5218 *Organometallics* **1997,** *16,* 5218−5222

Molecular Dynamics of Solid $(Me_3Si)_3C-C\equiv C-C(SiMe_3)_3$ As Seen by One- and Two-Dimensional CP/MAS NMR[†]

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

Received June 27, 1997[⊗]

Variable-temperature solid-state NMR studies (^{13}C, ^{29}Si) of polycrystalline $(Me_3Si)_3C-C\equiv C-C(SiMe_3)_3$ (**1**) are reported. These studies prove the simultaneous occurrence of two different reorientational modes in solid **1** in the temperature range $T \approx 150-240$ K: reorientation around the molecular $C-C\equiv C-C$ axis and internal reorientation of the Me_3Si groups. Two-dimensional ^{13}C exchange spectroscopy (2D EXSY) at low temperatures provides the correct assignment permutation for the ^{13}C resonances of the nine crystallographically inequivalent methyl groups into groups of three, each representing one Me_3Si ligand. Unequal exchange rate constants for the internal Me_3Si reorientation of the three crystallographically inequivalent Me_3Si groups in solid **1** are unambiguously established by the ^{13}C 2D EXSY experiments and by the spectral line shape simulations of the variable-temperature one-dimensional ^{13}C CP/MAS NMR spectra of **1**, while the ^{29}Si 2D EXSY experiments yield direct proof of reorientation around the molecular $C-C\equiv C-C$ axis.

Introduction

High-resolution solid-state NMR methods represent an ideally suited analytical tool for in-depth investigations of the dynamic properties of polycrystalline solids. In particular, detailed information about the kinetics and energy barriers, and hence about the mechanistic details on a molecular level, of thermally activated internal reorientational processes in solid organometallic compounds may be obtained.[1,2]

Recently, we have shown for solid $Si_2{}^tBu_6$ that considerable *intra*molecular steric crowding does not suppress the internal reorientation of the ^tBu groups around the respective Si−C bonds.[3] The activation barrier determined for this process of simultaneous, cooperative reorientation of the ^tBu groups is fairly low ($E_a \approx 20-25$ kJ mol^{-1}). A second molecular reorientational mode, reorientation around the central Si−Si bond, is also active for solid $Si_2{}^tBu_6$ in the temperature range $T \approx 180-240$ K. Owing to very short longitudinal relaxation times T_1 of the methyl-^{13}C resonances in $Si_2{}^tBu_6$, preventing the use of two-dimensional NMR experiments such as ^{13}C exchange spectroscopy (2D EXSY), extraction of the kinetic parameters and estimation of the activation barriers for that particular compound had to rely on iterative fitting of the variable-temperature one-dimensional ^{13}C CP/MAS NMR spectra and on molecular dynamics calculations.[3]

It is the purpose of the present study to unambiguously demonstrate, on a structurally related organosilicon compound of known single-crystal X-ray structure, that the two reorientational modes found for solid $Si_2{}^tBu_6$ are not unique to this particular compound. The compound chosen for the present solid-state NMR study is di[tris(trimethylsilyl)methyl]acetylene $(Me_3Si)_3C-C\equiv C-C(SiMe_3)_3$ (**1**). The criteria for the selection of **1**, therefore, also had to include the possibility to perform ^{13}C and ^{29}Si 2D EXSY NMR experiments in order to be able to directly prove the simultaneous occurrence of two different reorientational modes in solid **1**.

Results and Discussion

The single-crystal X-ray structure, obtained at T = 297 K, shows $(Me_3Si)_3\underline{C}-C\equiv C-C(SiMe_3)_3$, **1**, to crystallize in space group $P\bar{1}$, with half a (centrosymmetric) molecule representing the asymmetric unit.[4] The three $SiMe_3$ groups within the $C(SiMe_3)_3$ moiety are crystallographically inequivalent, corresponding to nine independent methyl groups and three independent Si sites. The central $C\equiv C$ bond in **1** acts as a spacer between the two bulky $C(SiMe_3)_3$ groups in the molecule, resulting in intramolecular *inter*-$C(SiMe_3)_3$ contacts approximately equal to the sum of the usual van der Waals radii, while there is considerable steric strain within the $C(SiMe_3)_3$ groups.[4] The molecular structure of **1** is illustrated schematically in Chart 1, including the possible modes of the intramolecular reorientational processes.

