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Comparative Solid-State NMR Study of the Molecular Dynamics of $Si(SiMe_3)_4$ and $C(SiMe_3)_4$

Xavier Helluy,[†] Jörg Kümmerlen,[‡] and Angelika Sebald*,[‡]

Rhône-Poulenc Rorer, Department of Pharmaceutical Sciences, Preformulation/Physical Analysis, Research Center of Vitry-Alfortville, 13 quai Jules Guesde, B.P. 14, 94403 Vitry sur Seine Cedex, France, and Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

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Variable-temperature ^{13}C and ^{29}Si one- and two-dimensional MAS NMR experiments are reported for the low-temperature phases of $Si(SiMe_3)_4$ (**1**) and $C(SiMe_3)_4$ (**2**). Quantitative determination of exchange rate constants from ^{13}C and ^{29}Si NMR spectra of **1** and **2** proves considerable dissimilarities of the molecular solid-state dynamic properties of **1** and **2**, despite the chemically and structurally homologous nature of these two compounds. In the low-temperature phase of **1**, internal $SiMe_3$ *and* whole-molecule reorientation occurs, while for the low-temperature phase of **2** no internal $SiMe_3$ reorientation but only whole-molecule reorientation is observed.

Introduction

Compounds $E(SiMe_3)_4$ (with E = Si, C; Me = methyl), which may be viewed as higher homologues of methane, CH_4, belong to a class of solids with nearly spherically shaped and nonpolar molecular units. Such molecular solids are known to undergo structural solid-state phase transitions, often including a plastically crystalline state ("rotator phase") at elevated temperatures. These structural phase transitions are closely related to thermally activated solid-state molecular dynamics such as internal modes of reorientation or whole-molecule reorientational modes.[1]

Solid $Si(SiMe_3)_4$, **1**, and $C(SiMe_3)_4$, **2**, exist as strongly orientationally disordered phases at ambient temperatures and undergo structural phase transitions upon cooling. The low-temperature phase of **1** exists at temperatures $T < 238-241$ K;[2] for **2** the low-temperature phase is stable up to $T = 213$ K.[3] Neither for **1** nor for **2** have single-crystal X-ray diffraction investigations been reported; the gas-phase structures of **1** and **2** have been examined by electron diffraction.[4,5] Empirical force field calculations[6,7] have indicated that **1** and **2** exhibit molecular *T* symmetry in the gas phase. On the basis of previous variable-temperature ^{13}C and ^{29}Si CP/MAS NMR results, molecular point group symmetry C_3 has been proposed for the low-temperature phases of **1** and **2**; similar dynamic solid-state properties of **1** and **2**, that is, the occurrence of both internal $SiMe_3$ reorientation and reorientation of the entire molecule around preferred axes, have been inferred from these NMR results.[8,9]

Here we will focus on the quantitative analysis of variable-temperature one- and two-dimensional ^{13}C and ^{29}Si MAS NMR experiments on the low-temperature phases of **1** and **2**. It will be shown that quantitative determination of exchange rate constants as a function of temperature from ^{13}C and ^{29}Si MAS NMR experiments on **1** and **2** is necessary for unambiguous identification of different reorientational modes. Quantification of exchange rate constants in addition reveals distinct differences in the thermally activated molecular solid-state dynamics of the low-temperature phases of **1** and **2**.

Results and Discussion

In the following we will concentrate on the molecular dynamic properties of the low-temperature phases of compounds $Si(SiMe_3)_4$, **1**, and $C(SiMe_3)_4$, **2**, as viewed by solid-state ^{13}C and ^{29}Si NMR. The low-temperature phases of **1** and **2** have recently been shown, by means of synchrotron powder diffraction techniques, to crystallize in space group $P2_13$,[10] confirming molecular C_3 point group symmetry. The possible modes of reorientation of a molecule $E(SiMe_3)_4$ with molecular C_3 symmetry (apart from internal reorientation of the methyl groups themselves) are illustrated schematically in Chart 1. Two different reorientational modes have to be taken into account: internal reorientation of the $SiMe_3$ groups around the respective E−Si bond (E = Si, C) directions, and reorientational jumps of the entire molecule around

