ELSEVIER

Journal of Organometallic Chemistry 655 (2002) 1–6

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Proton catalysis of nucleophilic substitution at pentacoordinate silicon

Alan R. Bassindale [a], Yuri I. Baukov [b], Peter G. Taylor [a,*], Vadim V. Negrebetsky [b,*]

[a] The Chemistry Department, The Open University, Walton Hall, Milton Keynes, Buckinghamshire MK7 6AA, UK
[b] Department of General and Bioorganic Chemistry, Ostrovityanov St., 1, Moscow 117869, Russia

Received 1 June 2001; received in revised form 13 March 2002; accepted 13 March 2002

Abstract

Addition of acid to the pentacoordinate fluorosilane **8**, leads to enhanced exchange of fluorine and loss of diastereotopicity of the silicon methyl groups. A DNMR study of the ^{1}H-NMR spectra suggests a dissociative mechanism involving protonation of the fluorine leaving group. Variable temperature studies suggest that at lower temperatures the tetracoordinate form is favoured.

Keywords: Silicon; Pentacoordinate; Electrophilic; Substitution

1. Introduction

The mechanism of substitution at silicon has interested chemists for many years [1–4]. Most of the research has focussed on nucleophilic mechanisms, particularly for substitution at four coordinate silicon. We have been interested in the mechanism of substitution at pentacoordinate silicon and support a dissociative mechanism, as shown in Scheme 1 [5]. In the inversion process the oxygen–silicon bond of the pentacoordinate species **1** cleaves to give a tetracoordinate species **2**, that undergoes an S_N2 type exchange to give **3** which recoordinates to give the pentacoordinate species **4**. Evidence for this mechanism comes from dynamic NMR studies of the rates of exchange in compounds of the type **5** and **6**. In **5**, the NCH_2 protons are diastereotopic and on going from **2** to **3**, with inversion of configuration, the methyl and the phenyl are exchanged. Thus, if this inversion is slow on the NMR timescale separate peaks will be obtained for each CH_2 proton. However, if inversion is fast, a single time averaged peak will be seen. A similar situation obtains in **6** where the two silylmethyl groups are diastereotopic but can be exchanged on inversion at silicon [6]. A dynamic NMR study of the reaction of **5** (X = Cl) with *N*-methylimidazole (NMI) gave the total rate of NMI exchange (inversion and retention) and the rate of inversion, from which the rate of retentive substitution could also be obtained [5]. Analysis of the kinetics, order of reaction and substituent effects favoured the inversion mechanism shown in Scheme 1. In this paper we report the effect of acids in promoting the inversion of configuration at silicon.

