

Conformational Studies by Dynamic NMR, Part 68<sup>[\*]</sup>

## Correlated Rotation of the Me<sub>3</sub>Si Groups in Tris(trimethylsilyl)methanes

Daniele Casarini,<sup>[b]</sup> Elisabetta Foresti,<sup>[c]</sup> Lodovico Lunazzi,<sup>[a]\*</sup> and Andrea Mazzanti<sup>[a]\*</sup>

*Dedicated to Dr. Keith U. Ingold on the occasion of his 70th birthday*

**Abstract:** Low-temperature NMR spectra of (Me<sub>3</sub>Si)<sub>3</sub>CH (**1**) allowed the restricted rotation of the Me<sub>3</sub>Si groups to be detected; the barrier was 5.1 kcal mol<sup>-1</sup>. On the basis of molecular mechanics calculations, this motion was assigned to a correlated disrotatory process with an eclipsed, staggered, staggered (ESS) transition state. In (Me<sub>3</sub>Si)<sub>3</sub>CMe (**2**), both a correlated ESS disrotatory process and a correlated conrotatory SSS process were distinguished, with rotational barriers of 6.7 and 5.15 kcal mol<sup>-1</sup>, respectively. Thus, **2** appears to adopt a chiral conformation (point group C<sub>3</sub>) at low temperature. For

more hindered derivatives such as (Me<sub>3</sub>Si)<sub>3</sub>CCH<sub>2</sub>Me (**3**) and (Me<sub>3</sub>Si)<sub>3</sub>CCH<sub>2</sub>Et (**4**), the ESS and SSS processes involving rotation about the Si–C bonds were also detected, but in addition a third process became evident. This process corresponds to restricted rotation about the C–C bond and seems to be correlated with the SSS conrotatory process at the C–Si bond, since both

display essentially the same barrier. Although in (Me<sub>3</sub>Si)<sub>3</sub>CCH<sub>2</sub>Ph (**5**) the effects of restricted rotation about the C–CH<sub>2</sub>Ph bond could not be observed, the same chiral conformation adopted by **3** and **4** (point group C<sub>1</sub>) was nonetheless assigned on the basis of molecular mechanics calculations and X-ray diffraction studies. The <sup>13</sup>C spectra (CP-MAS) of crystalline **5** also showed that the pairs of *ortho* and *meta* phenyl carbon atoms are diastereotopic due to restricted Ph–CH<sub>2</sub> bond rotation in the solid state.

**Keywords:** conformational analysis  
• molecular mechanics calculations  
• NMR spectroscopy • stereodynamics

### Introduction

The stereomutation processes occurring in compounds of the type (tBu)<sub>3</sub>MX were analysed by Mislow et al.,<sup>[2–4]</sup> who showed that the rotation of the tBu groups is a correlated motion in which a single-step process leads to permutational rearrangement in more than one of the three tBu groups. As exemplified by (tBu)<sub>3</sub>SiH, two possible pathways, termed SSS (staggered, staggered, staggered) and ESS (eclipsed, staggered, staggered), were taken into account.<sup>[2]</sup>

In the transition state of the SSS pathway, all the tBu groups are in a staggered arrangement, and in that of the ESS pathway, one of the tBu groups eclipses the Si–H and Si–C bonds, while the remaining two are still staggered. In (tBu)<sub>3</sub>SiH the calculated barrier for the SSS process was predicted<sup>[2]</sup> to be lower than that of the ESS process (5.1 and 6.8 kcal mol<sup>-1</sup>, respectively). In the SSS pathway the correlated rotation of the three tBu groups occurred in the same direction (conrotation), whereas in the ESS pathway the rotation of one of the three tBu groups had an opposite sense to the other two (disrotation). When the motion with the higher barrier (ESS) is slow and the SSS pathway is still fast, the three methyl groups lose their complete equivalence. One of them experiences an environment different from that of the other two, which remain symmetry equivalent since the fast SSS process still averages two of the three methyl environments. An analogous behaviour was observed in tBu<sub>3</sub>SiMe, in which the barrier for the ESS pathway (7.9 kcal mol<sup>-1</sup><sup>[4]</sup>) is higher than that measured<sup>[2]</sup> for tBu<sub>3</sub>SiH (6.1 kcal mol<sup>-1</sup>).<sup>[5]</sup>

Since the Me–Si bonds of Me<sub>3</sub>Si groups are longer than the Me–C bonds of tBu groups, steric crowding will be lower, and the barriers for rotation about the Si–C bond in (Me<sub>3</sub>Si)<sub>3</sub>CH (**1**) and (Me<sub>3</sub>Si)<sub>3</sub>CMe (**2**) are expected to be lower than those for the C–Si bonds in tBu<sub>3</sub>SiH and tBu<sub>3</sub>SiMe. We therefore

[a] Prof. Dr. L. Lunazzi, Dr. A. Mazzanti  
Department of Organic Chemistry “A. Mangini”  
University of Bologna  
Risorgimento, 4 Bologna I-40136 (Italy)  
Fax: (+39) 051-2093654  
E-mail: lunazzi@ms.fci.unibo.it

[b] Prof. Dr. D. Casarini  
Department of Chemistry, Università della Basilicata  
Potenza (Italy)

[c] Prof. Dr. E. Foresti  
Department of Chemistry “G. Ciamician”  
University of Bologna  
Via Selmi, Bologna (Italy)

[\*] For Part 67, see ref. [1]

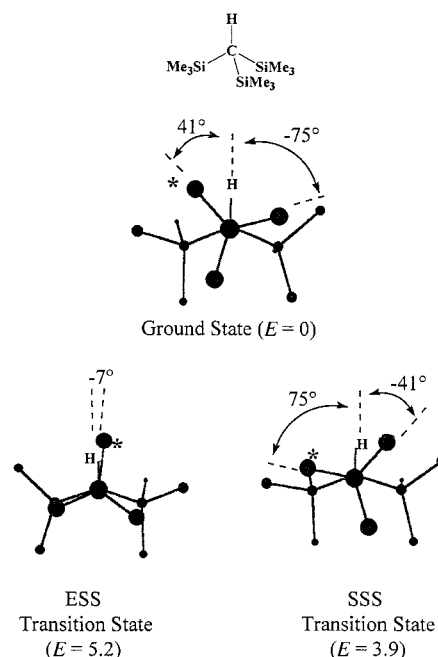
investigated the conformations and rotational pathways of compounds of general formula  $(\text{Me}_3\text{Si})_3\text{CR}$  (**1–5**) by means of molecular mechanics (MM) calculations,<sup>[6]</sup> X-ray diffraction and dynamic NMR measurements.

