

Intramolecular Motions in Polymetallacycles

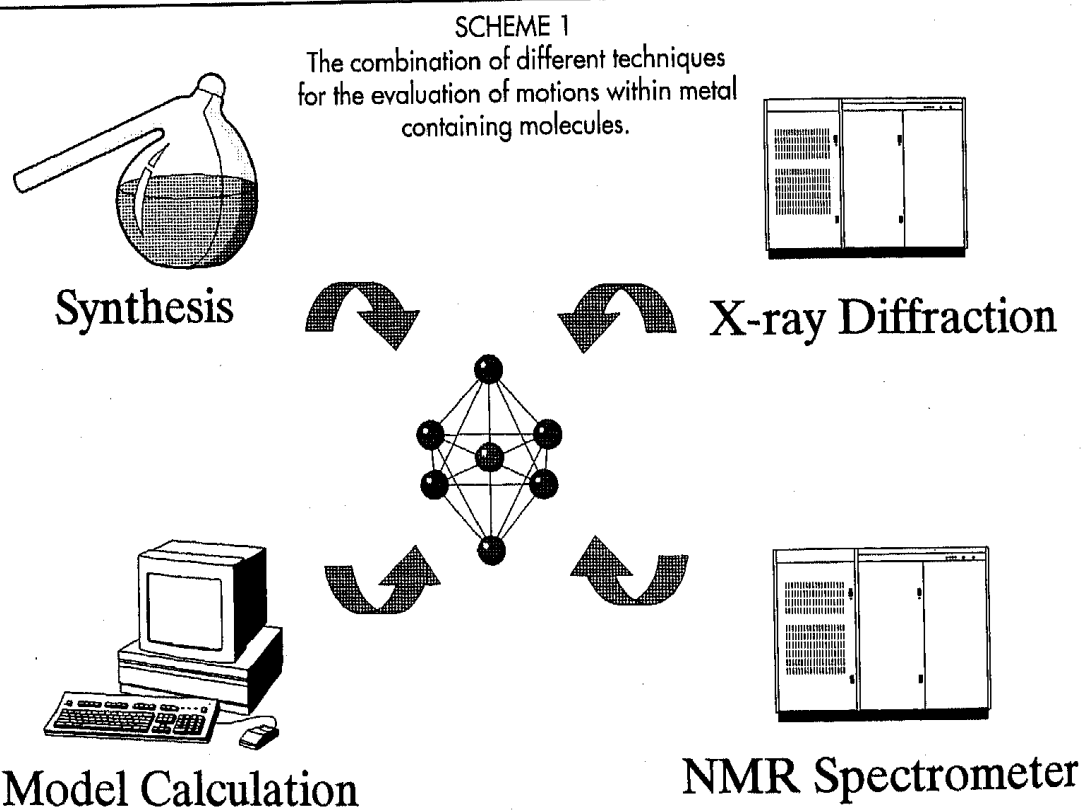
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Molecules with metallic elements tend to have much more intramolecular flexibility and mobility than molecules which are only composed of non-metallic elements. This flexibility is attributed to the fact that the metallic atom seems to use less directional bonds to other atoms compared to a non-metallic element [1]. Due to the metallic atom's ability to assemble as many ligands as possible in a coordination

sphere, competition with other metallic elements in the same molecule occurs when only a few sites are available. This competitive situation seems to be responsible for the high mobility of molecules [2].

How can these motions within molecules be visualized? In Scheme 1, several techniques are shown, which can be combined in order to evaluate the mechanism of fluctuation processes.



The X-ray structure determination may be used to establish the "frozen" structure of a molecule in a crystal. Hence, because of the packing of the molecules, only small oscillations of the atoms are observed (isotropic and anisotropic U-values). The same crystalline powder can be inserted in an NMR using MAS (magic angle spinning) techniques. The spectrum can then be compared to the results of the X-ray structure determination. Principally, any signals of atoms which are not symmetrical should show up. If fewer signals than expected are found, the cause may either be due to resolution problems of the NMR or by motions of the atoms.

Even more information can be gained by temperature-dependent NMR spectroscopy in solution—a method which is well established [3]. The models which may be extracted from the spectra can be compared to results obtained by molecular dynam-

ics or molecular mechanics calculations. In this report, we would like to illustrate the combination of all these techniques by a class of compounds which have recently been synthesized in our laboratory [4].