The multiplicity of the ^{13}C and ^{29}Si resonances, as predicted from the single-crystal X-ray structure of **1**, is not observed in the ^{13}C and ^{29}Si CP/MAS NMR

---

* Author to whom correspondence should be addressed. E-mail: angelika.sebald@uni-bayreuth.de.

[†] Dedicated to M. Weidenbruch on the occasion of his 60th birthday.

[‡] Rhône-Poulenc Rorer.

[§] Bayerisches Geoinstitut.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

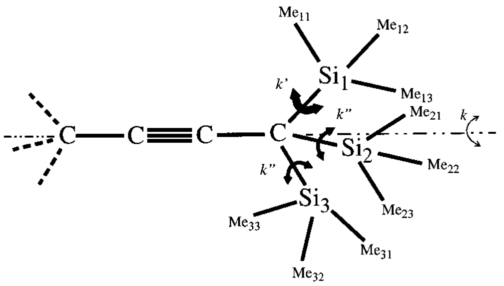
(1) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, 1994.

(2) (a) Kümmerlen, J.; Sebald, A. In *Encyclopedia of NMR*; Grant, D. M., Harris, R. K., Eds.; Wiley: New York, 1995; pp 4127−4132, and references given therein. (b) Sebald, A. In *Advanced Applications of NMR to Organometallic Chemistry*; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; Wiley: Chichester, England, 1996; pp 123−157, and references given therein.

(3) Kümmerlen, J.; Sebald, A. *Organometallics* **1997**, *16*, 2971.

(4) Fronczek, F. R.; Lickiss, P. D. *Acta Crystallogr., Sect. C* **1993**, *49*, 331.

Chart 1. Schematic Illustration of the Molecular Structure of 1[a]



[a] Also indicated are the different modes of reorientation, where k, k', and k'' denote the exchange rate constant of the respective dynamic process.

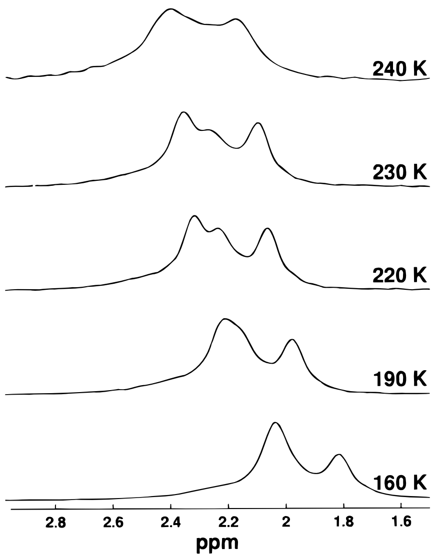


Figure 1. ^{29}Si CP/MAS NMR spectra ($\omega_0/2\pi = 59.6$ MHz) of **1** at different temperatures, as indicated.

spectra obtained at ambient temperature: the ^{29}Si CP/MAS NMR spectrum displays one slightly broadened resonance (δ ^{29}Si = 2.3 ppm); the ^{13}C CP/MAS NMR spectrum shows only one resonance for the nine inequivalent methyl groups (δ ^{13}C(Me) = 3.8 ppm), in addition to the ^{13}C resonances of the quaternary carbon atom (δ ^{13}C(CSi$_3$) = 6.5 ppm) and of the acetylenic carbon atom (δ ^{13}C(C≡) = 79.9 ppm). Only when performing the ^{13}C and ^{29}Si one-and two-dimensional CP/MAS NMR experiments on **1** at low temperatures, can information concerning the molecular dynamics of solid **1** be obtained.

