl]silane[8e] (2.07 g, 5.6 mmol) 59% yield, mp 147–149 °C (lit.[8e] 151 °C).

$K[H_2Si(OPr\text{-}i)_3]$ with PhMgBr. The following procedure (C) is given as an example. The obtained dihydrosilanes are known and were characterized by ^1H NMR.

To a solution of $K[H_2Si(OPr\text{-}i)_3]$ (1.84 g 7.48 mmol) in 30 mL of THF cooled at −78 °C was added dropwise a solution of

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PhMgBr in ether (15.0 mmol). The mixture was allowed to warm up to room temperature and was stirred 3 h. After hydrolysis and standard workup, Ph_2SiH_2 (1.06 g, 5.8 mmol), 77% yield, bp 55–65 (2 mmHg) and Ph_3SiH (0.2 g, 0.76 mmol), 10% yield, bp 110–115 °C (0.2 mmHg), were obtained.

$K[H_2Si(OPr\text{-}i)_3]$ with $PhCH_2MgCl$. Procedure C, using $K[H_2Si(OPr\text{-}i)_3]$ (2.36 g, 9.59 mmol) and $PhCH_2MgCl$ (19.2 mmol), gave $(PhCH_2)_2SiH_2$ (1.3 g, 6 mmol), 63% yield, bp 80–90 °C (0.1 mmHg). The distillation residue was chromatographed (silica plate, CH_2Cl_2/hexane, 1:1) to give $(PhCH_2)_3SiH$ (0.55 g, 1.8 mmol), 19% yield.

$K[H_2Si(OPr\text{-}i)_3]$ with *n*-BuMgBr. Procedure C, using $K[H_2Si(OPr\text{-}i)_3]$ (3.19 g, 12.97 mmol) and *n*-BuMgBr (26.0 mmol), gave *n*-Bu_2SiH_2 (0.90 g, 6.3 mmol), 48% yield, bp 40–50 °C (10 mmHg) and *n*-Bu_3SiH (0.4 g, 2.0 mmol) 15% yield, bp 90–95 °C (10 mmHg).

$K[H_2Si(OPr\text{-}i)_3]$ with PhLi. General procedure C using $K[H_2Si(OPr\text{-}i)_3]$ (1.94 g, 7.9 mmol) and PhLi (15.8 mmol) in ether gave, after distillation, Ph_2SiH_2 (0.17 g, 0.9 mmol), 12% yield, bp 55–60 °C (0.2 mmHg) and Ph_3SiH (0.9 g, 3.6 mmol), 46% yield, bp 100–105 °C (0.1 mmHg).

3. Reduction of Carbonyl Compounds with $K[H_2Si(OPr\text{-}i)_3]$. The following procedure (D) is given as an example. The obtained alcohols are characterized by comparison with an authentic sample.

Benzaldehyde. A solution of benzaldehyde (3.01 g, 28.4 mmol) in 15 mL of THF was added dropwise, at room temperature, to a solution of $K[H_2Si(OPr\text{-}i)_3]$ (3.50 g, 14.2 mmol) in 15 mL of THF. The mixture was stirred for 1 h and then hydrolyzed by using a 2 N HCl solution. Standard workup gave an oil, which was purified by column chromatography (silica gel; eluent, CH_2Cl_2) to give $PhCH_2OH$ (2.28 g, 21.1 mmol), 74% yield.

Octaldehyde. Procedure D (reaction time 2 h) gave $CH_3(CH_2)_7OH$ in 62% yield.

Benzophenone. Procedure D (reaction time 6 h) gave Ph_2CHOH, 50% yield, and 26% of benzophenone was recovered.

Acetophenone. Procedure D (reaction time 4 h) gave the corresponding alcohol, $PhCH(OH)CH_3$, in 36% yield. 40% of $PhCOCH_3$ was recovered.

Cyclohexanone. Procedure D (reaction time 15 h) gave cyclohexanone in 73% yield, and 24% of the starting ketone was recovered.

4. Reduction of Organic Halides with $K[H_2Si(OPr\text{-}i)_3]$. The following procedure (E) is given as an example.

1-Bromododecane. A solution of $CH_3(CH_2)_{11}Br$ (2.3 g, 9.3 mmol) in 10 mL of THF was added dropwise to a solution of $K[H_2Si(OPr\text{-}i)_3]$ (2.29 g, 9.30 mmol) in 20 mL of THF at room temperature. The reaction mixture wa stirred for 15 h and filtered. Gas chromatographic analysis showed a quantitative transformation to the corresponding alkane. Distillation gave $CH_3(CH_2)_{10}CH_3$ (1.28 g, 7.5 mmol) 81% yield, bp 60–65 °C (1.5 mmHg).