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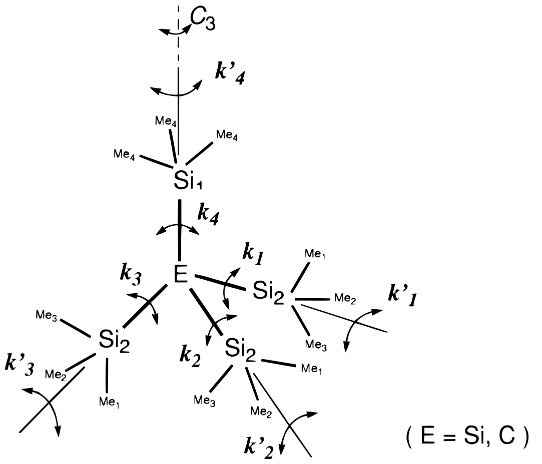
Chart 1. Schematic Representation of Molecular Reorientational Modes in the Low-Temperature Phases of E($SiMe_3$)$_4$, E = C, Si, with Molecular C_3 Symmetry[a,10]



[a] *k* and *k′* denote exchange rate constants for internal $SiMe_3$ (*k*) and for whole-molecule (*k′*) reorientation. The numbering scheme $Me^{(1)}$ to $Me^{(4)}$ and $Si^{(1)}$, $Si^{(2)}$ denotes symmetry-equivalent/inequivalent sites. See text for detailed description.

preferred molecular axes, also coincident with the E−Si bond directions.

From the schematic representation of a molecule E($SiMe_3$)$_4$ with molecular C_3 symmetry in Chart 1, we expect the following ^{13}C and ^{29}Si MAS NMR features for the low-temperature phases of **1** and **2**. At sufficiently low temperatures, in the so-called slow-exchange regime (on the one-dimensional ^{13}C and ^{29}Si MAS NMR time scale), we expect two ^{29}Si resonances in a 1:3 relative intensity ratio for the $Si^{(1)}Me_3$ and $Si^{(2)}Me_3$ groups. The 12 methyl groups will give rise to four ^{13}C resonances in a relative 1:1:1:1 intensity ratio for the four crystallographically distinct types of methyl−carbon sites $Me^{(1)}$ to $Me^{(4)}$ (see Chart 1). For reasons of symmetry, exchange rate constants $k_1 = k_2 = k_3$ for internal $Si^{(2)}Me_3$ reorientation and $k'_1 = k'_2 = k'_3$ for whole-molecule reorientation, while exchange rate constants k_4 and k'_4 for internal and whole-molecule reorientation around the molecular 3-fold axis of symmetry may differ from k_1, k_2, k_3 and k'_1, k'_2, k'_3 since the $Si^{(1)}Me^{(4)}{}_3$ group is crystallographically distinct from the remaining three $Si^{(2)}Me^{(1)}Me^{(2)}Me^{(3)}$ groups. In fact, unequal exchange rate constants for internal reorientation of chemically equivalent but crystallographically inequivalent sites ER_3 in solid organosilicon compounds have previously been reported for moieties $ER_3 = {}^tBu$[11] and $ER_3 = SiMe_3$.[12,13] Under conditions of fast magic-angle spinning, exchange rate constants k_4 and k'_4 for **1** and **2** cannot be measured: reorientations around the proper 3-fold axis of symmetry lead to mutual exchange of equivalent sites (mutual interchange of $Me^{(4)}$ sites for k_4, mutual interchange of $Me^{(4)}$ sites and of $Si^{(2)}Me^{(1)}Me^{(2)}Me^{(3)}$ groups for k'_4) and hence do not contribute to one- and two-dimensional ^{13}C and ^{29}Si NMR spectral line shapes. In principle, it would be possible to also determine k_4 and k'_4 from MAS NMR experiments recorded under slow magic-angle spinning conditions. For instance, the ODESSA experiment,[14] or a time-reversed version thereof,[15] would be a suitable approach. In practice, however, it turns out impossible to determine k_4 and k'_4 because for **1** and **2** very slow magic-angle spinning would be necessary ($\omega_{rot}/2\pi < 200$ Hz), resulting in severe spectral overlap problems.