Reorientation Around the Molecular C−C≡C−C Axis. Information about this reorientational mode is contained in the one- and two-dimensional ^{29}Si CP/MAS NMR spectra of **1**. On lowering the temperature, the ^{29}Si resonance line shapes change as a function of temperature; for instance at $T = 160$ K, a splitting into two resonances of relative intensities 2:1 (δ^{29}Si = 2.2 and 2.0 ppm) is observed; at $T = 220$ K, a splitting into three resonances, as predicted from single-crystal X-ray diffraction, is observed (see Figure 1). There are no indications of solid **1** undergoing any structural phase transitions in the relevant temperature range. Thus, the temperature-dependent line shape changes in the ^{29}Si CP/MAS NMR spectra of **1** have to be ascribed to the combined effects of molecular reorientation and of the intrinsic temperature-dependence of δ ^{29}Si: the only mode of molecular reorientation leading to coalescence of the ^{29}Si resonances of the three independent Si sites in the C(SiMe$_3$)$_3$ moiety is reorientation around the molecular C−C≡C−C axis. Whether this process is reorientation of the entire molecule around this axis or whether individual reorientation of the two C(SiMe$_3$)$_3$ moieties is being observed is not possible to derive from the variable-temperature NMR results alone. The temperature-dependent splittings in the ^{29}Si CP/MAS NMR spectra of **1** are very small. Hence, for solid **1**, the molecular-dynamics contribution to the overall line shape changes will only be of the same order of magnitude as are typical intrinsic temperature shifts of the isotropic ^{29}Si chemical shift(s)—fractions of a part per million per degree. This circumstance has two immediate consequences: (i) variable-temperature one-dimensional ^{29}Si CP/MAS NMR alone does not represent unambiguous proof for the presence of reorientation around the molecular C−C≡C−C axis; (ii) meaningful line shape simulations of these variable-temperature ^{29}Si CP/MAS NMR spectra of **1** for the extraction of *precise* exchange rate constants and the determination of the corresponding activation energy E_a are not feasible.

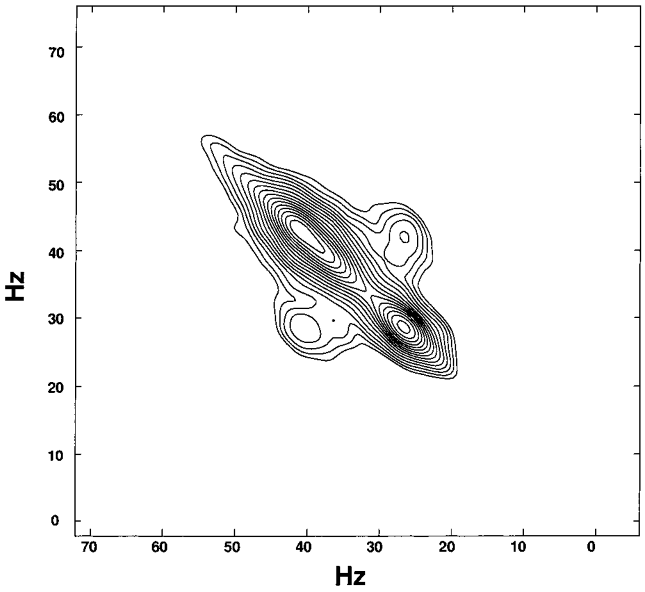


Figure 2. Contour plot of the ^{29}Si 2D EXSY spectrum ($\omega_0/2\pi = 59.6$ MHz) of **1** at $T = 190$ K and for a mixing time of $\tau_m = 4$ s. Note the off-diagonal exchange peaks due to reorientation around the molecular C−C≡C−C axis.