$(\text{Me}_3\text{Si})_3\text{CH}$	<b>1</b>
$(\text{Me}_3\text{Si})_3\text{Me}$	<b>2</b>
$(\text{Me}_3\text{Si})_3\text{CH}_2\text{Me}$	<b>3</b>
$(\text{Me}_3\text{Si})_3\text{CH}_2\text{Et}$	<b>4</b>
$(\text{Me}_3\text{Si})_3\text{CH}_2\text{Ph}$	<b>5</b>

## Results and Discussion

In the MM calculated<sup>[6]</sup> ground state of **1**, each of the three  $\text{Me}_3\text{Si}$  groups has the same three H-C-Si-Me dihedral angles (163, 41, and  $-75^\circ$ ). Hence, one methyl group is approximately *anti* (*a*) to the C-H bond and the other two occupy two different *gauche* environments (*g* and  $-g$ ) with respect to this bond (ground state structure *a*, *g*,  $-g$  (Scheme 1). As a consequence, the three methyl groups within each homotopic  $\text{Me}_3\text{Si}$  moiety would appear diastereotopic (symmetry group  $C_3$ ) when all the internal motions are slow.

**Abstract in Italian:** Gli spettri NMR a bassa temperatura di **1**,  $(\text{Me}_3\text{Si})_3\text{CH}$ , hanno permesso di identificare la rotazione ristretta dei gruppi  $\text{SiMe}_3$ , la cui barriera risulta pari a  $5.1 \text{ kcal mol}^{-1}$ . Sulla base di calcoli di meccanica molecolare questo processo è stato attribuito ad un moto disrotatorio correlato, il cui stato di transizione corrisponde ad una situazione identificata come ESS (cioè eclissata, sfalsata, sfalsata). Nel derivato **2**,  $(\text{Me}_3\text{Si})_3\text{CMe}$ , sono stati identificati sia un moto disrotatorio correlato, sia un moto conrotatorio correlato, identificato, quest' ultimo, come SSS (sfalsato, sfalsato): le corrispondenti barriere rotazionali risultano, rispettivamente, pari a  $6.7$  e  $5.15 \text{ kcal mol}^{-1}$ . Come conseguenza **2** assume una conformazione chirale (gruppo di simmetria  $C_3$ ) a bassa temperatura. Quando vengono esaminati composti maggiormente impediti, quali **3**  $(\text{Me}_3\text{Si})_3\text{CCH}_2\text{Me}$  e **4**,  $(\text{Me}_3\text{Si})_3\text{CCH}_2\text{Et}$ , si osservano ancora i due processi ESS e SSS ma, in aggiunta a questi, risulta osservabile un terzo processo dinamico. Quest' ultimo è dovuto alla rotazione ristretta attorno al legame C-C ed appare correlato con il processo conrotatorio SSS attorno al legame C-Si, dal momento che entrambi presentano la medesima barriera. Nel caso di **5**  $(\text{Me}_3\text{Si})_3\text{CCH}_2\text{Ph}$  non è stato possibile identificare la rotazione ristretta attorno al legame C-C, tuttavia **5** sembra comunque preferire la stessa conformazione chirale di **3** e **4**, come confermato dai calcoli di meccanica molecolare e dalla diffrazione ai raggi X. Gli spettri  $^{13}\text{C}$  di **5** allo stato cristallino mostrano, inoltre, come i due carboni orto e i due carboni meta dell' anello fenilico siano diastereotopici poichè, nel solido, la rotazione attorno al legame  $\text{Ph-CH}_2$  risulta impedita.



Scheme 1. Schematic calculated ground state (top) and rotational transition states (bottom) of **1**; selected Me-Si-C-H dihedral angles are given. The relative calculated energies  $E$  are in  $\text{kcal mol}^{-1}$ .

Our MM calculations indicate that the ESS pathway of **1** is a correlated disrotatory process with a calculated barrier of  $5.2 \text{ kcal mol}^{-1}$ . In the transition state, the Me-Si bonds of one of the three  $\text{Me}_3\text{Si}$  groups nearly eclipse the C-H and the two Si-CH bonds (Scheme 1),<sup>[7]</sup> whereas in the remaining pair of  $\text{Me}_3\text{Si}$  groups, the corresponding Me-Si bonds are nearly staggered with respect to the C-H and Si-CH bonds and have equal values of the three H-C-Si-Me dihedral angles. The calculated H-C-Si-Me dihedral angles for the two staggered  $\text{Me}_3\text{Si}$  groups are  $-163$ ,  $75$ , and  $-41^\circ$ ; the opposite sign with respect to the ground state means that the two *gauche* methyl groups have exchanged their positions. To reach the ESS transition state, one of the three dihedral angles (H-C-Si-Me\*; see Scheme 1) decreases from  $41$  to  $-7^\circ$ , whereas the corresponding angles of the other two  $\text{Me}_3\text{Si}$  groups increase from  $41$  to  $75^\circ$ . Hence, a disrotatory process has taken place. This pathway, together with the concomitant SES and SSE pathways,<sup>[2]</sup> would make all nine methyl groups dynamically equivalent.

The same calculations indicate that the SSS process in **1** is a correlated conrotatory motion with a barrier of  $3.9 \text{ kcal mol}^{-1}$ . This pathway corresponds to an enantiomerization process which makes the two *gauche* methyl groups dynamically equivalent and leaves the *anti* methyl group diastereotopic (average  $C_{3v}$  symmetry). In the SSS transition state, one of the three  $\text{Me}_3\text{Si}$  groups (indicated by an asterisk in Scheme 1) appears to have almost exchanged the positions of its two *gauche* methyl groups with respect to the ground state, whereas the Me groups of the other two  $\text{Me}_3\text{Si}$  groups are still close to their ground-state positions. When the rotational process is complete, however, the latter also appear to have exchanged the positions of their *gauche* methyl groups to give the enantiomer of the ground state conformation. In this

process (SSS) all three dihedral angles of  $41^\circ$  increase to  $75^\circ$ , and those of  $-75^\circ$  decrease to  $-41^\circ$ ; hence the motion is conrotatory.

As anticipated, both calculated barriers are lower than the corresponding barriers calculated for  $t\text{Bu}_3\text{SiH}$ .<sup>[2]</sup> Nevertheless, the higher of the two ( $5.2 \text{ kcal mol}^{-1}$  for the ESS pathway of **1**) should still be amenable to experimental verification by NMR spectroscopy, provided the chemical shift separation of the methyl signals is sufficiently large.