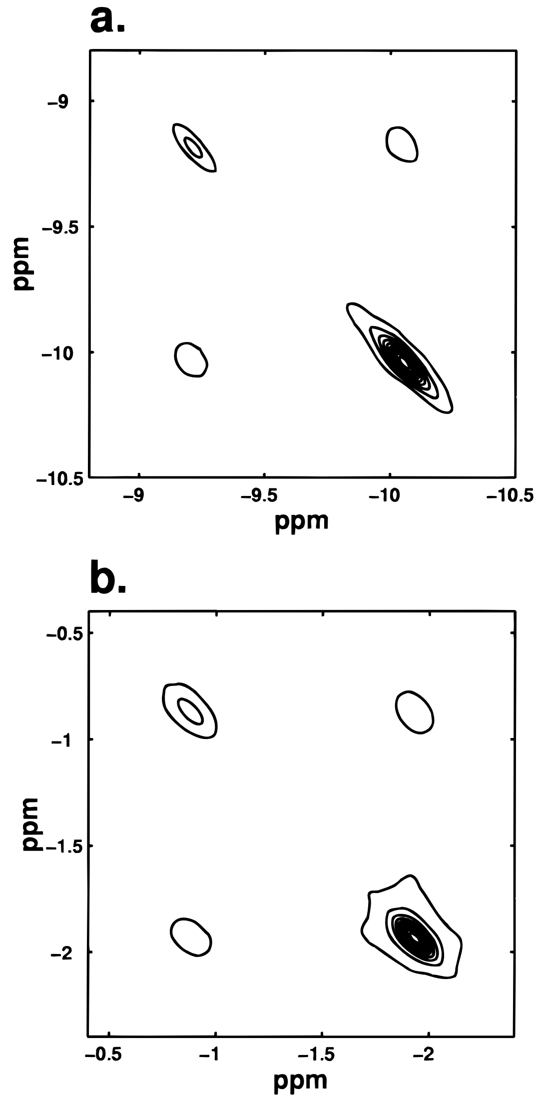


Figure 1. 2D ^{29}Si EXSY experiments on **1** and **2**: (a) **1**, $T = 160$ K, mixing time $\tau_{mix} = 300$ ms, only the $SiMe_3$ region is shown; (b) **2**, $T = 170$ K, mixing time $\tau_{mix} = 75$ ms. For long mixing times relative intensities corresponding to complete exchange in a four-site exchange (diagonal 1:9 and off-diagonal 3:3) are observed for **1** and **2**.

Under fast magic-angle spinning conditions, for **1** and **2** we can only determine the exchange rate constants $k = k_1$, k_2, k_3 and $k' = k'_1$, k'_2, k'_3 (see Chart 1) as these exchange processes lead to mutual exchange of inequivalent sites. We have to be able to distinguish internal $SiMe_3$ reorientation (*k*) from whole-molecule reorientation (*k′*). Under fast-spinning MAS conditions, the two ^{29}Si resonances of the $SiMe_3$ groups selectively

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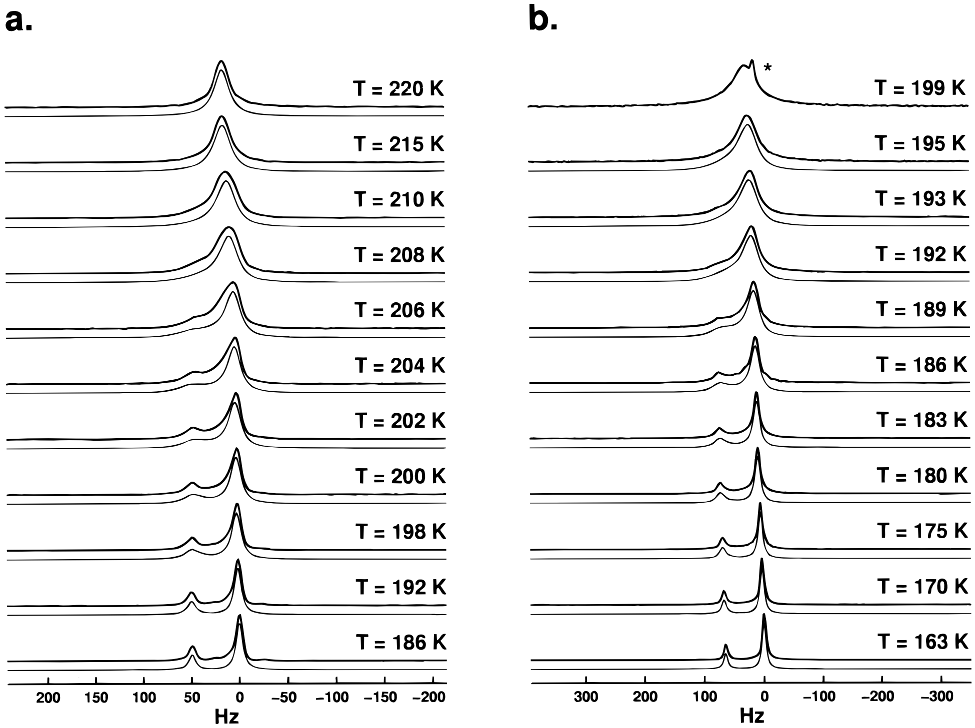