Direct and unambiguous proof for reorientation around the molecular C−C≡C−C axis in solid **1** is provided by ^{29}Si CP/MAS 2D exchange spectroscopy (EXSY) at low temperatures. The contour plot of a ^{29}Si CP/MAS EXSY experiment on **1** at $T = 190$ K, with a mixing time $\tau_m = 4$ s, is shown in Figure 2 and displays off-diagonal intensity which can only be explained by the mutual exchange of the different SiMe$_3$ groups in the C(SiMe$_3$)$_3$ unit. Integration of the relative intensities of the exchange peaks as a function of mixing time τ_m allows an *estimate* of the exchange rate constant $k \approx 0.02$ s^{-1} at $T = 190$ K for reorientation around the molecular C−C≡C−C axis in solid **1**. Equipped with this estimate of k at $T = 190$ K from the ^{29}Si CP/MAS 2D EXSY results, we may return to the variable-temperature one-dimensional ^{29}Si CP/MAS NMR spectra for closer inspection of k at slightly higher temperatures. Using k,

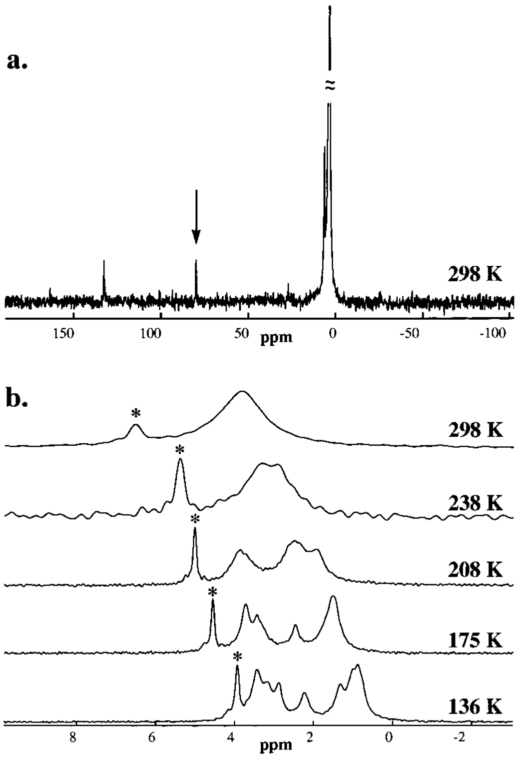


Figure 3. ^{13}C CP/MAS NMR spectra of **1**, obtained at (a) $\omega_0/2\pi$ = 50.3 MHz, full spectral range at T = 298 K, ↓ denotes isotropic ^{13}C chemical shift for C≡C; (b) $\omega_0/2\pi$ = 75.5 MHz, expansion of the methyl region at different temperatures, as indicated, $*$ denotes the isotropic ^{13}C chemical shift for C_{quat}. Note the onset of additional line broadening from the interference between coherent MAS averaging and incoherent molecular dynamic effects, leading to inefficient ^{1}H decoupling at temperatures T > 220 K.[1,2,9]

as estimated from the ^{29}Si CP/MAS EXSY results at T = 190 K, as the input parameter for the line shape simulations of the ^{29}Si CP/MAS NMR spectra of **1** in the temperature range up to $T \approx 240$ K, then permits a further *estimation* of $k \approx 6$ s^{-1} at T = 240. In turn, estimation of k as a function of temperature from combined consideration of the one- and two-dimensional ^{29}Si CP/MAS NMR yields an *estimate* of the activation barrier E_a for reorientation of solid **1** around the molecular C−C≡C−C axis of $E_a \approx 40$ kJ mol^{-1}. We would like to stress that owing to the very small splittings in the variable-temperature ^{29}Si CP/MAS NMR spectra of **1**, exchange rate constants k and, correspondingly, E_a for this thermally activated process can only be derived within fairly large error limits. Nevertheless, an estimate of the exchange rate constant k as a function of temperature is important information for the analysis of the temperature-dependent effects observed in ^{13}C CP/MAS NMR spectra of **1**.

