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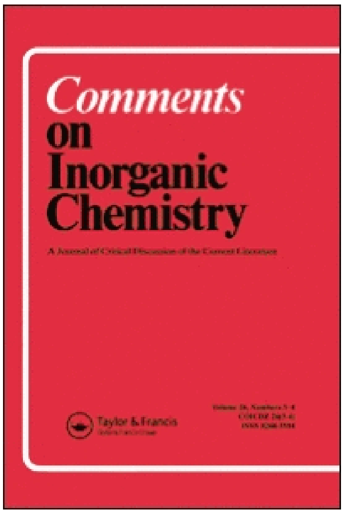

Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
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Cyclotrisilanes and Related Compounds

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To cite this Article Weidenbruch, Manfred(1986) 'Cyclotrisilanes and Related Compounds', Comments on Inorganic Chemistry, 5: 5, 247 — 261

To link to this Article: DOI: 10.1080/02603598608079841

URL: http://dx.doi.org/10.1080/02603598608079841

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Cyclotrisilanes and Related Compounds

Cyclotrisilanes are easily obtained by reductive halogen elimination from sterically congested dihalomono-dihalodi-, or dihalotrisilanes. Ring contraction of cyclotetrasilanes containing medium-sized substituents also provides access to the three-membered cycles. Their molecular structures reveal considerable lengthenings of the Si–C and mainly the Si–Si bonds. The photochemically induced ring cleavage leads to the corresponding disilenes or to silylenes and disilenes which can either be isolated or trapped by a variety of multiply-bonded compounds. Cyclotrigermanes and cyclotristannanes, which can be obtained by a similar route, can also be cleaved to yield digermenes and distannenes, respectively.

INTRODUCTION

Although cyclosilanes have been known for a long time,[1] it is only recently that the smallest members of this series, the cyclotrisilanes, have become available. Interest in cyclosilanes continues for several reasons: they exhibit unusual spectral properties, they can extrude silylenes by light-induced activation yielding ring-contracted compounds and, in general, they can serve as chemical models for the bond properties of silicon surfaces.

The synthesis of cyclosilanes often leads to the simultaneous formation of rings of different sizes, but the thermodynamically favored ring is generally the main product. Recently it has been shown[2] that there exists a definite correlation between the ring size and steric requirements of the substituents bonded to the silicon atoms. This can be proved by the evaluation of the Hammet–Taft values Es(Si)[3] of the two substituents R and R′ in cyclosilanes $(RR'Si)_n$. Thus one finds that the six-membered ring is

Comments Inorg. Chem.
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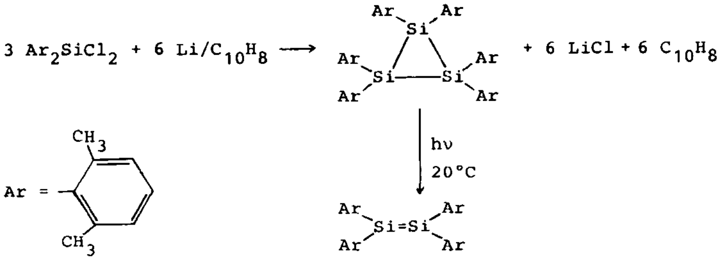
predominant at R = R′ = methyl (Σ Es(Si) = 0.00), while the four-membered ring dominates at two bulky isopropyl groups per silicon atom (Σ Es(Si) = −1.12). Upon further increasing the steric bulk of the substituents, the three-membered ring should be preferably formed, despite the high strain in the ring, as the "van der Waals" interactions between the H-atoms of adjacent groups are less pronounced than in the larger rings.

The progress in the synthesis of sterically congested mono- and oligosilanes[4] achieved during the last few years has opened up different routes to the cyclotrisilanes. These will be discussed next.

