Solid-State Molecular Dynamics of (Ph$_3$Si)Si(SiMe$_3$)$_3$ Studied by Variable Temperature ^{13}C and ^{29}Si MAS NMR Spectroscopy

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Summary. One- and two-dimensional ^{13}C and ^{29}Si solid-state NMR experiments at variable temperature demonstrate that crystalline (Ph$_3$Si)Si(SiMe$_3$)$_3$ lacks all molecular symmetry and that internal $2\pi/3$ reorientation of all three crystallographically inequivalent SiMe$_3$ groups in the molecule occurs. Quantitative analysis of one-dimensional MAS NMR spectra and of two-dimensional NMR exchange experiments by spectral lineshape simulations yields exchange rate constants for internal SiMe$_3$ reorientation as a function of temperature. The activation energies determined from these kinetic data are $E_a = 21 \pm 4$, 22 ± 4, and $30 \pm 5\,\mathrm{kJ \cdot mol^{-1}}$ for internal reorientation of the three inequivalent SiMe$_3$ groups in solid (Ph$_3$Si)Si(SiMe$_3$)$_3$.

Keywords. Molecular solid-state dynamics; Solid-state NMR; ^{13}C and ^{29}Si MAS NMR; Exchange rate constants; Spectral lineshape simulations.

Untersuchung der molekularen Dynamik von (Ph$_3$Si)Si(SiMe$_3$)$_3$ im Festkörper mittels ^{13}C- und ^{29}Si-MAS-NMR-Spektroskopie bei variabler Temperatur

Zusammenfassung. Ein- und zweidimensionale ^{13}C- und ^{29}Si-NMR-Experimente am Festkörper bei verschiedenen Temperaturen zeigen, daß kristallines (Ph$_3$Si)Si(SiMe$_3$)$_3$ keine molekulare Symmetrie besitzt und daß interne $2\pi/3$-Reorientierung der drei kristallographisch unterschiedlichen SiMe$_3$-Gruppen auftritt. Quantitative Analyse von eindimensionalen MAS-NMR-Spektren und zweidimensionalen Austauschexperimenten mittels Linienformsimulation ergibt die Geschwindigkeitskonstanten des obengenannten Austauschs als Funktion der Temperatur. Daraus erhält man für die interne Reorientierung der drei nichtäquivalentem SiMe$_3$-Gruppen in festem (Ph$_3$Si)Si(SiMe$_3$)$_3$ die folgenden Aktivierungsenergien: 21 ± 4, 22 ± 4 und $30 \pm 5\,\mathrm{kJ \cdot mol^{-1}}$.

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Introduction

$Si(SiMe_3)_4$ and $C(SiMe_3)_4$ are highly disordered crystalline phases at ambient temperatures, similar to the disordered crystalline phases which exist for several nonpolar, spherically shaped organic molecules such as *e.g.* adamantane [1]. Both compounds undergo structural phase transitions to less disordered low-temperature phases ($Si(SiMe_3)_4$ at $T < 238$ K [2], $C(SiMe_3)_4$ at $T < 213$ K [3]); the molecular dynamic properties of these two low-temperature phases have been investigated by variable temperature ^{13}C and ^{29}Si MAS NMR. The molecular point group symmetry in the low-temperature phases of $Si(SiMe_3)_4$ and $C(SiMe_3)_4$, as inferred from MAS NMR experiments, is C_3 [4–6] and is confirmed by X-ray diffraction analysis [7]. Despite identical molecular symmetry in these two low-temperature phases, the two compounds differ strongly with regard to the dynamic properties of their low-temperature phases. Quantitative analysis of one- and two-dimensional variable temperature ^{13}C and ^{29}Si MAS NMR experiments permits to distinguish and precisely determine exchange rate constants for internal $SiMe_3$ reorientation and for whole-molecule reorientation around preferred molecular axes as a function of temperature. The dynamic solid-state properties of the low-temperature phases of $Si(SiMe_3)_4$ and $C(SiMe_3)_4$ may be briefly summarized as follows. In the low-temperature phase of $Si(SiMe_3)_4$ we observe internal $SiMe_3$ reorientation and additional whole-molecule reorientation; the exchange rate constants for internal $SiMe_3$ reorientation always considerably exceed those for whole-molecule reorientation. The situation is different for solid $C(SiMe_3)_4$: over the entire temperature range of existence of the low-temperature phase, only whole-molecule reorientation is observed, whereas exchange rate constants for internal $SiMe_3$ reorientation are negligibly small [6]. We have interpreted this difference in the solid-state molecular dynamic properties of $Si(SiMe_3)_4$ and $C(SiMe_3)_4$ in relation to higher intramolecular steric crowding in $C(SiMe_3)_4$. This interpretation is qualitatively supported by empirical force-field calculations based on the gas-phase structures of $Si(SiMe_3)_4$ [8] and $C(SiMe_3)_4$ [9].

