

Asymmetric Bis(organylamino)dimethylsilanes - Synthesis and Application

Conny Wiltzsch, Konstantin Kraushaar, Anke Schwarzer and Edwin Kroke

Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg

Introduction

Aminosilanes and silazanes are used as precursors for Si/N-, Si/N/C- or Si/N/C/O-ceramics (e.g. fibers, layers)^[1,2]. Alternatively these compounds may be used for the synthesis of useful molecular and polymeric products. Urea can be synthesized from silylcarbamates^[3]. Asymmetrically substituted bis(organylamino)silanes were synthesized^[4], and their use for the synthesis of urea and silicones by reaction with carbon dioxide was investigated^[5] (Fig. 1).

Aminosilane Synthesis

For the reaction of *n*-propylamine and cyclohexylamine with dichlorodimethylsilane different pathways are possible^[4] (For reaction I, III and V see Tab. 1):

I RNH₂ and R'NH₂ as well as Me₂SiCl₂, were put together in the reaction vessel at once.

II Reaction of Me₂SiCl₂ with RNH₂. No isolation of **2a**. Filtration of the hydrochloride and addition of R'NH₂.

III Reaction of Me₂SiCl₂ and RNH₂ and isolation of compound **2a**, followed by reaction with R'NH₂.

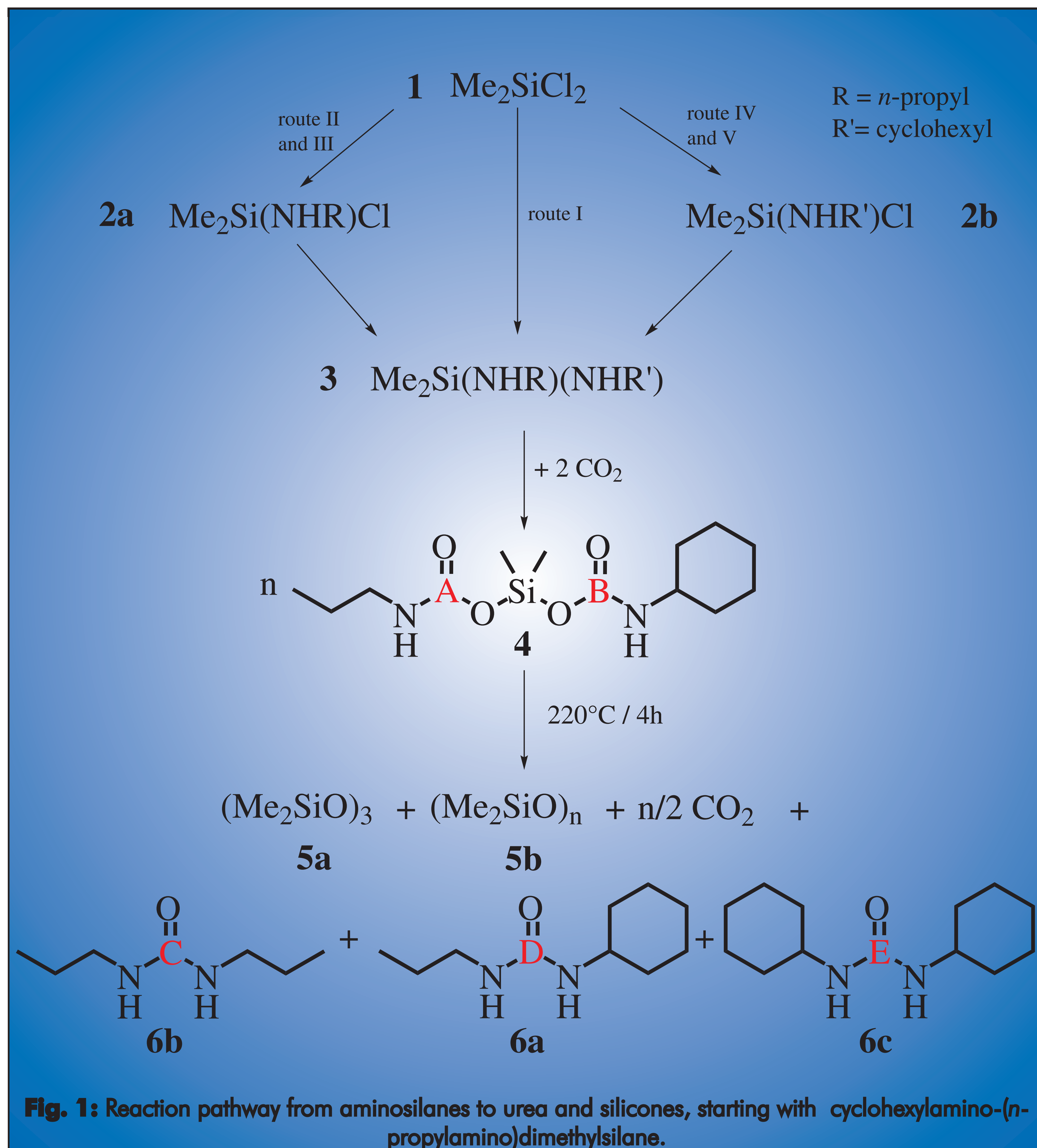
IV Reaction of Me₂SiCl₂ with R'NH₂. No isolation of **2b**. Filtration of the hydrochloride and addition of RNH₂.

