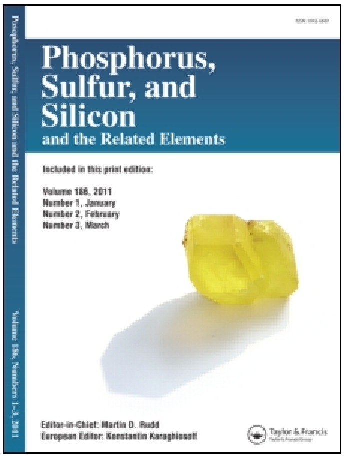

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Interconversions in Cyclosilazanes and their Application to Sin - Ceramics

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INTERCONVERSIONS IN CYCLOSILAZANES AND THEIR APPLICATION TO SIN - CERAMICS

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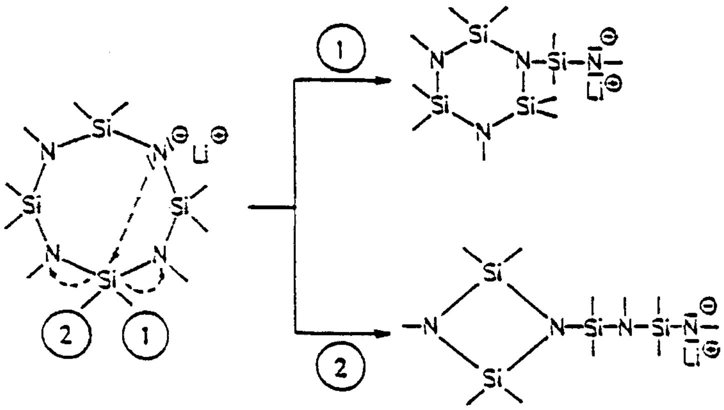
Abstract

Rearrangements occur very frequently in reactions of cyclosilazanes. We have found an equilibrium between the eight-, six-, and four-membered ring anions, which is strongly dependent on thermal and kinetic effects, the choice of substituents and the properties of the attacking group.



Knowledge of the interconversion mechanisms has enabled us to prepare silyl-bridged and coupled cyclosilazanes of high molecular weight. These coumpounds are useful precursors of SiN-ceramics.

INTRODUCTION

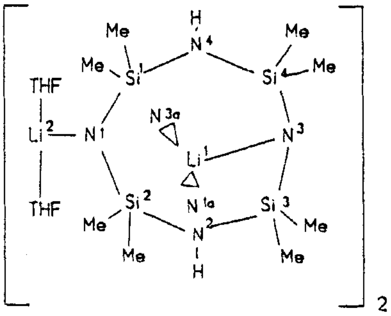
The six-membered cyclotri - and the eight-membered cyclotetrasilazane were the first well-defined silicon-nitrogen-rings. They were prepared by Brewer and Haber by ammonolysis of dimethyldichlorosilane in 1948.[1]

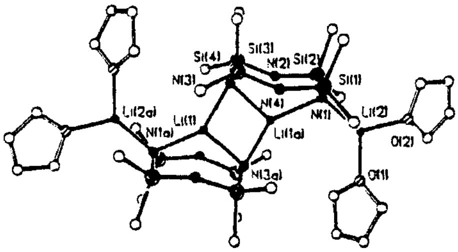
$$n\ Me_2SiCl_2 + 3n\ NH_3 \longrightarrow (Me_2SiNH)_{n=3,4} + 2n\ NH_4Cl$$

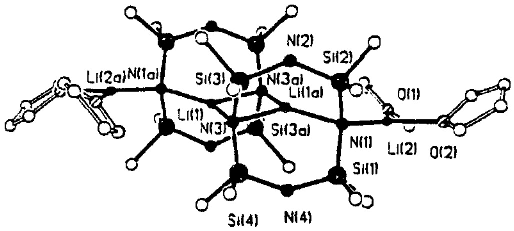
The eight -membered ring is formed in about 40 percent yield. However, no reaction of this ring had been reported until 1988.

From our investigations in the six-membered ring we learnt that rearrangements occur very frequently in reactions of alkaliderivatives of cyclosilazanes.