Internal Reorientation of the Me_3Si Groups. The ^{13}C CP/MAS NMR spectrum of **1** at room temperature is shown in Figure 3a, while Figure 3b displays the expanded methyl region in low-temperature ^{13}C CP/MAS NMR spectra of **1**. Even at T = 136 K, we do not observe full spectral resolution of the expected nine methyl-^{13}C resonances but the molecular dynamics of solid **1** are clearly in the slow-exchange regime on the one-dimensional ^{13}C NMR time scale at T < 160 K. In principle, if occurring at sufficiently fast exchange rate constants k, molecular reorientation around the C−C≡C−C axis could account for coalescence of the entire methyl region in the ^{13}C CP/MAS NMR spectra of **1**. However, in the temperature range $T \approx 140-210$ K, exchange rate constants k are so small (*vide supra*) that contributions of this dynamic process to the observed line shape changes in the methyl region of the ^{13}C CP/MAS NMR spectra are negligible. Another molecular reorientational process, occurring at faster rates, must be responsible for these effects observed in the variable-temperature ^{13}C CP/MAS NMR spectra of **1**. This second mode of molecular reorientation in solid **1** is simultaneous internal reorientation of the three Me_3Si groups around the respective Si−C_{quat} bond directions, despite considerable steric crowding within the $C(SiMe_3)_3$ moieties.[3] More light is shed on this dynamic process by the ^{13}C 2D EXSY experiments. Figure 4 compares the contour plots (methyl region only) of the ^{13}C 2D EXSY experiments on **1**, with mixing time τ_m = 300 ms, obtained at T = 166 and 190 K. We cannot quantify these ^{13}C 2D EXSY experiments in terms of exchange rate constants k' and k'' for internal $SiMe_3$ reorientation; spectral overlap, in combination with relatively short methyl-^{13}C T_1 relaxation times, prevents a meaningful integration of the relative off-diagonal exchange peak intensities as a function of mixing times and temperature. Despite this incomplete spectral resolution, the ^{13}C 2D EXSY experiments on **1** provide two pieces of unambiguous information of importance for the subsequent quantitative analysis of the variable-temperature ^{13}C CP/MAS NMR spectra by means of spectral line shape simulations: (i) one of the three independent $SiMe_3$ groups undergoes internal reorientation with an exchange rate constant k' much faster than the remaining two $SiMe_3$ groups within the $C(SiMe_3)_3$ unit (see Figure 4a); (ii) although spectral resolution is incomplete in both the one- and two-dimensional ^{13}C CP/MAS NMR spectra of **1**, spectral resolution in the 2D EXSY spectra is sufficient to provide the correct assignment permutation of the methyl-^{13}C resonances into groups of three, each representing one $SiMe_3$ group.

Before we address the quantitative analysis of the variable-temperature ^{13}C CP/MAS NMR spectra of **1**, two comments seem to be appropriate. First, we do not know which of the three crystallographically inequivalent $SiMe_3$ groups in solid **1** displays internal reorientation faster than the remaining two $SiMe_3$ groups. Second, and perhaps more importantly, for solid **1**, the ^{13}C 2D EXSY experiments at low temperatures directly show the presence of unequal exchange rate constants k' and k'' for internal $SiMe_3$ reorientation. With respect to the molecular dynamics of solid $Si_2{}^tBu_6$,[3] where no ^{13}C 2D EXSY experiments could be performed, the finding of unequal exchange rate constants k' and k'' for internal $SiMe_3$ reorientation in **1** is identical to our finding of unequal exchange rate constants for internal ^{t}Bu reorientation of the three crystallographically inequivalent ^{t}Bu groups in solid $Si_2{}^tBu_6$. However, for solid $Si_2{}^tBu_6$, this finding was the result of having to iteratively fit the ^{13}C CP/MAS NMR spectra as a function of temperature for all possible assignment permutations, without preliminary information about the exchange rate constants. The possibility to perform ^{13}C 2D EXSY experiments on solid **1**, regardless of incomplete spectral resolution, as a preparative step for