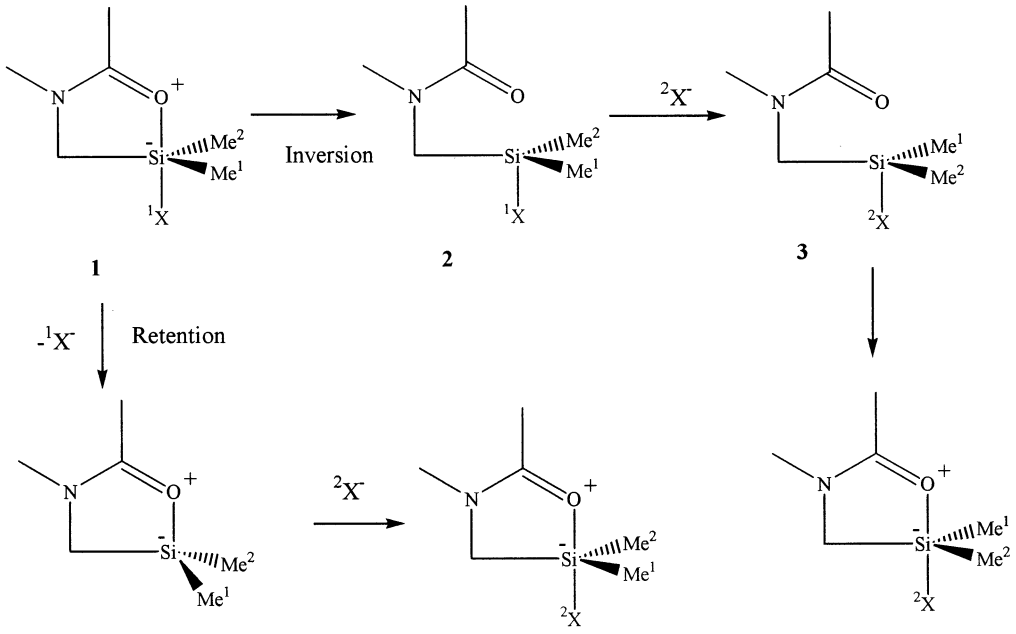
2. Results and discussion

At room temperature the ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra of **7** all exhibit doublets for the $SiMe_2$ group owing to coupling from the fluorine ($^{1}J_{Si-F} = 255$, $^{2}J_{C-F} = 48$, $^{3}J_{HSiF} = 6.8$ Hz). Variable temperature studies between −50 and +50 °C show no changes to the spectrum indicating that exchange of the fluorine is slow on the NMR timescale. However, addition of a drop of hydrofluoric acid leads to complete loss of coupling for all nuclei.

This exchange could arise from electrophilic catalysis by the proton or nucleophilic catalysis by fluoride ion. At room temperature the ^{1}H-, ^{13}C- and ^{29}Si-NMR spectrum of the $SiMe_2$ group in **8** also exhibit coupling from the fluorine ($^{1}J_{Si-F} = 248$, $^{2}J_{C-F} = 41$, $^{3}J_{HSiF} = 4.9$

* Corresponding author. Tel.: +44-1908-652512; fax: +44-1908-858327.
E-mail address: p.g.taylor@open.ac.uk (P.G. Taylor).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01395-5



Scheme 1.

Hz), however, if the concentration of **8** is increased the fluorine coupling is lost, although the diastereotopicity is retained. Similar behaviour is observed if the spectra are obtained at higher temperatures. These results suggest that flourine exchange occurs rapidly without inversion at the silicon. The X-ray crystal structure of **8** shows some evidence for dimerisation of the type **9** [6,7]. Thus, one possibility involves a bimolecular mechanism involving a transition state and/or intermediate of the type **9**. However, when the ^{1}H-NMR spectrum is obtained in the presence of the base, proton sponge, loss of fluorine coupling is observed only at higher concentrations and temperatures (ca. 0.4 M, +50 °C). This suggests that loss of the fluorine coupling arises from electrophilic catalysis by trace acid in the sample. We believe that fluorine exchange also occurs via a dissociative mechanism, as shown in Scheme 2. Any protons present in the solution will hydrogen bond with the fluorine increasing the leaving group ability of the fluorine and thus catalysing exchange.