At ambient temperature the  $^{13}\text{C}$  NMR spectrum (75.5 MHz) of **1** displays two sharp Me and CH peaks ( $\delta = 4.29$  and  $3.69$ , respectively) with a 9:1 intensity ratio (Figure 1). Even at  $-140^\circ\text{C}$  their line widths remain equal to

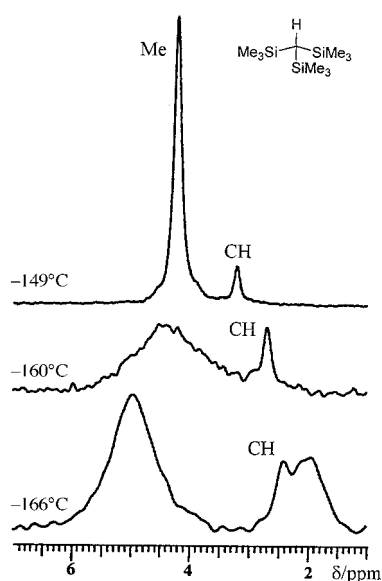


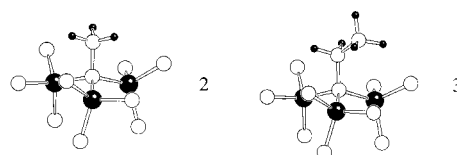
Figure 1. Temperature dependence of the  $^{13}\text{C}$  NMR spectrum (75.5 MHz) of **1**, showing the splitting due to the ESS process (see text).

those of the solvent. Below  $-150^\circ\text{C}$ , however, the signal of the Me groups broadens much more than that of the CH carbon atom and eventually splits, at  $-166^\circ\text{C}$ , into a pair of signals separated by 225 Hz, with a relative intensity of 2:1 ( $\delta = 4.93$  and  $1.94$ , respectively). The CH signal, in contrast, remains a relatively sharp singlet (shifted to  $\delta = 2.41$  at this temperature) between the two signals of the methyl groups.

Computer line shape simulation yielded a  $\Delta G^\ddagger$  value of  $5.1 \pm 0.2 \text{ kcal mol}^{-1}$  for the exchange process. The observation of only two types of diastereotopic methyl groups indicates that solely the ESS pathway is slow on the NMR

time scale, and this was further confirmed by the experimental barrier being almost coincident with that calculated for this process. Also, the fact that at the lowest attainable temperature ( $-166^\circ\text{C}$ ), the major and the minor methyl signals of **1** still have essentially the same line width indicates that the SSS pathway is too fast to be experimentally observed. In agreement herewith is the theoretical prediction of a rotational barrier of  $3.9 \text{ kcal mol}^{-1}$  which is too small for detection by NMR spectroscopy.<sup>[8]</sup>

When applied to **2** the same calculations give analogous results to those of **1** with regard to the conformation and the stereodynamics: **2** can also undergo correlated conrotatory SSS and disrotatory ESS pathways. In the MM calculated structure of the ground state of **2** (Scheme 2) the three methyl groups of the three homotopic  $\text{Me}_3\text{Si}$  groups are diastereotopic. Substitution of the C–H hydrogen atom of **1** by the bulkier methyl group is expected to raise the rotational barriers of **2** with respect to those **1**. Indeed the barrier calculated for the SSS pathway becomes 5.0, and that for the ESS pathway  $7.3 \text{ kcal mol}^{-1}$ . Both should be therefore accessible to an experimental determination by NMR spectroscopy.



Scheme 2. Calculated ground state conformation of **2** (left) and **3** (right). The hydrogen atoms of the  $\text{SiMe}_3$  groups have been omitted for clarity; the other hydrogen atoms and the Si atoms are shaded black.

In the  $^{13}\text{C}$  NMR spectrum of **2** (Figure 2), the singlet of the nine equivalent methyl carbon atoms ( $\delta = 1.2$ ) broadens below  $-100^\circ\text{C}$  much more than those of the other methyl and quaternary carbon atoms ( $\delta = 14.3$  and  $-2.30$ , respec-

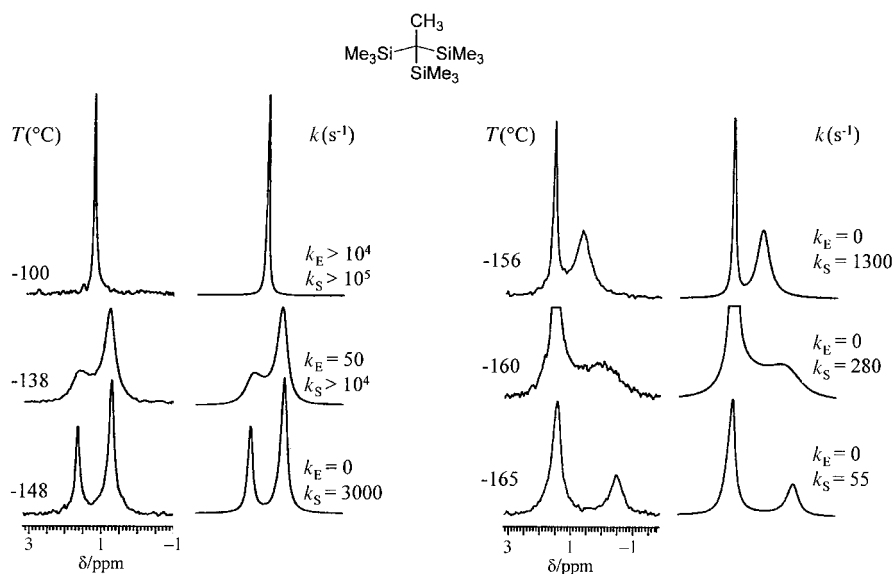


Figure 2. Experimental and simulated  $^{13}\text{C}$  spectrum of the  $\text{SiMe}$  signal of **2** in the temperature range  $-100$  to  $-148^\circ\text{C}$  (left), showing essentially the effects of the ESS process (described by the rate constant  $k_E$ ). Experimental and simulated  $^{13}\text{C}$  NMR spectrum of the  $\text{SiMe}$  signal of **2** in the temperature range  $-156$  to  $-165^\circ\text{C}$  (right), showing essentially the effects of the SSS process (described by the rate constant  $k_S$ ).

tively), and eventually splits at  $-148^{\circ}\text{C}$  into a pair of signals separated by 70 Hz ( $\delta = 1.65$  and  $0.71$ ), with a intensity ratio of 1:2. The experimental  $\Delta G^{\ddagger}$  value for this process (assigned to the ESS pathway) is  $6.7 \pm 0.2 \text{ kcal mol}^{-1}$ , a value in agreement with theoretical predictions.