Therefore the first question was, is the ring size retained in the alkaliderivative of the eight-membered ring ? We isolated the anion, and even the dianion, and got crystal structure determinations.[3]



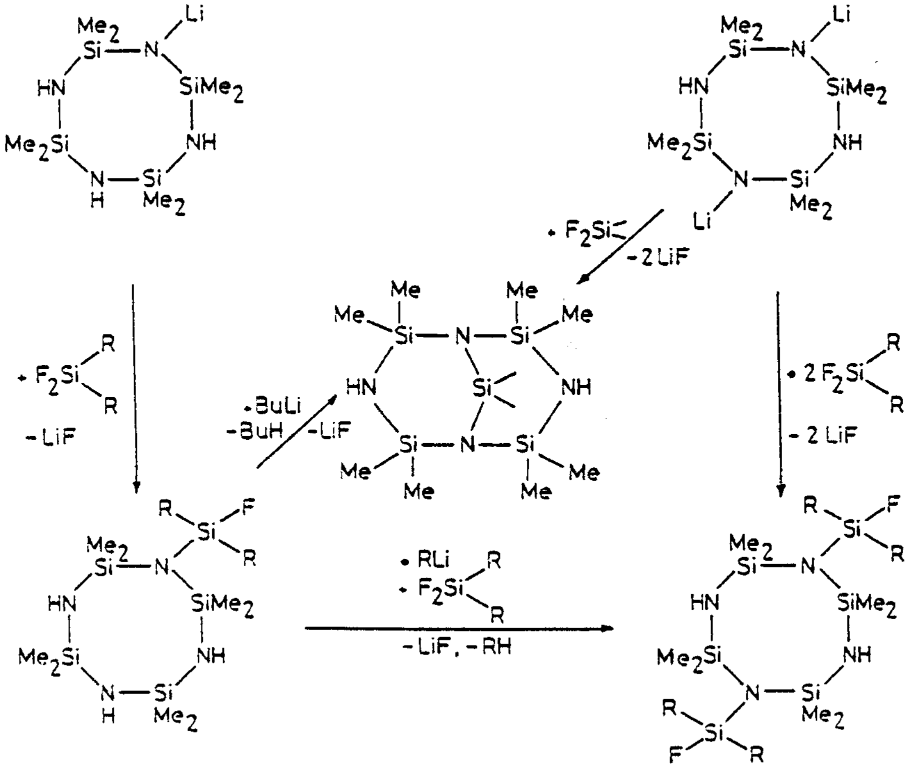




Different views of the dianion show some interesting features. The compound is a dimer. The eight-rings form a boat and they are connected by a planar $(LiN)_2$ four-membered ring which is perpendicular to the eight-rings. However, lithium is not located above the centroids of the eight-membered rings. The lithium atoms are threefold coordinated. The exocyclic Li-atoms are each coordinated to two THF-molecules.

Now we knew that the ring could e metallated with retention of the ring size and we started some reactions.

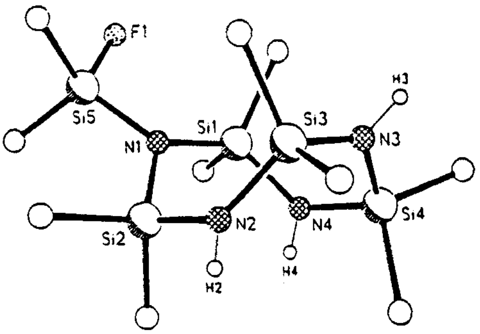
The lithium derivatives react with fluorosilanes in a molar ratio 1:1 or 1:2 to give mono- and disubstituted "monomeric" products containing eight-membered rings.[5]

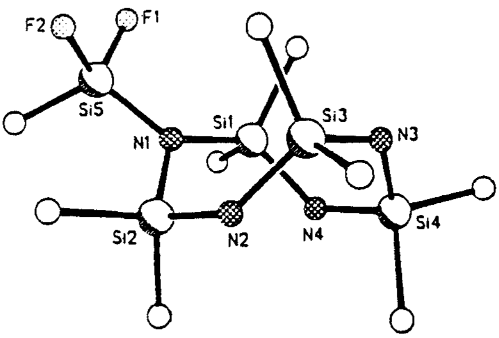


Some examples:

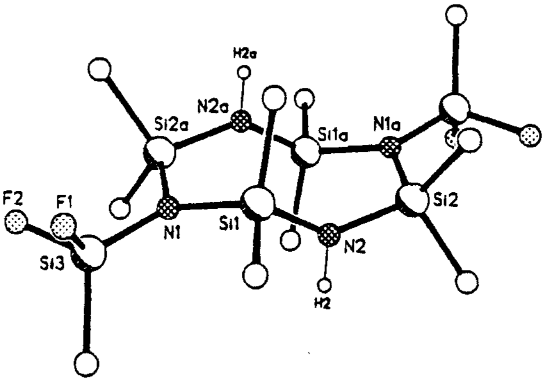
First the $SiFMe_2$-monosubstituted ring. It crystallizes, like all monosubstituted eight-membered rings, in boat conformation. There is only one fluorine atom in the molecule. Therefore the rings form chains via H-F-bridges.