Figure 2. Variable-temperature ^{29}Si MAS NMR spectra of **1** (a) and **2** (b); only the $SiMe_3$ region is shown. Temperatures are indicated and $*$ denotes the presence of resonances from the coexisting high-temperature phase. Upper traces represent experimental spectra; lower traces are the corresponding best-fit calculated spectra.

monitor the exchange rate constants k' for whole-molecule reorientation, that is, interchanging $Si^{(1)}$ with $Si^{(2)}$. Formally, this exchange process may be described as a four-site exchange with three degenerate sites. ^{13}C one- and two-dimensional MAS NMR spectra will be affected by both molecular reorientational modes. Internal $Si^{(2)}Me_3$ reorientation only interchanges the $Me^{(1)}$, $Me^{(2)}$, $Me^{(3)}$ sites with rate constant k, while whole-molecule reorientation with rate constant k' leads to mutual interchange of $Me^{(1)}$, $Me^{(2)}$, $Me^{(3)}$ sites, as well as to interchange of ($Me^{(1)}$, $Me^{(2)}$, $Me^{(3)}$) sites with the $Me^{(4)}$ sites. Only reorientation of the entire molecule can lead to exchange between all four ^{13}C-methyl resonances. Exchange rate constants k, k' for two simultaneously occurring processes are additive;[16] hence, the simultaneous presence of both reorientational modes would lead to, for example, exchange peaks of unequal integrated intensities in a two-dimensional ^{13}C exchange MAS NMR spectrum (2D EXSY). Since the ^{13}C resonance of the $Me^{(4)}$ sites is only affected by whole-molecule reorientation, it would always be possible to determine k' directly from the relative integrated intensities of those exchange peaks involving the ^{13}C resonance of the $Me^{(4)}$ sites. Alternatively, the observation of exchange between all four ^{13}C-methyl resonances with *all* exchange peaks of identical integrated intensities is consistent only with the presence of whole-molecule reorientation in the absence of additional internal $Si^{(2)}Me_3$ reorientation.

We may now inspect more closely the various one- and two-dimensional, variable-temperature ^{13}C and ^{29}Si NMR results on the low-temperature phases of **1** and **2**. In accord with the predictions for molecular C_3 symmetry from the above discussion of Chart 1, ^{29}Si MAS NMR spectra of **1** and **2** at low temperatures display two ^{29}Si resonances in a relative intensity ratio of 1:3 for the $Si^{(1)}Me_3$ and $Si^{(2)}Me_3$ groups.This slow-exchange limit on the one-dimensional ^{29}Si NMR time scale is reached at temperatures $T \leq 190$ K for **1** and at $T \leq 170$ K for **2**. ^{29}Si 2D EXSY experiments on **1** and **2** in the respective ^{29}Si slow-exchange limit provide proof that for both compounds, even at low temperatures, whole-molecule reorientation does take place: in both cases off-diagonal exchange peaks connecting the two ^{29}Si resonances are observed (see Figure 1). Exchange rate constants k' for whole-molecule reorientation as a function of temperature in this slow-exchange regime for **1** and **2** are obtained from a series of ^{29}Si 2D EXSY experiments, recorded at different temperatures and with different mixing times. At temperatures $T \geq 190$ K (for **1**) or $T \geq 170$ K (for **2**) the line shapes of one-dimensional ^{29}Si MAS NMR spectra become affected by whole-molecule reorientation, as can be seen in Figure 2. Spectral line shape simulations of the exchange-broadened ^{29}Si resonances yield exchange rate constants k' for whole-molecule reorientation of **1** and **2** up to the temperature ranges where the onset of the phase transition to the high(er)-temperature phase starts to interfer by the coexistence of high- and low-temperature phase. For **1**, the one-dimensional ^{29}Si spectral line shapes can be exploited to determine exchange rate constants in the temperature range $T \approx 190-215$ K; for **2**, the corresponding informative temperature range is $T \approx 170-195$ K (see Figure 2).