SYNTHESIS OF CYCLOTRISILANES

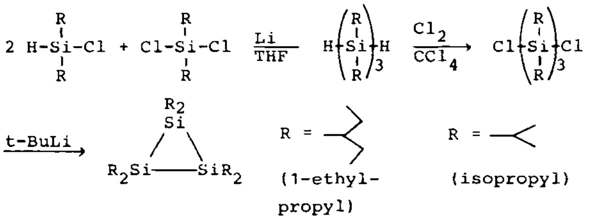
In 1982 Masamune and co-workers[5] successfully performed the first synthesis of a cyclotrisilane by reaction of dichlorobis(2,6-dimethylphenyl)silane with lithium naphthalenide. The authors also showed that the photolysis of hexakis(2,6-dimethylphenyl) cyclotrisilane leads to the corresponding disilenes without any by-products (Eq. (1)).



(1)

The molecular structure of the hexaarylcyclotrisilane reveals some unexpected details. The three silicon atoms form an isosceles triangle with two different Si–Si bond lengths. One of these bonds is shorter (237.5 pm) than the two other equivalent Si–Si bonds of 242.4 pm (normal single bond length 234 pm). It has been suggested that the steric congestion of the molecule is partly responsible for the extraordinarily long bond lengths, at that time the longest ever observed.

In order to eliminate the perturbation of the electronic structure of the cyclotrisilane framework caused by the aryl substituents, the groups of Masamune[6] (Eq. (2)) and of Watanabe and Nagai[7] (Eq. (3)) have synthesized the first alkyl substituted derivatives.



(2)

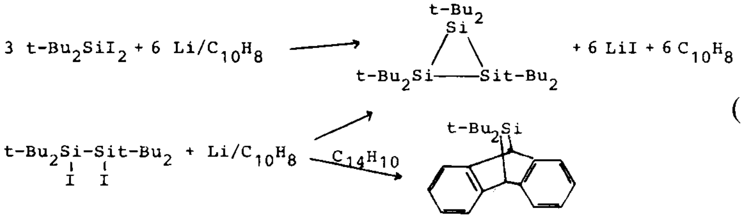
$$3\ (t\text{-}BuCH_2)_2SiCl_2 + 6\ Li \longrightarrow [(t\text{-}BuCH_2)_2Si]_3 + 6\ LiCl \qquad (3)$$

The Si–Si bond lengths of the two independent molecules of hexaneopentylcyclotrisilane (239.1; 240.7 (average) pm) are also considerably longer than in unstrained rings. It was claimed that these bond lengths are the largest ever observed for an alkylcylopolysilane.[8]

Irradiation of octaisopropylcyclotetrasilane also provided evidence for the formation of hexaisopropylcyclotrisilane[9] (see Eq. (2)), but the prolonged photolysis of the three-membered cycle afforded a new compound. The band in its UV spectrum at 400 nm has been attributed to tetraisopropyldisilene[9] (Eq. (4)).

$$(i\text{-}Pr_2Si)_4 \xrightarrow[\{-\ i\text{-}Pr_2Si:\}]{h\nu} (i\text{-}Pr_2Si)_3 \xrightarrow{h\nu} \{i\text{-}Pr_2Si{=}Si\text{-}i\text{-}Pr_2\} \qquad (4)$$

We obtained hexa-tert-butylcyclotrisilane, the most strained cyclotrisilane prepared so far, by treatment of di-tert-butyldiiodosilane or of 1,2-dibromotetra-tert-butyldisilane with lithium naphthalenide.[10]

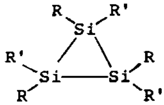


(5)

In this context it is interesting to note that the reaction of di-tert-butyldichlorosilane with lithium naphthalenide yields only acyclic compounds.[11,12]

Hexa-tert-butylcyclotrisilane (Fig. 1) exhibits Si–C bond distances of 197.0 pm and Si–Si distances of 251.1 pm—the largest Si–Si bond lengths found in a molecule up to this time.[10] These exceed those observed in unstrained silicon compounds by 17 pm and correspond to Pauling's bond orders of 0.54 (calculated by $d(\text{PBO}) = d(1) - 60 \log(\text{PBO})$ with $d(1)$ = normal single bond length).[10,27]

Several other cyclotrisilanes have been synthesized according to the methods developed for the formation of compounds already mentioned. These cyclotrisilanes include the following molecules:



R = R' = 2,6-diethylphenyl[13]
R = t-Bu, R' = mesityl, and substituents interchanged at one silicon atom[14]
R = t-Bu, R' = cyclohexyl[15]

Irradiation of these cyclotrisilanes also leads to the corresponding disilenes which, in some instances, can be isolated as thermally stable compounds[13,14] (see also Refs. 16 and 17).