Here we report on the solid-state dynamic properties of a compound chemically closely related to $Si(SiMe_3)_4$. In $(Ph_3Si)Si(SiMe_3)_3$ (**1**) the molecular symmetry is lowered by chemical substitution as compared to the fully $SiMe_3$ substituted parent molecule. We have investigated the dynamic solid-state properties of **1** by variable temperature one- and two-dimensional ^{13}C and ^{29}Si CP/MAS NMR experiments. The experimental NMR results on **1** are compared to the dynamic properties of the low-temperature phase of $Si(SiMe_3)_4$.

Results and Discussion

Apart from internal reorientation of the methyl groups themselves (which will not be considered in the following) and possible π-flips of the phenyl groups in the $SiPh_3$ moiety, *a priori* there are two modes of molecular dynamics to be considered for solid $(Ph_3Si)Si(SiMe_3)_3$ (**1**):

i) internal reorientation of the individual R_3Si groups ($R = Ph$, Me) around the $R_3Si\text{-}Si_{central}$ bond directions, leading to mutual exchange of the groups R within a SiR_3 unit (referred to as internal reorientation), and

ii) reorientation of the Si(SiMe$_3$)$_3$ moiety around the Ph$_3$Si-Si$_{central}$ bond direction axis, leading to mutual exchange of the three SiMe$_3$ groups as a whole (referred to as Si(SiMe$_3$)$_3$ reorientation).

These two reorientational modes, if present, may occur simultaneously. Our experimental solid-state NMR tools to investigate and possibly distinguish these two reorientational modes consist of one- and two-dimensional variable temperature ^{13}C and ^{29}Si NMR experiments in conjunction with spectral lineshape simulations.

Many solid organosilicon compounds undergo structural phase transitions upon cooling or heating. Differential scanning calorimetry (DSC) of **1** gives no indication for the occurrence of such structural phase transitions in solid **1** in the temperature range of $T = 180$–290 K. Accordingly, observation of temperature dependent spectral lineshapes in ^{13}C and ^{29}Si MAS NMR experiments on **1** cannot be ascribed to the effects of structural phase transitions in this temperature range.

