

Preliminary communication

ENHANCEMENT OF Si–H BOND REACTIVITY IN PENTACOORDINATED STRUCTURES

J. BOYER, C. BRELIERE, R.J.P. CORRIU, A. KPOTON, M. POIRIER and G. ROYO

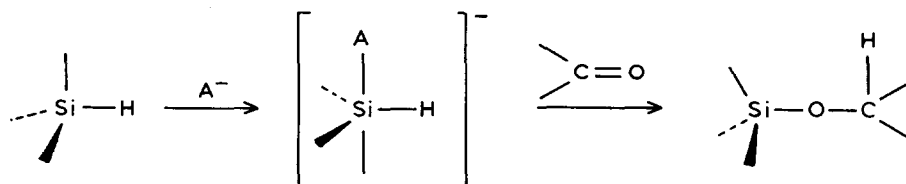
Institut de Chimie Fine, Hétérochimie et Amino-acides, UA 1097, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cedex (France)

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Summary

The reactions of pentacoordinated silicon dihydrides with alcohols, carboxylic acids and carbonyl compounds have been studied. The dihydrides are markedly more reactive than the corresponding tetraordinated species.

In previous communications, we have described the coordination of an internal amine nucleophile in hydrogenosilanes [1]. In all cases the X-ray structure shows apical coordination of the chelating nitrogen atom with H atoms occupying equatorial positions in a trigonal bipyramid [2]. In solution the ^{29}Si NMR signals are shifted upfield by comparison with the normal range for tetrahedral structures, confirming that the pentacoordination persists [3]. Furthermore in the presence of activating nucleophiles (F^- , for instance) the Si–H bond becomes a good reducing agent for carbonyl groups [4,5], and we interpreted this in terms of a nucleophilic activation mechanism [6].



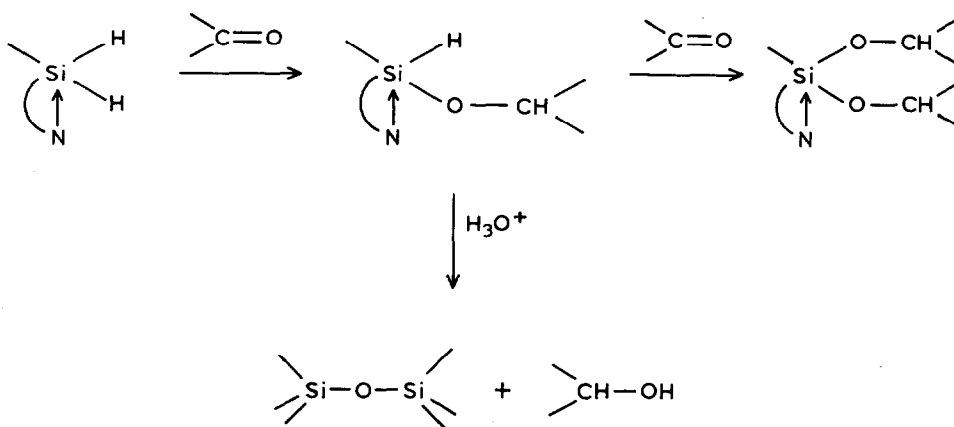
We describe here experiments which reveal an increase in Si–H reactivity towards nucleophiles in pentacoordinated structures compared with that in tetraordinated analogues.