In contrast to the one- and two-dimensional variable-temperature ^{29}Si MAS NMR experiments, selectively monitoring exchange rate constants k' of whole-molecule

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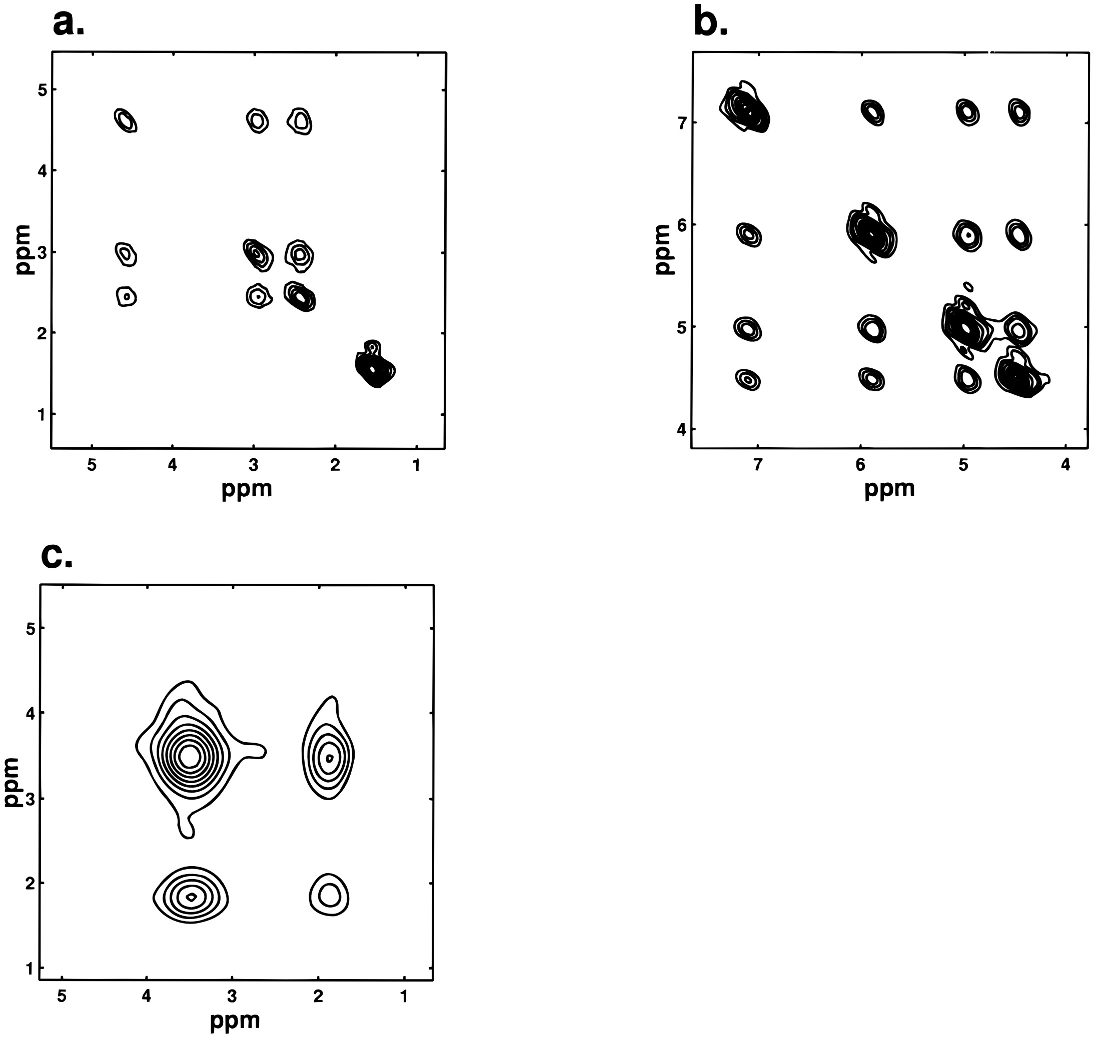

Figure 3. 2D ^{13}C EXSY experiments on **1** and **2**; only the methyl region is shown: (a) **1**, $T = 154$ K, mixing time $\tau_{\text{mix}} =$ 500 ms; (b) **2**, $T = 164$ K, mixing time $\tau_{\text{mix}} = 250$ ms; (c) **1**, $T = 190$ K, mixing time $\tau_{\text{mix}} = 1$ s.

