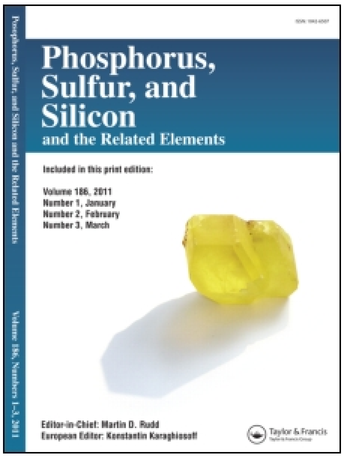

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Siloxane, Phosphate, and Hypervalent Formation in Cyclic Silicon and Phosphorus Reactions

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SILOXANE, PHOSPHATE, AND HYPERVALENT FORMATION IN CYCLIC SILICON AND PHOSPHORUS REACTIONS

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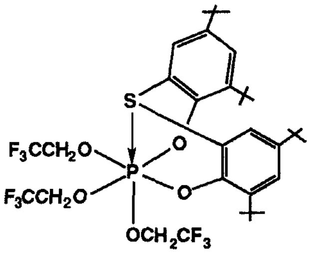
Comparative reactions of phosphites and chlorosilanes with diols, $S[R_1R_2C_6H_2OH]_2$, capable of forming eight-membered ring systems, were studied. With $(CH_2)_4SiCl_2$ a bicyclic silane formed, $S[R_1R_2C_6H_2O]_2Si(CH_2)_4$, whereas with $SiCl_4$, a hydrolysis reaction dominated yielding a cyclic disiloxane product, $\{S[(t\text{-}Bu)_2C_6H_2O]_2Si(OCH_2CF_3)\}_2O$, whose X-ray structure showed a ~50% displacement toward a trigonal bipyramid from a tetrahedron due to a Si–S interaction. Hydrolysis reactions also ensued in reactions of $P(OXyl)_3$ and $P(OCH_2CF_3)_3$ with diols giving acyclic and cyclic phosphates, respectively, e.g., $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$ and $S[(t\text{-}Bu)MeC_6H_2O]_2P(O)(OCH_2CF_3)$. With the rigorous exclusion of moisture, the diol reaction with $P(OCH_2CF_3)_3$ led to a hexacoordinated structure, via a P–S interaction, $S[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$, shown to be ~70% displaced toward an octahedron from a square pyramid based on X-ray analysis. With $P(NMe_2)_3$, a bicyclic oxyphosphorane formed, $[S(Me_2C_6H_2O)_2]_2PNMe_2$, which showed no evidence for P–S coordination. Hydrolysis processes in the case of phosphorus are shown to correlate with the nature of the leaving group and are proposed to involve a hexacoordinated intermediate.

Key Words: Disiloxane, bicyclic, silane, phosphate, hydrolysis, hexacoordinated phosphorus.

INTRODUCTION

Recent studies in our laboratory have revealed that sulfur containing cyclic pentaoxyphosphoranes which have eight-membered rings are capable of P–S interactions,[1-6] e.g., **1**.[1]



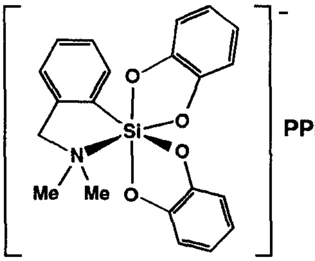
1

The eight-membered ring acts as a spatial support to position the sulfur atom in the vicinity of the phosphorus atom. In this way, the potential donor action of the sulfur atom was explored as a function of ring substituents and ligands attached to the phosphorus atom. This type of interaction appears unknown in silicon chemistry, although we recently found that comparable Si–S interactions occur in a new cyclic disiloxane formulation.[7]

The interest in achieving higher coordinate forms for both phosphorus[8,9] and silicon[10] stems from their role as models in nucleophilic displacement reactions. Earlier most mechanistic work on substitution reactions of tetracoordinated phosphorus[9,11-14] and silicon[10,15-19] compounds have involved pentacoordinated activated states or intermediates. More recently, mechanisms indicating possible hexacoordinated formations in both phosphorus[19] and silicon[19,20] reactions have been advanced. Most of the silicon chemistry in this area has been carried out by Corriu and coworkers.[20]

However, an extensive structural basis is lacking to support many of these mechanistic proposals. Earlier X-ray studies have revealed hexacoordinated structures for $[SiF_6]^{=}$ [21] and the neutral adducts $F_4Si{\bullet}2$ py[22] and $Cl_4Si{\bullet}2$ PMe_3.[23] All have distorted octahedral arrangements. Likewise, some comparable structures for phosphorus are $[PF_6]^{-}$ [24] and the neutral adducts $F_5P{\bullet}Py$[25] and $F_5P{\bullet}NH_3$.[26] The adducts have P–N distances of 1.899 and 1.842Å, respectively, which are very close to the covalent distance of 1.85Å.

Examination of the results of recent X-ray studies centers on silicon compounds that achieve increased coordination largely by intramolecular nitrogen atom donation.[20] For example, **2**[27] and **3**[28] have nearly octahedral structures with very short Si–N distances, 2.15Å and 2.21Å, respectively.