Under MAS conditions, that is at MAS rates sufficiently high to average out all ^{29}Si chemical shielding anisotropies, ^{29}Si MAS NMR spectra of **1** can report on the molecular symmetry of **1** as well as – selectively – on Si(SiMe$_3$)$_3$ reorientational processes, whereas ^{13}C MAS NMR spectra of **1** will be affected by both internal R_3Si and Si(SiMe$_3$)$_3$ reorientation [6]. With this aspect in mind, we first consider the ^{29}Si MAS NMR spectra of **1** (Fig. 1). At $T = 150$ K we observe three barely resolved ^{29}Si resonances ($\delta_{iso} = -9.3, -9.9, -10.2$ ppm), corresponding to three nonequivalent SiMe$_3$ groups, one resonance for the SiPh$_3$ group ($\delta_{iso} = -11.7$ ppm), and one resonance for the central Si atom ($\delta_{iso} = -133.4$ ppm). ^{29}Si CP NMR spectra of **1**, obtained under static conditions, display a ^{29}Si chemical shielding tensor with a large asymmetry parameter ($-\delta_{iso} = \sigma_{iso} = 133.4$ ppm, $\sigma_{11} = 124.0$ ppm, $\sigma_{22} = 132.6$ ppm, $\sigma_{33} = 143.4$ ppm, $\eta = 0.85$) for the resonance of the central Si atom (see Fig. 1). Accordingly, solid **1** lacks all molecular symmetry and, if present, we should be able to detect Si(SiMe$_3$)$_3$ reorientation from one- and two-dimensional variable temperature ^{29}Si MAS NMR experiments. Figure 2a shows the SiMe$_3$/SiPh$_3$ region of the ^{29}Si MAS NMR spectra of **1** in the
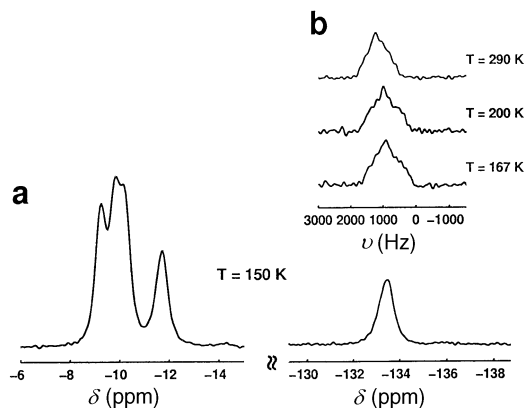

Fig. 1. ^{29}Si CP NMR experiments on **1** ($\omega_0/2\pi = 59.6$ MHz): a) ^{29}Si CP MAS NMR ($\omega_{rot}/2\pi = 4.0$ kHz, $T = 150$ K); b) ^{29}Si CP NMR, static conditions, only the chemical shielding powder pattern of the ^{29}Si resonance of the central Si atom at three different temperatures is shown
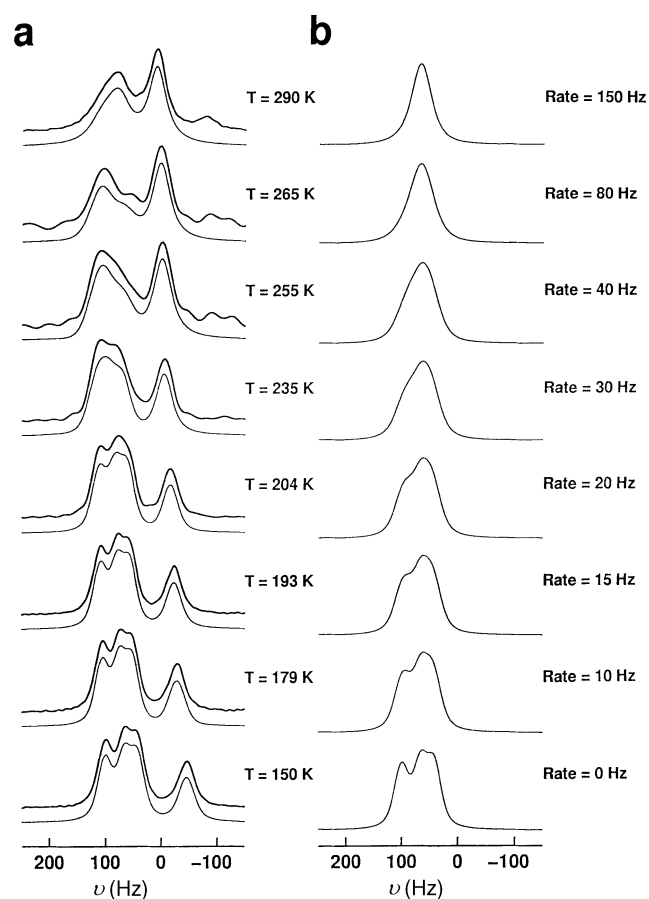
Fig. 2. Variable temperature ^{29}Si CP MAS NMR spectra of **1**; only the SiPh$_3$/SiMe$_3$ region is shown, temperatures are indicated ($\omega_0/2\pi = 59.6$ MHz, $\omega_{rot}/2\pi = 4.0$ kHz): a) upper traces represent experimental spectra, lower traces are the corresponding best-fit calculated spectra, assuming minor intrinsic temperature-dependence of $\delta_{iso}(^{29}\text{Si})$ of the four ^{29}Si resonances of the SiPh$_3$ and SiMe$_3$ groups in **1**; b) calculated hypothetical ^{29}Si MAS NMR spectra of **1**, assuming mutual exchange of the three SiMe$_3$ groups by Si(SiMe$_3$)$_3$ reorientation