The SiF_2Me-monosubstituted ring also crystallizes in boat form and both fluorine atoms form two dimensional H-F-bridges in the crystal.



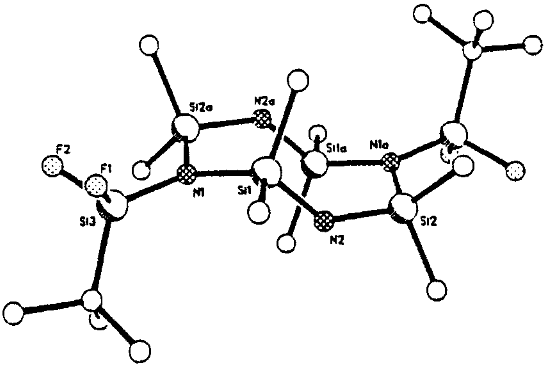


Now let us look a some disubstituted eight-rings. The $MeSiF_2$-disubstituted eight membered rings crystallizes in chair conformation.

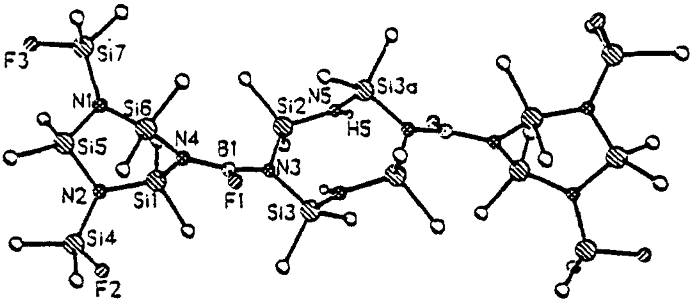


The molecule contains three dimensional H-F-bridges. The eight-membered rings are perpendicular to each other.

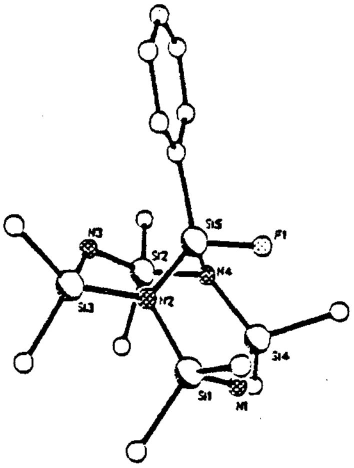
The bis(tert-butyldifluorosilyl)substituted eight-membered ring does not form H-F-bridges. Perhaps the tert-butylgroups are too bulky.



In other reactions disubstitution leads to coupled ring systems, for example this BF-bridged molecule.



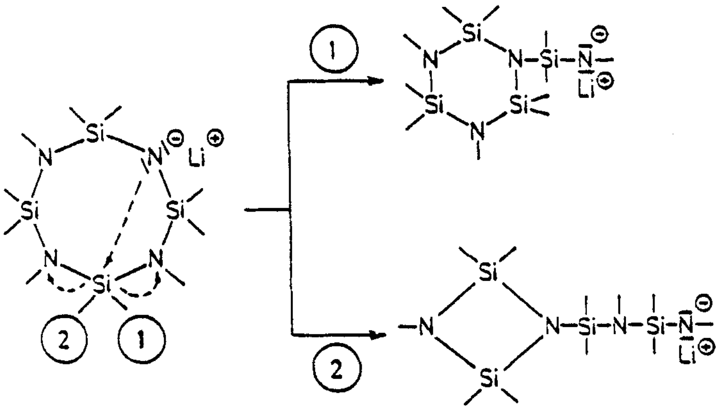
However, disubstitution can also lead to silyl bridged spirocyclic compounds.[3]



In the example of this novel bicyclic compound the N2-N4-Si2-Si3 and N2-N4-Si4-Si1 planes of the two six-membered rings of the bicyclic system are inclined
towards each other.

