Some aspects of the reactivity of hypervalent species of silicon in organic synthesis

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Abstract

The nucleophilic activation for nucleophilic displacements at silicon is extensively used in organic synthesis. This process involves pentacoordinated intermediates. The reactivity of pentacoordinated organosilanes, silicates and siliconates (neutral or anionic) is studied. All the examples reported here illustrate the great reactivity of hypervalent species. These species react faster than the corresponding tetracoordinated silanes.

The nucleophilic activation for nucleophilic displacements is a process extensively used at silicon mainly in the uses of organosilanes in synthesis: cleavage and activation of Si-O bonds (ref.1), activation of Si-H (ref.2), Si-C (ref.3), Si-N (ref.4) bonds, all processes performed using F- or HMPA or more generally using nucleophiles having a high affinity towards silicon, as catalysts. The same process was also observed at Phosphorus (ref.5). Since such a process is not known in carbon chemistry, we have proposed a mechanism involving the formation, in a pre-equilibrium, of a pentacoordinated intermediate formed with the nucleophilic catalyst. This step is followed by the nucleophilic attack of the incoming nucleophile in the rate determining step (Scheme 1).

Scheme 1

NUCLEOPHILIC ACTIVATION to
NUCLEOPHILIC SUBSTITUTION

R₃Si - X \rightarrow R₃Si - Nu + X⁻

Cot

\[ X + H, OR, NR₂, Cl \]

Cot = NON-SUBSTITUTING NUCLEOPHILE
(HMPA, F⁻, RCO₂⁻, X⁻)

Scheme 2

NUCLEOPHILIC ACTIVATION of Si-H

\[ FCs \rightarrow FK \]

Very Selective Reduction of CARBONYL GROUP

NO REDUCTION OF \{ C=Hal. Bonds \}

Amido, cyano groups

or R\(\equiv\)C

ABSOLUTE SELECTIVITY FOLLOWING

Aldehydes > Ketones > Esters

Some examples of this mechanism will be given in the following reduction reactions. The activation of Si-H bond by F- is a very efficient and very selective way for the reduction of carbonyl groups. It is possible to reduce a >C=O group without reduction of NO₂, >C=C-, -C≡C-, halo, CN, and -CONH₂ groups. There is also a very selective reduction of 2-Enones in 1-2 position, even with the chalcone (ref.6) (Scheme 2).
The mechanism involves a nucleophilic activation of Si-H bond at
the surface of F- in heterogeneous conditions, or by coordination
of F- in homogeneous conditions, and the attack of carbonyl group
with hydride transfer in the rate determining step.

In order to support this mechanism we have studied the reactivity
of pentacoordinated hydrogenosilanes we have prepared. The Si-H
bond is a very interesting one for comparison since we have
obtained a very good evidence for the formation of pentacoor-
dinated structures in solid state (XR) (ref.7) and in solution
(Si²⁴ NMR)(ref.8). The Si-H bond has a good ability to form
pentacoordinated structures and the hydrogen was always in equato-
rial position (Scheme 3).

Scheme 3

It is well known that the tetravalent dihydrogenosilanes do not
react with alcohols or carboxylic acids, or carbonyl groups. On
the other hand the same reagents are able to substitute the Si-H
bond when the silicon is in a pentacoordinated state. We have even
found the possible hydrosilylation of carbonyl groups (ref.9)
(Scheme 4).

Scheme 4

The reactivity of pentacoordinated hydrogenosilanes support very
well the mechanism we have proposed for the hydrosilylation of
alcohol and carbonyl groups. More generally it was interesting to
consider the reactivity of hypervalent species of silicon towards
nucleophiles. Since recently Damrauer (ref.10) reported a very
good method for the preparation of hypervalent fluorosilanes, it
was possible to perform a direct study. We have observed a very
high reactivity for the trifluorosilicates (Scheme 5) and a faster
reactivity of the pentacoordinated towards the tetracoordinated
ones (Scheme 6).

The same increase of reactivity was also observed in the case of
neutral pentacoordinated species. The case of (IV) is particularly
illustrative since the tri, bi, and monofluorosilanes are penta-
coordinated. The tri-substitution takes place much faster than in
the case of trifluoronaphthysilane (Scheme 7).

We have extended successfully the Damrauer procedures to the
preparation of hypervalent methoxysilanes. These compounds are
very reactive. For instance the pentamethoxysiliconate is hydro-
lysed very quickly giving a gel (Scheme 8).
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![Scheme 5](image)

We have observed once again a higher reactivity for the pentacoordinated silicon (Scheme 9).

The comparison was also performed in the case of neutral species and the reactivity was found always in favour of pentacoordinated silicon (Scheme 10).
The very high reactivity of hypervalent species containing Si-O bonds confirms the possible formation of pentacoordinated silicon in the course of the nucleophilic activation of Si-O bond (activation of enoxysilanes) (ref.1a) (Scheme 11-12).

