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Supplementary Material Available: Tables of thermal parameters and all bond lengths and angles for **2a** (5 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Pentacoordinated Silicon Anions: Synthesis and Reactivity[1]

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Pentacoordinated anionic siliconates $Ph_3Si(OMe)_2^-K^+$(18-crown-6), $Ph_2Si(OMe)_3^-K^+$(18-crown-6), $Ph_3SiF_2^-K^+$(18-crown-6), and $MePhSiF_3^-K^+$(18-crown-6) reacted with nucleophiles (RMgX, RLi, ROLi, $LiAlH_4$) to give the neutral tetravalent substituted silicon derivatives. Reactivity comparisons between $Ph_3SiX_2^-K^+$(18-crown-6) and Ph_3SiX (X = F, OMe) showed that the pentavalent anionic species is more reactive than the tetravalent analogue toward nucleophiles. Hydrolysis reactions of $Ph_3SiF_2^-K^+$(18-crown-6) and $Ph_3Si(OMe)_2^-K^+$(18-crown-6) gave respectively Ph_3SiF and a mixture of Ph_3SiOMe and Ph_3SiOH. Results clearly indicate that nucleophilic attack at pentacoordinated silicon species is a general process. Moreover, the data point out the enhanced reactivity of these species that may mainly arise from a general loosening of the bonds around silicon.

Over the last 20 years interest in hypervalent silicon compounds has grown considerably, and many isolable organosilicon compounds with coordination number greater than 4 are known.[2]

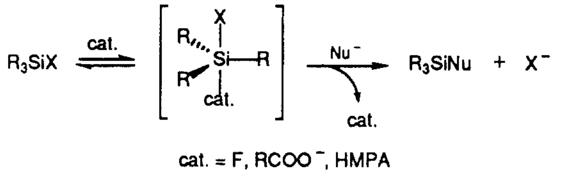
Our interest in the reactivity of pentacoordinated anionic silicon species is derived from several sources.

(1) Nucleophilic displacements in tetravalent organosilicon derivatives, R_3SiX, have been assumed to pass through the formation of a pentacoordinated anionic silicon intermediate.[3]

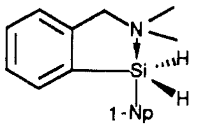
(2) Nucleophilic displacement at silicon can be activated by catalytic amounts of nucleophiles that are good coordinating agents for silicon.[3,4] The rate-determining step of the proposed mechanism (Scheme I) is attack of the nucleophile Nu^- at a pentacoordinated silicon center.

(3) The reaction of silicon hydrides, $RSiH_3$ and R_2SiH_2, with KH as a catalyst gives redistribution processes that are interpreted as involving intermediate formation of a pentacoordinated silicon complex.[5] In the same way, fast racemization of MePh-1-NpSiH(D), (1-Np = 1-naphthyl) catalyzed by hydrides (KH, $LiAlH_4$, $LiAlD_4$) was rationalized through formation of a pentacoordinated hydridoorganosiliconate anion.[6]

Scheme I



(4) The reduction of carbonyl compounds with silicon hydrides and fluoride[7] or alcoholate[8] ions as activators is well-known and proceeds through a pentacoordinated silicon intermediate. Recently anionic hydridosilicates have been isolated and have been shown to be the active species in the reduction of carbonyl compounds.[9,10] Finally, the intramolecularly coordinated silicon dihydride 1 has also been shown to possess a much more reactive hydrogen function than 1-naphthylphenylsilane.[11,12]



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(5) The transfer of an allyl group to a carbonyl compound from an allylsilane activated by fluoride ions (n-Bu_4NF)[13] is also a general process in organic synthesis. Furthermore, isolated pentacoordinated allyl derivatives may undergo allyl group transfer to a carbonyl compound.[14]

(6) The group transfer polymerization (GTP) of acrylates, activated by fluoride ions, was demonstrated to proceed through hypervalent silicon species.[15]

(7) Studies on the organo bis(benzene-1,2-diolato) complexes of silicon $RSi(o\text{-}O_2C_6H_4)_2^-Na^+$ (R = Me, Ph, 1-Np)[13] and hydridoalkoxosiliconates $H_nSi(OR)_{5-n}^-K^+$ (n = 1, 2)[10,17] show that these derivatives are very reactive toward nucleophilic reagents such as organometallic compounds, RMgX,[10,13,17] RLi,[13] and hydrides.[13]

In this paper we describe the synthesis of the methoxosiliconates **2**, **3**, and **4** and discuss the reactions of pentacoordinated fluoro- (**5**, **6**) and methoxosiliconates (**3**, **4**) toward strong nucleophiles (RO^-, R^-, H^-) and water: $Ph_3Si(OMe)_2^-K^+$(18-crown-6) (**2**); $Ph_2Si(OMe)_3^-K^+$(18-crown-6) (**3**); $PhSi(OMe)_4^-K^+$(18-crown-6) (**4**); $Ph_3SiF_2^-K^+$(18-crown-6) (**5**); $MePhSiF_3^-K^+$(18-crown-6) (**6**).

