

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

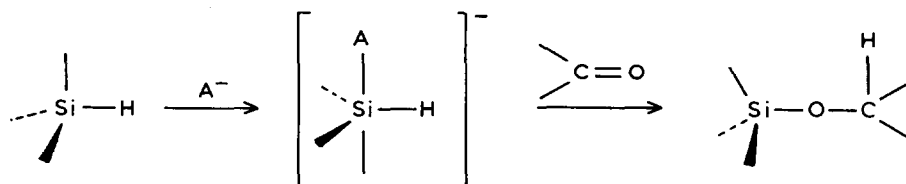
Institut de Chimie Fine, Hétérochimie et Amino-acides, UA 1097, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cedex (France)

(Received June 2nd, 1986)

Summary

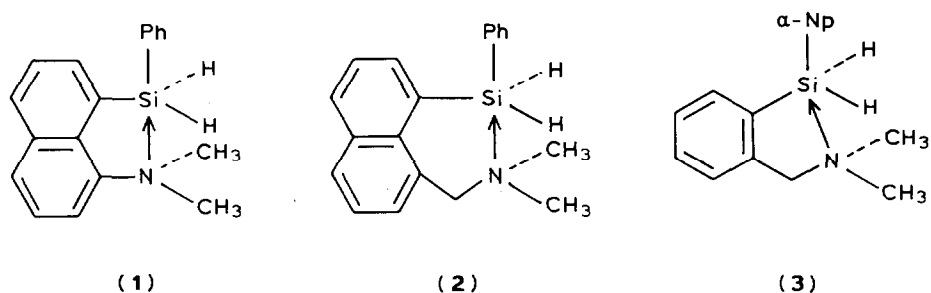
The reactions of pentacoordinated silicon dihydrides with alcohols, carboxylic acids and carbonyl compounds have been studied. The dihydrides are markedly more reactive than the corresponding tetracoordinated species.

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].



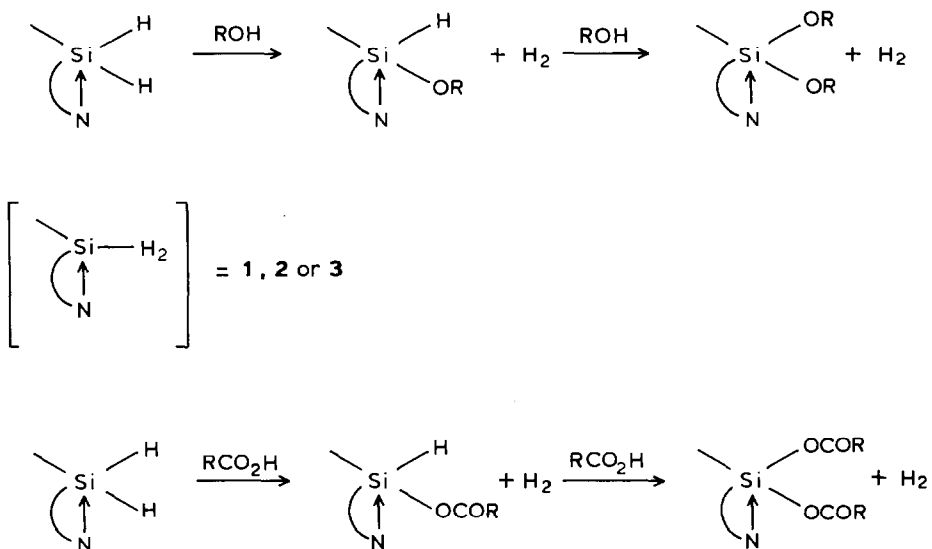
We describe here experiments which reveal an increase in Si–H reactivity towards nucleophiles in pentacoordinated structures compared with that in tetracoordinated analogues.

The silicon hydrides **1**, **2** and **3** were selected for these studies because they have been shown to be pentacoordinate species by X-ray structure or ^{29}Si NMR analysis.



The trigonal bipyramidal geometry is well defined, with Si-H bonds occupying equatorial positions.

Alcohols and carboxylic acids react with silicon dihydrides to form alkoxy- or acyloxy-silanes with evolution of hydrogen (see Table 1).



We confirmed that CH_3COOH or CH_3OH do not react under the same conditions with the corresponding tetracoordinated dihydrogensilanes: $\alpha\text{-Np(Ph)SiH}_2$ (**5**) (Table 1); even in the presence of added amine no reaction occurred. There are however, some reports of amine catalysis of the reactions of alcohols with hydrogensilanes [7].

Very interestingly, the pentacoordinate species react even with bulky alcohols such as isopropyl alcohol and 1-menthol.

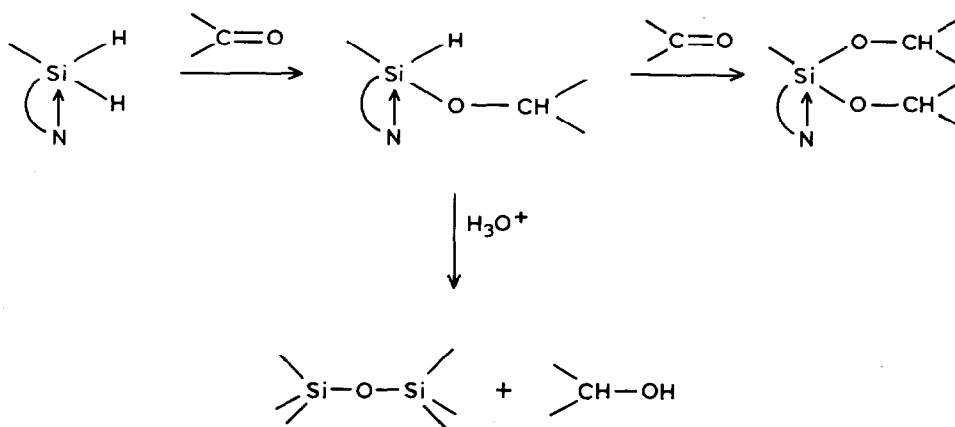
We also studied the reactivity of **1**, **2** and **3** towards carbonyl groups. Compound **3** does not react, but dihydrogensilanes **1** and **2** hydrogenate aldehydes and ketones without any catalyst (Table 2).