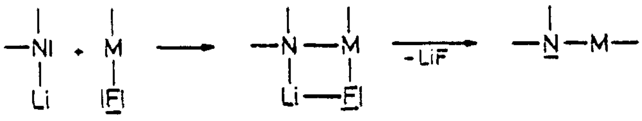
N2, Si1, N1, Si4, and N4 are coplanar, whereas N3 of the second six-membered ring is bent towards the bridging atom Si5, so that N3, Si2, N4, Si6, N2 and Si3 form a tub-shaped moiety.

You see, substitution of the cyclotetrasilazane is possible. Now let us have a look at interconversion reactions. There are two possible ways of isomerisation. A six- and a four-membered isomer can be formed.



I.	Low temperature	High temperature
II.	Ligands with $^{-}$M- and I-effect	Ligands with $^{+}$M- and I-effect
III.	Small substituents	Bulky substituents

IV.



We found out that the equilibrium between the eight-, six-, and four-membered ring anion depends on several factors.

First, reaction temperature:

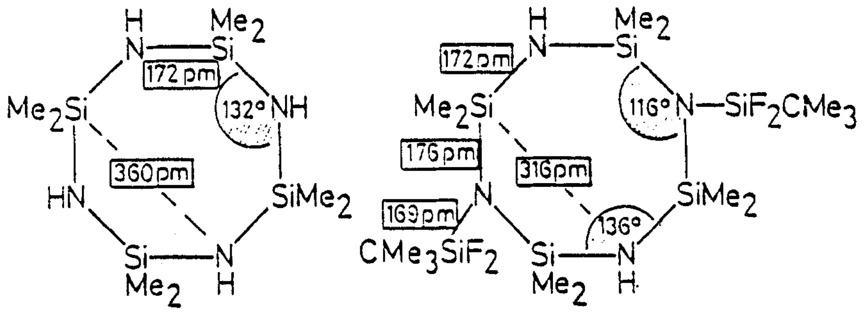
Higher temperatures lead to a better Si-N-contact across the ring, which favoures isomerisation. Substitution with retention of the eight ring is preferred at low temperatures.

Second, electronic effects of the first substituents:

SiF or BF-groups have electron withdrawing effects. They decrease the basicity of the anion and therefore the tendency to ring contration.

Third, kinetic effects:

Bulky groups increase the tendency to ring contration



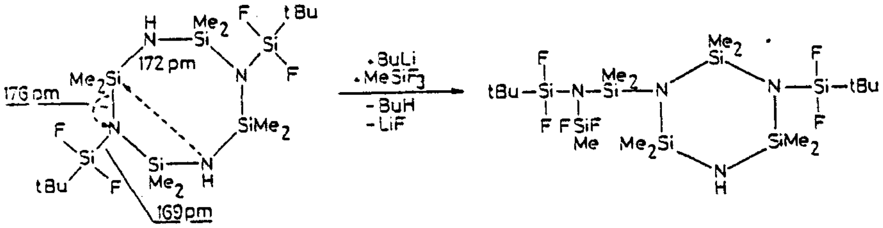
Because of the CMe_3SiF_2-group the SiNSi angle gets smaller compared with the same angle in the unsubstituted compound. However, the N- and Si-atoms try to save their sp^2- and sp^3-character. So that the N-Si-distance aross the ring decreases and a ring contraction is possible.

Fourth, electronic effects of the attacking ligand : If the reacting agent is a Lewis acid, the basicity of the nitrogen is decreased, as shown by this four centre mechanism.

The ring size is retained.