TABLE 1

REACTIONS OF SILICON DIHYDRIDES WITH ALCOHOLS AND CARBOXYLIC ACIDS 1, 2 AND 3

Compound	Reagent (excess)	Conditions (°C/time)	Product ^a	Yield (%)
1	MeOH	60/48 h	Ar ¹ (Ph)SiH(OMe)	25
1	MeOH	60/ 8 days	Ar ¹ (Ph)SiH(OMe)	60
2	MeOH	25/ 1 h	Ar ² (Ph)SiH(OMe)	100
2	MeOH	70/12 h	Ar ² (Ph)Si(OMe) ₂	100
2	1-Menthol	70/ 4 h	Ar ² (Ph)SiH(OMen)	75
2	PhCOOH (1 equiv.)	25/ 1 h	Ar ² (Ph)SiH(OCO-Ph)	100
2	PhCOOH (2 equiv.)	25/ 1 h	Ar ² (Ph)Si(OCOPh)	100
3	MeOH	25/12 h	Ar ³ (α-Np)Si(OMe) ₂	94
3	Me ₂ CHOH	70/48 h	Ar ³ (α-Np)SiH(OCHMe ₂)	88
3	t-BuOH	60/72 h	Ar ³ (α-Np)SiH(O-t-Bu)	25
3	1-Menthol	70/48 h	Ar ³ (α-Np)SiH(OMen)	75
3	CH ₃ COOH (1 equiv.)	25/ 1 h	Ar ³ (α-Np)SiH(OCOMe)	97
3	CH ₃ COOH (2 equiv.)	25/ 1 h	Ar ³ (α-Np)Si(OCOMe) ₂	85
5	MeOH	70/48 h	no reaction	
5	MeOH, Et ₃ N	70/48 h	no reaction	
5	CH ₃ COOH	80/80 h	no reaction	
5	CH ₃ COOH + PhCH ₂ N(CH ₃) ₂	25/ 1 h	degradation	

^a Ar¹ = 8-*N,N*-dimethylamino-1-naphthyl; Ar² = 8-(*N,N*-dimethylaminomethyl)-1-naphthyl; Ar³ = 2-(*N,N*-dimethylaminomethyl)phenyl.

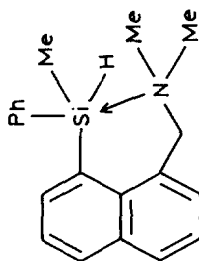


Interestingly, the monohydrogensilane 4 (see Table 2) also reacts with aldehydes although tetracoordinated hydrogensilanes do not react with carbonyl groups even in the presence of a catalyst; we confirmed that the related species α -Np(Ph)SiH₂ does not react with aldehydes even in presence of an amine at room temperature during 17 days.

These results clearly reveal the increase in reactivity associated with extension of the coordination at silicon. The Si-H bond is more reactive in the pentacoordinated than in the tetracoordinated state, and the results support the explanation of Si-H bond activation by F⁻ ions [5,6].

TABLE 2
REACTIONS OF HYDROGENOSILANES TOWARDS CARBONYL GROUPS

Compound	Carbonyl derivative	Conditions (°C/time)	Product	Yield (%)
1	<i>p</i> -NO ₂ C ₆ H ₄ CHO (1 equiv.)	25/12 h	Ar ¹ (Ph)Si(H)OCH ₂ (<i>p</i> -NO ₂ C ₆ H ₄)	100
1	<i>p</i> -NO ₂ C ₆ H ₄ CHO (2 equiv.)	25/15 days	Ar ¹ (Ph)Si(OCH ₂ (<i>p</i> -NO ₂ C ₆ H ₄)) ₂	100
1	<i>p</i> -MeOC ₆ H ₄ CHO (1 equiv.)	25/ 3 days	Ar ¹ (Ph)Si(H)OCH ₂ (<i>p</i> -MeOC ₆ H ₄)	100
2	Fluorenone (1 equiv.)	25/12 h	Fluorenone ^a	100
2	<i>p</i> -NO ₂ C ₆ H ₄ CHO (1 equiv.)	25/12 h	<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ OH	100
2	<i>p</i> -MeOC ₆ H ₄ CHO (1 equiv.)	25/12 h	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	100
	<i>p</i> -MeOC ₆ H ₄ CHO (1 equiv.)	25/12 h	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH + disiloxane	90
5	<i>p</i> -MeOC ₆ H ₄ CHO (1 equiv.)	25/17 days	no reaction	
5	<i>p</i> -MeOC ₆ H ₄ CHO (1 equiv.) + PhCH ₂ N(CH ₃) ₂	25/17 days	no reaction	



(4)

^a After hydrolysis with 4 N HCl.

Interestingly the silanes **1** and **4**, in which Si-H bonds are in equatorial positions [2], react more quickly with carbonyl groups than hydrogenated silatranes in which the Si-H bond is in an apical position (100% reduction at room temperature in 12 h compared with 25% at 140°C in 72 h) [8]. The relative configuration of the Si-H bond and the coordinated nucleophile seems to have a very important influence on the reactivity [9,10].

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