V Reaction of Me₂SiCl₂ and R'NH₂, isolation followed by reaction with RNH₂.

Tab. 1 summarize the results of the different pathways. In all cases mixtures of the different possible products are formed.

The question was now, how to separate the three aminosilanes.

In previous work, iso-propylamine instead of cyclohexylamine was used. The boiling points in this case are very close. But distillation of the three products Me₂Si(NHR)₂, Me₂Si(NHR')₂ and the desired product Me₂Si(NHR)(NHR') was successful. In the first fraction the Me₂Si(NHR)₂ was obtained and in the second the asymmetrically substituted aminosilane.



Synthesis of Carbamoyloxysilanes

Bubbling CO₂ into a mixture of the asymmetric aminosilane **3** with THF yields the expected silylcarbamate **4**.

The ¹³C-NMR spectra (Fig. 2) show the two carbonyl-groups appear at ~ 155 ppm. Also elementary analysis proved the generation of cyclohexylcarbamoyloxy(*n*-propylcarbamoyloxy)dimethylsilane.

Thermal Treatment

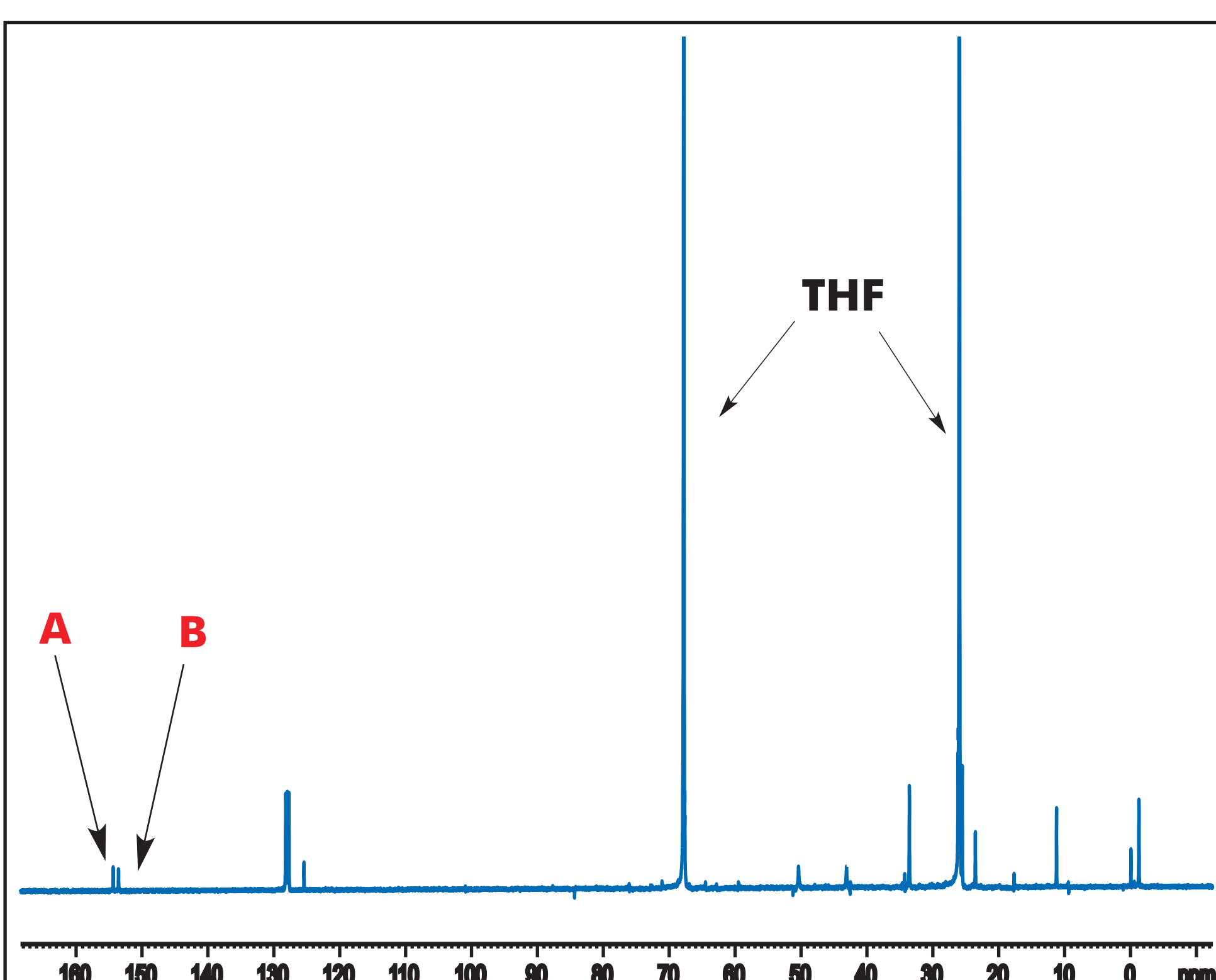
Tab. 2 shows the molecular mass peaks, of the product obtained by the thermal treatment of **4**. All these possible urea **6a**, **6b** and **6c** are detected.

Heating of cyclohexylcarbamoyloxy(*n*-propylcarbamoyloxy)dimethylsilane **4** up to 220°C results in the symmetric, asymmetric urea and the polydimethylsilicone (Fig. 1).

The ¹³C-NMR spectrum (Fig. 3), shows three different signals near 160 ppm. This is the typical region of carbonyl-groups and stand for the three different urea **6a-c** which are generated by thermal treatment.