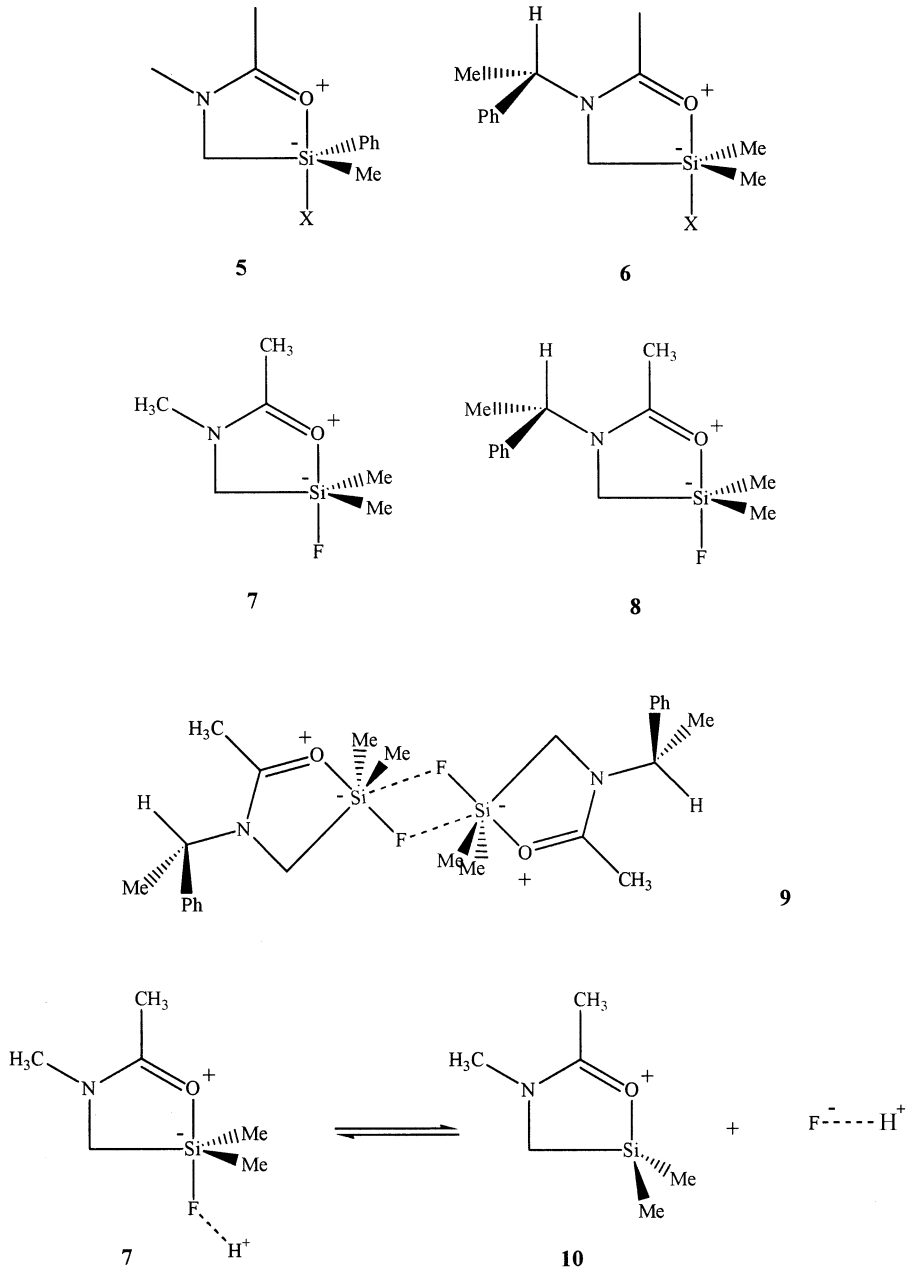
To confirm this mechanism we separately studied the effects of acid and fluoride ion. Addition of tetrabutylammonium fluoride to **8** at room temperature had no effect on the observed fluorine coupling suggesting that nucleophilic exchange of F^- is a minor route. As expected addition of trifluoroacetic acid led to collapse of the doublet arising from the fluorine coupling in the ^{1}H-NMR spectrum. Variable temperature NMR studies, Fig. 1, confirmed that as the concentration of acid is increased the rate of fluorine exchange increases in a regular fashion in accord with an acid catalysed process, as shown in Table 1.

Addition of acid also catalyses the permutational isomerism of the diastereotopic $SiMe_2$ group in **8**. This process is slower than fluorine exchange by a factor of about 100 (Table 1). Variable temperature NMR studies with different concentrations of acid again suggested a simple acid catalysed process, as shown in Table 1. Presumably, this catalysis occurs via protonation of the carbonyl oxygen, increasing its leaving group ability and thus the dissociative process **1** to **2**.

An alternative mechanism for the permutational isomerism involves loss of fluoride as in Scheme 2, but instead of attack of the fluoride on **10** at the face opposite the electronegative group, attack occurs at the face opposite the CH_2 group, as shown in Scheme 3 [6,9]. Route (b) leads to exchange of fluorine without inversion, whereas route (a) after pseudorotation, leads to exchange with inversion. Face attack opposite the more electronegative group is the favoured process such that retentive exchange is the faster process. Route (b) is a minor pathway that is only revealed because it involves inversion at silicon, thus, it does not violate the law of microscopic reversibility.

Use of the Eyring equation gives the activation parameters for the acid catalysed permutational isomerism, as listed in Table 2. These values are very similar to those obtained in the absence of electrophilic catalysis and reflect a common dissociative process [10,11].