Results and Discussion

1. Synthesis of Pentacoordinated Siliconates. Previous work[18] has demonstrated the formation of the five-coordinate anionic fluorosiliconates $R_nSiF_{5-n}^-$ (n = 0–3); these acyclic derivatives result largely from the reaction of fluoride ion with four-coordinated fluorosilanes, as illustrated by the preparation of the 18-crown-6 potassium salt of difluorotriphenyl- and trifluoromethylphenylsiliconates that was carried out by Damrauer et al.[19] (eqs 1 and 2).

$$\underset{\mathbf{7}}{Ph_3SiF} + KF(\text{18-crown-6}) \xrightarrow{THF} \underset{\mathbf{5}}{Ph_3SiF_2^-K^+(\text{18-crown-6})} \quad (1)$$

$$\underset{\mathbf{8}}{MePhSiF_2} + KF(\text{18-crown-6}) \xrightarrow{THF} \underset{\mathbf{6}}{MePhSiF_3^-K^+(\text{18-crown-6})} \quad (2)$$

The use of 18-crown-6 facilitates the solubility of potassium fluoride in aprotic solvents and may also stabilize the fluorosiliconates formed. The formation of pentacoordinated silicon derivatives by use of the 18-crown-6 potassium salt is a general process. It has been extended by Holmes and co-workers for the preparation of $Si(OMe)_5^-K^+$(18-crown-6)[20] and by ourselves in the case of methoxosiliconates **2**, **3** and **4** (eq 3). It is interesting to

$$\underset{\substack{n = 3,\ \mathbf{9}\\ n = 2,\ \mathbf{10}\\ n = 1,\ \mathbf{11}}}{Ph_nSi(OMe)_{4-n}} + KOMe(\text{18-crown-6}) \rightarrow \underset{\substack{n = 3,\ \mathbf{2}\\ n = 2,\ \mathbf{3}\\ n = 1,\ \mathbf{4}}}{Ph_nSi(OMe)_{5-n}K^+(\text{18-crown-6})} \quad (3)$$

emphasize the following structural features of the pentacoordinated siliconates. Damrauer et al.,[19] working with a 80-MHz instrument, found in ^{19}F NMR spectra that the fluorines of $Ph_2SiF_3^-K^+$(18-crown-6) and $MePhSiF_3^-K^+$(18-crown-6) exchange at room temperature; variable-temperature experiments showed the coalescence temperature to be −12 °C for $Ph_2SiF_3^-$ and +2 °C in the case of $MePhSiF_3^-$. With the methoxosiliconate **3**, ^1H NMR studies (200 MHz) showed only one relatively sharp singlet of the methoxy groups even at −90 °C, indicating that the energy barrier of the process is quite low (<10 kcal mol^{-1}).

Table I. Reactions of $Ph_3SiF_2^-K^+$(18-crown-6) (5) with Nucleophiles[a]

run no.	reagent	solvent, temp, reacn time	product (yield, %)
1	$LiAlH_4$	Et_2O, −30 °C, 1 h	Ph_3SiH (88)
2	EtMgBr	THF, room temp, 3 h	Ph_3SiEt (79)
3	i-PrMgBr	THF, room temp, 3 h	Ph_3Si-i-Pr (68)
4	(allyl)MgBr	THF, room temp, 1 h	Ph_3Si(allyl) (73)
5	$PhCH_2MgBr$	THF, room temp, 1 h	Ph_3SiCH_2Ph (69)
6	n-BuLi	Et_2O, −30 °C, 30 min	Ph_3Si-n-Bu (93)
7	$PhC{\equiv}CLi$	THF, −30 °C, 1 h	$Ph_3SiC{\equiv}CPh$ (50)
8	MeONa	THF, −30 °C, 1 h	Ph_3SiOMe (62)
9	PhOLi	THF, room temp, 30 min	Ph_3SiOPh (69)
10	p-MeO-C_6H_4OLi	THF, room temp, 30 min	$Ph_3SiOC_6H_4OCH_3$ (82)
11	i-PrOLi	THF, room temp, 30 min	Ph_3SiO-i-Pr (92)

[a] Reaction conditions: 2 mol of reagent/mol of siliconate. Room temp = room temperature.

$Ph_3Si(OMe)_2^-K^+$(18-crown-6) showed one methoxy signal in ^1H NMR spectra at room temperature, which suggests that both methoxy groups are axial. Since it is well accepted that, in trigonal bipyramids, the electronegative groups prefer to be axial,[2] one can assume that both methoxy groups are axial as observed in the case of $Ph_3SiF_2^-K^+$(18-crown-6).[19]

A special reaction was observed in the case of $MePhSi(OEt)_2$; it reacts with potassium ethoxide in the presence of 18-crown-6 with rupture of the silicon–phenyl bond (eq 4). Very recently, Holmes and co-workers[21] observed an

$$\underset{\mathbf{12}}{MePhSi(OEt)_2} + KOEt(\text{18-crown-6}) \rightarrow \underset{\mathbf{13}}{MeSi(OEt)_4^-K^+(\text{18-crown-6})} \quad (4)$$

analogous reaction in an attempt to prepare $(t\text{-}Bu)_2SiF_3^-K^+$(18-crown-6) (eq 5). All the pentacoordinated

$$(t\text{-}Bu)_2SiF_2 + KF(\text{18-crown-6}) \xrightarrow{Tol} t\text{-}BuSiF_4^-K^+(\text{18-crown-6}) \quad (5)$$