Contrary to the case of **1**, however, the more intense signal is broader than the minor one, and the width at half-height further increases on cooling below  $-150^{\circ}\text{C}$  (Figure 2, right). The major signal ( $\delta = 0.71$ ) eventually splits into a pair of equally intense lines with a separation of 145 Hz at  $-165^{\circ}\text{C}$  ( $\delta = 1.45$  and  $-0.47$ ). They correspond to the pair of diastereotopic *gauche* methyl groups that are anisochronous at this temperature: the signal at lower field is coincidentally superimposed at  $-165^{\circ}\text{C}$  on that of the methyl group in the *anti* position,<sup>[9]</sup> as revealed by the 2:1 integrated intensity ratio. The existence of three anisochronous Me groups that render **2** chiral at low temperature ( $C_3$  symmetry) has been thus verified. This second dynamic process, corresponding to the disrotatory SSS pathway, has an experimental  $\Delta G^{\ddagger}$  value ( $5.15 \pm 0.2 \text{ kcal mol}^{-1}$ ) in good agreement with the calculated value ( $5.0 \text{ kcal mol}^{-1}$ ).

If the threefold symmetry axis that coincides with the C–Me bond of **2** is eliminated by replacing the Me group with an Et group, the resulting 1,1,1-tris(trimethylsilyl)propane (**3**) will become a totally asymmetric molecule (symmetry group  $C_1$ ) once rotation about the C–Et and Si–C bonds is frozen. The calculated (MM) ground state structure of **3** is shown in Scheme 2. The three  $\text{Me}_3\text{Si}$  groups of **3** are thus expected to lose their equivalence and give rise to three diastereotopic silicon atoms and nine diastereotopic Si-bonded methyl groups. The  $^1\text{H}$  NMR spectrum would accordingly display, in principle, nine signals for the 27 methyl hydrogen atoms, whereas the signals of the ethyl group would be unaffected by these dynamic processes. Indeed the  $^1\text{H}$  NMR signal of the  $\text{Me}_3\text{Si}$  groups remains a singlet down to  $-140^{\circ}\text{C}$  but decoalesces into a 1:2 doublet at  $-148^{\circ}\text{C}$  owing to the restriction of the same ESS process described for **1** and **2**. At  $-164^{\circ}\text{C}$  three signals are eventually detected (Figure 3, top), but their relative intensities are not in the 1:1:1 ratio expected if solely the SSS process were frozen. The actual ratio of 5:2:2 can be accounted for by nine anisochronous overlapping lines, generated by the simultaneous restriction of both the SSS and C–Et rotations.<sup>[10]</sup> This interpretation is additionally supported by the  $^{13}\text{C}$  NMR spectrum of the corresponding nine methyl carbon atoms, which at the same temperature give rise to five signals (Figure 3, bottom) with approximate integrated relative intensities of 2:3:1:1:2. The wider chemical shift range of  $^{13}\text{C}$  NMR spectra (in the present case 350 Hz at 75.5 MHz) lowers the probability of accidental coincidences, so that five signals, as opposed to three in the  $^1\text{H}$  NMR spectrum, could be resolved.

In principle the three and five lines of the  $^1\text{H}$  and  $^{13}\text{C}$  spectra, respectively, could be also explained by assuming that the ESS and the C–Et rotations are slow, while the SSS rotation is still fast. In this case the molecule would retain a dynamic plane of symmetry, and the  $^1\text{H}$  spectrum would comprise five lines in a ratio of 1:2:2:2:2, and the accidental coincidence of three of them might reproduce the 5:2:2 experimental intensity ratio of the three signals. The  $^{13}\text{C}$

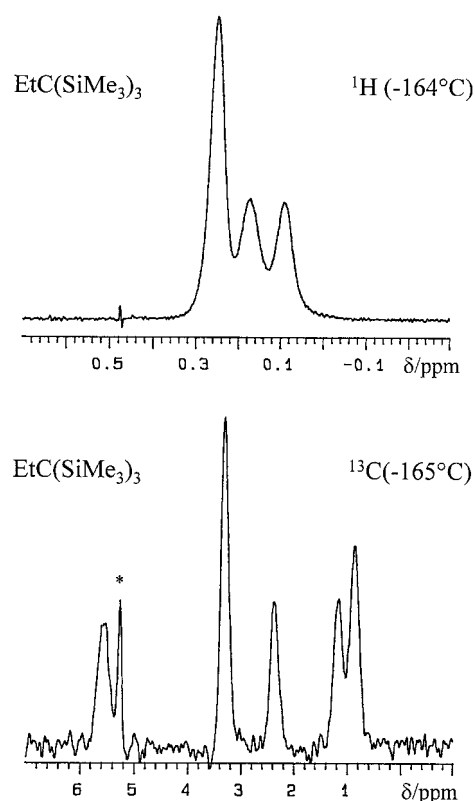


Figure 3.  $^1\text{H}$  NMR spectrum (300 MHz) of the  $\text{SiMe}_3$  groups of **3** at  $-164^{\circ}\text{C}$  (top), displaying three lines with a 5:2:2 intensity ratio.  $^{13}\text{C}$  NMR spectrum (75.5 MHz) of the silicon-bonded carbon atoms of **3** at  $-165^{\circ}\text{C}$  (bottom), showing five different signals (integrated intensity ratio 2:3:1:1:2) for the nine  $\text{SiMe}_3$  carbon atoms (the sharp line with an asterisk is that of the quaternary carbon atom).

spectrum would likewise comprise five lines in a ratio of 1:2:2:2:2, but this result is not consistent with the experimental intensity distribution (i.e., 2:3:1:1:2). Accordingly this model can be safely dismissed.

Finally we monitored the  $^{29}\text{Si}$  NMR (59.6 MHz) singlet of the three isochronous silicon atoms. It broadens significantly on lowering the temperature below  $-130^{\circ}\text{C}$  and splits, at  $-166^{\circ}\text{C}$ , into a pair of signals with a ratio of 1:2 (Figure 4). This indicates that the silicon atoms too are diastereotopic: the coincidence of two of the three expected lines can be understood in terms of the conformation calculated for **3**.