The variable temperature studies also revealed some interesting structural changes. Fig. 2 shows how the ^{19}F chemical shift of **8** changes as a function of temperature in the presence of acid. A tetrahedral fluorosilane exhibits a fluorine chemical shift of about −160 ppm,



Scheme 2.

thus *N*-(amidomethyl)-fluorosilanes that involve little silicon oxygen coordination have fluorine chemical shifts in the range −150 to −160 ppm. However, pentacoordinate *N*-(amidomethyl)-fluorosilanes, which involve substantial silicon oxygen coordination have fluorine chemical shifts in the range −110 to −120ppm [12,13]. This is presumably due to a reduction in the silicon–fluorine bond order in pentacoordinate species. At high temperature compound **8** has a fluorine chemical shift of −138 ppm suggesting a reasonable amount of pentacoordination, however, the results in Fig. 1 suggest that on lowering the temperature compound **8** becomes less pentacoordinate. This is confirmed by the ^{29}Si-NMR chemical shift of **8** that changes from −1.7 ppm at 25 °C, to +19.3 ppm at −60 °C. Fully pentacoordinate silicon compounds have ^{29}Si chemical shifts of around −40 ppm, whereas tetracoordinate species have ^{29}Si chemical shifts around +30 ppm again suggesting compound **8** is more pentacoordinate at room temperature than at low temperature [14]. Variable temperature studies show that as the temperature is lowered such a silicon usually becomes more pentacoordinate [15]. This study suggests that preferential coordination of the carbonyl with a proton at low temperatures disfavours coordination with the silicon leading to tetracoordinate silicon.

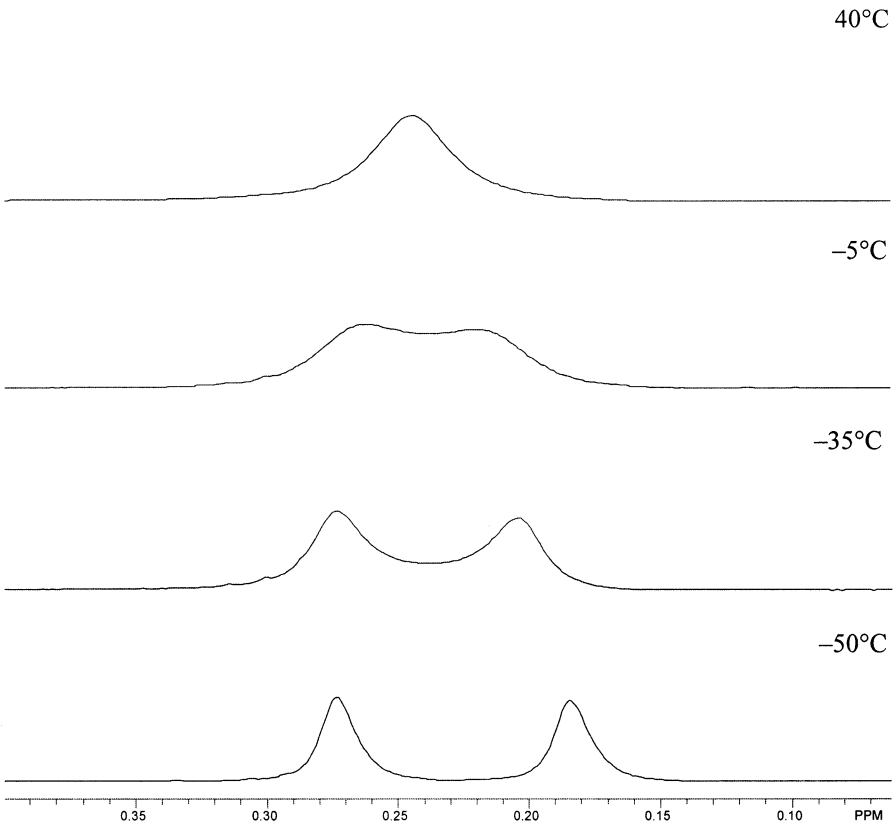


Fig. 1. ^{1}H-DNMR spectra of compound **8** showing the Si(Me)$_2$ resonance at various temperatures (400 MHz, mixture of $CDCl_3$ and CF_3COOH, 1–0.5).

Kummer has suggested that an equilibrium exists between the fully pentacoordinate compound and the tetracoordinate extremes, as shown in Scheme 4 [16,17]. On changing the temperature the position of equilibrium shifts between **7** and **10** or **7** and **11**. Since lowering the temperature leads to a less pentacoordinate species with a larger fluorine–silicon bond order, this suggests the equilibrium would be between **11** and **7**. Nevertheless, throughout the temperature range only one ^{19}F peak was observed. The ^{19}F-NMR chemical shift difference between the species **7** and **11** is estimated to be around 20 ppm, suggesting that exchange between the two species must be very fast if the equilibrium in Scheme 4 were operating.