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Table II. Reactions of $MePhSiF_3^-K^+$(18-crown-6) (6) with Nucleophiles[a]

run no.	reagent	solvent, temp	product (yield, %)
1	$LiAlH_4$	Et_2O, 0 °C	$PhMeSiH_2$ (77)
2	*i*-Bu_2AlH	Et_2O, −30 °C	$PhMeSiH_2$ (quant)
3	$NaBH_4$	THF, 0 °C	$PhMeSiH_2$ (77)
4	Li(*t*-BuO)$_3$AlH	THF, −50 °C → room temp	$PhMeSiH_2$ (quant)
5	MeMgBr	Et_2O, −30 °C	$PhSiMe_3$ (73)
6	MeMgBr[b]	Et_2O, −30 °C	$PhMe_2SiF$[c]
7	*i*-PrMgBr	Et_2O, 0 °C	PhMeSi(F)-*i*-Pr (75)
8	*t*-BuMgBr	Et_2O, 0 °C	PhMeSi(F)-*t*-Bu (79)
9	*n*-BuLi	Et_2O, −30 °C	PhMeSi(*n*-Bu)$_2$ (83)
10	PhC≡CLi	Et_2O, −30 °C	PhMeSi(C≡CPh)$_2$ (76)
11	MeONa	Et_2O, −30 °C	$PhMeSi(OMe)_2$ (92)

[a] Reaction conditions: 2 mol of reagent/mol of siliconate; reaction time 30–60 min. Room temp = room temperature. [b] Reactions conditions: 1 mol of reagent/mol of siliconate. [c] Some $PhSiMe_3$ is also present.

Table III. Reactions of $Ph_3Si(OMe)_2^-K^+$(18-crown-6) (2) with Nucleophiles[a]

reagent	solvent, temp, reacn time	products (yield, %)
$LiAlH_4$	THF, 0 °C, 30 min	Ph_3SiH (85)
$NaBH_4$	THF, room temp, 5 days	no reacn
MeMgBr	THF, room temp, 12 h	Ph_3SiMe (72)
EtMgBr	THF, room temp, 12 h	Ph_3SiEt (68)
i-PrMgBr	THF, room temp, 7 days	Ph_3Si-*i*-Pr (67)
PhMgBr[b]	THF, room temp, 2 days	Ph_4Si (65)
(allyl)MgBr	THF, room temp, 7 days	Ph_3Si(allyl) (63)
$PhCH_2MgBr$	THF, room temp, 9 days	Ph_3SiCH_2Ph (61)
n-BuLi	THF, −30 °C, 30 min	Ph_3Si-*n*-Bu (83)
PhLi	THF, room temp, 30 min	Ph_4Si (93)
p-$MeOC_6H_4OLi$	THF, room temp, 8 days	$Ph_3SiOC_6H_4OMe$ (86)

[a] Reaction conditions: 2 mol of reagent/mol of siliconate. Room temp = room temperature. [b] Reaction conditions: 1 mol of PhMgBr/mol of siliconate.

Table IV. Reactions of $Ph_2Si(OMe)_3^-K^+$(18-crown-6) (3) with Nucleophiles[a]

reagent	solvent, temp, reacn time	product (yield, %)
$LiAlH_4$	THF, 0 °C, 30 min	Ph_2SiH_2 (87)
MeMgBr	THF, room temp, 2 days	Ph_2SiMe_2 (95)
MeMgBr[b]	THF, room temp, 2 h	$Ph_2Si(OMe)Me$ (57)
EtMgBr	THF, room temp, 5 days	$Ph_2Si(OMe)Et$ (58) Ph_2SiEt_2 (26)
EtMgBr[b]	THF, room temp, 2 days	$Ph_2Si(OMe)Et$ (80) Ph_2SiEt_2 (10)
i-PrMgBr	THF, room temp, 6 h	$Ph_2Si(OMe)$-*i*-Pr (74)
s-BuMgBr	THF, room temp, 6 h	$Ph_2Si(OMe)$-*s*-Bu (74)
(allyl)MgBr	THF, room temp, 2 days	$Ph_2Si(allyl)_2$ (68)
$PhCH_2MgBr$	THF, room temp, 2 days	$Ph_2Si(CH_2Ph)_2$ (72)
n-BuLi	Et_2O, room temp, 2 h	Ph_2Si(*n*-Bu)$_2$ (50)
PhLi	THF, room temp, 2 h	Ph_4Si (85)

[a] Reaction conditions: 4 mol of reagent/mol of siliconate. Room temp = room temperature. [b] Reaction conditions: 1 mol of reagent/mol of siliconate.

derivatives we have synthesized, **2**, **3**, **4**, and **13**, are obtained as white powders in good yields. They are stable at room temperature under inert gas, but they are air- and moisture-sensitive.

The preparation of these pentacoordinated silicon anions allows a direct comparison of their chemical behavior with that of the corresponding tetravalent silanes.

2. Reactivity of Fluoro- and Methoxosiliconates with Nucleophiles. The fluorosiliconates **5** and **6** reacted easily with nucleophilic reagents to give the substituted neutral derivatives in good yields (Tables I and II). For instance, reduction of $Ph_3SiF_2^-$ (anion of **5**) with $LiAlH_4$ gave Ph_3SiH in 88% yield (Table I, run 1). Grignard reagents (Table I, runs 2–5) and organolithium derivatives (Table I, runs 6 and 7) reacted with **5** to give Ph_3SiR (R = Et, *i*-Pr, allyl, benzyl, *n*-Bu, PhC≡C–) in high yield. Other nucleophiles such as alcoholates or phenolates (Table I, runs 8–11) also reacted with complex **5** to give the corresponding neutral alkoxysilanes.

Table II gives the analogous reactions performed with $MePhSiF_3^-$ (anion of **6**). This pentacoordinated fluorosiliconate is readily reduced with use of $LiAlH_4$, *i*-Bu_2AlH, $NaBH_4$, or Li(*t*-BuO)$_3$AlH (Table II, runs 1–4). Whereas MeMgBr reacted with **6** to give the disubstituted (Table II, run 5) or the monosubstituted derivative (Table II, run 6), depending on the reaction conditions, more hindered Grignard reagents (*i*-PrMgBr, *t*-BuMgBr) (Table II, runs 7 and 8) gave only the monosubstituted compound. Organolithium derivatives (Table II, runs 9 and 10) and MeONa (Table II, run 11) reacted with **6** to give the disubstituted $MePhSiR_2$ compounds (R = *n*-Bu, PhC≡C–, OMe) in good yields.