A Newman projection along the C–Et bond shows that the silicon atoms occupy the  $-g$ ,  $+g$ ,  $a$  positions with respect to the methyl group of the ethyl substituent (Scheme 3). The corresponding Si–C–CH<sub>2</sub>–Me dihedral angles were calculated to be  $-72$  ( $-g$ ),  $51$  ( $+g$ ) and  $170^{\circ}$  ( $a$ ). If we take into account the approximations of the MM approach and the occurrence of fast libration processes (requiring a low-barrier displacement of a few degrees with respect to the perfectly staggered arrangement), the *gauche* silicon atoms can be considered to lie on almost identical positions, with essentially equal absolute values of their dihedral angles (close to  $-60$  and  $+60^{\circ}$ ). Therefore, whereas the *anti* silicon atom lies in a site very different from those of the two *gauche* silicon atoms, the latter are located in essentially identical positions and hence have coincident chemical shifts. Indeed, they are diastereo-

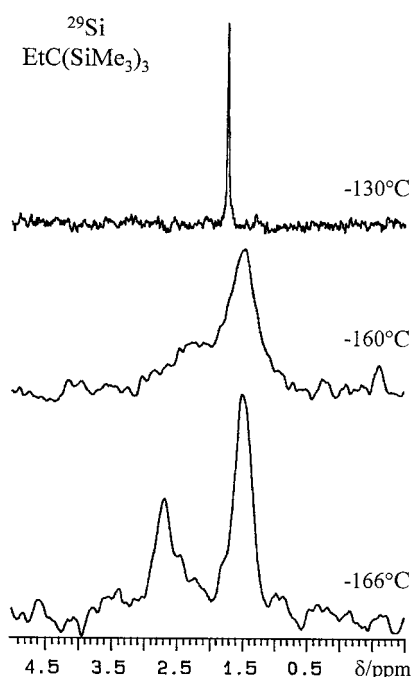
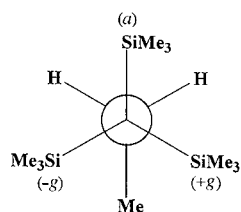


Figure 4. Temperature dependence of the  $^{29}\text{Si}$  NMR spectrum (59.6 MHz) of **3**, displaying (at  $-166^\circ\text{C}$ ) two lines (ratio 1:2) separated by 75 Hz.

topic only in an indirect way, in that they are bonded to methyl groups that experience different environments. This is because the three methyl groups bonded to  $-g$  silicon atoms



Scheme 3. Newman projection of **3** along the C–Et bond (conformation *a*, *g*,  $-g$ ).

have a spatial relationship (e.g., with respect to the methyl group of the ethyl moiety) that differs from that of the methyl bonded to the  $+g$  silicon atom, as demonstrated by the multiplicity of the corresponding  $^{13}\text{C}$  signals.<sup>[11]</sup>

The barrier for the ESS process in **3** was determined by simulating the  $^1\text{H}$  NMR signal of the Si-bonded methyl groups. Its value of  $\Delta G^\ddagger = 6.7 \pm 0.15 \text{ kcal mol}^{-1}$  at  $-144^\circ\text{C}$  is equal to that measured for **2**. The effects on the line shape due to the subsequent SSS process occurred simultaneously with the rotation about the C–Et bond, both in the  $^1\text{H}$  and  $^{13}\text{C}$  spectra. This seems to indicate that these two processes have a unique free energy of activation and therefore share a common transition state; this suggests that the two processes are strongly correlated. However, the complexity of the spectral patterns in the temperature range of interest prevented a reliable determination of this value either at the  $^1\text{H}$  or at the  $^{13}\text{C}$  frequency.

The shape of the  $^{29}\text{Si}$  line depends solely on the restriction of rotation about the C–Et bond because the direct effects of the ESS and SSS processes are not observable at the silicon NMR frequency. As a consequence a simpler spectral shape was observed (Figure 4), which allowed us to determine a free energy of activation of  $5.55 \pm 0.15 \text{ kcal mol}^{-1}$ . This value represents the barrier for rotation about the C–Et bond in interaction with the SSS process since these two motions do

not take place independently of each other. These conclusions are supported by the observation that very similar low-temperature spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$ ) were also observed for the analogous compound **4**, in which the ethyl group of **3** is replaced by an *n*-propyl group. The barriers measured for the latter were essentially equal to those of **4** (Table 1).

Table 1. Experimental free energies of activation  $\Delta G^\ddagger$  [ $\text{kcal mol}^{-1}$ ] for rotation about the  $\text{Me}_3\text{Si}-\text{C}$  (ESS and SSS processes) and C–C bonds in **1–5**.

Compound	ESS process	SSS process	C–C rotation
<b>1</b>	5.1	–	–
<b>2</b>	6.7	5.15	–
<b>3</b>	6.7	5.55	5.55
<b>4</b>	6.7	5.5	5.5
<b>5</b>	7.05 (10.1 <sup>[a]</sup> )	–	–

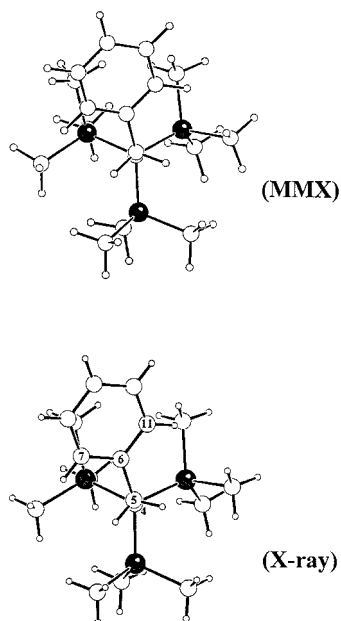
[a] Measured in the solid state (see text).

Having the same overall symmetry, **5** is expected to display stereodynamic processes analogous to those of **3** and **4**, although the size and the position of the Ph group might significantly affect the values of the activation energies. In both the  $^1\text{H}$  and  $^{13}\text{C}$  spectra the Me signal split into a 1:2 pair of lines in the range  $-130$  to  $-140^\circ\text{C}$ ; the barrier for the corresponding motion was  $7.05 \pm 0.15 \text{ kcal mol}^{-1}$ . Contrary to the case of **3** and **4**, however, a further lowering of the temperature did not produce additional modifications of the spectral multiplicity. Two possible models should be considered for explaining such a different behavior.

The ESS process could be responsible for the observed barrier of  $7.05 \text{ kcal mol}^{-1}$  (a value similar to those of **3** and **4**), whereas the SSS and the C– $\text{CH}_2\text{Ph}$  rotations might have a barrier too low to be detected by NMR spectroscopy. Alternatively, the ESS and SSS barriers may have become too low to be observed, so that the restricted rotation about the C– $\text{CH}_2\text{Ph}$  bond would be responsible for the 1:2 pair of lines observed below  $-130^\circ\text{C}$  (and for the related barrier of  $7.05 \text{ kcal mol}^{-1}$ ). Indeed the conformation calculated for **5** and its X-ray crystal structure (Scheme 4), show that one  $\text{Me}_3\text{Si}$  group is *anti* and two  $\text{Me}_3\text{Si}$  groups are *gauche* with respect to the benzyl substituent (a conformation essentially identical to that discussed for **3**; see Scheme 3).