Previously [5], we reported our investigations concerning the dynamic properties of a particular heterometal amide, containing indium and lithium in the same molecular unit. As a result of extensive variable temperature and multinuclear NMR measurements in solution (and taking into account its crystal structure), we found evidence of coupled intramolecular dynamic processes in which the lithium atom migrates with regard to the other heavy atoms. Here, we want to present and illustrate our results concerning the dynamic behavior of a special class of silylamides containing the main group metal germanium. All the new molecular compounds can easily be prepared according to Scheme 2.

SCHEME 2

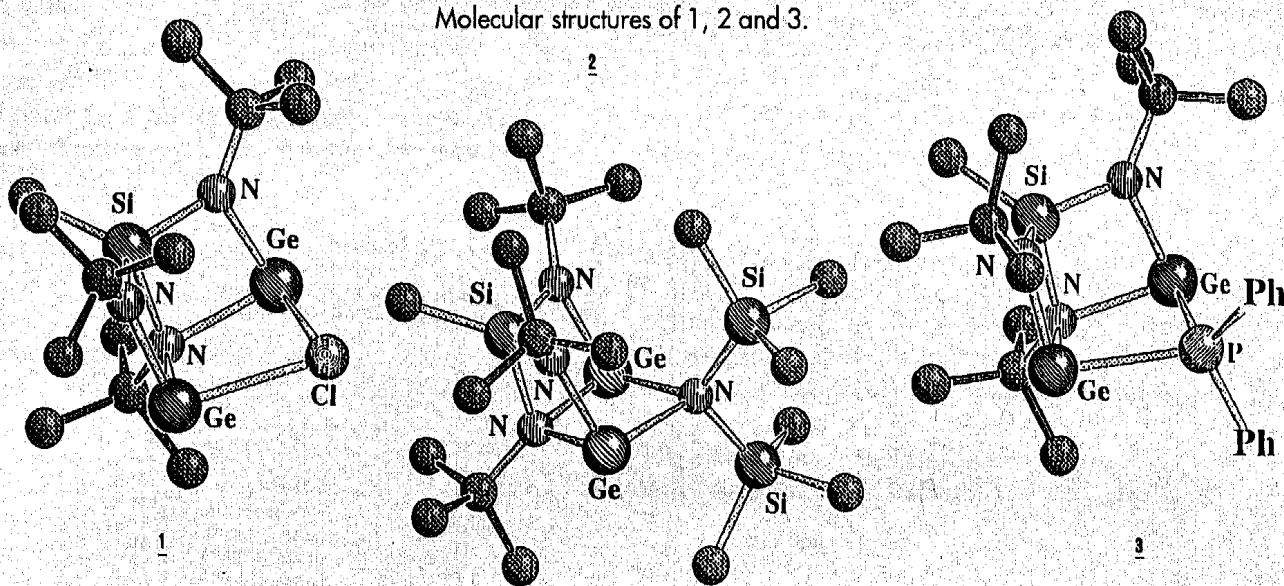


The results of the X-ray structure analyses (Figure 1) show 1, 2 and 3 as monomeric cage compounds consisting of three, fused, four-membered rings forming a distorted cube with one missing cor-

ner. The cage is made up of Si, three N atoms, two Ge atoms and a non-metallic element, which either can be Cl (1) N (2) or P (3).