reorientation in the low-temperature phase of **1** and **2**, ^{13}C MAS NMR experiments can report on the kinetics of internal Si$^{(2)}$Me$_3$ reorientation as well as on whole-molecule reorientation. In agreement with the requirements of molecular C_3 symmetry for the low-temperature phases of **1** and **2**, four ^{13}C-methyl resonances of relative intensities 1:1:1:1 are observed for both compounds in ^{13}C CP/MAS NMR spectra, recorded in the slow-exchange temperature regimes on the one-dimensional ^{13}C NMR time scale. This temperature regime is reached at $T \leq 150$ K for **1** and at $T \leq 170$ K for **2**. 2D ^{13}C EXSY experiments on **1** and **2** at low temperatures reveal major differences in the molecular dynamics of **1** and **2**. As illustrated in Figure 3, for **1** only exchange between three methyl sites, Me$^{(1)}$, Me$^{(2)}$, Me$^{(3)}$, is observed at low temperatures, while exchange between all methyl sites Me$^{(1)}$ to Me$^{(4)}$ occurs for **2**. Obviously, for **1** at low temperatures only internal Si$^{(2)}$Me$_3$ reorientation takes place with nonnegligible exchange rate constants k; at higher temperatures additional whole-molecule reorientation occurs (see Figure 3c). In solid **2** the only low-temperature dynamic process occurring with substantial exchange rate constants k' is whole-molecule reorientation. The integrated intensities of all 12 exchange peaks in the 2D ^{13}C EXSY spectra of **2** are equal within experimental error and thus exclude the simultaneous presence of additional internal Si$^{(2)}$Me$_3$ reorientation. The dissimilarities in the solid-state molecular dynamics of **1** and **2** are also evident in the temperature range where one-dimensional ^{13}C MAS NMR spectra display temperature-dependent exchange broadening. Variable-temperature ^{13}C MAS NMR spectra of **1** and **2** in this temperature range are shown in Figure 4. For **1** there are two different coalescence regimes: one occurs in the $T = 160-180$ K temperature range and affects only the three ^{13}C-methyl resonances for sites Me$^{(1)}$, Me$^{(2)}$, Me$^{(3)}$ (internal Si$^{(2)}$Me$_3$ reorientation); a second coalescence regime is reached in the temperature range $T = 180-210$ K, brought about by the additional onset of whole-molecule reorientation (see Figure 4a). For **2** the evolution of the one-dimensional ^{13}C MAS NMR spectral line shape as a function of temperature is quite different (see Figure 4b). Over the temperature range $T = 160-190$ K all four ^{13}C-methyl resonances are part of the emerging coalescence pattern. From qualitative inspection of this coalescence pattern we cannot safely exclude that at somewhat elevated temperatures also for **2** additional internal Si$^{(2)}$Me$_3$ reorientation may take place as well.

However, if we take into consideration *all* exchange rate constants k, k' determined from 2D ^{13}C and ^{29}Si

