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Silicon–nitrogen bond formation by nucleophilic activation of silicon–hydrogen bonds

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Abstract

A method of forming Si–N bonds by dehydro-coupling of Si–H and N–H bonds in the presence of a nucleophilic catalyst is reported. The method is useful for the preparation of silylamines and silazanes and for crosslinking of organometallic polymers.

The potential usefulness of polysilazanes as precursors of silicon nitride (Si_3N_4) or silicon carbonitride [1–8] has prompted studies of new methods of forming Si–N bonds [4,7]. The classical method of forming silanamines involves the aminolysis (or ammonolysis) of Si–Cl bonds, as shown in eq. 1:

$$R_3SiCl + 2\,R'_2NH \longrightarrow R_3NR'_2 + R'_2NH_2Cl \qquad (1)$$

Such reactions give ammonium salts as by-products, and this means that a filtration step is required.

Dehydro-coupling between Si–H and N–H bonds provides an alternative route in which the by-product is dihydrogen, as illustrated in eq. 2:

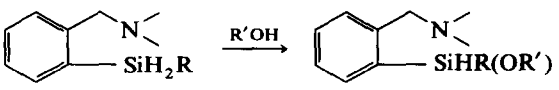
$$R_3SiH + HNR'_2 \longrightarrow R_3SiNR'_2 + H_2 \qquad (2)$$

This reaction is known to be catalyzed by transition metal catalysts [9,10] or by strong bases such as KH [7,11].

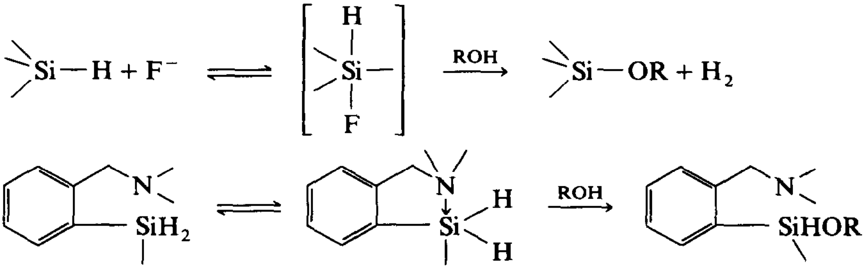
However, recent work in our laboratory revealed that the reactivity of Si–H bonds toward alcoholysis is enhanced by the presence of nucleophilic catalysts [12,13] as shown in eqs. 3–5:

$$PhSiH_2R \xrightarrow{R'OH} \text{no reaction} \qquad (3)$$

$$PhSiH_2R \xrightarrow[F^-]{R'OH} PhSiHR(OR') + PhSiR(OR')_2\ [12] \qquad (4)$$



[13] (5)



Scheme 1

This activation of the Si–H bond which can be inter- or intra-molecular, is attributed to the formation of a pentacoordinate intermediate (Scheme 1) that is more reactive towards nucleophiles than the tetracoordinated species.

As part our program on the synthesis of preceramic polymers we have investigated the reactivity of Si–H bonds towards aminolysis in the presence of fluoride anions. As a model of the reaction we first studied the reaction of secondary amines with various silanes. The catalyst tetrabutylammonium fluoride, as 1 *M* solution in THF (Aldrich), carefully dried over a 4 Å molecular sieve, was added dropwise to the mixture of amine and silane. Under the conditions given in the Table 1 the products obtained were silylamine and unchanged silane; the formation of siloxane was negligible.

The reaction is evidently very sensitive to hindrance in the amine; the order of reactivity based on the turnover frequency (TF = moles product per moles catalyst