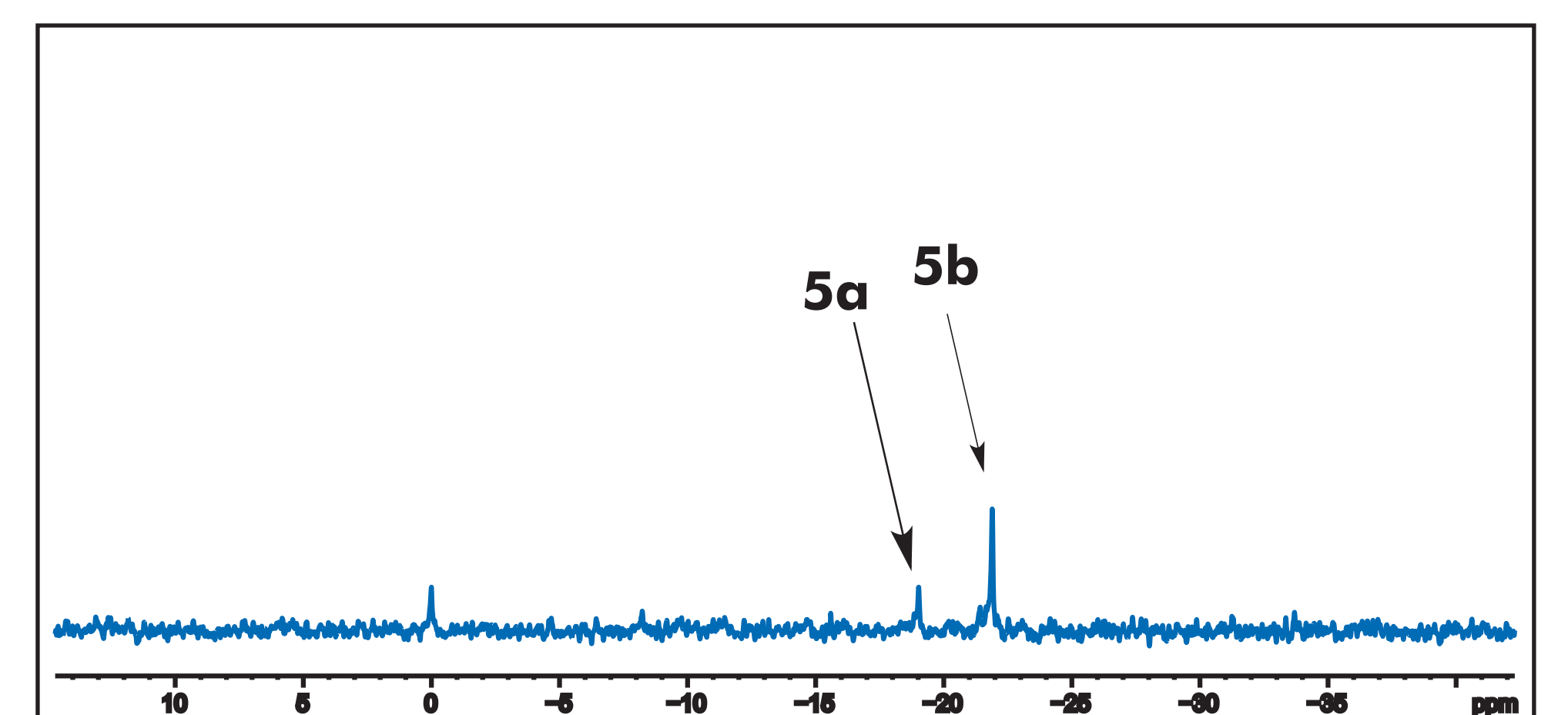
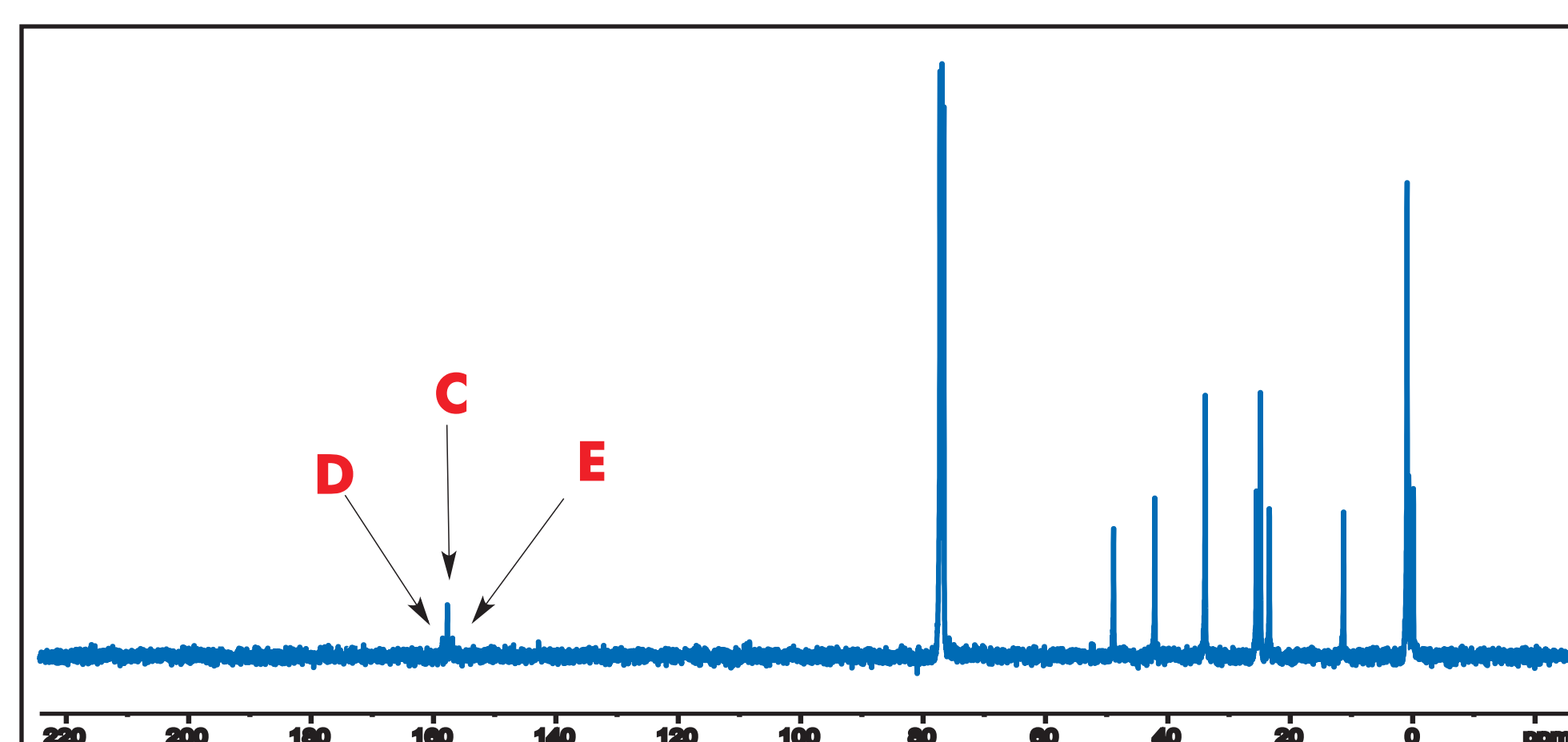
An evidence for the formation of polydimethylsilicone are the two signals at -19 and -21.9 ppm in the ²⁹Si-NMR spectrum (Fig. 4) representing the Si atom typical in **5a** and **5b**.