FIGURE 1

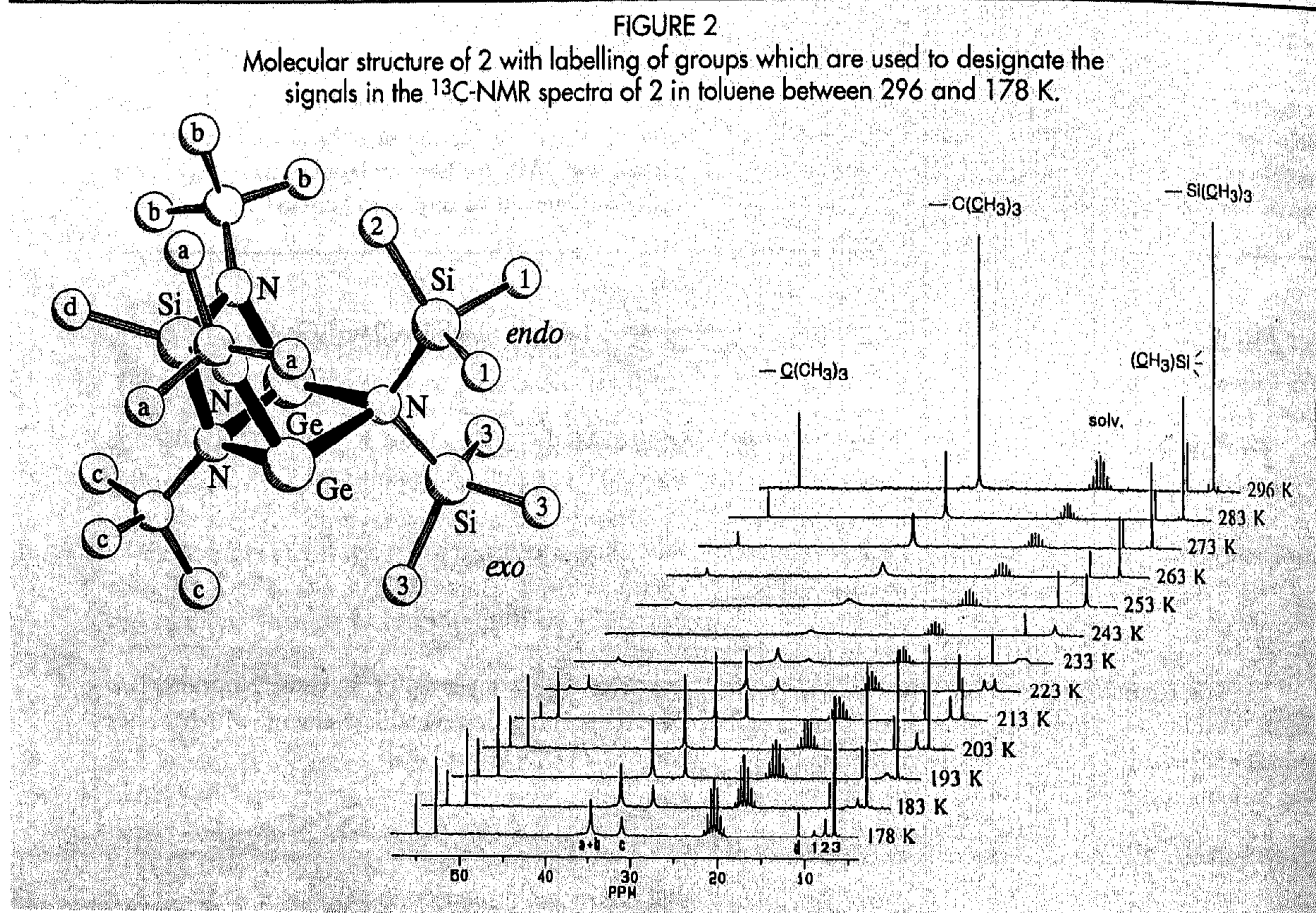
Molecular structures of 1, 2 and 3.



The two metal atoms are coordinated three-fold by nitrogen in compound 2, while in compounds 1 and 3, the third coordination site is occupied by a chlorine and phosphorus atom, respectively. The low C_s -symmetry of 1 and the absence of any symmetry element in 2 and 3 (results from the X-ray structure analyses (see Figure 1)) are not consistent with the NMR spectra in solution or in the solid state. Taking compound 2 as an example, we would like to show, in

detail, the different intramolecular motions of groups and atoms which can be detected by NMR techniques (in 1 and 3 a similar dynamical behavior has been found).

In Figure 2, the molecular structure of compound 2, as a result of the crystal structure analysis, is opposed to a series of temperature-dependent ^{13}C -NMR-spectra in solution.