Analogous reactions with nucleophiles were performed in the case of the methoxosiliconates $Ph_3Si(OMe)_2^-$ (anion of **2**) and $Ph_2Si(OMe)_3^-$ (anion of **3**). Grignard reagents, hydrides, and alcoholates reacted with **2** and **3** to give the corresponding tetracoordinated neutral silicon compounds (Tables III and IV). These reactions were usually performed in THF at room temperature and gave good yields of the products. For instance, $LiAlH_4$ reacted with **2** and **3** to give Ph_3SiH (85% yield) and Ph_2SiH_2 (87%), respectively. With $Ph_3Si(OMe)_2^-$ (anion of **2**), as in the case of the corresponding fluorosiliconate **5**, no reaction was observed with $NaBH_4$. With use of the pentavalent silicon complex $Ph_2Si(OMe)_3^-$ (anion of **3**) (Table IV) the $Ph_2Si(OMe)R$ derivatives were obtained with the hindered Grignard reagent (*i*-Pr) or with 1 equiv of the organomagnesium compound (Me, Et). Organolithium derivatives (PhLi, *n*-BuLi) also reacted with **2** (Table III) and **3** (Table IV) to give Ph_3SiR and Ph_2SiR_2, respectively (R = Ph, *n*-Bu), in good yield.

3. Reactions with Nucleophiles: Reactivity Comparisons between Pentacoordinated Siliconates and the Corresponding Tetravalent Silicon Species. The chemical behavior of the fluoro- (**5** and **6**) and methoxosiliconates (**2** and **3**) has been compared with that of the corresponding neutral fluoro- (**7** and **8**) and methoxysilanes (**9** and **10**), respectively, with use of Grignard reagents and alkoxides; the results obtained are summarized in tables V and VI. These tables show reactivity studies that compare the rates of nucleophilic substitution of pentacoordinated silicon derivatives with those for the analogous neutral compounds. The reaction half-lives (determined by ^1H NMR techniques with respect to the starting silane) are not precise values; however, in most cases the numbers are large enough to leave no doubt as to the qualitative difference between the chemical behaviors of the penta- and tetravalent silicon species.

As observed previously,[11,12,16,17] the pentacoordinate species are more reactive than the tetravalent ones. The difference in rate observed is more important with fluoro than with methoxy derivatives, and diphenyl- and methyl phenyl derivatives are also found to be more reactive than the triphenyl compounds. The larger rate accelerations, i.e. 10–10^2 times faster, are observed in the case of fluoro- or methoxosiliconates with the most hindered nucleophiles (*i*-PrMgBr, *t*-BuMgBr). The reactions of $Ph_3SiF_2^-$ (anion of **5**) and Ph_3SiF (**7**) with phenolates (PhOLi, *p*-$MeOC_6H_4OLi$) are too fast in both cases to be able to measure a rate difference between them. The same remark may be valid when hydrides ($LiAlH_4$, Li(O-*t*-Bu)$_3$AlH, *i*-Bu_2AlH) are used; a direct reactivity comparison is made

Table V. Reactivity Studies of the Fluorosiliconate/Fluorosilane Couples 5/7 and 6/8 with Nucleophiles[a]

run no.	compd	reagent	reacn conditions	reacn half-life, min[b]	ratio
1	6	*i*-PrMgBr	Et_2O, -10 °C	<5	6:8 > 150
2	8			780	
3	6	*t*-BuMgBr	Et_2O, 0 °C	<3	6:8 > 100
4	8			360	
5	5	*i*-PrMgBr	THF, room temp	32	5:7 ≃ 10
6	7			320	
7	7 (18-crown-6)	*i*-PrMgBr	THF, room temp	300	
8	7 (MgF_2)	*i*-PrMgBr	THF, room temp	320	
9	5	$PhCH_2MgBr$	THF, room temp	*c*	5:7 ≃ 2.5
10	7				
11	5	MeONa	THF, -30 °C	20	5:7 ≃ 2
12	7			10	
13	5	PhOLi	THF, room temp	*d*	5:7 ≃ 1
14	7				
15	5	*p*-$MeOC_6H_4O$-Li	THF, room temp	*d*	5:7 ≃ 1
16	7				

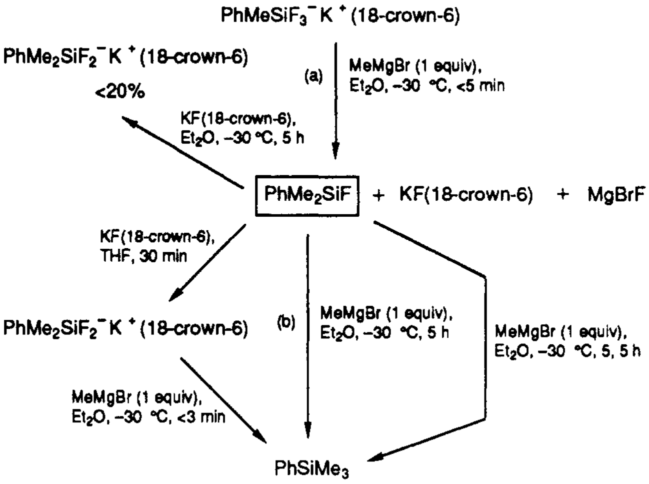
[a] Reaction conditions: 2 mol of reagent/mol of silicon derivative; [Si] = 0.1 M; total volume 10 mL; aliquot 2 mL. [b] Reaction half-lives determined by ^1H NMR technique with respect to the starting silicon derivative. [c] 5, 70% reaction after 10 min; 7, 90% reaction after 5 min. [d] Reactions with 5 and 7 are complete after 6 min; they are too fast to measure a difference of rate.