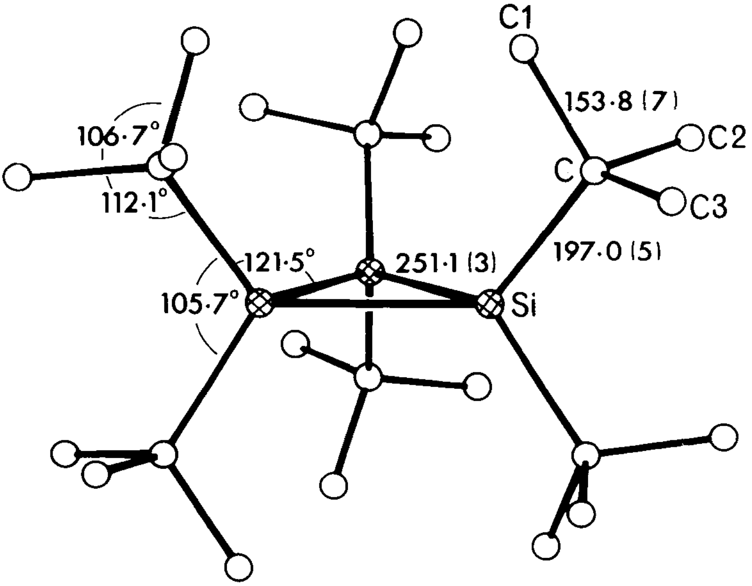
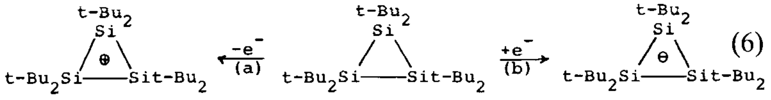


FIGURE 1 Structure of hexa-tert-butylcyclotrisilane showing bond lengths (pm) and bond angles.

PHYSICAL PROPERTIES AND CHEMICAL REACTIVITY OF CYCLOTRISILANES

One of the most important properties of linear or cyclic polysilanes is their electronic absorption at relatively low energy.[1] These compounds exhibit UV absorption bands that can be attributed to a delocalized $\sigma \rightarrow \sigma^*$ or $\sigma \rightarrow 3d$ transition, near the visible region.[1,18] The absorption maxima of acyclic polysilanes increase with increasing chain length, whereas in cyclic polysilanes, the red shift increases as ring size decreases; eg., from approximately 250 nm in cyclohepta- or cyclohexasilanes to 320 nm in cyclotrisilanes. Hexa-tert-butylcyclotrisilane, the most strained three-membered cycle, reveals the largest bathochromic shift with shoulders at 350 and 390 nm.[10]

Cyclic polysilanes exhibit properties resembling those of aromatic compounds.[1] Consistent with this behavior, these rings are easily converted to cation or anion radicals which can be detected by ESR spectroscopy or can be determined by cyclic voltammetry. Hexa-tert-butylcyclotrisilane, e.g., can either lose or gain one electron forming, respectively, the radical cation or anion (Eq. (6)).

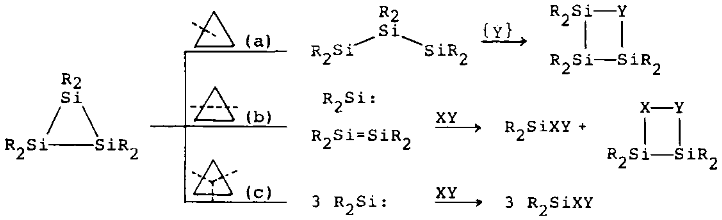


(6)

(a) CV: +0.84 V
vs. SCE in DME[19]

(b) ESR: <200 K.
$a_{si} = 0.07$;
$a_H = 0.038$ mT[20]

The chemical behavior of the cyclotrisilane skeleton should be characterized by three possible paths, which can be classified according to the number of Si–Si bond cleavages.