1-Chlorododecane. Procedure E was used with a reaction time of 24 h and a reaction temperature of 40–45 °C. The gas chromatography analysis gave 25% $CH_3(CH_2)_{10}CH_3$ and 75% of starting material, $CH_3(CH_2)_{11}Cl$, was recovered.

Benzyl Chloride. Procedure E was used with a reaction time of 18 h. Gas chromatographic analysis showed a 49% of toluene and 12% $(PhCH_2)_2$ (24% of benzyl group used).

Benzyl Bromide. Procedure E was used with a reaction time of 4 h. Gas chromatographic analysis gave 29% $PhCH_3$ and 22% $PhCH_2CH_2Ph$ (44% of benzyl group used), identified with an authentic sample.

Chlorodiphenylmethane. Procedure E was used with a reaction time of 10 h. The corresponding reduced product Ph_2CH_2 and dimer $Ph_2CHCHPh_2$ were obtained in 30 and 25% (50% of diphenylmethyl group used) yield, respectively, after TLC purification (silica gel; hexane/dichloromethane, 5:1).

6-Bromo-1-hexene. Procedure (E) was used and gave 1-hexene in 89% yield and methylcyclopentane in less 5% yield (gas chromatographic analysis).

Bromotriphenylmethane. A solution of Ph_3CBr (1.45 g, 4.5 mmol) in 20 mL of THF was added to a solution of $K[H_2Si(OPr\text{-}i)_3]$ (1.15 g, 4.7 mmol) in 30 mL of THF and the reaction was stirred for 4 h. The reaction mixture was then hydrolyzed by using a saturated solution of NH_4Cl, extracted with Et_2O, and the organic phases were dried over $MgSO_4$. Removal of the solvents under vacuum gave a white powder, which was treated with 50 mL of Et_2O, leading to a solution A and a solid B. Solution A was concentrated and gave triphenylmethane (0.66 g, 2.7 mmol), 60% yield. Solid B was recrystallized from CH_2Cl_2/hexane (1:1) to give (0.17 g, 0.35 mmol) 7.5% *p*-$Ph_2CHC_6H_4CPh_3$[25] (15% of triphenylmethyl group recovered).

5. Miscellaneous. Reduction of $Cp(CO)_2FeI$ with $K[H_2Si(OPr\text{-}i)_3]$. A solution of $Cp(CO)_2FeI$ (1.37 g, 4.51 mmol) in 10 mL of THF was added dropwise to a solution of $K[H_2Si(OPr\text{-}i)_3]$ (1.11 g, 4.51 mmol) in 20 mL THF at 0 °C. After 1 h of stirring, IR spectrum of the reaction medium showed only the presence of $[Cp(CO)_2Fe]_2$. Gas chromatographic analysis of the medium showed nearly quantitative yield of $HSi(OPr\text{-}i)_3$, traces of $Si(OPr\text{-}i)_4$, and $[Fe(CO)_2Cp]_2$. Elimination of the solvent under vacuum followed by recrystallization from hexane gave $[Cp(CO)_2Fe]_2$ (0.74 g, 2.09 mmol), 93% yield, mp 194 °C. IR identical with that of an authentic sample.

Reaction of $K[H_2Si(OPr\text{-}i)_3]$ with $PhC{\equiv}CH$. A solution of $PhC{\equiv}CH$ (0.5 g, 5 mmol) in 5 mL of THF was added to a solution of $K[H_2Si(OPr\text{-}i)_3]$ (1.23 g, 1.23 mmol) in the same solvent (5 mL) and the mixture was stirred at room temperature for 18 h. Me_3SiCl (0.65 g, 6 mmol) was added and the reaction mixture was stirred for 4 h. Hydrolysis, using a saturated solution of NH_4Cl, followed by standard workup gave an oil, which was purified by TLC (silica plate; eluent, hexane) to give $PhC{\equiv}CSiMe_3$[34] (0.7 g, 4.1 mmol), 82% yield. ^1H NMR (CCl_4) δ 7.0–7.5 (m, 5 H, Ar), 0.1 (s, 9 H, $SiMe_3$); IR (neat) $\nu_{C{\equiv}C}$ 2159 cm^{-1}.

ESR Experiments. The following procedure is given as an example. One milliliter of a dilute solution (5–10 mg in 3 mL of THF) of Ph_3CBr was added via a cannula and under argon to 1 mL of a dilute solution of $K[H_2Si(OPr\text{-}i)_3]$ (5–10 mg in 3 ml THF) in a 2 mm diameter glass tube, which was then put in the field of the instrument. The same procedure was used in the case of 2,6-di-*tert*-butyl-1,4 benzoquinone and *p*-dinitrobenzene. The ESR spectra were compared with those described in the literature.[18a,23a,28–30]

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