Table 1

Aminolysis of silanes catalysed by $^{n}Bu_4NF$

Silane	Amine/temperature	TF [a]	Product [b]	^{29}Si chemical shift (ppm)
$PhMe_2SiH$	Me_2NH (10 equiv.) 0 °C	1	$PhMe_2SiNMe_2$	+0.57
$PhMeSiH_2$	Me_2NH (2.8 equiv.) 0 °C	7.25	$PhMe_2SiHNMe_2$	−7.6 (*J*(SiH) 197 Hz)
	Et_2NH (4 equiv.) 20 °C	4	$PhMe_2SiHNEt_2$	−11.6 (*J*(SiH) 199 Hz)
	$(Me_3Si)_2NH$ (1.2 equiv.) 100 °C	0.75	$PhMe_2SiHN(SiMe_3)$	−20.0 (*J*(SiH) 196 Hz) +4.66
Ph_2SiH_2	Me_2NH (2.8 equiv.) 0 °C	33	$Ph_2SiHNMe_2$	−11.4
	Et_2NH (4 equiv.) 40 °C	1.6	$Ph_2SiHNEt_2$	−14.4 (*J*(SiH) 204 Hz)
	$(Me_3Si)_2NH$ (2 equiv.) 67 °C	10.3	$Ph_2SiHN(SiMe_3)_2$	−24.4 (*J*(SiH) 202 Hz) +5.8
$OctSiH_3$	Me_2NH (4 equiv.) 0 °C	47.5	$OctSiH(NMe_2)_2$	−7.23 (*J*(SiH) 205 Hz)
	Et_2NH (5 equiv.) 40 °C	1.8	$OctSiH_2NEt_2$	−20.1 (*J*(SiH) 197 Hz)
	$(Me_3Si)_2NH$ (2.5 equiv.) 50 °C	15	$OctSiH_2N(SiMe_3)_2$	−28.4 (*J*(SiH) 198 Hz) +2.4

[a] TF = turnover frequency (moles product per moles catalyst per hour). [b] Identified by IR and ^{1}H NMR spectroscopy.

$$\begin{tikzcd}
MeHSiCl_2 \arrow[r, "NH_3"] & (MeHSiNH)_n \arrow[r, "1000\,^\circ C"] \arrow[d, "NH_3/0\,^\circ C" right, "{}^nBu_4NF" right] & \text{Yield } 20\% \ [7] \\
& \text{Insoluble and non-melting product} \arrow[r, "1000\,^\circ C"] & \text{Yield } 48\%
\end{tikzcd}$$

Scheme 2

per hour) is: $Me_2NH > (Me_3Si)_2NH > Et_2NH$. The reactivity of the silanes falls the following sequence: $OctSiH_3 > PhMeSiH_2 > Ph_2SiH_2 > PhMe_2SiH$.

The reaction is selective in the case of dihydrosilanes, only one of the hydrogen atoms being replaced even when an excess of the amine is used. In the case of octylsilane, use of an excess of the amine leads to mono- or di-substitution depending on the amine. Thus dimethylamine gives bis(dimethylamino)octylsilane, whereas diethylamine gives diethylaminooctylsilane. It is noteworthy that under the conditions used there is no reaction when $^nBu_4NF$ is replaced by CsF.

In the field of preceramic polysilazanes this approach has been tested for: (a) the synthesis of polysilazanes; and (b) crosslinking of oligosilazanes, in order to increase the yield of the ceramic in the polymer pyrolysis [1]:

Ammonolysis of methylphenylsilane gives only oligocyclosilazane and no polymer is obtained (eq. 6):

$$MePhSiH_2 \xrightarrow[THF/20\,^\circ C/16\ h]{NH_3/^nBu_4NF} (MePhSiNH)_n \qquad (6)$$

Yield 76%, $\delta(^{29}Si)$ −12.3 ppm, $M_n = 469$, $M_w = 509$. It is noteworthy both of the hydrogeno atoms are displaced by ammonia.

Crosslinking of oligocyclosilazane by ammonia was performed starting from the ammonolysis product of dichloromethylsilane [7], as shown in Scheme 2. This reaction appears to be very efficient for crosslinking of oligocyclosilazanes containing Si−H bonds.

The activation of Si−H bonds through formation of pentacoordinate intermediates allows formation of Si−N bonds. This method is convenient for preparation of functional aminosilanes such as $R_2SiHNR'_2$ or $RSiH_2NR'_2$.

This dehydro-coupling reaction is also useful for the preparation of oligosilazanes and for the low temperature crosslinking of oligosilazanes containing Si−H bonds, and avoids the use of expensive metal catalysts.

A more extensive study of the crosslinking of organometallic polymers containing Si−H bonds is in progress.

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