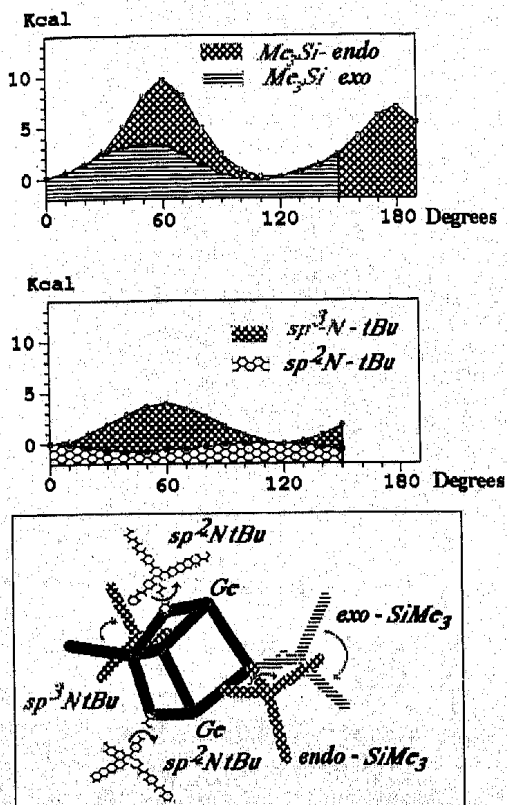
The appearance of only one single resonance line for either the two trimethylsilyl or the three *tert*-butyl groups at room temperature proves that the whole molecular unit has a higher average point symmetry in solution in contrast to the solid state. When the temperature is lowered, different coalescence points for the signals of the trimethyl element groups are observed. The resultant doubling of the resonances of the trimethyl element groups at lower temperature is in accordance with the determined molecular structure of 2 in the solid state, assuming trimethyl element groups rotate quickly around their Si-N bonds. On further lowering of the

temperature, another doubling of one of the two signals of the trimethylsilyl groups (in a 1:2 ratio) indicates its loss of rotary freedom, suggesting its classification as a "cage-inner" endocyclic trimethylsilyl group.

As a result of molecular dynamic model calculations [6] (Figure 3), we observed a very good match between the calculated and experimentally determined activation energies for the reorientation of the endocyclic trimethylsilyl group and others. Simple classical potential calculations can thus be used to probe mechanistic ideas.

FIGURE 3

Energy profiles concerning the rotation of the different $\text{E}(\text{Me}_3)$ groups in compound 2 from results of molecular mechanics calculations.

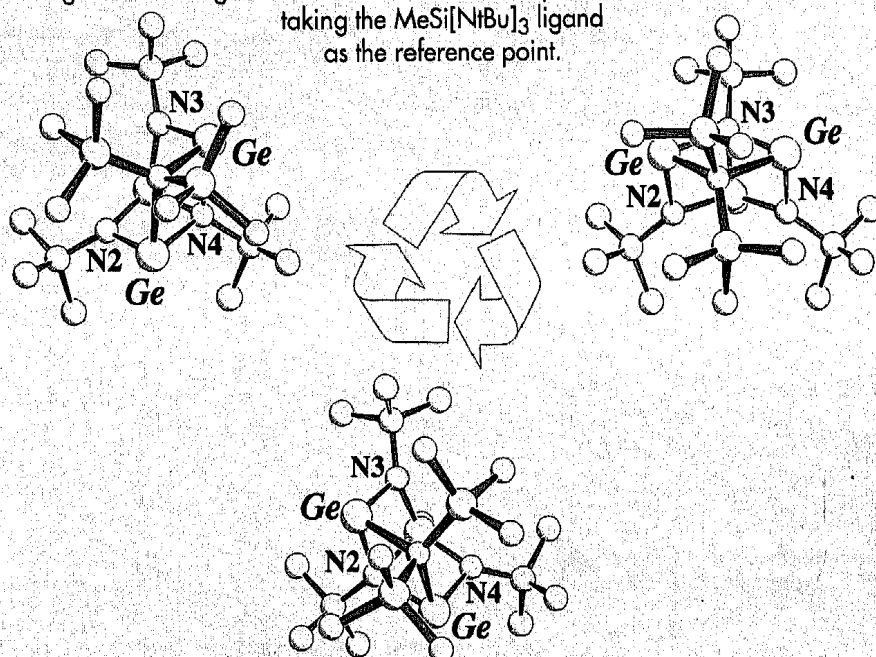


Summarizing the results of the crystal structure analysis, NMR studies and molecular mechanics calculations, we are able to establish a model of the intramolecular dynamical behavior of compound 2 in solution.