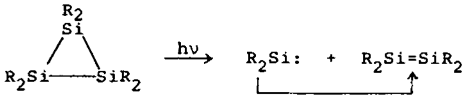


(7)

Route (a) involves a cleavage of one Si–Si bond and leads, depending on the reactants, to either open-chained trisilanes or ring insertion products.

Route (b) brings about a simultaneous formation of silylene and disilene as cleavage products, which can either be trapped by an insertion reaction or by an addition reaction.

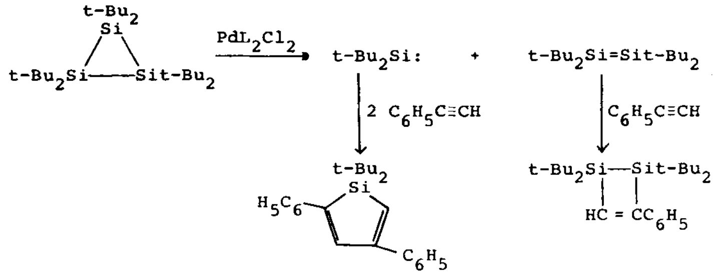
For route (c) a cleavage of cyclotrisilane into three silylenes and their trapping reactions is suggested. Although the extremely stretched Si–Si bond lengths in cyclotrisilanes should favor route (c), no reaction consistent with this suggestion has been found so far. The cleavages of cyclotrisilanes that have been the most studied at present are those which are either photolytically or catalytically induced since they offer good access to the disilenes.[21]



(8)

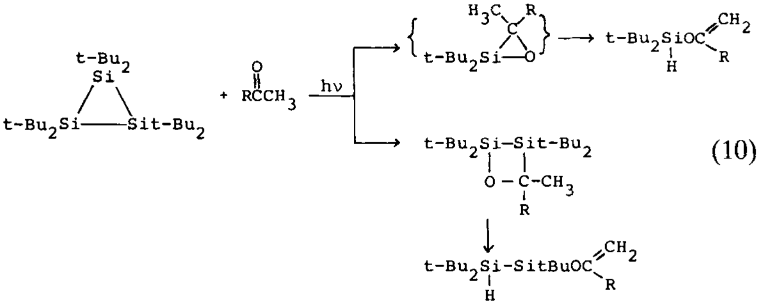
The thermally less stable disilenes and silylene intermediates can also be obtained by this route and can be isolated by trapping reactions.

Equation (9) shows the cleavage of the three-membered ring catalyzed by palladium and the trapping of cleavage products by phenylacetylene.[22]



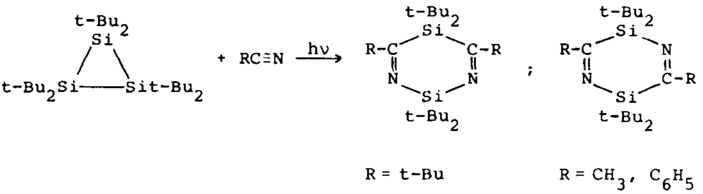
(9)

Reactive trapping products such as the silaoxiranes can be detected as rearranged products[22] (Eq. (10)).



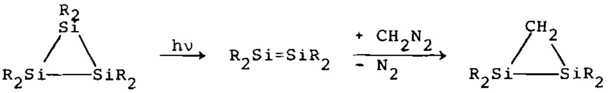
(10)

Photolysis of hexa-tert-butylcyclotrisilane in the presence of nitriles leads to novel ring systems of the 3,6-disila-3,6-dihydropyrazines or of the 2,5-disila-2,5-dihydropyrimidines[23] (Eq. (11)).



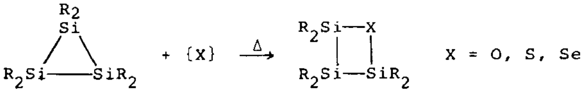
(11)

On irradiation of hexakis (2,6-dimethylphenyl)cyclotrisilane and subsequent reaction with diazomethane, disilacyclopropane[24] was obtained, which is one of the few stable examples for this ring system (Eq. (12)).