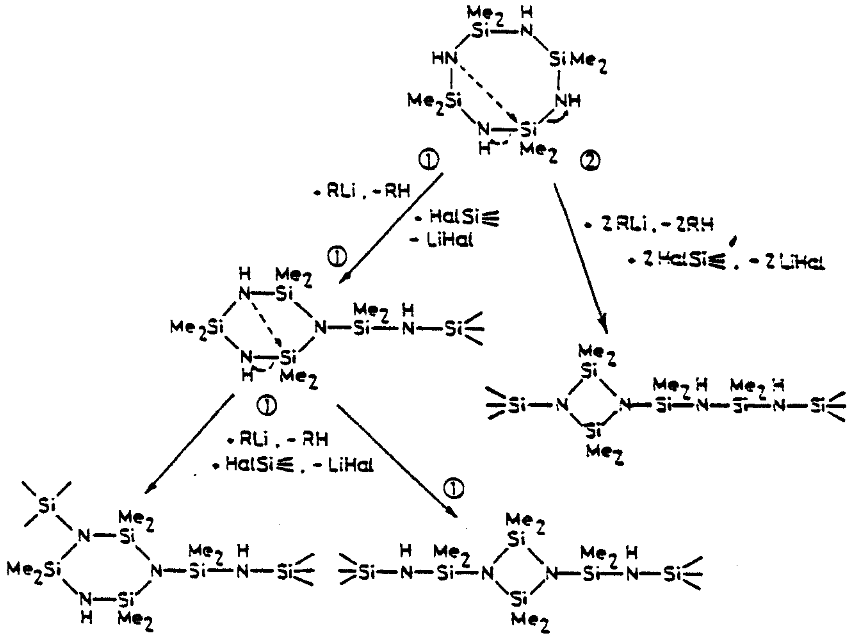
Now let us concentrate on the question which of the two isomers is formed. The cleavage of the Si-N-bond of the ring depends on the substituents. The Si-N-bond in the neighborhood of a SiF_2-group is, because of its electron withdrawing effect, longer and therefore weaker than the one in the neighbor hood of an Me_3Si-group. The weakest bond cleaves.[6]

For example: When the CMe_3SiF_2 disubstituted eight-ring isomerizes, a six-ring is formed in the interconversion reaction. The longest and therefore weakest Si-N-bond of eight-ring is cleaved.



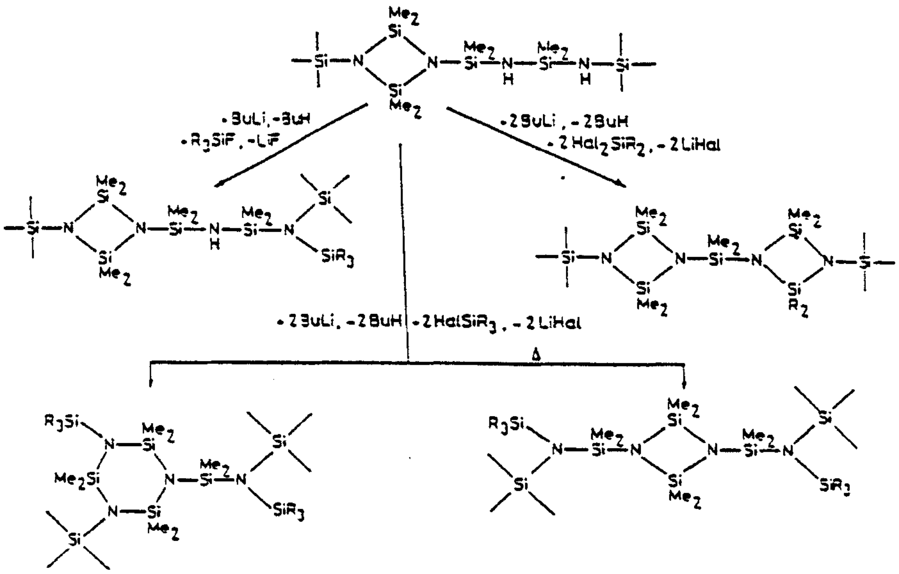
Let me summarize our investigations:

The mono anion of the eight-membered ring contracts forming a six-ring, according to way (1). This six-ring can be substituted or contracts with formation of a symmetrically disubstituted four-membered ring.



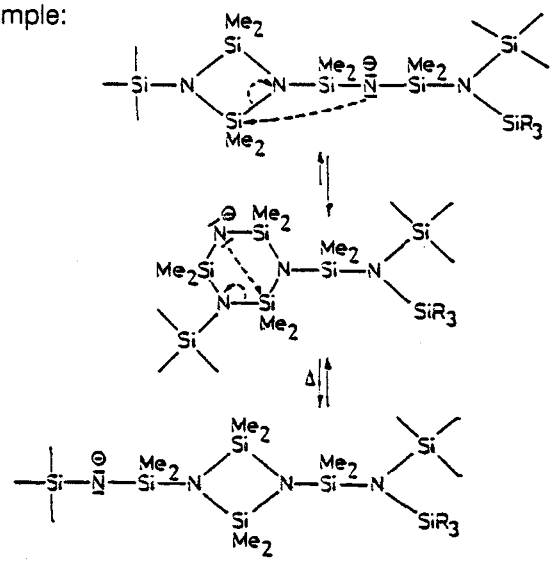
The dilithiated eight-ring, the dianion, contracts according to way (2) with formation of the unsymmetrically disubstituted four-membered ring.