temperature range of $T = 150$–290 K. It is tempting to ascribe the minor changes of isotropic chemical shifts in the SiMe$_3$ region, observed as a function of temperature, to Si(SiMe$_3$)$_3$ reorientation around the Ph$_3$Si-Si$_{central}$ bond direction and leading to coalescence of the three ^{29}Si resonances of the three SiMe$_3$ groups at higher temperatures. This explanation can be ruled out by calculating expected exchange broadened ^{29}Si NMR spectral lineshapes for mutual exchange of the three SiMe$_3$ groups in **1** and comparing them to the experimental ^{29}Si MAS NMR spectra. Temperature dependent spectral lineshapes caused by Si(SiMe$_3$)$_3$ reorientation around the Ph$_3$Si-Si$_{central}$ bond direction would have to display an asymmetric shape in the spectral SiMe$_3$ region with a shoulder at higher frequencies at temperatures approaching coalescence (Fig. 2b), whereas the experimentally observed ^{29}Si spectral lineshapes display an inversely asymmetric

shape in this temperature region with an unresolved shoulder towards lower frequencies. Bearing in mind that the entire $SiMe_3$ region in the ^{29}Si MAS NMR spectra of **1** ($\omega_0/2\pi = 59.6$ MHz) only spans a frequency range of approximately 100 Hz and that we consider a temperature range of roughly 150 degrees, it is reasonable to ascribe the observed changes in ^{29}Si spectral lineshapes to minor intrinsic temperature shifts of $\delta_{iso}(^{29}Si)$. With this assumption, the temperature dependent ^{29}Si NMR spectral lineshapes can be well reproduced (Fig. 2a); the simulated spectral lineshapes correspond to intrinsic temperature shifts of $\delta_{iso}(^{29}Si)$ for the $SiMe_3$ and $SiPh_3$ groups in solid **1** of 0.003, 0.006, 0.005 ppm/K ($SiMe_3$) and 0.007 ppm/K ($SiPh_3$). Furthermore, within experimental error the ^{29}Si chemical shielding tensor of the resonance of the central Si atom does not change as a function of temperature (see Fig. 1), and also ^{29}Si 2D EXSY experiments on **1** (data not shown) under MAS ($T = 204$ and 224 K, mixing times of $\tau_{mix} = 4$ and 3 s) and under static conditions ($T = 290$ K, $\tau_{mix} = 5$ s and 50 µs) give no indication for the presence of a molecular dynamic process leading to mutual exchange of the three crystallographically nonequivalent $SiMe_3$ sites in **1**. In short, on the frequency scales accessible by one- and two-dimensional variable temperature ^{29}Si MAS NMR experiments ($10^{-2}–10^3$ s^{-1}) on solid **1**, the molecule in the crystal lattice does not undergo $Si(SiMe_3)_3$ reorientational jumps around the Ph_3Si-$Si_{central}$ bond direction. The absence of this kind of dynamic disorder in solid **1** is in contrast to the dynamic properties of the (chemically) symmetrically substituted derivative $Si(SiMe_3)_4$. For the latter, whole-molecule reorientational jumps do occur at temperatures of $T \approx 170–220$ K with exchange rate constants of the order of $k \approx 10^{-1}–10^2$ s^{-1} [6].