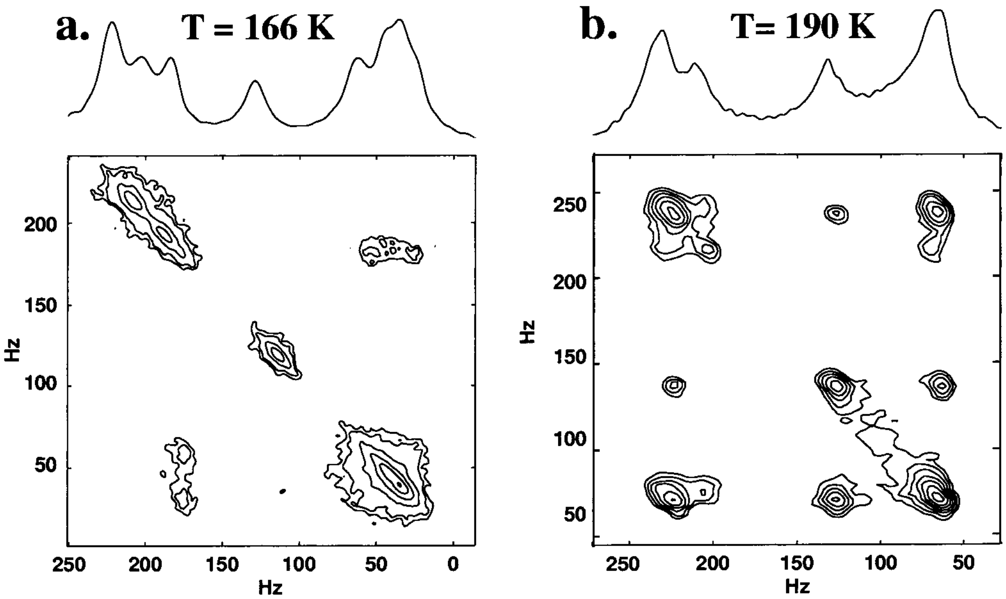


Figure 4. Contour plots of the ^{13}C 2D EXSY spectra ($\omega_0/2\pi = 75.5$ MHz) of **1**, obtained with a mixing time $\tau_m = 300$ ms. Only the methyl region is shown. (a) $T = 166$ K; (b) $T = 190$ K. Note the strongly differing (i.e., much faster) buildup of the exchange off-diagonal intensity for one of the three inequivalent $SiMe_3$ groups. Also shown along the respective $F2$ dimensions are the corresponding one-dimensional ^{13}C CP/MAS NMR spectra.

line shape simulations creates a far less tedious initial condition for quantitative analysis of the variable-temperature ^{13}C CP/MAS NMR spectra of **1** than was the case for solid $Si_2{}^tBu_6$.

The following represents the starting point for the determination of the exchange rate constants k' and k'' for internal $SiMe_3$ reorientation in solid **1** from the line shape simulations of the variable-temperature ^{13}C CP/MAS NMR spectra: (i) from the ^{13}C 2D EXSY experiments on **1**, the correct assignment permutation of the methyl-^{13}C resonances into groups of three is known, and we know that we have to use at least two unequal exchange rate constants k' and k'' for the simulation; (ii) from the one- and two-dimensional ^{29}Si CP/MAS NMR (*vide supra*) it is known that in the low-temperature range $T \approx 160-220$ K, reorientation around the molecular $C{-}C{\equiv}C{-}C$ axis occurs at a rate so slow that we may safely ignore its influence on the ^{13}C variable-temperature line shapes in this temperature range. Thus, a formal description of the internal $SiMe_3$ reorientation dynamics in solid **1** as a superposition of three independent three-site exchange processes[3,5] is an adequate model for the simulation of the exchange-broadened ^{13}C CP/MAS NMR spectra of **1** in the temperature range $T \approx 160-220$ K. The best fit, in comparison to the respective experimental ^{13}C CP/MAS NMR spectra, is depicted in Figure 5, where the bar code at the bottom denotes the assignment of the methyl-^{13}C resonances into groups of three (as derived from inspection of ^{13}C 2D EXSY spectra), the broader width of the bar code for one set of three resonances symbolizes the exchange rate constant k' for the faster three-site exchange process. The three $SiMe_3$ groups within the $C(SiMe_3)_3$ unit are crystallographically inequivalent, which, in principle, would be consistent with the occurrence of three different exchange rate constants k', k'', and k''' for internal $SiMe_3$ reorientation in **1**. Within the error limits of our spectral line shape simulations, the two (slower) $SiMe_3$ exchange processes have equal exchange rate constants k''. The kinetics of the internal $SiMe_3$ reorientation in **1**, thus, are very similar to the dynamics of the internal ^{t}Bu group reorientation in solid $Si_2{}^tBu_6$ where one “fast” and two “slow” ^{t}Bu groups have been identified also,[3] except that the difference between k' and k'' for **1** is more pronounced than that for $Si_2{}^tBu_6$.