Table 1
First order rate constants at 298 K obtained by NMR for fluorine exchange and permutational isomerism of **8** in the presence of acid in $CDCl_3$

$[H^+]$, M	k (s) for fluorine exchange	k (s) for permutational isomerism
0.25	120	53.0
0.32	504	48.2
0.43	710	39.1
0.5	–	35.3
2	–	34.0

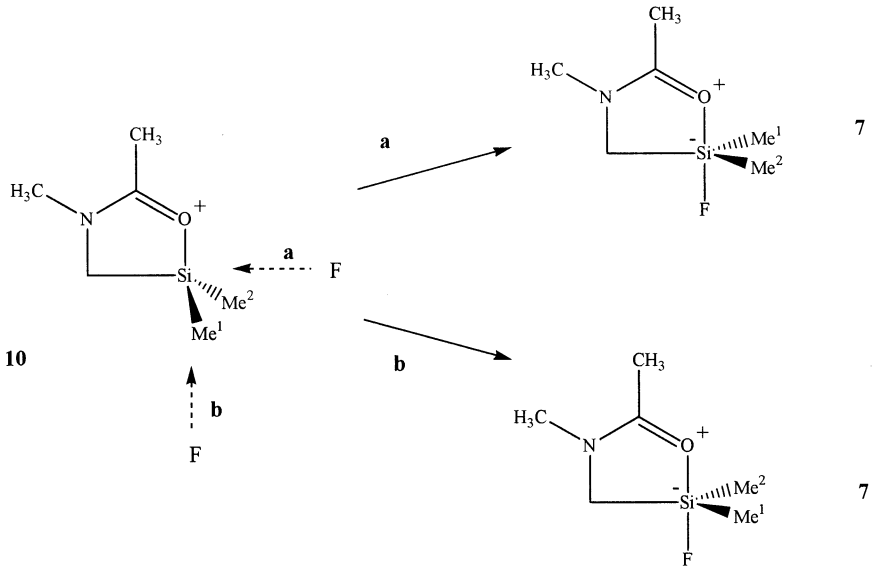
3. Experimental

The preparation and characterisation of compounds **7** and **8** are given in Refs. [18,7], respectively. The ^{1}H-, ^{13}C-, ^{19}F- and ^{29}Si-NMR spectra were recorded on a JEOL JNM-EX400 and Varian XL-400 spectrometer at 399.9, 110.1 and 79.5 MHz, respectively. A standard 5 mm ^{13}C–^{1}H probe head was used. The ^{1}H, ^{13}C and ^{29}Si chemical shifts were measured using Me_4Si as internal references for 0.5 M solutions in deuterochloroform or deuterodichloromethane. The ^{19}F chemical shifts were

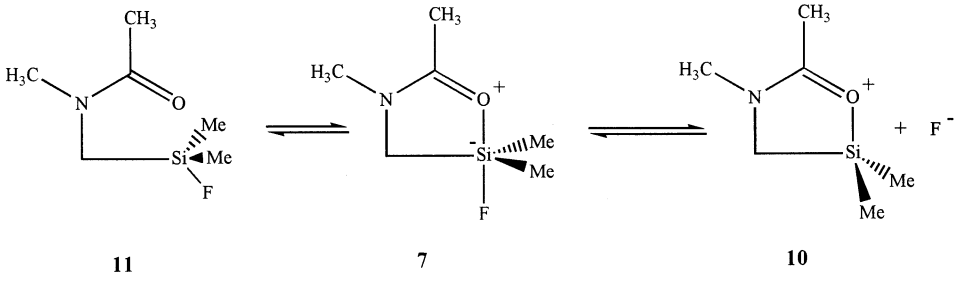
Table 2
Activation parameters for permutational isomerism in compound **8** in $CDCl_3$

$[H^+]$, M	$\Delta G^{\ddagger}$ (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (kcal K^{-1} mol^{-1})
0	> 24		
0 [a]	14.4±0.1	6.7±0.1	−26±8
0.25	14.9±0.1	12.9±0.3	−7±3
0.32	14.6±0.1	12.3±0.2	−10±3
0.43	14.0±0.1	11.9±0.1	−13±6
0.5	13.8±0.1	12.3±0.1	−5±2
2	13.7±0.2	10.5±0.2	−11±3

[a] In the presence of $(Bu)_4N^+F^- \cdot 3H_2O$ (0.01 M.).