Having established the complete lack of molecular symmetry and the absence of $Si(SiMe_3)_3$ reorientation for solid **1** by means of ^{29}Si MAS NMR, we may next inspect the solid-state dynamic properties of **1** as seen by one- and two-dimensional variable temperature ^{13}C MAS NMR. The lack of molecular symmetry for **1** leads us to expect up to eighteen resonances in the phenyl region and nine resonances in the methyl region of the ^{13}C MAS NMR spectrum of **1**. Not so surprisingly, even at $T = 150$ K (Fig. 3) these multiple carbon sites are only
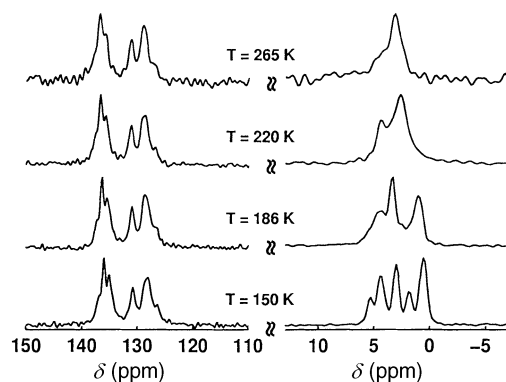

Fig. 3. ^{13}C CP MAS NMR spectra of **1** ($\omega_0/2\pi = 75.5$ MHz, $\omega_{rot}/2\pi = 4.0$ kHz) at different temperatures; left column displays ^{13}C-phenyl spectral region, right column ^{13}C-methyl spectral region

partially resolved in the ^{13}C MAS NMR spectrum ($\omega_0/2\pi = 75.5\,MHz$). As far as the phenyl-$^{13}C$ region is concerned, hardly any changes are observed in the ^{13}C MAS NMR spectra of **1** as a function of temperature. On the timescale of one-dimensional ^{13}C MAS NMR experiments in the temperature range of $T = 150$–$290\,K$, we have no indication for the occurrence of either reorientation of the SiPh$_3$ group around the Ph$_3$Si-Si$_{central}$ bond direction or for π-flips of the individual phenyl groups in the SiPh$_3$ moiety. A different situation is found for the methyl-^{13}C region for which we do observe a strong temperature dependence in the ^{13}C MAS NMR spectra of **1** (Fig. 3). The only remaining possible dynamic process to account for these temperature dependent ^{13}C MAS NMR effects is internal $2\pi/3$ reorientation of the three crystallographically inequivalent SiMe$_3$ moieties in solid **1**. Given the incomplete spectral resolution in the methyl-^{13}C region of these ^{13}C MAS NMR spectra, it would be a rather hopeless task to immediately attempt quantitative analysis of these spectral lineshapes in terms of exchange rate constants of internal SiMe$_3$ reorientation as a function of temperature by means of spectral lineshape simulations. There are too many unknown parameters, such as the unknown assignment of the nine incompletely resolved ^{13}C resonances into groups of three, each group representing one SiMe$_3$ unit. Furthermore, with the three SiMe$_3$ groups in solid **1** being crystallographically inequivalent, these three SiMe$_3$ moieties do not necessarily have to undergo internal SiMe$_3$ reorientation with identical exchange rate constants k, k', and k''. Unequal exchange rate constants of internal $2\pi/3$ reorientation for crystallographically inequivalent ^tBu groups in a Si$^tBu_3$ moiety [10] or SiMe$_3$ groups in a C(SiMe$_3$)$_3$ unit [11] have previously been observed.

Here we can take advantage of 2D ^{13}C MAS NMR EXSY experiments. As an example, the contour plot of a two-dimensional ^{13}C MAS NMR exchange experiment of **1** at $T = 169\,K$ and with a mixing time $\tau_{mix} = 250\,ms$ is displayed in Fig. 4. 2D ^{13}C EXSY experiments on **1**, obtained with different mixing times τ_{mix} and at various different temperatures, permit unambiguous assignment of the
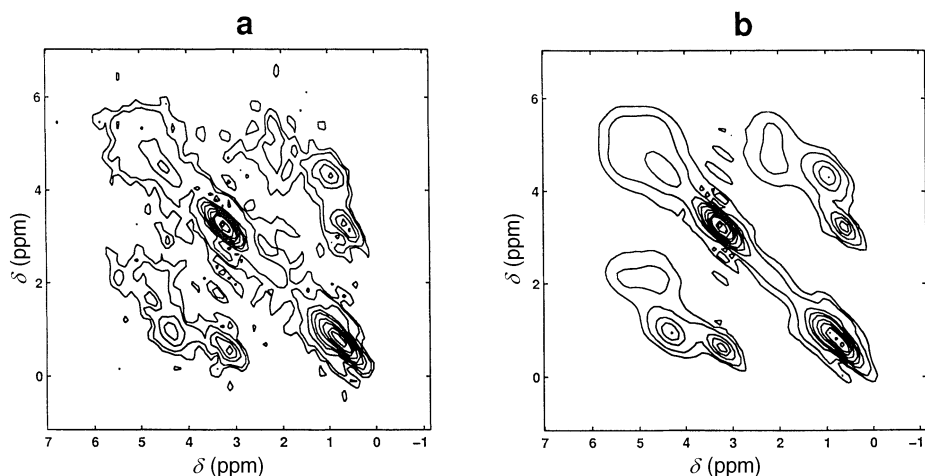