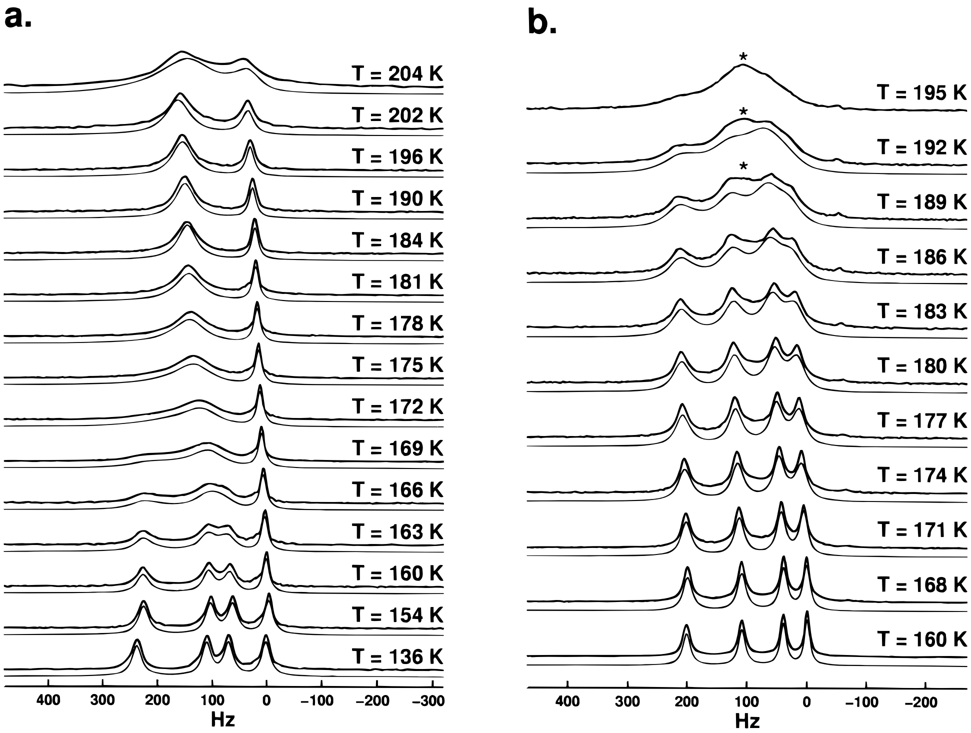

Figure 4. Variable-temperature ^{13}C MAS NMR spectra of **1** (a) and **2** (b); in b only the methyl region is shown. Temperatures are indicated, and $*$ denotes the presence of resonances from the coexisting high-temperature phase. Upper traces represent experimental spectra; lower traces are the corresponding best-fit calculated spectra.

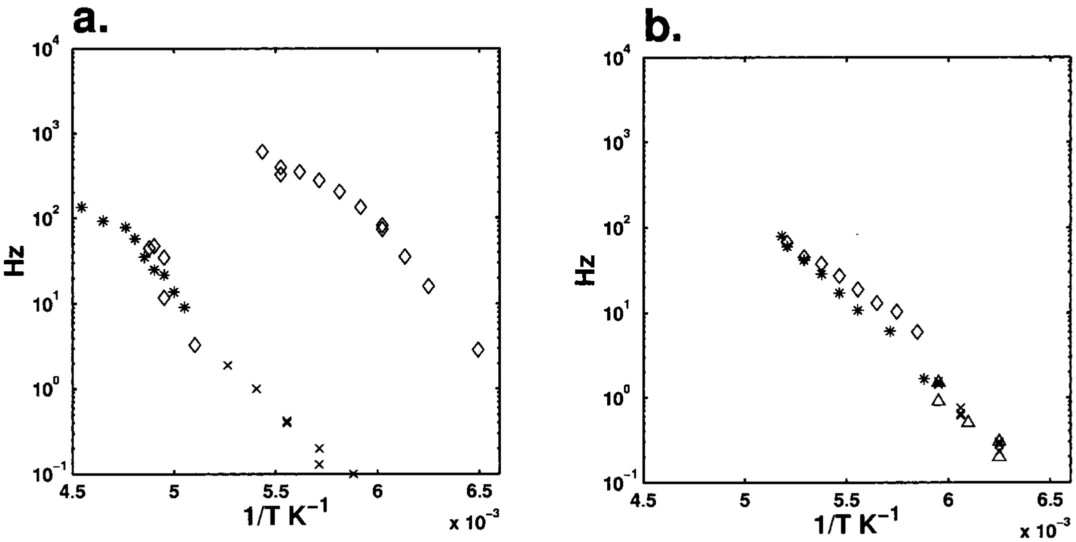

Figure 5. Semilogarithmic plots of exchange rate constants k, k' for **1** (a) and **2** (b) versus $1/T$. The symbols refer to exchange rate constants determined from ^{29}Si MAS ($*$), ^{29}Si 2D EXSY ($\times$), ^{13}C MAS ($\diamond$), and ^{13}C 2D EXSY ($\triangle$) NMR experiments, respectively.

EXSY experiments and from iterative fitting of the spectral line shapes of variable-temperature one-dimensional ^{13}C and ^{29}Si MAS NMR spectra, the following picture is obtained for the low-temperature phases of **1** and **2**. Figure 5 displays semilogarithmic plots of all exchange rate constants k, k' versus $1/T$ for the low-temperature phases of **1** and **2**. The Arrhenius plot for **1** (Figure 5a) clearly shows the two exchange rate constants k for internal Si$^{(2)}$Me$_3$ reorientation and k' for whole-molecule reorientation to differ considerably. Note that the exchange rate constant k for internal Si$^{(2)}$Me$_3$ reorientation in the low-temperature phase of **1** is always higher than k' and that k exhibits a significant deviation from Arrhenius behavior at elevated temperatures. From the data displayed in Figure 5a, the activation barrier for internal Si$^{(2)}$Me$_3$ reorientation in **1** at temperatures up to $T \approx 185$ K is determined as $E_a = 53.3 \pm 6.0$ kJ mol^{-1}. The exchange rate constants k' accessible for whole-molecule reorientation of **1** permit determination of the activation barrier for this process as $E_a = 49.3 \pm 3.0$ kJ mol^{-1}. A different situation is found in the Arrhenius plot for **2** (see Figure 5b). Over the entire accessible temperature range, the exchange rate constants at a given temperature, as obtained from ^{13}C *and* ^{29}Si NMR data, are identical within experimental error, leading to the conclusion that the only dynamic process occurring in the low-temperature phase of **2** is whole-molecule reorientation with an activation barrier $E_a = 44.7 \pm 3.0$ kJ mol^{-1}.