Scheme 3.



Scheme 4.

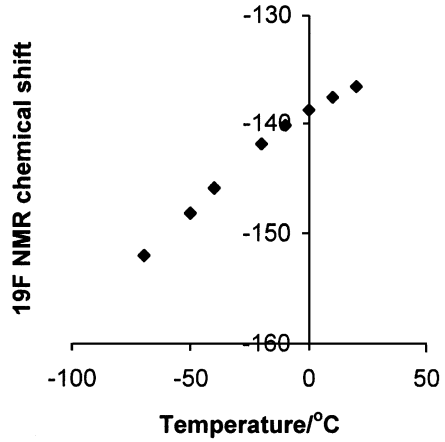


Fig. 2. Plot of the ^{19}F-NMR chemical shift against temperature.

measured using BF_3 as external references. Negative values are to high field.

Coalescence of the separate ^{1}H resonances resulting from diastereotopic $SiMe_2$ groups could be determined visually with a precision of ± 0.5 °C.

Activation parameters for the stereodynamic processes resulting in coalescence of NMR signals were calculated using a DNMR-SIM program [8].

Acknowledgements

This work was financially supported by the Russian Foundation for Basic Research (Project 01-03-32216).

References

[1] L.H. Sommer, Intra-Sci. Chem. Rep. 7 (1973) 1.
[2] R.R. Holmes, Chem. Rev. 90 (1990) 17.
[3] C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371.
[4] A.R. Bassindale, S.J. Glynn, P.G. Taylor, in: Z. Rappaport, Y. Apeloig (Eds.), The Chemistry Chemistry of Organosilicon Compounds, vol. 2 (Part 1), Wiley, Chichester, 1998, pp. 495–511.
[5] A.R. Bassindale, in: B. Marciniec, J. Chojnowski (Eds.), Progress in Organosilicon Chemistry, Gordon and Breach, Basel, 1995, pp. 191–208.
[6] Vad.V. Negrebetsky, A.G. Shipov, E.P. Kramarova, V.V. Negrebetsky, Yu.I. Baukov, J. Organomet. Chem. 530 (1997) 1.

[7] Yu.I. Baukov, Yu.E. Ovchinnikov, A.G. Shipov, E.P. Kramarova, Vad.V. Negrebetsky, Yu.T. Struchkov, J. Organomet. Chem. 536 (1997) 399.
[8] G. Haegele, R. Fuhler, Th. Lenzen, Comp. Chem. 19 (1995) 277.
[9] Vad.V. Negrebetsky, Yu.I. Baukov, Russ. Chem. Bull. 46 (1997) 1807.
[10] A.R. Bassindale, J.C.-Y. Lau, P.G. Taylor, J. Organomet. Chem. 499 (1995) 137.
[11] R.J.P. Corriu, J.C. Young, in: S. Patai, Z. Rappaport (Eds.), The Chemistry Chemistry of Organic Silicon Compounds, vol. 1 (Part 2), Wiley, Chichester, 1989, pp. 1242–1288.
[12] A.R. Bassindale, M. Borbaruah, S.J. Glynn, D.J. Parker, P.G. Taylor, J. Chem. Soc. Perkin Trans. 2 (1999) 2099.
[13] A.R. Bassindale, M. Borbaruah, S.J. Glynn, D.J. Parker, P.G. Taylor, J. Organomet. Chem. 606 (2000) 125.
[14] A.R. Bassindale, M. Borbaruah, J. Chem. Soc. Chem. Comm. (1991) 1499.
[15] D. Kost, I. Kalikhman, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organosilicon Compounds, vol. 2 (Chapter 23), Wiley, New York, 1998, pp. 1339–1445.
[16] D. Kummer, S.C. Chaudhry, J. Seifert, B. Deppisch, G. Mattern, J. Organomet. Chem. 382 (1990) 345.
[17] D. Kummer, S.H. Abdel Halim, Z. Anorg. Allg. Chem. 622 (1996) 1388.
[18] Yu.I. Baukov, O.A. Zamyshlyaeva, S.A. Pogozhikh, E.P. Kramarova, A.G. Shipov, Vad.V. Negrebetsky, Yu.E. Ovchinnikov, Russ. Chem. Bull. 48 (1999) 1796.