Fig. 4. Contour plots of 2D ^{13}C MAS EXSY spectra of **1** ($T = 169\,K$, $\tau_{mix} = 250\,ms$); only the ^{13}C-methyl region is shown; a) experimental spectrum, b) best-fit simulated spectrum

methyl-^{13}C spectral region into three groups of three methyl-^{13}C resonances, each representing one SiMe$_3$ group. We already know that the only molecular dynamic process we have to take into account for **1** is internal $2\pi/3$ SiMe$_3$ reorientation. Accordingly, off-diagonal peaks in the methyl-^{13}C spectral region in 2D ^{13}C EXSY spectra of **1** can only occur between methyl-^{13}C resonances belonging to methyl groups within the same SiMe$_3$ group. Careful inspection of 2D ^{13}C EXSY spectra of **1** (Fig. 4) reveals these "3 × 3 assignment connectivities" and thus provides valuable information input for subsequent spectral lineshape simulations of the one-dimensional variable temperature ^{13}C MAS NMR spectra of **1**. Beyond this assignment aspect from 2D ^{13}C EXSY spectra of **1**, differing relative off-diagonal intensities for ^{13}C-methyl resonances belonging to different SiMe$_3$ groups directly and clearly indicate unequal exchange rate constants k, k', and k'' for internal $2\pi/3$ SiMe$_3$ reorientation of the three crystallographically inequivalent SiMe$_3$ groups in solid **1**.

Most commonly, 2D ^{13}C EXSY experiments are carried out at temperatures low enough to be able to operate in the so-called slow-exchange regime. In this regime, exchange rate constants of the dynamic process under consideration are small enough to allow to take into account only exchange occuring during the mixing time of the two-dimensional NMR experiment and to neglect all motion occuring during the evolution and detection period. 2D ^{13}C EXSY NMR data obtained in this slow-exchange regime yield exchange rate constants in a straightforward manner directly from the relative integrated intensities of off-diagonal peaks as a function of the mixing time τ_{mix}; there is no need for a full simulation of the two-dimensional NMR experiment in order to extract kinetic parameters. For ^{13}C NMR experiments on solid **1**, this slow-exchange regime is only reached at inconveniently low temperatures ($T < 160$ K). Hence, 2D ^{13}C EXSY experiments on **1** have to be obtained in the so-called intermediate-exchange regime where exchange occuring during the evolution and detection period can no longer be neglected for meaningful analysis. In order to extract exchange rate constants from 2D ^{13}C EXSY experiments carried out in the intermediate-exchange regime, a full simulation of the two-dimensional NMR experiment, including the effects of exchange occuring during evolution and detection period, is necessary. Methods to fully analyze and simulate such experimental 2D EXSY data have been described in detail in the literature [12]; the contour plot of the best-fit simulated 2D ^{13}C EXSY spectrum of **1** is shown in Fig. 4b in comparison to the contour plot of the corresponding experimental spectrum. Qualitatively, it is obvious from inspection of the 2D ^{13}C EXSY experiment that internal SiMe$_3$ reorientation for one of the three SiMe$_3$ groups in **1** occurs at a lower exchange rate than for the other two SiMe$_3$ groups in the molecule. Of course, full simulation of such intermediate-regime 2D ^{13}C EXSY experiments yields exchange rate constants.