The formation of hypervalent species was also demonstrated in the case of the polymerisation of the acrylate through the group transfer polymerisation (ref.7). In this case the activating nucleophile activates the Si-O bond and the transfer takes place through an hexacoordinate intermediate (ref.11) (Scheme 13).

Scheme 11

Scheme 13

MICHAEL REACTION EXTENSION

Scheme 12

POLYMERISATION with TRANSFER of SiMe3

PMMA - SOGAH - WEBSTER - FARNHAM - JACS 1831 5706 DUPONT de NEMOURS

PMMA - PBMA - OnBu - SOGAH - FARNHAM - WEBSTER
The activation of Si-C bond by F\(^-\) was reported in the case of the transfer of the allyl group (ref. 12). The mechanism can be either an heterolytic cleavage of Si-O bond or a nucleophilic activation through hyper-coordinated silicon intermediate (Scheme 14).

Scheme 14

In order to check the possible reaction with pentacoordinate silicon, the reactivity of the allyl siliconates having an anionic pentacoordinated structure has been studied. These species react with carbonyl groups. It is possible to perform the reaction in different conditions (ref. 13): without any activation, with electrophilic activation using Zn\(\times\)\(X\), and also with nucleophilic activation (Scheme 15-16).

All these results are in good agreement with the activation of Si-C bond taking place through a nucleophilic activation instead of an heterolytic cleavage of Si-C bond.

Scheme 15

Scheme 16
The higher reactivity of pentacoordinated Si-Cl bond was also observed in the reaction of the organolithium (V) towards Me₂SiCl₂. This reaction gives the exclusive formation of disubstituted product (VII) whatever is the ratio between V and Me₂SiCl₂ (even with a fixed time excess of Me₂SiCl₂). The conclusion is that the mono-substituted pentacoordinated chlorosilanes VI reacts faster with (V) than Me₂SiCl₂. This high reactivity of VI was checked by separated preparation and reaction (Scheme 17).

All these experiments illustrate very well the great reactivity of hypervalent species. They confirm the possibility of pentacoordinated intermediate in the nucleophilic activation, of nucleophilic substitution at silicon. This possibility cannot be ruled out only on the basis of the argumentation of a more crowded and less electrophilic species than tetracoordinated silicon. Furthermore after these results, it becomes interesting to understand why these hypercoordinated species react faster than the tetracoordinated ones. The two possible explanations are one part the increase of the length of Si-X bonds which corresponds to an higher lability and other part the increase of the electrophilicity of the central Si atom (14). The illustration of that is the reactivity observed between dihydrogenosilanes (III) and CS₂ which gives a rearrangement never reported in silicon chemistry. Interestingly the process started with a double hydrosilylation of CS₂ (Scheme 18).

Scheme 17

In order to explain the reaction of (III) with CS₂ we have treated it with molecular S and we have obtained a product (VIII) identified as a silathione stabilized by intramolecular coordination with the NMe₂ group. This product is highly oxidable; it is stable in anaerobic conditions and reacts instantaneously with air, with formation of the trisiloxane (IX) (Scheme 19).

Besides the microanalysis, the spectroscopic arguments supporting the structure of the silathione are:

1) the mass spectrum obtained at two different electronic impacts
2) the H¹ NMR showing a clean diastereotopism of -CH₂- and NMe₂ groups due to the strong coordination of the nitrogen atom to silicon
3) the Si⁴²⁸ chemical shift which is just between the low-valent and hypervalent species chemical shifts (Scheme 20).

The reaction of CO₂ is a very interesting one, we have observed the elimination of H₂C=O and formation of trisiloxane when the reaction is performed in vacuum line, using dry and degased solvents; the mechanism of this reaction is illustrated below (Scheme 21).
The silyl ester of formic acid was obtained by an independent route and its pyrolysis at 120° gives elimination of \( \text{H}_2\text{C}=\text{O} \) and silanone which can be trapped by \((\text{Me}_2\text{SiO})_3\) giving the compound \((\text{X})\). We have extended this reactivity to the case of carboxylic acids. The hydrogenosilanes react very well with formation of aldehydes and trisiloxane (ref.15) (Scheme 22). Schemes 23-24-25 report the results obtained and the selectivity of the reaction.

Scheme 19

Mass Spectrum

\[
\text{Si}_{29} = 22.4
\]

Scheme 20

Scheme 21

Scheme 22

Scheme 23

Scheme 24

Scheme 25

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Another unexpected reaction of pentacoordinated hydrogenosilanes is the very clean hydrogen-halogen exchange; this exchange takes place in very mild conditions (ref. 15) (Scheme 26). We have used this reaction for obtaining a very simple and useful synthesis of aldehydes from acyl chlorides. Scheme 27 reports the main results obtained and the selectivity of the reaction.

Acknowledgement
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REFERENCES
5 G.F. LANNEAU Phosphorus and Sulfur (1986) 27
6 Ref la and Ref. therein.