The urea **6a-c** may be formed during transamination or via intermolecular reaction between two carbamoyloxysilanes (Fig. 1).



Tab. 1: Different pathways for the synthesis of Me₂Si(NHR)(NHR').

rct.	Me ₂ Si(NHR)(NHR')	Me ₂ Si(NHR) ₂	Me ₂ Si(NHR') ₂	Me ₂ Si(NHR)Cl	Me ₂ Si(NHR')Cl
I	0.5	1			
III			1	isolated	
V	0.6	1			isolated



Tab. 2: MS data for 6a-c.

molpeak (m/z)	compound
184	<i>N</i> -propyl- <i>N'</i> -cyclohexylurea
144	<i>N,N'</i> -Dipropylurea
224	<i>N,N'</i> -Dicyclohexylurea

Summary

It was possible to synthesize asymmetrically substituted aminosilanes starting from chlorosilane **1** and addition of the *n*-propyl- and cyclohexylamine. Distillation of the product mixture results in pure cyclohexylamino(*n*-propylamino)dimethylsilane. The reaction with carbon dioxide gave the expected carbamoyloxysilane **4**. The thermal treatment results in three possible urea **6a-c** and siloxanes **5a-b**.

References

[1] M. Jansen, Structure & Bonding, High Performance Non-Oxide Ceramics I. Springer-Verlag, Berlin, Heidelberg, 2002. [2] E. Kroke, Ya-Li Li, C. Konetschny, E. Lecomte, C. Fasel, A. Riedel, Materials Science & Engineering 26, Elsevier April 2000, 97-199. [3] M. J. Fuchter, C. J. Smith, M. W. S. Tsang, A. Boyer, S. Saubern, Chem. Comm. 2008, 2152-2154. [4] U. Wannagat, S. Klemke, Monatshefte Chemie, 110, 1979, 1077-1088. [5] C. Wiltzsch, J. Wagler, G. Roewer, E. Kroke, Patentanmeldung, DE102009045849.2, PCTWO 2011048159 A1 20110428.