At very low temperatures, movements in the freely dissolved molecules begin with low-energy rotations of the peripheral trimethyl element groups, either *tert*-butyl or trimethylsilyl. At higher temperatures, the molecule gains more flexibility, even allowing the endocyclic trimethylsilyl group to rotate around the Si-N bond. By further raising the temperature, a subsequent process is started in which the two germanium atoms are competing for coordination sites at the $(\text{tBuN})_3\text{SiMe}$ moiety of the molecule. From a dynamic point of view, the germanium atoms are equally distributed over the three nitrogen atoms of the $\text{MeSi}(\text{tBuN})_3$ part of the molecule. Moreover the metal fluctuation causes—taking the $\text{MeSi}(\text{NtBu})_3$ subunit as a reference—a rotation of the complete $\text{N}(\text{SiMe}_3)_2$ ligand with the nitrogen atom as a fulcrum around an average C_3 -axis of the molecule (see Figure 4).

FIGURE 4

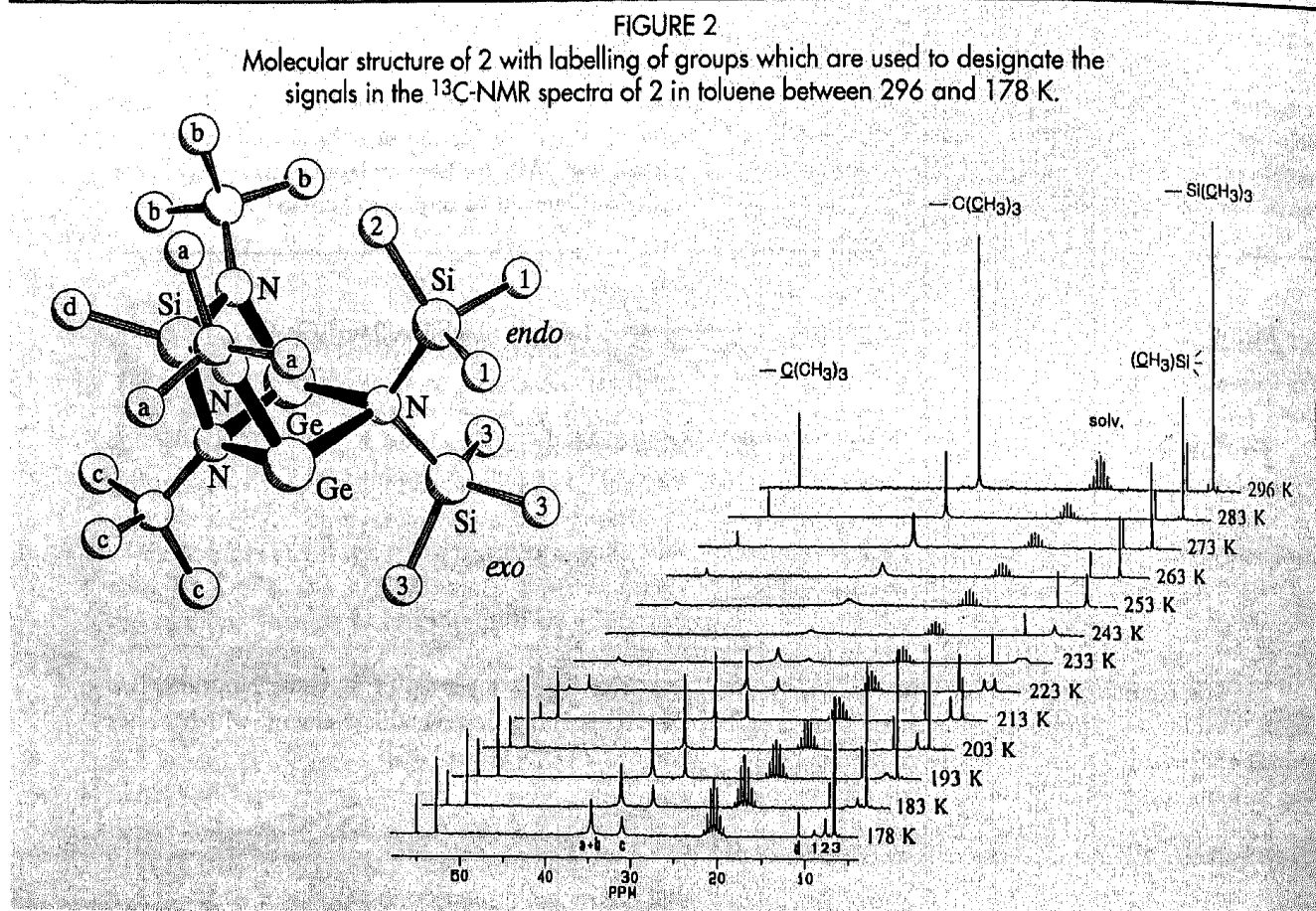
The circular migration of the germanium atoms and the cooperative rotation of the $\text{N}(\text{SiMe}_3)_2$ ligand taking the $\text{MeSi}[\text{NtBu}]_3$ ligand as the reference point.