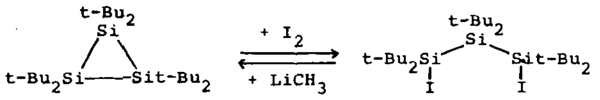
(12)

In the absence of light or a catalyst, the reactions of cyclotrisilanes follow route (a), i.e., one Si–Si bond is cleaved. In the presence of chalcogenes, for example, the ring-extended oxa-,[6,25] thia- and selenatrisiletanes are obtained[25] (Eq. (13)).



(13)

On the other hand, treatment of hexa-tert-butylcyclotrisilane with halogens leads to open chain 1,3-dihalotrisilanes. Surprisingly, these compounds can be converted into the three-membered ring by methyllithium although the angular strain in the ring seems to be unfavorable for this reaction[26] (Eq. (14)).



(14)

The fact that the ring can easily be reestablished indicates a higher decrease in bond strength in open-chained trisilanes. This assumption is confirmed by the molecular structure (Fig. 2).[27] Even in comparison with hexa-tert-butylcyclotrisilane, the Si–Si bond lengths are drastically extended and correspond to Pauling bond orders of only 0.41 and 0.32, respectively. The $\bar{d}$(Si–C) and $\bar{d}$(Si–I) bond lengths only have Pauling bond orders of 0.66 and 0.71, respectively, so that the molecular skeleton consisting of

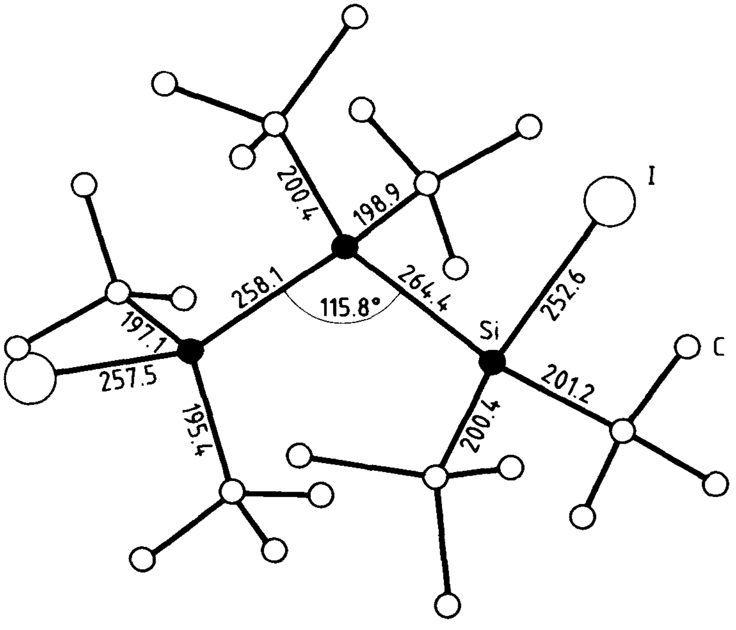


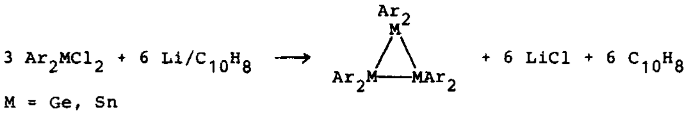
FIGURE 2 Structure of hexa-tert-butyl-1,3-diiodotrisilane.

Si–Si, Si–I, and Si–C bonds merely holds a PBO value of 6 instead of Σ PBO = 10. Accordingly it has to cope with the loss of four bonds.

The existing theoretical studies on cyclotrisilanes[28] or tetrasilabicyclo [1.1.0] butane[29] do not take into consideration this effect, because only the hydrogen substituted compounds can be reasonably calculated by *ab initio* methods. These calculations do not reveal the strong influence of the substituents on the bond lengths and the bond angles.

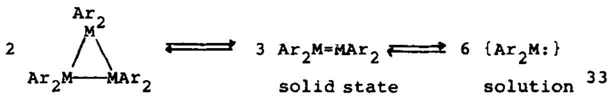
CYCLOTRIGERMANES AND CYCLOTRISTANNANES

Masamune *et al.* prepared hexakis (2,6-dimethylphenyl) cyclotrigermane[30] and hexakis (2,6-diethylphenyl) cyclotristannane,[31] the first homoatomic three-membered cycles of these elements, using a route analogous to the one used for the formation of the first cyclotrisilane (Eq. (15)).