TABLE 1

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

Compound	Reagent (excess)	Conditions ($^{\circ}\text{C}/\text{time}$)	Product ^a	Yield (%)
1	MeOH	60/48 h	$\text{Ar}^1(\text{Ph})\text{SiH}(\text{OMe})$	25
1	MeOH	60/ 8 days	$\text{Ar}^1(\text{Ph})\text{SiH}(\text{OMe})$	60
2	MeOH	25/ 1 h	$\text{Ar}^2(\text{Ph})\text{SiH}(\text{OMe})$	100
2	MeOH	70/12 h	$\text{Ar}^2(\text{Ph})\text{Si}(\text{OMe})_2$	100
2	1-Menthol	70/ 4 h	$\text{Ar}^2(\text{Ph})\text{SiH}(\text{OMen})$	75
2	PhCOOH (1 equiv.)	25/ 1 h	$\text{Ar}^2(\text{Ph})\text{SiH}(\text{OCO-Ph})$	100
2	PhCOOH (2 equiv.)	25/ 1 h	$\text{Ar}^2(\text{Ph})\text{Si}(\text{OCOPh})$	100
3	MeOH	25/12 h	$\text{Ar}^3(\alpha\text{-Np})\text{Si}(\text{OMe})_2$	94
3	Me_2CHOH	70/48 h	$\text{Ar}^3(\alpha\text{-Np})\text{SiH}(\text{OCHMe}_2)$	88
3	t-BuOH	60/72 h	$\text{Ar}^3(\alpha\text{-Np})\text{SiH}(\text{O-t-Bu})$	25
3	1-Menthol	70/48 h	$\text{Ar}^3(\alpha\text{-Np})\text{SiH}(\text{OMen})$	75
3	CH_3COOH (1 equiv.)	25/ 1 h	$\text{Ar}^3(\alpha\text{-Np})\text{SiH}(\text{OCOMe})$	97
3	CH_3COOH (2 equiv.)	25/ 1 h	$\text{Ar}^3(\alpha\text{-Np})\text{Si}(\text{OCOMe})_2$	85
5	MeOH	70/48 h	no reaction	
5	MeOH, Et_3N	70/48 h	no reaction	
5	CH_3COOH	80/80 h	no reaction	
5	$\text{CH}_3\text{COOH} + \text{PhCH}_2\text{N}(\text{CH}_3)_2$	25/ 1 h	degradation	

^a $\text{Ar}^1 = 8\text{-}N,N\text{-dimethylamino-1-naphthyl}$; $\text{Ar}^2 = 8\text{-}(N,N\text{-dimethylaminomethyl})\text{-1-naphthyl}$; $\text{Ar}^3 = 2\text{-}(N,N\text{-dimethylaminomethyl})\text{phenyl}$.

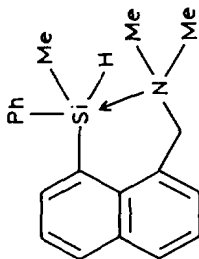


Interestingly, the monohydrogensilane 4 (see Table 2) also reacts with aldehydes although tetracoordinated hydrogensilanes do not react with carbonyl groups even in the presence of a catalyst; we confirmed that the related species $\alpha\text{-Np}(\text{Ph})\text{SiH}_2$ does not react with aldehydes 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].

References

- 1 J. Boyer, R.J.P. Corriu, A. Kpton, M. Mazhar, M. Poirier and G. Royo, *J. Organomet. Chem.*, 301 (1986) 131.
- 2 C. Brelière, F. Carré, R.J.P. Corriu, M. Poirier and G. Royo, *Organometallics*, 5 (1986) 388.
- 3 B.J. Helmer, R. West, R.J.P. Corriu, M. Poirier, G. Royo and A. de Saxcé, *J. Organomet. Chem.*, 256 (1983) 295.
- 4 J. Boyer, R.J.P. Corriu, R. Perz and C. Reyé, *Tetradron*, 37 (1981) 2165; J. Boyer, R.J.P. Corriu, M. Poirier and C. Reyé, *Synthesis*, 7 (1981) 558.
- 5 J.L. Fry and M.A. Mc Adam, *Tetradron Lett.*, 25 (1984) 5859.
- 6 R.J.P. Corriu, R. Perz and C. Reyé, *Tetradron*, 39 (1983) 999 and ref. therein.
- 7 E. Lukevics and M. Dzintara, *J. Organomet. Chem.*, 271 (1984) 307 and ref. therein.
- 8 M.T. Attar-Bashi, C. Eaborn, J. Venci and D.R.M. Walton, *J. Organomet. Chem.*, 117 (1976) C87.
- 9 J.A. Deiters and R.R. Holmes, Oral communication, Organosilicon symposium Baton Rouge, USA, 1985.
- 10 W.H. Stevenson and J.C. Martin, *J. Amer. Chem. Soc.*, 107 (1985) 6352.