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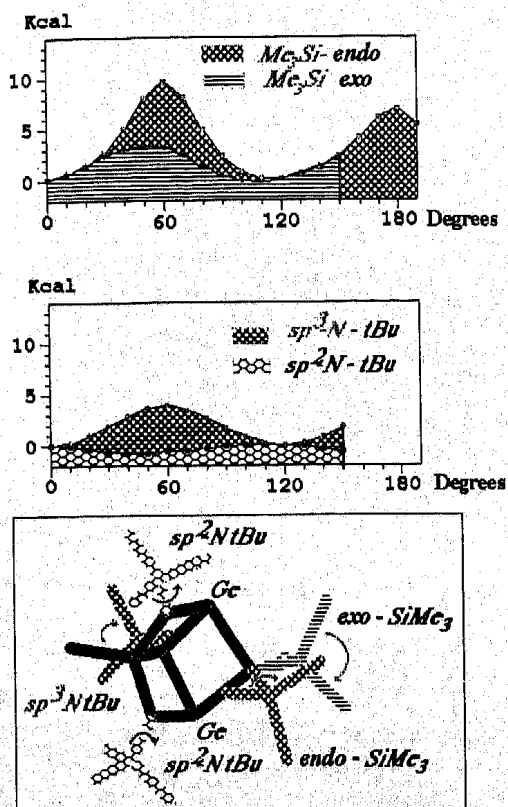
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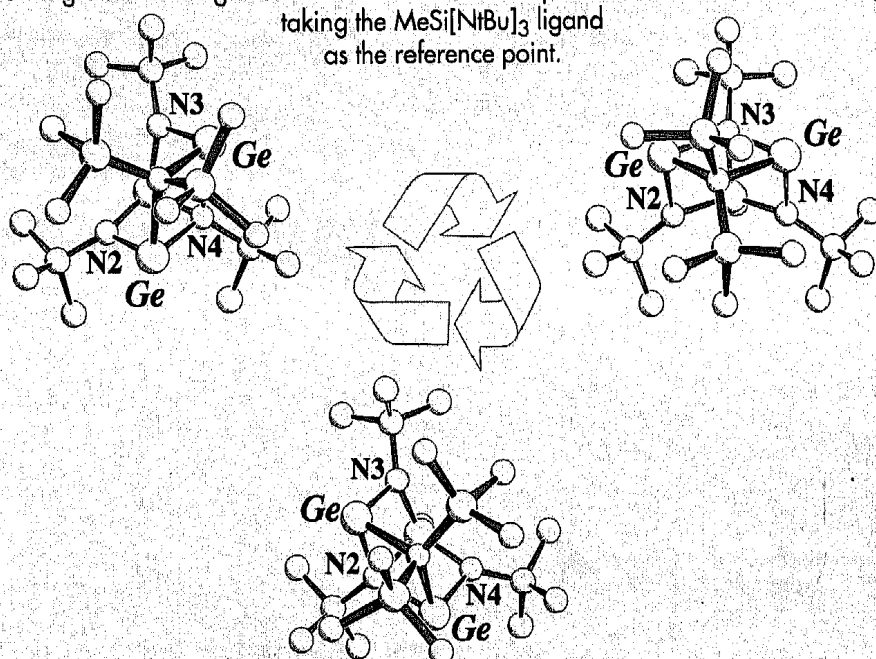