Consequently, a restricted rotation about the C– $\text{CH}_2\text{Ph}$  bond might well be responsible for the observed line splitting in the  $^1\text{H}$  and  $^{13}\text{C}$  spectra. This hypothesis, however, also requires the  $^{29}\text{Si}$  signal of **5** to split in the same temperature range; however, a single sharp line is always observed, even at  $-165^\circ\text{C}$ . Hence, no doubt remains that the measured barrier corresponds to that of the ESS process in each of the three dynamically equivalent  $\text{Me}_3\text{Si}$  groups, a process which does not require splitting of the  $^{29}\text{Si}$  signal. The reason why the other two processes have an energy lower than those of **3** and **4** is probably a consequence of the destabilization of the ground state due to steric interactions of the large phenyl group in the position it assumes in the conformation of **5** shown in Scheme 4.

Although the X-ray structure indicates that the Me groups of **5** are diastereotopic in the solid state, the high-resolution



Scheme 4. Calculated MMX structure (top) and X-ray diffraction structure (bottom) of **5** (the three silicon atoms are shaded black).

solid-state CP-MAS  $^{13}\text{C}$  NMR spectrum exhibits a single line for the nine methyl carbon atoms at ambient temperature. This indicates that rotations about the C–Si and  $\text{PhCH}_2\text{--C}$  bonds are both still fast on the NMR time scale. Below  $-20^\circ\text{C}$  this line begins to broaden and eventually splits, at  $-90^\circ\text{C}$ , into a 1:2 pair of signals corresponding to three and six methyl carbon atoms, respectively. This feature is the result of slow rotation about the C–Si bond (ESS mode), which is the same process as that observed in solution, although this process occurs at temperatures  $50^\circ\text{C}$  lower than in the solid state. Accordingly, the corresponding barrier in the solid state ( $\Delta G^\ddagger = 10.1 \text{ kcal mol}^{-1}$ ) is significantly higher than in solution. The difference of about  $3 \text{ kcal mol}^{-1}$  is due to crystal-lattice effects, as reported in a number of analogous cases.<sup>[12]</sup> Contrary to what observed in solution, the more intense upfield signal is much broader at  $-90^\circ\text{C}$  than its companion (85 vs 60 Hz), and this suggests that the other dynamic processes (i.e., rotation about the C–Si bond in the SSS mode and rotation about the  $\text{PhCH}_2\text{--C}$  bond) possibly begin to take place. Therefore, it seems that in the solid state not only the ESS but also the other motions have higher barriers than in solution. Indeed at  $-120^\circ\text{C}$  further splitting occurred and eventually six methyl carbon signals, with a 1:2:1:1:3:1 intensity ratio, were detected using a 100.6 MHz solid state spectrometer (courtesy of Varian GmbH, Darmstadt). An example of restricted rotation about the C–SiMe<sub>3</sub> bond was detected in the solid state at similar temperatures,<sup>[13]</sup> whereas in another case this motion was not observed to take place, even below  $-100^\circ\text{C}$ .<sup>[14]</sup>

Steric effects due to the position assumed by the phenyl ring might affect the barriers of two dynamic processes (SSS and  $\text{PhCH}_2\text{--C}$  rotations) in **5**; if this is the case, such a conformational arrangement should also affect the solid-state NMR spectra. In fact, the phenyl carbon signals of **5** display a multiplicity different in the solid than in solution, where the pairs of *ortho* and *meta* carbon atoms give rise to only two

lines, having been made homotopic by rapid rotation about the  $\text{Ph--CH}_2$  bond, even at the lowest attainable temperature of  $-165^\circ\text{C}$  (see, for example the spectrum at  $-110^\circ\text{C}$ ; Figure 5, top). In the solid-state spectrum, in contrast, the *ortho* and *meta* carbon atoms give rise to four closely spaced signals (Figure 5, bottom). Since the multiplicity of the methyl signals in the solid-state spectra showed that rotation about the  $\text{PhCH}_2\text{--C}$  bond is fast on the NMR time scale, the four lines must be a consequence of restricted rotation about the  $\text{Ph--CH}_2$  bond in the solid state.

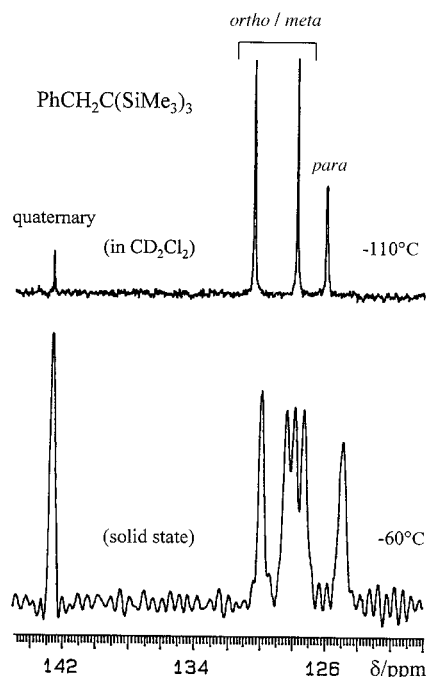


Figure 5. 75.5 MHz  $^{13}\text{C}$  NMR phenyl signals of **5** (top) at  $-110^\circ\text{C}$  (in  $\text{CD}_2\text{Cl}_2$ ), displaying four lines, that is, one for the quaternary (C6) and three for the CH (*ortho*, *meta*, and *para*) carbon atoms. The CH lines have a 2:2:1 intensity ratio because the pairs in *ortho* and *meta* positions are homotopic in solution. 75.5 MHz  $^{13}\text{C}$  solid-state CP-MAS NMR spectrum of the same region at  $-60^\circ\text{C}$  (bottom), showing six lines for the phenyl carbon atoms due to the diastereotopicity of the two *ortho* and of the two *meta* positions in the solid state.

Furthermore, the observed diastereotopicity of the pairs of *ortho* and *meta* carbon atoms also requires that the plane of the phenyl ring adopt an angle other than  $90^\circ$  with respect to the plane defined by the carbon atoms C6–C5–C4 (numbering as in Scheme 4), otherwise a local plane of symmetry, which would render the *ortho* and *meta* carbon atoms homotopic, would be maintained, even in the presence of a slow rotation about the  $\text{Ph--CH}_2$  bond. Accordingly, the dihedral angles C7–C6–C5–C4 and C11–C6–C5–C4 of Scheme 4 must have different values, and this agrees well with the X-ray diffraction data, which yield values of  $+106^\circ$  and  $-77^\circ$ , respectively, for these angles.