Figure 6 shows a semilogarithmic plot of the exchange rate constants k' and k'' as determined by the spectral line shape simulations of the variable-temperature ^{13}C CP/MAS NMR spectra of **1** *versus* $1/T$. Again, the observed deviation from an Arrhenius-type behavior is similar to the findings for internal ^{t}Bu group reorientation in solid $Si_2{}^tBu_6$:[3] for internal $SiMe_3$ group reorientation also in solid **1**, the height of the activation barrier, E_a, depends on the temperature and decreases with increasing temperatures. From the slopes of the plot for k' near $T = 175$ K, E_a is estimated as ca. 40 kJ mol^{-1} while $E_a \approx 22$ kJ mol^{-1} near $T = 196$ K.

Conclusions

There seems to be repeated patterns of molecular solid-state dynamics of organosilicon compounds containing a preferred molecular axis and sterically highly crowded moieties $X(EMe_3)_3$ (X, E = C, Si): molecular reorientation around the preferred molecular axis with slow rates and simultaneous internal reorientation of the EMe_3 groups at faster rates, whereby crystallographically inequivalent groups EMe_3 give rise to unequal exchange rate constants. No direct clue concerning these unequal exchange rate constants is obtained from the respective single-crystal X-ray structures. Known single-crystal X-ray structures of such compounds, though, may play a key role for more extended molecular dynamics simulations by providing the relevant geometric parameters. Naturally, the generality of these statements requires confirmation by further experimental and theoretical studies.

---

(5) Mehring, M. *Principles of High Resolution NMR in Solids*; Springer: Berlin, 1983.