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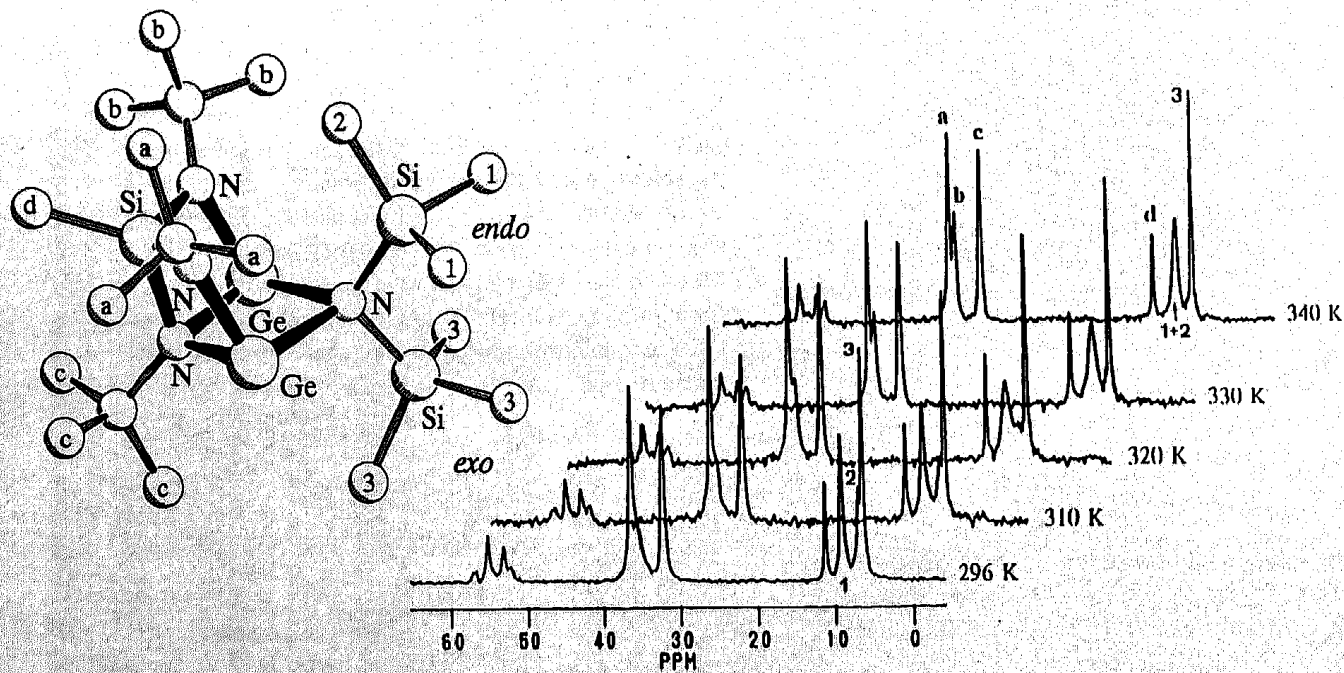


The influence of crystal packing on the dynamic properties of molecule 2 has been examined by solid state NMR spectroscopy under variations of the temperature (Figure 5). The ^{13}C CP-MAS-NMR-spectrum of 2 at room temperature, being in agreement

with the low temperature ^{13}C -NMR-spectra in solution, proves the presence of a rigid molecular $\text{SiN}_3\text{Ge}_2\text{N}$ frame in accordance with the crystal structure analysis.

FIGURE 5

^{13}C CP-MAS-NMR spectrum of 2 and its temperature dependence between 296 and 340 K. Notice the asymmetrical quadrupole splittings of the carbon atoms bonded to nitrogen between 50 and 60 ppm.



But as can be deduced from the series of ^{13}C CP-MAS-NMR spectra in Figure 5, there are still movements going on which can be classified as reorientation of trimethyl element groups around the E1-N bonds. With increasing temperature, the endocyclic trimethylsilyl group undergoes a transition from a fixed group with regard to the metal atoms to a rotating one, the signals for methyl groups 1 and 2 merging to a single resonance line. ❖

References

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