Another possible interpretation of the equivalence of the pairs of *ortho* and *meta* carbon atoms in the solution spectra of **5** might be advanced. In principle rotation about the  $\text{Ph--CH}_2$  bond could become slow at low temperature also in solution, but the phenyl ring might undergo a fast libration of  $\pm 15^\circ$  about the  $90^\circ$  equilibrium position, rapidly oscillating be-

tween  $|77^\circ|$  and  $|106^\circ|$  (i.e., the dihedral angles determined by X-ray diffraction). In this way a dynamic symmetry equal to that created by a fixed  $90^\circ$  angle would be achieved, and this process (which is evidently forbidden in the solid state) might generate equivalent *ortho* and *meta* carbon atoms even in the presence of restricted rotation about the Ph–CH<sub>2</sub> bond. We feel, however, that this interpretation is quite unrealistic, since the restricted rotation about the Ph–CH<sub>2</sub> bond has never been detected in nonhindered benzyl groups by NMR spectroscopy in solution. Furthermore, our calculations<sup>[6]</sup> predict a barrier of 4.2 kcal mol<sup>−1</sup> for rotation about the Ph–CH<sub>2</sub> bond in **5**, clearly too low a value to be relevant to the NMR time scale.

In conclusion, although X-ray diffraction and NMR data indicate that **5** is chiral in the solid state, it exhibits dynamic planes of symmetry in solution even at the lowest attainable temperature. In other words, **1** and **5** display, in solution, achiral conformations of the same dynamic symmetry by virtue of fast dynamic processes, whereas **2**, **3**, and **4** exhibit asymmetric, that is chiral, conformations in solution in the appropriate temperature range.

## Experimental Section

**Materials:** Tris(trimethylsilyl)methane was commercially available; tris(trimethylsilyl) compounds were prepared by a known procedure.<sup>[15]</sup> To a solution of tris(trimethylsilyl)methane (5 mmol in 10 mL of anhydrous THF) a solution of methylolithium (1.6 M in Et<sub>2</sub>O, 6 mmol) was added at room temperature. The mixture was heated to reflux for 5 h, during which it turned yellow, and then cooled to room temperature. A solution of the appropriate electrophile (MeI, EtI, PrI, PhCH<sub>2</sub>Br; 10 mmol in 2 mL of anhydrous THF) was added, and after 12 h the reaction mixture was quenched with an aqueous solution of NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O. The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by crystallization (CH<sub>3</sub>OH) to obtain the desired products in 30–50% yields.

**1,1,1-Tris(trimethylsilyl)ethane (2):** White solid, m.p. 153–154 °C (ref. [15]; 155 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 0.06 (s, 27H, SiMe<sub>3</sub>), 1.06 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 1.21 (CH<sub>3</sub>), 3.41 (q), 14.44 (CH<sub>3</sub>).

**1,1,1-Tris(trimethylsilyl)propane (3):** White solid, m.p. 208–209 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 0.13 (s, 27H, SiMe<sub>3</sub>), 1.12 (t, 3H, Me), 1.79 (q, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 2.77 (CH<sub>3</sub>), 3.20 (q), 15.50 (CH<sub>2</sub>), 23.3 (CH<sub>3</sub>); C<sub>12</sub>H<sub>32</sub>Si<sub>3</sub> (260.6): calcd C 55.30, H 12.38, Si 32.33; found C 55.36, H 12.34, Si 32.31.

**1,1,1-Tris(trimethylsilyl)butane (4):** White waxy solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 0.12 (s, 27H, SiMe<sub>3</sub>), 0.86 (t, 3H, Me), 1.42–1.62 (m, 4H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 2.69 (CH<sub>3</sub>), 5.50 (q), 15.87 (CH<sub>3</sub>), 24.35 (CH<sub>2</sub>), 34.00 (CH<sub>2</sub>); C<sub>13</sub>H<sub>34</sub>Si<sub>3</sub> (274.6): calcd C 56.85, H 12.48, Si 30.68; found C 56.88, H 12.42, Si 30.72.

**1,1,1-Tris(trimethylsilyl)-2-phenylethane (5):** White solid, m.p. 77–78 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 0.14 (s, 27H, SiMe<sub>3</sub>), 3.2 (s, 2H, CH<sub>2</sub>), 7.20–7.38 (m, 5H, Ph); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 2.05 (CH<sub>3</sub>), 11.40 (q), 36.02 (CH<sub>3</sub>), 126.90 (CH), 128.43 (CH), 131.55 (CH), 143.65 (q); C<sub>17</sub>H<sub>34</sub>Si<sub>3</sub> (322.7): calcd C 63.27, H 10.62, Si 26.11; found C 63.31, H 10.66, Si 26.05.

**NMR measurements:** The samples for the low-temperature measurements were prepared by connecting to a vacuum line NMR tubes containing the desired compounds and some C<sub>6</sub>D<sub>6</sub> for locking purpose. The gaseous solvents (CF<sub>2</sub>Cl<sub>2</sub> and CF<sub>3</sub>Br, in a 2:1 proportion) were subsequently condensed with liquid nitrogen, and the tubes, sealed under vacuum, were introduced in the precooled probe of the spectrometer. The temperature was independently calibrated with an Ni/Cu thermocouple inserted in the NMR probe (Varian, Gemini 300) before recording the spectra.

The high-resolution <sup>13</sup>C NMR solid-state CP-MAS spectra (Bruker, CXP 300) were recorded at 75.5 MHz. The sample, a white crystalline powder, was packed in a 7-mm zirconia rotor spun at the magic angle with a speed of about 3000 Hz. The number of transients was varied to give good signal to noise ratios in the VT experiments. The chemical shifts were measured with respect to the lower frequency signal of adamantane ( $\delta$  = 29.4). The sample was cooled by a stream of dry nitrogen, precooled in a heat exchanger immersed in liquid nitrogen. The temperatures of the solid-state spectra were calibrated by means of the shift dependence of the <sup>13</sup>C signals of 2-chlorobutane adsorbed on solid Dicalite,<sup>[16]</sup> by assuming a dependence equal to that observed in the neat liquid, which was previously calibrated with the same Cu/Ni thermocouple.

**Calculations:** The molecular mechanics calculations<sup>[6]</sup> were carried out by driving the R-C-Si-Me dihedral angle of one of the three Me<sub>3</sub>Si groups in steps of 10° (near the transition states by 1°) about the corresponding Si–CR axis and allowing all the other bonds and angles of the molecule to relax. In so doing the other two R-C-Si-Me dihedral angles also spontaneously change, as described in the text, and hence the motion is correlated.