Based on the 2D ^{13}C EXSY information (signal assignment as well as knowing that internal SiMe$_3$ reorientation of one of the three SiMe$_3$ groups occurs at a considerably slower rate than for the other two SiMe$_3$ groups), we can now proceed and simulate the one-dimensional variable temperature ^{13}C MAS NMR exchange broadened lineshapes in terms of exchange rate constants of internal SiMe$_3$ reorientation. Formally, the exchange broadened lineshapes can be described as a superposition of three (independent) three-site exchange processes. The results
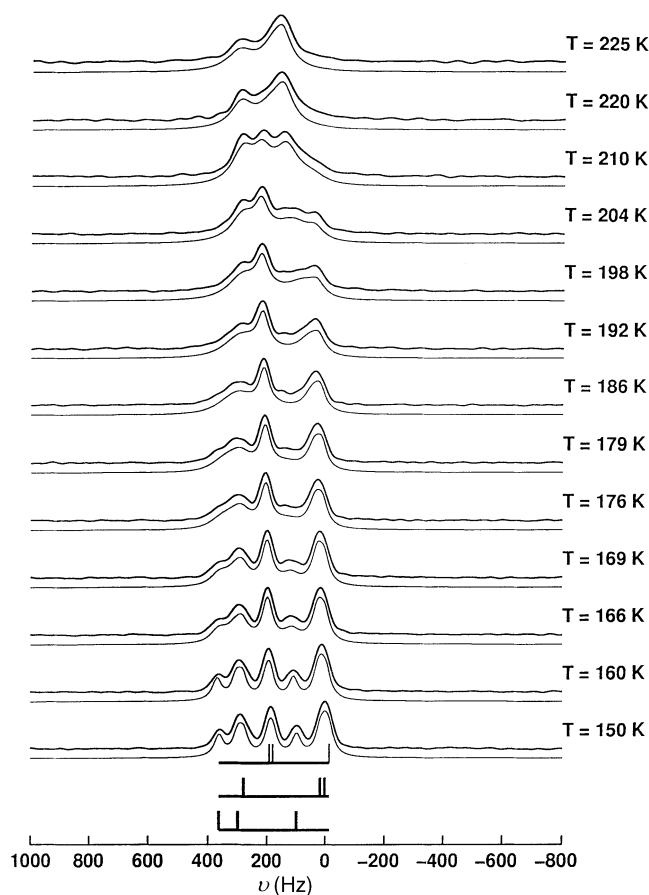
Fig. 5. Variable temperature ^{13}C MAS NMR spectra of **1**; only the ^{13}C-methyl region is shown and temperatures are indicated. Upper traces represent experimental spectra, lower traces are the corresponding best-fit calculated spectra; the bar code at the bottom indicates assignment of the ^{13}C-methyl resonances into groups of three, each group representing one SiMe$_3$ group; the smaller linewidth of the bars for one SiMe$_3$ group indicates slower exchange than for the other two SiMe$_3$ groups (see also Fig. 6)