We need to answer the question why there should be such differences in the intramolecular (internal Si$^{(2)}$Me$_3$ reorientation) solid-state dynamics of **1** and **2**. Obviously, the difference in intramolecular steric crowding in E(SiMe$_3$)$_4$ on going from E = Si (**1**) to E = C (**2**), caused by different bond lengths E−Si (236 pm (**1**) and 192 pm (**2**)[10]), has a significant impact on the molecular dynamic properties of the two compounds. It renders internal Si$^{(2)}$Me$_3$ reorientation in C(SiMe$_3$)$_4$, **2**, a highly unfavorable process, while "conventional" solid-state dynamic properties (where internal Si$^{(2)}$Me$_3$ reorientation is thermally activated at lower temperatures, followed by the onset of global reorientation at more elevated temperatures) are found for the low-temperature phase of Si(SiMe$_3$)$_4$, **1**. It appears reasonable to consider intramolecular steric strain as the dominating cause of hindrance to internal Si$^{(2)}$Me$_3$ reorientation in solid **1** and **2**, although crystal-packing effects should not be completely ignored. With the crystal structure of the low-temperature phases of **1** and **2** determined,[10] it becomes feasible to compare ab initio and force-field calculations based on the gas-phase and crystal structures in order to understand better the molecular dynamic properties of **1** and **2**, as well as the relationship between solid-state molecular dynamics and structural phase transitions. This work is in progress and will be reported elsewhere.[10]

Experimental Section

Compound **1**, Si(SiMe$_3$)$_4$, is commercially available (ABCR Chemikalien, Karlsruhe) and has been used without further purification. Compound **2**, C(SiMe$_3$)$_4$, was kindly donated by G. Fritz, Karlsruhe.

All ^{13}C and ^{29}Si NMR experiments were carried out on a Bruker MSL 300 NMR spectrometer, corresponding to Larmor frequencies of 75.5 (^{13}C) and 59.6 (^{29}Si) MHz, respectively. Standard 4 and 7 mm ZrO$_2$ rotors and double-bearing probes were used. For variable-temperature MAS NMR experiments, purified N$_2$ gas served as the drive and bearing gas. MAS frequencies were in the range 2−3 kHz, ^{1}H $\pi/2$ pulse durations were 3−5 μs, recycle delays had to be 3−5 s, and the contact times for Hartmann−Hahn cross-polarization (^{13}C and ^{29}Si) were 5 ms. 2D exchange spectroscopy (EXSY)[16−19] employed phase cycling according to the TPPI method.[20] Spectral line shape simulations of the exchange-broadened ^{13}C and ^{29}Si MAS NMR spectra of **1** and **2** were carried out as described elsewhere;[11,21] iterative fitting employed the MATLAB[22] simplex routine for nonlinear least-squares minimization.

Isotropic chemical shifts δ (^{13}C) and δ (^{29}Si) are quoted with respect to external SiMe$_4$. Selected data are as follows. **1**: ^{13}C, 3.5 ppm (T = 297 K), and 4.6, 3.0, 2.4, 1.5 ppm (T = 154 K); ^{29}Si, −9.9 (SiMe$_3$), −135.6 ppm (T = 297 K), and −9.3, −10.0 (SiMe$_3$), −140.9 ppm (T = 168 K). **2**: ^{13}C, 6.4 (Me), −1.2 ppm (T = 297 K), and 7.1, 5.9, 5.0, 4.5 (Me), −2.6 ppm (T = 164 K); ^{29}Si, −1.5 ppm (T = 297 K), and −0.9, −1.9 ppm (T = 163 K).

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