**Crystal structure of 1,1,1-tris(trimethylsilyl)-2-phenylethane (5):** C<sub>17</sub>H<sub>34</sub>Si<sub>3</sub>, *M*<sub>r</sub> = 322.7, triclinic, space group *P* $\bar{1}$ , *a* = 8.896(3), *b* = 9.433(2), *c* = 12.820(8) Å,  $\alpha$  = 81.79(5),  $\beta$  = 91.45(6),  $\gamma$  = 76.20 (3)°, *V* = 1034(1) Å<sup>3</sup>, *Z* = 2,  $\rho_{\text{calcd}}$  = 1.036 Mg m<sup>−3</sup>, *F*(000) = 356,  $\lambda$  = 0.71069 Å, *T* = 298 K, MoK $\alpha$  radiation,  $\mu$  = 0.222 mm<sup>−1</sup>, crystal dimensions 0.40 × 0.40 × 0.60 mm. A total of 3812 reflections was collected (3634 unique reflections, *R*<sub>int</sub> = 0.0347). Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated MoK $\alpha$  radiation,  $\omega/2\theta$  scan mode, range 2.24 <  $\theta$  < 24.97°. The unit cell parameters were determined by least-squares refinement on diffractometer angles for 25 automatically centered reflections with 3.74 <  $\theta$  < 6.08°. The structure was solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> with the SHELX program packages.<sup>[17]</sup> In the final refinement cycles 3206 reflections having *I* > 2 $\sigma$ (*I*) were used, and 181 parameters varied. Weights in accord with the Scheme  $w = 1/[\sigma^2(F_o^2) + (0.0893 P)^2 + 0.1947 P]$  were used, where  $P = (F_o^2 + 2F_c^2)/3$ . The hydrogen atoms were located by geometrical calculation and refined with a riding model. The final agreement indices were *R*<sub>1</sub> = 0.0457 and *wR*<sub>2</sub> = 0.1207. GOF on *F*<sup>2</sup>: 1.05. Largest difference peak and hole were 0.239 and −0.399 e Å<sup>−3</sup>. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116793. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

## Acknowledgements

Thanks are due to the I.Co.C.E.A. Institute of CNR (Bologna) for access to the solid-state NMR facilities. Financial support was received from MURST (national project “Stereoselection in Organic Synthesis”) and from the University of Bologna (Finanziamento triennale d’Ateneo 1997–1999).

- [1] D. Casarini, L. Lunazzi, A. Mazzanti, *J. Org. Chem.* **1998**, *63*, 9125.
- [2] W. D. Hounshell, D. L. Iroff, R. J. Wroczynski, K. Mislow, *J. Am. Chem. Soc.* **1978**, *100*, 5212.
- [3] R. J. Wroczynski, K. Mislow, *J. Am. Chem. Soc.* **1979**, *101*, 3980.
- [4] R. J. Wroczynski, D. L. Iroff, K. Mislow, *J. Org. Chem.* **1978**, *43*, 4226. Similar barriers were also measured for the halosilanes *t*Bu<sub>3</sub>SiX (X = Cl, Br, I): M. Weidenbruch, W. Peter, C. Pierrand, *Angew. Chem.* **1976**, *88*, 26; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 43.
- [5] Whereas in *t*Bu<sub>3</sub>SiH and *t*Bu<sub>3</sub>SiMe the SSS pathway is still fast at the lowest attainable temperature (as revealed by a two-line NMR spectrum), in [*t*Bu<sub>3</sub>PMe]<sup>+</sup> and *t*Bu<sub>3</sub>CH, this process could be rendered slow in the NMR time scale.<sup>[3]</sup> Accordingly, the three lines expected for the three diastereotopic *t*Bu methyl carbon atoms were detected, and two different  $\Delta G^\ddagger$  values were obtained.<sup>[3]</sup>
- [6] Use was made of the MMX force field as implemented in the program PC Model, Serena Software, Bloomington, IN.

- [7] The H-C-Si-Me dihedral angles of the eclipsing Me<sub>3</sub>Si group are  $-7$  (asterisked Me group in Scheme 1),  $-126$ , and  $113^\circ$ .
- [8] In such a temperature range the NMR spectra are likely to reveal only those dynamic processes that have barriers larger than about  $5 \text{ kcal mol}^{-1}$ . See F. A. L. Anet, R. Anet in *Determination of Organic Structures by Physical Methods, Vol 3* (Eds: F. C. Nachod, J. J. Zuckerman), Academic Press, New York, **1971**, p. 343; F. A. L. Anet, L. Kozerski, *J. Am. Chem. Soc.* **1973**, *95*, 3407.
- [9] The signal of the *anti* methyl group ( $\delta = 1.65$  at  $-148^\circ\text{C}$ , Figure 2) shifted to about 1.45 on lowering the temperature to  $-165^\circ\text{C}$  (Figure 3).
- [10] These lines are viscosity-broadened at  $-164^\circ\text{C}$  (width at half-height of 12 Hz) and lie in a quite narrow shift range (47 Hz at 300 MHz); this explains the poor resolution which reduces the nine peaks to three signals with such an unusual intensity ratio.
- [11] For instance, the calculated distances between the Me carbon atom of the ethyl group and the three Me carbon atoms bonded to the  $-g$  silicon atom of 3.23, 4.40, and  $5.11 \text{ \AA}$  are quite different to the distances between the same carbon atom and the three Me carbon atoms bonded to the  $+g$  silicon atom (3.62, 3.82,  $5.28 \text{ \AA}$ ), even for the perfectly staggered conformation of Scheme 3.
- [12] F. G. Riddell, S. Arumagam, J. E. Anderson *J. Chem. Soc. Chem. Comm.* **1991**, 1525; P. J. Barrie, J. E. Anderson, *J. Chem. Soc. Perkin Trans 2* **1992**, 2031; F. G. Riddell, S. Arumagam, K. D. M. Harris, M. Rogerson, J. H. Strange, *J. Am. Chem. Soc.* **1993**, *115*, 1881.
- [13] X. Helluy, J. Kümmerlen, A. Sebald, *Organometallics* **1997**, *16*, 5218.
- [14] X. Helluy, J. Kümmerlen, A. Sebald, *Organometallics* **1998**, *17*, 5003.
- [15] M. A. Cook, C. Eaborn, E. Jukes, D. R. M. Walton, *J. Organomet. Chem.* **1970**, *24*, 529.
- [16] A. E. Aliev, K. D. M. Harris *Magn. Reson. Chem.* **1994**, *32*, 366.
- [17] G. M. Sheldrick, SHELXS86, *Acta Crystallogr. Sect. A*, **1990**, *46*, 467; G. M. Sheldrick, SHELXL93, Program for Crystal Structure Refinement, Universität Göttingen, Germany, **1993**.

Received: March 26, 1998 [F 1698]