Table VI. Reactivity Studies of the Methoxosiliconate/Methoxysilane Couples 2/9 and 3/10 with Nucleophiles[a]

run no.	compd	reagent	reacn conditions	progress of the reacn,[b] %	ratio
1	2	MeMgBr	THF, room temp	75 (1.5 h)	2:9 ≃ 1.3
2	9			70 (2 h)	
3	2	EtMgBr	THF, room temp	36 (2 h)	2:9 ≃ 4.5
4	9			37 (9 h)	
5	2	*i*-PrMgBr	THF, room temp	50 (40 h)	2:9 > 20
6	9			15 (15 h)	
7	2	*n*-BuLi	THF, -30 °C	100 (3 min)	2:9 ≃ 4.4
8	9			90 (13 min)	
9	2	$LiAlH_4$	THF, 0 °C	70 (3 min)	2:9 ≃ 1.2
10	9			55 (3 min)	
11	3	*i*-PrMgBr	THF, room temp	50 (2 h 15 min)	3:10 ≃ 11
12	10			50 (25 h)	
13	3	*s*-BuMgBr	THF, room temp	50 (2 h 20 min)	3:10 ≃ 25
14	10			50 (55 h)	

[a] Reaction conditions: 2 mol of reagent/mol of silicon derivative; runs 1-4, [Si] = 0.5 M, total volume 30 mL; runs 7-10, [Si] = 0.1 M, total volume 10 mL; runs 5 and 6 and 11-14, [Si] = 0.25 M, total volume 30 mL; aliquot 2 mL. Room temp = room temperature. [b] The progress of the reactions is determined by ^1H NMR techniques with respect to the starting silicon derivative.

Scheme II



impossible because of the insolubility of the potassium salts at lower temperature.

The fluorosiliconate 5 reacted with *i*-PrMgBr with a reaction half-life of 32 min (Table V, run 5); the same reaction with Ph_3SiF (7) took 320 min (Table V, run 6). When 18-crown-6 or MgF_2 was added to the reaction mixture with 7 (Table V, runs 7 and 8), no change in the reaction half-life was observed. The complexing agent itself or MgF_2 does not significantly alter the reactivity of the Grignard reagent. These results show that the observed activation actually comes from coordination of the fluoride ion at silicon. To prove this assertion, the reactions summarized in Scheme II were performed. Treatment of the fluorosiliconate 6 with 1 equiv of MeMgBr in diethyl ether at -30 °C led, within 5 min, to formation of the monofunctional silane $PhMe_2SiF$ (8) with concomitant formation of MgBrF and KF(18-crown-6) (Scheme II, step a). The subsequent addition of 1 equiv of MeMgBr at -30 °C gave in 5 h $PhSiMe_3$ (Scheme II, step b). Reaction between pure $PhMe_2SiF$ and 1 equiv of MeMgBr in diethyl ether as solvent was also slow and was complete only after 5.5 h. Starting from $PhMe_2SiF$ and KF(18-crown-6) at -30 °C in diethyl ether as solvent, the pentavalent fluorosiliconate is formed slowly (Scheme II); less than 20% of $PhMe_2SiF_2^-K^+$(18-crown-6) (determined by ^1H NMR spectroscopy) was formed after 5 h, indicating that under our reaction conditions (Scheme II, step b) the concentration of the pentavalent species will be always quite low. In contrast, the reaction of $PhMe_2SiF_2^-K^+$(18-crown-6) with MeMgBr in diethyl ether at -30 °C leads quantitatively to $PhSiMe_3$ within 3 min. Scheme II shows also that formation of $PhMe_2SiF_2^-K^+$(18-crown-6) is rapid when the reaction is performed in tetrahydrofuran instead of diethyl ether (reaction complete in 0.5 h at room temperature). These data clearly indicate that the rate enhancement observed with either $PhMe_2SiF_2^-$ or $Ph_3SiF_2^-$ results solely from coordination of the fluoride anion at silicon.

This interpretation may be extended to the methoxosiliconates. Table VI summarizes the comparison of the progress of the reactions between $Ph_3Si(OMe)_2^-$ (anion of 2) and $Ph_2Si(OMe)_3^-$ (anion of 3) and the corresponding neutral methoxysilanes 9 and 10, respectively. The pentavalent silicon anions are more reactive toward nucleophiles (RMgX, *n*-BuLi, AlH_4Li) than the corresponding neutral methoxysilanes. These results parallel those obtained in the case of fluorosiliconates (vide supra). The differences in reaction rates are less important with methoxy leaving groups than with fluorosiliconates, but as observed in the latter cases, larger differences were obtained with hindered Grignard reagents (11 and >20 with *i*-PrMgBr, runs 5, 6 and 11, 12).

