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Pentacoordinated Silicon Anions: Reactivity toward Strong Nucleophiles

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Summary: The reactivity of 18-crown-6 potassium salts of the trifluoromethylphenyl-, difluorodimethylphenyl-, difluorotriphenyl-, and dimethoxytriphenylsiliconates toward strong nucleophiles (RLi, RMgX, H^-, RO^-) is reported and compared to that of the corresponding tetravalent neutral species. Results clearly show enhanced reactivity of the pentavalent species in such nucleophilic reactions.

Our interest in the reactivity of pentacoordinated anionic silicon species toward nucleophiles is derived mainly from three sources:

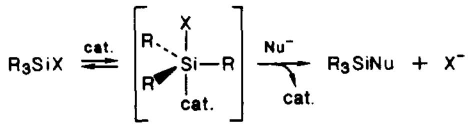
1. Nucleophilic displacements at silicon in tetravalent $R_3Si–X$ compounds can be activated by catalytic amounts of nucleophiles which are good coordinating agents for silicon.[1,2] We have proposed a mechanism in which the rate-determining step is the attack of the nucleophile Nu^- at a pentacoordinated silicon center (Scheme I). Such a process has been also proposed in the case of phosphorus.[3] However, it has been considered controversial since the pentacoordinated center is more sterically hindered and should be less electrophilic than the tetracoordinated one and consequently less susceptible to nucleophilic attack.

2. The activation of organosilicon compounds with F^- is very useful in organic synthesis[5] and group-transfer polymerization reactions.[6]

3. Recent studies conducted on anionic pentacoordinated siliconates of catechol, $RSi(o\text{-}O_2C_6H_4)_2^-NMe_4^+$ (R = Me, Ph, 1-Np), show clearly that pentacoordinated anionic silicon species can undergo nucleophilic attack by hydrides, R′MgX and R′Li.[7]

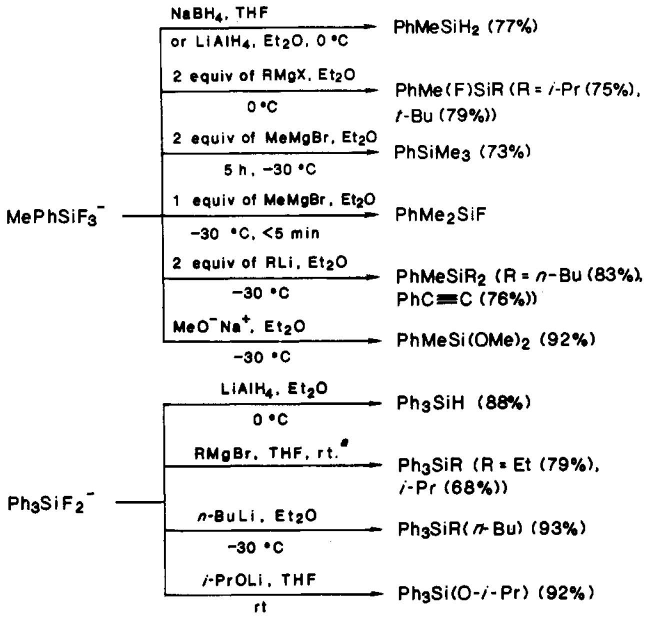
We describe here the reactivity of strong nucleophiles toward the 18-crown-6 potassium salts of the trifluoromethylphenyl- and difluorotriphenylsiliconates, **1** and **2**, respectively. The preparation of salts containing pentacoordinated silicon anions in pure state carried out by Damrauer et al.[8] allows comparison of their chemical behavior with that of the corresponding tetravalent fluorosilanes, **3** and **4**. Compounds **1** and **2** are very reactive.

Scheme I[a]



[a] cat. = F^-, HMPA, $RCOO^-$.

Scheme II



[a] rt = room temperature in this and subsequent schemes.

Table I[a]

run	substrate	nucleophile	half-reaction time, min
1	$PhMeSiF_3^-$ (**1**)	*i*-PrMgBr[b]	<5
			$t_3/t_1 > 150$
2	$PhMeSiF_2$ (**3**)	*i*-PrMgBr[b]	780
3	$PhMeSiF_3^-$ (**1**)	*t*-BuMgBr[b]	<3
			$t_3/t_1 > 100$
4	$PhMeSiF_2$ (**3**)	*t*-BuMgBr[b]	360
5	$Ph_3SiF_2^-$ (**2**)	*i*-PrMgBr[b]	32
			$t_4/t_2 \approx 10$
6	Ph_3SiF (**4**)	*i*-PrMgBr[b]	320
7	Ph_3SiF (18-crown-6)	*i*-PrMgBr[c]	300
8	Ph_3SiF (MgF_2)	*i*-PrMgBr[d]	320

[a] Half-reaction times (determined by ^1H NMR technique with respect to the starting silane) are not precise values; however, the numbers are large enough to leave no doubt to the qualitative difference between the chemical behaviors of **1** and **3** or **2** and **4**. Concentrations of the silicon substrates are identical in each experiment ([substrate] = 0.3 mol L^{-1}, v = 50 mL). [b] Runs 1 and 2: RMgX (2 equiv), Et_2O, -10 °C. Runs 3 and 4: RMgX (2 equiv), Et_2O, 0 °C. Runs 5 and 6: RMgX (2 equiv), THF, room temperature. [c] Run 7: 18-crown-6 (1 equiv), RMgX (2 equiv), THF, room temperature. [d] Run 8: MgF_2 (1 equiv), RMgX (2 equiv), THF, room temperature.