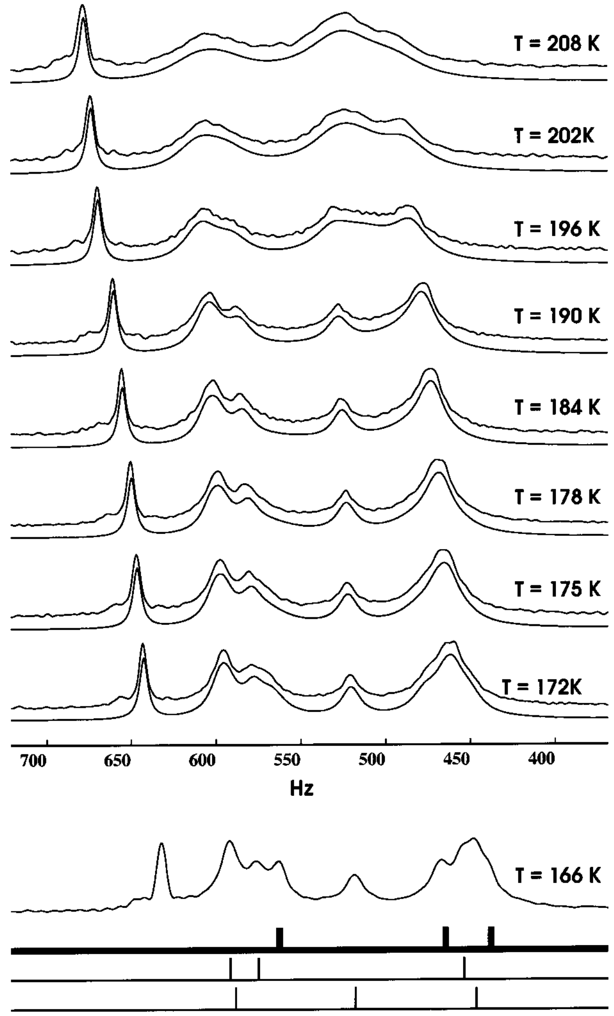


Figure 5. Experimental (upper trace) ^{13}C CP/MAS NMR spectra ($\omega_0/2\pi = 75.5$ MHz) of **1** at different temperatures, as indicated, shown in comparison to the respective best-fit calculated (lower trace) spectra. At the bottom, the bar codes indicate the assignment of the methyl-^{13}C resonances into three groups of three; the broader width of the bars for one set of three resonances denotes faster reorientation with exchange rate constant k'.

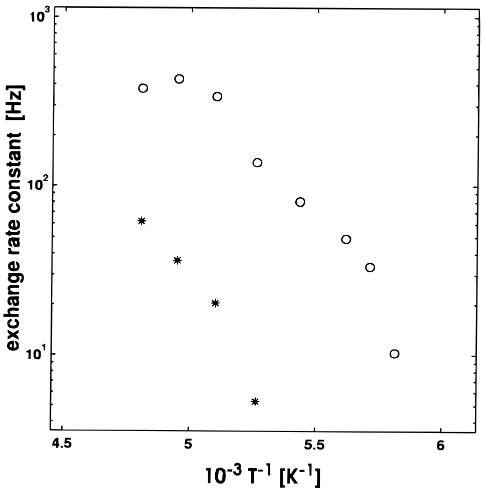


Figure 6. Semilogarithmic plot of the exchange rate constants k' (○) and k'' (∗), obtained from spectral line shape simulations, *versus* $1/T$. Note the deviation from an Arrhenius-type behavior.

Experimental Section

Our sample of compound **1** was kindly supplied by P. D. Lickiss, Salford, U.K. All ^{13}C and ^{29}Si CP/MAS NMR experiments on **1** were run on Bruker MSL 300 and MSL 200 NMR spectrometers (Larmor frequencies ^{13}C 75.5 and 50.3 MHz, respectively; ^{29}Si 59.6 MHz), using standard 4 mm ZrO$_2$ rotors, standard double-bearing probes, and temperature-control units. For the low-temperature MAS experiments, purified N$_2$ gas was used as the drive and bearing gas. MAS frequencies were in the range 1.9–2.7 kHz, isotropic chemical shifts δ ^{13}C, δ ^{29}Si are given with respect to external SiMe$_4$ ≡ 0 ppm. The ^{1}H $\pi/2$ pulse durations were 5 μs, the contact times for the Hartmann–Hahn cross polarization were 5 ms (^{13}C) and 2 ms (^{29}Si), respectively, and recycle delays of 3–5 s have been employed. Phase cycling for the 2D EXSY sequence[6] was according to the TPPI method;[7] rotor-synchronization of mixing times τ_m was unnecessary for both ^{13}C and ^{29}Si 2D EXSY experiments on **1**: working at an external magnetic field strength $B_0 = 7$ T and with MAS frequencies in the range of ca. 1.9–2.7 kHz corresponds to the so-called fast-spinning regime for the methyl-^{13}C and SiMe$_3$-^{29}Si resonances of **1**. Spectral line shape simulations of the variable-temperature ^{13}C CP/MAS NMR spectra of **1** were carried out as decribed previously;[3,5] error minimization in iterative fitting employed the MATLAB[8] simplex routine.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We would like to thank P. D. Lickiss, University of Salford, U.K., for the donation of compound **1**.

OM9705463

---

(6) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: Oxford, 1987.

(7) Marion, D.; Wüthrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 467.

(8) *MATLAB*, Version 4.2; The Math Works Inc.: Natick, MA, 1992.

(9) Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1981**, *74*, 2721.