A probable interpretation of the enhanced reactivity of pentacoordinate silicon species was suggested recently by Holmes and co-workers;[22] ab initio calculations on SiH_nF_{4-n} and $[SiH_nF_{5-n}]^-$ showed only a small change in charge at

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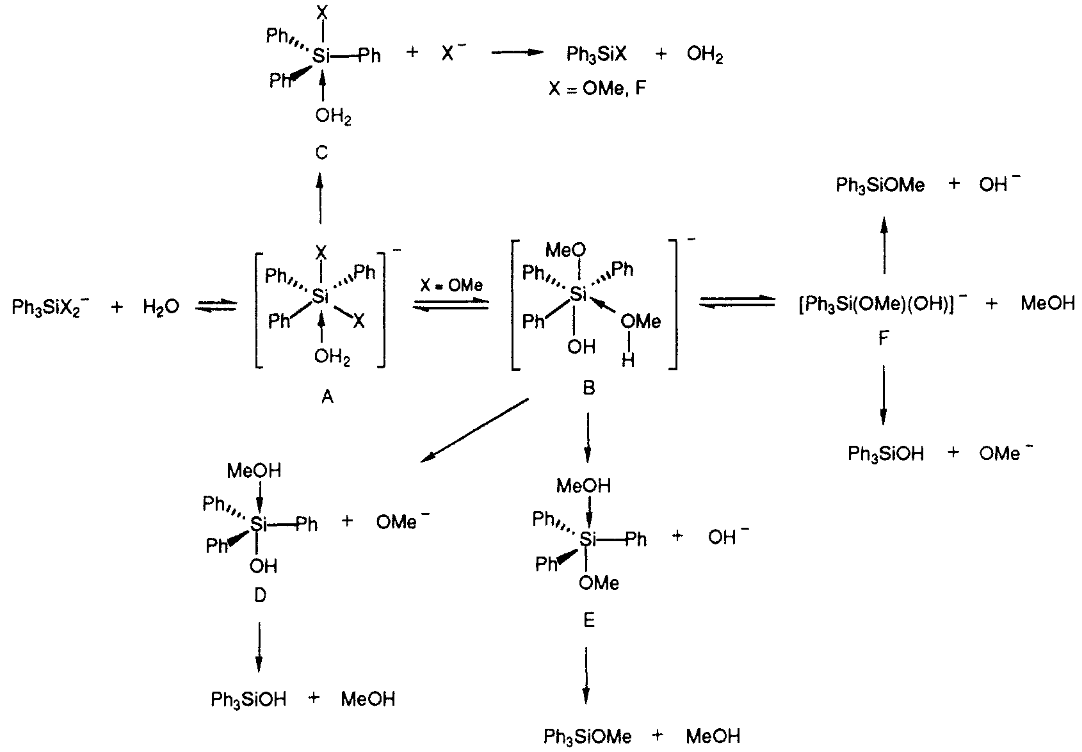
(22) Deiters, J. A.; Holmes, R. R. 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; INOR 423.

(23) Johnson, S. E.; Deiters, J. A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 3250.

Scheme III



silicon on going from the tetravalent to the pentacoordinate anionic species. However, a general loosening of all bonds in the pentacoordinate state occurs, which suggests that the enhanced reactivity is associated with a greater leaving group ability on going from tetra- to pentacoordinated species.

4. Hydrolysis of Anionic Pentacoordinated Silicon Derivatives. We have also analyzed the reaction of these pentavalent anionic species with water. A recent report from Holmes and co-workers[21] shows that hydrolysis of Mes_2SiF_2 with $Et_4NF{\cdot}2H_2O$ gives disiloxane with intermediate formation of $Mes_2SiF_3^-$ and $Mes_2Si(F)O{-}H{-}O{-}Si(F)Mes_2$. We have studied the hydrolysis of $Ph_3SiF_2^-$ and $Ph_3Si(OMe)_2^-$ and found that the hydrolysis reactions of these pentacoordinate silicon anions are functions of not only the complex and the reaction medium (neutral, acidic, or basic) but also the concentration of the reactants.

As previously observed with fluorosiliconates,[19] $Ph_3SiF_2^-K^+$(18-crown-6) (**5**) is stable in the presence of small amounts of water (100% recovered with 3.5 equiv of H_2O in THF after 10 min); however, after it is washed with a saturated solution of NH_4Cl and extracted with diethyl ether, decomposition takes place, since Ph_3SiF is quantitatively recovered.

The hydrolysis reactions of the methoxosiliconates depend on the reaction conditions; Table VII summarizes the results obtained in an extraction procedure under different conditions. With $Ph_3Si(OMe)_2^-$ (anion of **2**) hydrolysis with a saturated solution of NH_4Cl or a solution of NaOH (1 M) gave a mixture of Ph_3SiOMe and Ph_3SiOH, 40–48 and 30–60%, respectively. In contrast, with Ph_3SiOMe, under the same reaction conditions, only a small amount of Ph_3SiOH is observed (17% with NH_4Cl and 6% with the NaOH solution). Under acidic conditions Ph_3SiOH is the only compound obtained in the hydrolysis of methoxosiliconate **2**. Thus, the pentacoordinated methoxosiliconate seems to be more reactive toward hydrolysis than the corresponding neutral methoxysilane. In this particular case activation may be due to the pentacoordinated complex itself or to a base-catalyzed nucleophilic substitution. To investigate the hydrolysis mechanism, the reaction was performed under different experimental conditions. Table VIII summarizes the results obtained. The methoxosiliconate **2** reacted with water in THF to give a mixture of Ph_3SiOMe (55%) and Ph_3SiOH (45%) after 5 min of reaction (Table VIII, run 1). The same derivatives and ratio were obtained when water was added to the mixture of Ph_3SiOMe and KOMe(18-crown-6) in THF as solvent (Table VIII, run 2). This fast reaction may be interpreted by rapid formation of the pentacoordinated species followed by hydrolysis. The formation of **2** is effectively fast: when triphenylmethoxysilane reacted with potassium methoxide in the presence of crown ether, in THF as solvent, only 15% of the starting material was recovered after 10 min. When KOH(18-crown-6) was added to Ph_3SiOMe instead of KOMe(18-crown-6), the hydrolysis reaction with wet THF gave the same mixture of Ph_3SiOMe and Ph_3SiOH with an analogous ratio (Table VIII, run 3). These results show that it is the pentacoordinated species which reacts with water; formation of this anionic species is the first step of the reaction when Ph_3SiOMe is used as starting material in the presence of KOMe or KOH. As previously observed in the case of racemization of chlorosilanes or nucleophilic substitution in the presence of added nucleophiles,[4,24,25] a hexacoordinated silicon derivative may be formed in a second step (Scheme III, A); further evolution of the reaction