(15)

These compounds contain considerably elongated Ge–Ge and Sn–Sn bonds compared with the values which have been determined for less strained oligogermanes and -stannanes. As for the cyclotrisilanes, these homoatomic three-membered rings are photolytically converted into the corresponding digermenes and distannenes.

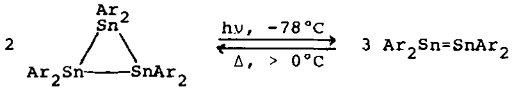


(16)

While it is not possible to obtain tetrakis (2,6-dimethylphenyl) digermene chemically pure,[30] the corresponding 2,6-diethylphenyl compound[32,33] is formed in high purity without any difficulty.

It is very interesting to note the Ge–Ge bond length of this digermene is 221.3 pm and is therefore clearly shorter than the Ge–Ge bond length of the tetrakis[bis(trimethylsilyl)methyl]digermene, synthesized by Lappert *et al.*,[34] which is 234.7 pm. As a consequence one cannot generalize the statement[34] that with increasing atomic number there is an increasing tendency for pyramidicity, and that the percentage of bond shortening of the M═M bond length in R_2MMR_2 compounds compared with the single bond length in the diamond form of the elements decreases in the sequence $C > Si > Ge > Sn$. While the bond shortening of Lappert's digermene only amounts to 4%, it is out of the line with the 2,6-diethylphenyl-derivative which has a bond shortening of 10%. Obviously the bond lengthenings in the three-membered rings, as well as the bond shortening in the M–M bonds, are much more dependent on the shape as well as on the steric bulk of the ligands than has been believed previously. In this context it definitely would be of considerable interest to compare the aliphatically substituted distannenes R_2SnSnR_2, R = bis(trimethylsilyl)methyl, with a distannene $Ar_2SnSnAr_2$ containing aromatic ligands.

In the case of the R_2SnSnR_2 the Sn–Sn bond length is 276.4 pm[35] which is only 2% shorter than in α-tin (281.0 pm). In addition there exists a pronounced trans-bent structure with $\chi_{Sn} = 41°$ in this molecule. Most recently the quantitative formation of a distannene has been shown to occur by photolysis of the sterically extremely congested hexakis(2,4,6-triisopropylphenyl)cyclotristannane,[36] but the distannene is again slowly converted into cyclotristannane at temperatures above 0°C. This is the reason why it has not yet been possible to perform a structure analysis of this distannene.

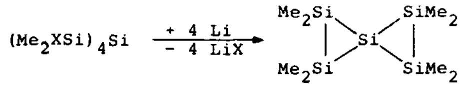


(17)

The electron spectra of the analogously substituted disilene[13] compared with that of the digermene[32] and of the distannene[36] point out similar structural properties of these dimetallenes. The x-ray structure analysis of this distannene may therefore not reveal a trans-bent structure as pronounced as that of Lappert's compound. Hexa-9-phenanthrylcyclotristannane[37] has recently been isolated, but a possible photolytic cleavage to the corresponding distannene is still lacking.

SILABICYCLO [1.1.0] BUTANES AND SPIROPENTASILANES

The first and, until now, only spiropentasilane as a rather sensitive compound has been obtained in THF solution and has been identified by several chemical reactions.[38]



(18)

In order to isolate a thermally more stable spiropentasilane, the methyl groups should be replaced by bulkier substituents in order to achieve sufficient shielding of the silicon atoms. On the other hand, the silabicyclo[1.1.0]butanes have been definitely proved to exist. 2,4-Disilabicyclo[1.1.0]butane was obtained by Fritz, von Schnering *et al.*[39] and its molecular structure determined. Characteristic of this compound is the strong puckering of the four-membered ring skeleton and the extremely long $(C–C)_{endo}$ bond (Fig. 3(a)) with a bond order of only 0.41.