of this iterative fitting procedure are shown in Fig. 5 where the ^{13}C-methyl region of experimental ^{13}C MAS NMR spectra of **1** in the temperature range of $T = 150-225\,\text{K}$ is compared to the best-fit calculated spectral lineshapes. The semilogarithmic plot of exchange rate constants *vs.* T^{-1} in Fig. 6 summarizes the exchange rate constants for internal SiMe$_3$ reorientation in solid **1** as determined by simulation of one- and two-dimensional variable temperature ^{13}C MAS NMR experiments. Over the temperature range considered, the exchange rate constants follow *Arrhenius'* law, and from the slope of the plots depicted in Fig. 6 we obtain activation energies $E_a = 21 \pm 4$, 22 ± 4, and $30 \pm 5\,\text{kJ mol}^{-1}$, respectively, for the internal reorientation of the three SiMe$_3$ groups in **1**. For Si(SiMe$_3$)$_4$, we find $E_a = 53 \pm 6\,\text{kJ mol}^{-1}$ for internal SiMe$_3$ reorientation [6]. For Si(SiMe$_3$)$_4$, the crystal structure has been determined [7], but not for **1**. Accordingly, any attempts
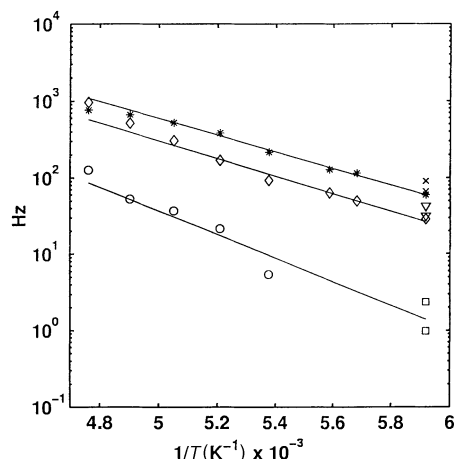
Fig. 6. Semilogarithmic plots of exchange rate constants k, k', and k'' for internal SiMe$_3$ reorientation in **1** *vs.* $1/T$; the symbols refer to exchange rate constants determined from ^{13}C MAS (∗, ◇, ○) and ^{13}C 2D EXSY (×, ▽, □) NMR experiments; note the difference in exchange rate constants for the three inequivalent SiMe$_3$ groups in solid **1**

to rationalize these differences in E_a for internal SiMe$_3$ reorientation necessarily have to be speculative. A major contribution towards energy barriers for internal SiMe$_3$ reorientation of predominantly intramolecular nature seems a reasonable assumption, and thus implies a lesser degree of intramolecular steric hindrance of the SiMe$_3$ groups in **1** as compared to Si(SiMe$_3$)$_4$.

Experimental

Compound **1**, (Ph$_3$Si)Si(SiMe$_3$)$_3$, was synthesized following a published procedure [13].

NMR experiments and data analysis

All ^{13}C and ^{29}Si NMR experiments were carried out on a Bruker MSL 300 NMR spectrometer at *Larmor* frequencies of 75.5 (^{13}C) and 59.6 (^{29}Si) MHz, respectively. Standard 4 mm and 7 mm ZrO$_2$ rotors and double-bearing probes were used. For variable temperature MAS NMR experiments, purified N$_2$ gas served as drive and bearing gas. MAS frequencies were in the range of 2.0–4.5 kHz, ^{1}H $\pi/2$ pulse durations were 3–5 μs, recycle delays were 3–5 s, and contact times for *Hartmann-Hahn* cross-polarization were 1.5 ms (^{13}C) and 2.0 ms (^{29}Si). 2D exchange spectroscopy (EXSY) [14] employed phase cycling according to the TPPI method [15]. Spectral lineshape simulations of the exchange broadened one-dimensional ^{13}C and ^{29}Si MAS NMR spectra of **1** were carried out as described elsewhere [6, 10, 14, 16]. Some ^{13}C 2D EXSY spectra of **1** have been obtained in the so-called intermediate motional regime. Simulation of such 2D spectra hence requires a suitably extended exchange matrix formalism as described in the literature [12] where also motion during the evolution and detection periods of the experiment is taken into account and where T_1 relaxation during the mixing time is still negligible. Iterative fitting procedures employed the MATLAB [17] simplex and quasi-*Newton* routines for nonlinear least-squares minimization.

Isotropic chemical shifts $\delta_{\text{iso}}(^{13}\text{C})$ and $\delta_{\text{iso}}(^{29}\text{Si})$ are given with respect to external SiMe$_4$, chemical shielding tensor eigenvalues are reported according to *Haeberlen*'s convention [18]; $\delta_{\text{iso}} = -\sigma_{\text{iso}}$; $|\sigma_{33} - \sigma_{\text{iso}}| \geq |\sigma_{11} - \sigma_{\text{iso}}| \geq |\sigma_{22} - \sigma_{\text{iso}}|$; $\eta = (\sigma_{22} - \sigma_{11})(\sigma_{33} - \sigma_{\text{iso}})^{-1}$.

Acknowledgements

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