Table VII. Hydrolysis of $Ph_3Si(OMe)_2^-K^+$(18-crown-6) (2) and Ph_3SiOMe (9) (in Parentheses) in THF as Solvent with Use of the Extraction Procedure

reactant	amt of Ph_3SiOMe, %	amt of Ph_3SiOH, %
NH_4Cl (satd), H_2O	40 (83)	48 (17)
NaOH (1 M), H_2O	30 (94)	60 (6)
HCl (1 M), H_2O	0 (≃30)	100 (≃70)

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(24) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1.

(25) Damrauer, R.; Burgraff, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601.

Table VIII. Hydrolysis of Ph$_3$Si(OMe)$_2^-$K$^+$(18-crown-6) (2) and Ph$_3$SiOMe (9) with Use of Wet THF^a

run no.		amt of Ph$_3$SiOMe, %	amt of Ph$_3$SiOH, %
1	Ph$_3$Si(OMe)$_2^-$K$^+$(18-crown-6)	54	45
2	Ph$_3$SiOMe + KOMe(18-crown-6)	55	45
3	Ph$_3$SiOMe + KOH(18-crown-6)	60	40

^{a} Reaction conditions: 8 mmol in 20 mL of THF + 1 mL of H$_2$O; reaction time 5 min.

depends on the relative labilities of the ligands attached to silicon. A possible pathway is given in Scheme III. The third step involves extrusion of X$^-$, leading to the pentacoordinated neutral silicon derivative C, which eliminates H$_2$O and gives Ph$_3$SiX (X = OMe, F). The driving force may be formation of KX. To explain the formation of Ph$_3$SiOH, one may assume fast exchange of a proton between the coordinated ligands OH and MeOH in B. This hexacoordinated species evolves in the same way as A by elimination of an anion (OMe$^-$ or OH$^-$), giving D and E, followed by the extrusion of MeOH to give the compounds Ph$_3$SiOMe and Ph$_3$SiOH. For symmetry reasons B may be in equilibrium with the pentacoordinated anionic species F, which evolves by extrusion of OH$^-$ or OMe$^-$ to give Ph$_3$SiOMe or Ph$_3$SiOH, respectively.

In conclusion, the comparison between neutral and pentacoordinated anionic silicon derivatives shows that the latter are more reactive toward nucleophilic substitutions than the corresponding neutral silicon compounds. These reactions may be proof that the formation of pentavalent anionic species as intermediates in nucleophilic activated substitution at silicon is a general process. The enhanced reactivity observed is also suggested by calculations[22] which show that in these pentavalent anionic species there is only a small change in charge at silicon; however, a general loosening of all bonds in the pentacoordinated state occurs, which suggests that the enhanced reactivity of the pentavalent silicon derivative is associated with a greater leaving group ability on going from four- to five-coordinate species.[22]

Experimental Section

All reactions were carried out under nitrogen or argon, with use of a vacuum line and Schlenk tubes. Diethyl ether and tetrahydrofuran were dried over sodium–benzophenone and distilled before use. The following starting materials were prepared by literature methods: Ph$_3$SiF$_2^-$K$^+$(18-crown-6);[19] MePhSiF$_3^-$K$^+$(18-crown-6).[19] Compounds RPhSi(OMe)$_2$ (R = Me, Ph) were prepared according to standard methods: reaction of PhMgBr with RSiCl$_3$ (R = Me, Ph) in diethyl ether afforded, after distillation, RPhSiCl$_2$ species (R = Me, Ph), which were methoxylated with MeOH and Et$_3$N in pentane as solvent. Ph$_3$SiOMe was prepared from HSiCl$_3$ and PhMgBr followed by methoxylation of Ph$_3$SiH with MeOH and Wilkinson's catalyst. Grignard reagents and organolithium derivatives were prepared by using the standard procedures; lithium alcoholate and phenolates (*i*-PrOLi, PhOLi, *p*-MeOPhLi) were prepared by reaction of the corresponding alcohol with *n*-BuLi (purchased from Janssen Chemical) in diethyl ether as solvent. Li(*t*-BuO)$_3$AlH was prepared according to the method of Brown.[26] The following starting materials were purchased: MeONa (Janssen), *i*-Bu$_2$AlH (Aldrich), LiAlH$_4$ (Merck), NaBH$_4$ (Janssen), HSiCl$_3$ (Fluka, PhSiCl$_3$ (Fluka), MeSi(OEt)$_3$ (Janssen). Silica gel 60 (70–230 mesh) was purchased from Merck.