Tetrasilabicyclo[1.1.0]butane[40] (Fig. 3(b)), which has been isolated by Masamune and co-workers, also contains a puckered four-membered ring, in which the dynamic behavior of the aryl protons in the variable temperature NMR spectra is best explained by reversible ring inversion. This process is accompanied by significant stretching of the central Si–Si bond which has to be considered as a very weak bond. Theoretical studies[29] support this assumption because an extremely long Si–Si bond distance of 285 pm has been found for the central Si–Si bond. An x-ray structure analysis,[45]

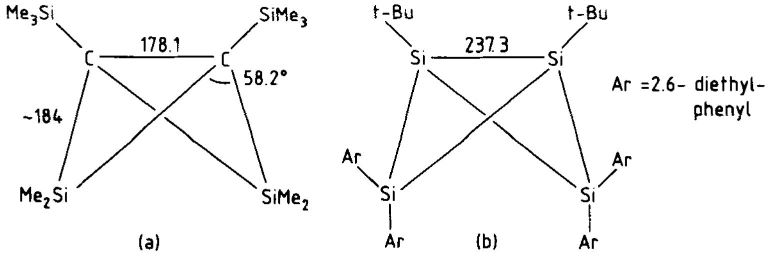


FIGURE 3 2,4-Disilabicyclo[1.1.0]butane (a) and tetrasilabicyclo[1.1.0]butane (b).

however, reveals a bond length of only 237 pm, surprisingly short for this series of compounds.

OUTLOOK

The chemistry of three-membered rings of silicon, germanium, and tin has made rapid progress within the last 5 years. Nevertheless, the results achieved raise further questions, of which two have been discussed in this Comment.

It has been demonstrated that some cyclotrisilanes and their open-chained derivatives show considerable to drastic lengthening of the Si–Si bonds. Despite the immense decrease in bond strength, these molecules are thermally stable. An extreme example is the recently isolated hexa-tert-butyldisilane,[41] which possesses the largest yet proved bond length of 269.7 pm corresponding to a Pauling bond order of only 0.26. It appears as if these molecules are kept together like a "droplet" by a "van der Waals skin." It may be that the increase of attractive van der Waals, dipole–quadrupole, and quadrupole–quadrupole forces exceeds the repulsive interactions within the "peripheral skin" of the compressed methyl groups.[42] In contrast to this, the Si· · ·Si contact in tetramesityldisiloxane (Fig. 4(a))[43] is only 231 pm, somewhat shorter than the normal Si–Si single-bond length of 234 pm. Although this very short distance suggests the existence of a Si–Si–σ bond (Fig. 4(b)), *ab initio* MO calculations on cyclodisiloxanes[44] reveal that the short Si···Si distance in these silicon–oxygen rings does not correspond to silicon–silicon bonding.

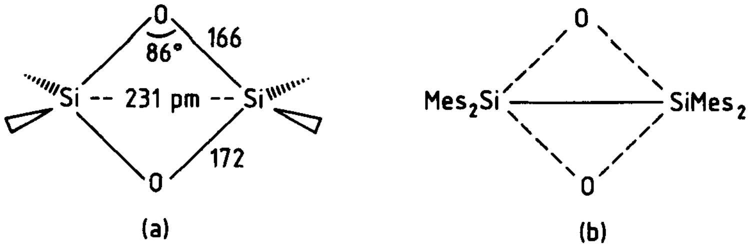


FIGURE 4 Structure of tetramesitylcyclodisiloxane (a) and suggested bonding in this compound (b).

The above phenomena will have to be substantiated by further physical evidence in order to explain why two silicon atoms form a thermally stable bond, despite a bond length of 270 pm, while two silicon atoms, which are forced to keep a distance of 231 pm by ring geometry, do not show any bonding interaction.

Another question which still remains open concerns the nature of the central bond in dimetallenes R_2MMR_2. Theoretical studies and initial experimental data suggest that there is an increasing tendency for pyramidicity with increasing atomic number of M but decreasing shortening of the M–M bond lengths compared with that in the diamond form of the element M.[34] Is it possible that dimetallenes are no longer molecules with a true double bond, but rather should be regarded as loosely adjoined germylenes or stannylenes in the solid state? Surely one cannot definitely answer this question based on only one or two representatives of this family; instead more experimental results are urgently required.

Acknowledgments

Financial support of our contributions by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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