Let's have a look at the third- and fourth-substitution starting with this unsymmetrical four-membered ring.



The substituent number three is bonded exocyclically at the four-ring. Difunctional halides react with the dilithium derivatives spontaneously and quantitatively forming a second four-membered ring. Ring closure is also observed with boronhalides, tindichloride or germaniumdichloride. Hydroxi- or amino groups are also stabilized in this position. They don't condensate.[7]

Ring expansion occurs with the fourth substituent. A six-membered ring is formed or a symmetrically substituted four-membered ring. That means, the tris(silyl)substituted unsymmetrical four-ring forms in an interconversion reaction the tetrakis(silyl)-substituted symmetrical four-ring. The formation of the symmetrical four-ring can be explained with the isomerisation of the anion of the (silyl)-substituted ring, for example:

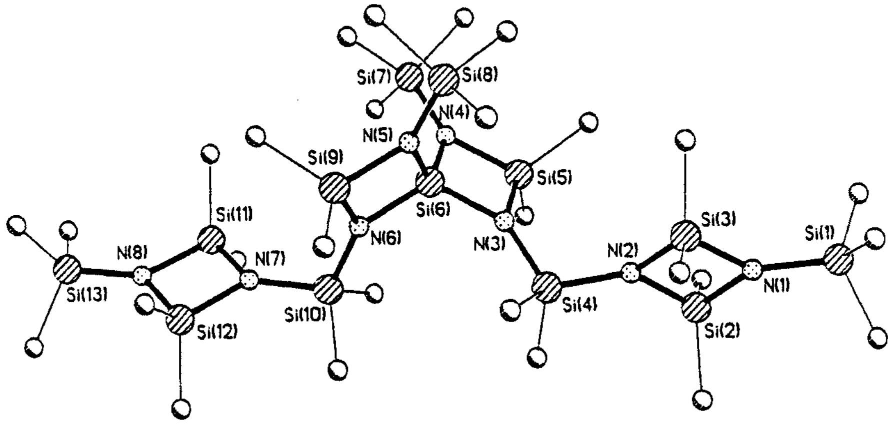


There is an equilibrium of the four- and six-ring anion, which depends on the temperature of the reaction. The formed six-ring contracts again with formation of a symmetrical four-ring.

So much for reaction mechanisms of cyclosilazanes. The knowledge of the interconversion conditions will surely lead to further interesting results in the Si-N-chemistry.

The next two slides give an impression what use can be made of these systems. As I told you, the reactivity of these ring anions allow facile preparation of high molecular systems, which already have properties of polymers. For example:

A spirocyclic system is obtained in the reaction of a dilithiated compound with a difluoro functional ring.[8]



Above 600°C these compounds form polymers and above 1200°C SiC and Si_3N_4 ceramics. Pure Si_3N_4-ceramics are obtained by pyrolysis in an NH_3 atmosphere.

Our investigations show that cyclosilazanes are excellent precursors for ceramics. The ceramic material obtained form this starting materials has a greater surface than the one obtained by other methods.

References

1. S.D. Brewer and C.P. Haber, J. Am. Chem. Soc. 70 (1948) 3888.
2. U. Klingebiel, Phosphorus, Sulfur and Silicon, Vol. 41 (1989) 361.
3. K. Dippel, U. Klingebiel, M. Noltemeyer, F. Pauer, and G.M. Sheldrick, Angew. Chem. 100 (1988) 1093.
4. K. Dippel, U. Klingebiel, F. Pauer, G.M. Sheldrick, and D. Stalke, Chem. Ber. 123 (1990) 237-241.
5. K. Dippel, U. Klingebiel, T. Kottke, F. Pauer, G.M. Sheldrick, and D. Stalke, Z. anorg. allg. Chem. 584 (1990) 87-104.
6. K. Dippel, U. Klingebiel, F. Pauer, G.M. Sheldrick, and D. Stalke, Chem. Ber. 123 (1990) 779-782.
7. K. Dippel, U. Klingebiel, Chem. Ber. 123 (1990) 1817-1820.
8. L. Marcus, K. Dippel, and U. Klingebiel, in press.