$MePhSiF_3^-$	$Ph_3SiF_2^-$	$PhMeSiF_2$	Ph_3SiF
1	**2**	**3**	**4**

For instance, **1** reacts even with the sterically hindered *i*-PrMgBr or *t*-BuMgBr (2 equiv) to completion within 10 min, leading to PhMe(F)SiR (R = *i*-Pr and *t*-Bu); reaction of **2** with *n*-BuLi (-30 °C, 10 min) leads quantitatively to Ph_3Si(*n*-Bu). Other relevant data are summarized in Scheme II.

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(1) Corriu, R.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 232; *Adv. Organomet. Chem.* **1982**, *20*, 265. Corriu, R.; Guerin, C.; Moreau, J. *Top. Stereochem.* **1982**, *15*, 43.

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(4) Chojnowski, J.; Cypryk, M.; Michalski, J. *J. Organomet. Chem.* **1978**, *161*, C31; Bassindale, A. R.; Stout, T. *Ibid.* **1982**, *238*, C41.

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(6) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. Hertler, W. R.; Sogah, D.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1415. Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Macromol. Sci., Chem.* **1984**, *A21*(8, 9), 943. Sogah, D. Y .; Farnham, W. B. In *Organosilicon and Bioorganosilicon Chemistry (Structure, bonding, reactivity and synthetic application)*; Ellis Horwood Ltd: Chichester, 1985; p 219 and references therein.

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(8) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490.

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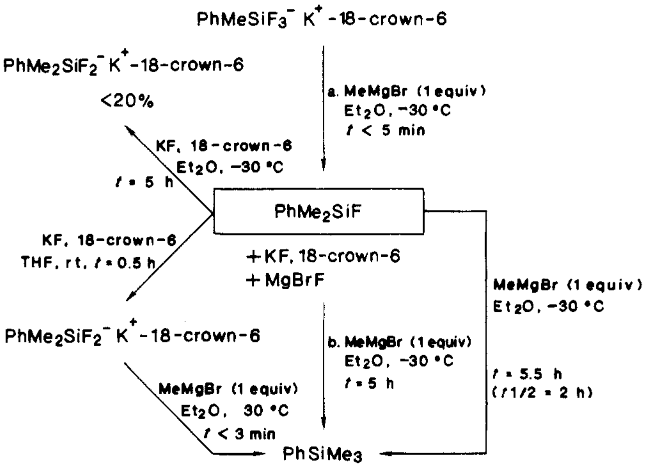
Scheme III



The chemical behavior of 1 and 2 has been compared with that of the corresponding fluorosilanes 3 and 4 using Grignard reagents as nucleophiles; results are summarized in Table I.

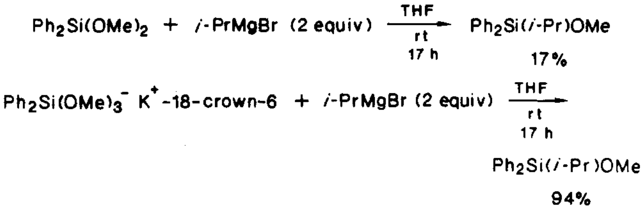
Apparently the pentacoordinated silicon species are more reactive than the tetracoordinated ones, as observed previously.[7,9] Compounds 1 and 2 always react faster than their tetravalent analogues. The larger rate accelerations, i.e., 10–10^2 times faster, are observed with the most hindered nucleophiles. When hydrides ($LiAlH_4$, $LiAlH(OMe)_3$, $LiAlH(O\text{-}t\text{-}Bu)_3$, $(i\text{-}Bu)_2AlH$) are used instead of Grignard reagents, the rates are very fast with both anionic and neutral compounds. A direct comparison is made impossible because of the insolubility of the potassium salts at lower temperatures.

When the reaction was carried out between Ph_3SiF and i-PrMgBr (2 equiv) in THF at room temperature in the presence of 18-crown-6 (Table I, run 7) or of MgF_2 (Table I, run 8), the corresponding half-reaction times are of the same order of magnitude as that measured in run 6; it clearly indicates that the complexing agent or MgF_2 does not alter significantly the reactivity of the Grignard reagent.