Melting points were taken in sealed tubes with a Gallenkamp apparatus. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer. ^{1}H NMR spectra were taken with a Bruker AW 60 spectrometer in deuterated benzene or acetone and are referenced to tetramethylsilane. ^{29}Si NMR spectra were recorded with Bruker 250 and Bruker 200 spectrometers operating at 49.694 and 39.76 MHz, respectively; tetrahydrofuran was used as solvent, and an internal capillary with deuterated benzene was used to lock the instrument; chemical shifts (δ) are referenced to tetramethylsilane.

Synthesis of Ph$_2$Si(OMe)$_3^-$K$^+$(18-crown-6) (3). This procedure is an extension of the preparation of phenylfluorosiliconate by Damrauer et al.[19]

To a dispersion of KOMe (0, 21 g, 3 mmol) and 18-crown-6 (0.792 g, 3 mmol) in 10 mL of toluene, at room temperature and under argon, was added a solution of Ph$_2$Si(OMe)$_2$ (0.732 g, 3 mmol) in 5 mL of toluene and the mixture stirred at room temperature for one night. Toluene was removed under vacuum, and the residue was washed with four 10-mL portions of dry pentane. A white powder was obtained and recrystallized from THF: 1.66 g, 96% yield; mp 89–92 °C; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.85–7.5 and 7.25–6.90 (2 m, 10 H, Ph), 3.53 (s, 24 H, 18-crown-6), 3.25 (s, 9 H, OMe);[26] ^{29}Si NMR −100.2 ppm. Anal. Calcd for C$_{27}$H$_{43}$O$_9$SiK: C, 56.03; H, 7.49. Found: C, 55.53; H, 7.62. In the pure complex only one OMe signal is observed in the proton NMR spectrum: at room temperature equatorial and axial positions exchanged rapidly. A relatively sharp singlet is observed even at −90 °C, indicating that the energy barrier of the process is very low. It must be underlined that at −90 °C the crown ether signal is very broad.

Synthesis of Ph$_3$Si(OMe)$_2^-$K$^+$(18-crown-6) (2). The same procedure as for 3 was applied, but with THF as solvent. Recrystallization from THF gave a 68% yield of 2: mp 76–77 °C; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.9–7.5 and 7.2–7.0 (2 m, 15 H, Ph), 3.51 (s, 24 H, 18-crown-6), 3.21 (s, 6 H, OMe). Anal. Calcd for C$_{32}$H$_{45}$O$_8$SiK: C, 62.03; H, 7.66. Found: C, 61.51; H, 7.61. No ^{29}Si NMR signal was observed in THF or C$_6$D$_6$ as solvent with use of the inverse gate decoupling technique and a 60-s delay (800 scans).

Synthesis of PhSi(OMe)$_4^-$K$^+$(18-crown-6) (4). The same procedure as for 3 was applied: 79% yield; mp 105–108 °C; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.95–7.7 and 7.3–7.05 (2 m, 5 H, Ph), 3.6 (s, 24 H, 18-crown-6), 3.3 (s, 12 H, OMe); ^{29}Si NMR −114.1 ppm. Anal. Calcd for C$_{22}$H$_{41}$O$_{10}$SiK: C, 49.61; H, 7.76. Found: C, 49.42; H, 7.64.

Synthesis of MeSi(OEt)$_4^-$K$^+$(18-crown-6) (13). The same procedure as for 3 was applied, but with MePhSi(OEt)$_2$ and KOEt as starting materials; MeSi(OEt)$_4^-$K$^+$(18-crown-6) is obtained in 45% yield with a 1:1 ratio of MePhSi(OEt)$_2$ and KOEt and in 82% yield with a 1:2 ratio 13 was also prepared from MeSi(OEt)$_3$ and KOEt with use of the general procedure: 78% yield; mp 71–75 °C; ^{1}H NMR (CD$_3$COCD$_3$) δ 4.28 (s + q, 32 H, 18-crown-6 + OCH_2), 1.28 (t, 12 H, CH$_2$CH_3), 0.21 (s, 3 H, SiCH$_3$); mass spectrum (*m*/*e*, assignment) FAB$^+$ 303 (K$^+$, 18-crown-6) FAB$^-$ 223 (MeSi(OEt)$_4$). The complex 13 was not obtained pure enough for analysis. No ^{29}Si NMR signal of MeSi(OEt)$_4^-$ was observed in THF or C$_6$D$_6$ as solvent, with use of the inverse gate decoupling technique and a 60-s delay (800 scans). The polarization transfer technique gave no signal in the pentacoordinate region. With both techniques, MeSi(OEt)$_3$ (−47.1 ppm (C$_6$D$_6$)) is the only signal observed.

Reactions of 2, 3, 5, and 6 with Nucleophiles. To a solution of 2.5 mmol of the silicon derivative was added 5 mmol of the reactant dissolved in the same solvent (Et$_2$O or THF). The reactions were followed by using TLC (10:90) toluene–pentane). After standard workup the crude compound was analyzed by ^{1}H NMR spectroscopy. If necessary, further purification was performed with preparative TLC or column chromatography (silica gel; (5–15):(95–85) CH$_2$Cl$_2$–pentane). The compounds obtained are known and identified by ^{1}H NMR spectra and melting points.

Reactivity Studies. Experimental conditions are given in Tables V and VI.

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[26] Brown, H. C.; McFarlin, R. F. *J. Am. Chem. Soc.* **1958**, *80*, 5372. Brown, H. C.; Sloaf, C. J. *Ibid.* **1964**, *86*, 1079. See also: Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1.

[27] In ref 1 we published two OMe signals. In the pure complex only one signal is observed.