Treatment of 1 with 1 equiv of MeMgBr at −30 °C leads to a mixture of the monofunctional $PhMe_2SiF$, MgBrF, and KF,18-crown-6 within 5 min (Scheme III, step a). The subsequent addition of 1 equiv of MeMgBr at −30 °C leads to $PhSiMe_3$ (reaction time 5 h) (Scheme III, step b). Reaction between $PhMe_2SiF$ and KF,18-crown-6 at −30 °C in ether is quite slow (Scheme III, <20% of $PhMe_2SiF_2^-$ K^+-18-crown-6 determined by ^1H NMR after 5 h), indicating that under our experimental conditions (Scheme III, step b), the concentration of the pentavalent species will be always quite low. Reaction between pure $PhMe_2SiF$ and 1 equiv of MeMgBr is also slow and complete only after 5.5 h. In contrast, the reaction of the preformed $PhMe_2SiF_2^-K^+$-18-crown-6 with MeMgBr (1 equiv) in ether at −30 °C leads quantitatively to $PhSiMe_3$ within 3 min. Thus, the above data clearly indicate that the rate enhancement observed either with $PhMe_2SiF_2^-$ and $Ph_3SiF_2^-$ only results from a coordination of the fluoride anion at silicon.

Such an activation is general. For instance, $Ph_2Si(OMe)_3K^+$-18-crown-6[10] is also quite reactive (Scheme IV) and reacts with i-PrMgBr (2 equiv) in THF at room temperature to completion within 2 h; in contrast, 17% of $Ph_2Si(OMe)_2$ is only converted after 17 h under identical conditions.

Scheme IV



In conclusion, we have evidence that nucleophilic attack at pentacoordinated silicon species is a general process. These species may be regarded as possible intermediates in nucleophilic activated substitutions at silicon. Morever, the present data point out the enhanced reactivity of these species that might arise from a greater electropositive character of the pentavalent silicon atom, as suggested also by calculations.[11]

Registry No. 1·k-18-crown-6, 102307-92-6; 2·k-18-crown-6, 47102-67-0; 3, 328-57-4; 4, 379-50-0; $PhMeSiH_2$, 766-08-5; PhMe(F)Si(i-Pr), 111268-12-3; PhMe(F)Si(t-Bu), 111268-13-4; PhMeSi(n-Bu)$_2$, 17903-10-5; PhMeSi(C≡CPh)$_2$, 23024-19-3; PhC≡CLi, 4440-01-1; Ph_3SiH, 789-25-3; Ph_3SiEt, 18666-24-5; Ph_3Si-i-Pr, 111268-14-5; $PhSiMe_3$, 768-32-1; $PhMe_2SiF$, 454-57-9; PhMeSi(OMe), 3027-21-2; $Ph_3Si(n\text{-}Bu)$, 2117-32-0; $Ph_3Si(O\text{-}i\text{-}Pr)$, 1829-43-2; 18-crown-6, 17455-13-9; MgF_2, 7783-40-6; Si, 7440-21-3.

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[9] Boyer, J.; Breliere, C.; Corriu, R.; Kpoton, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1986**, *311*, C39.

[10] $Ph_2Si(OMe)_3^-$ K^+-18-crown-6: mp 89–92 °C; ^1H NMR (δ, CD_3COCD_3) 3.25 (s, 6 H, OCH_3), 3.53 (s, 27 H, OCH_3 + OCH_2), 6.93–7.25 (m, 6 H, Ph), 7.47–7.85 (m, 4 H, Ph). Anal. Calcd for $C_{27}H_{43}O_9SiK$: C, 56.03; H, 7.49. Found: C, 55.53; H, 7.62.

[11] Sogah, D. Y., private communication.

Electrocatalytic Reduction of CO_2 by Associative Activation

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Summary: The complex *cis*-[Os(bpy)$_2$(CO)H][PF_6] (bpy is 2,2′-bipyridine) has been found to be an electrocatalyst for CO_2 reduction in CH_3CN/0.1 M tetra-*n*-butylammonium hexafluorophosphate solution at a Pt working electrode. Under anhydrous conditions CO is the dominant product, but addition of water results in up to 25% formate. Kinetic parameters derived by digital simulation of the cyclic voltammograms under electrocatalytic conditions are consistent with an associative step (k_1) where CO_2 reacts with the di-reduced complex [Os(bpy)$_2$(CO)H]$^-$ to form an intermediate that leads directly to CO or formate. When extended to a series of related complexes, the kinetic data provide the first example of a significant steric effect on CO_2 reduction as demonstrated by a linear correlation between ln k_1 and the cone angle of the cis ligand in the series *cis*-[M(bpy)$_2$(CO)R]$^-$ (M = Os, R = H, Me, or Ph; M = Ru, R = CH_2Ph) where k_1 is the rate constant for the initial second-order reaction between the di-reduced complex and CO_2.

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