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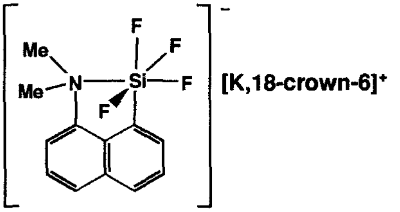
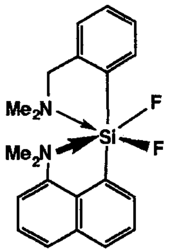


3

In contrast, with less electronegative ligands in neutral complexes, e.g., **4**[29] and **5**,[30] the X-ray structures are nearly tetrahedral at silicon with the two more weakly coordinating nitrogens located at greater distances, in the range of 2.50 to 2.81Å.



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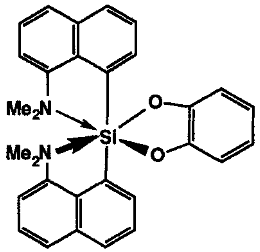
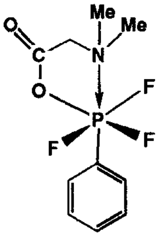


5

A similar situation prevails in phosphorus chemistry. For example, Krebs, Schmutzler, and Schomburg[31] found that an X-ray study of acetoxyphenyltrifluorophosphate **6** shows an octahedral geometry with a P–N distance of 2.013(4)Å.

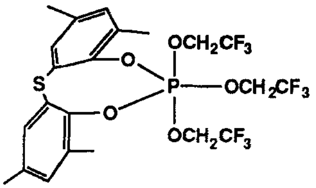


6

We report here a review of our current work in the area and show that silicon, like phosphorus, is capable of increased coordination in the presence of sulfur donor atoms. The geometrical consequences of such coordination in each of the two chemistries is explored as is their relevance as intermediates in hydrolysis processes.

CYCLIC OXYPHOSPHORANES

In addition to the octahedral structure found for **1**,[1] our recent work has revealed cyclic pentaoxyphosphoranes in trigonal bipyramidal geometries (TBP) with eight-membered rings positioned at diequatorial sites, **7** and **8**,[1,32] and at axial-equatorial sites, **9**.[1]



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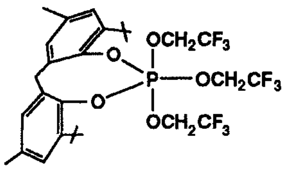

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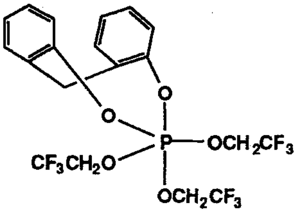
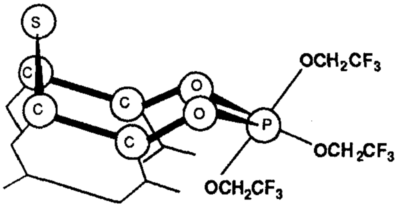


9

The rings are in symmetrical chair-like forms in **7** and **8** but in a very twisted boat-like form in **9**. In the octahedral geometry for **1**, the ring assumes a symmetrical boat shape. The variety in ring conformations present in the structures of **1** and **7-9** are displayed here.



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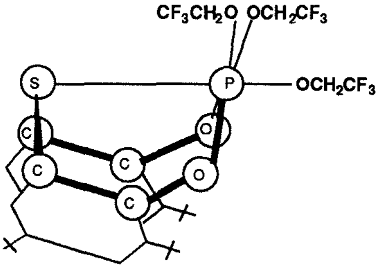

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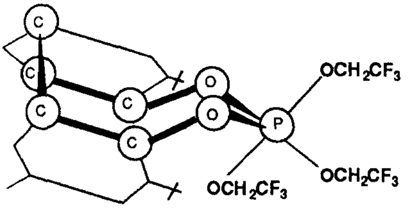

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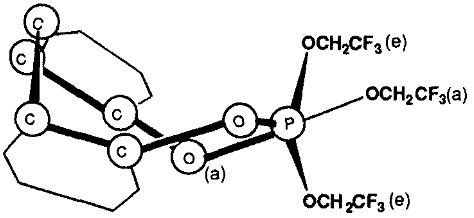
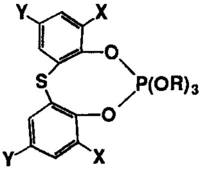


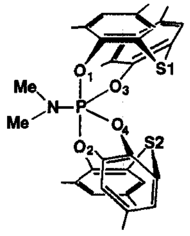
9

There is a correlation between decreasing ring distortion in the boat forms which parallels decreasing P–S distances in the series of pentaoxyphosphoranes like **1**. In this series, the structures are displaced along a coordinate from a square pyramid toward an octahedron. The displacement over the series of compounds extends from 44% to 69% with an accompanying decrease in the P–S distance from 2.880(1)Å to 2.362(2)Å[5] (Table I).

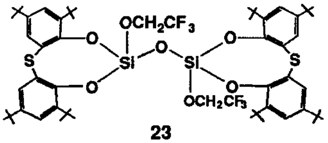
TABLE I
Selected Parameters for Oxyphosphoranes and the Disiloxane **23** with Sulfur-Bridging Eight-Membered Rings



	X	Y	R	% octa.[a]	P–S,Å	Ring Conformation[b]	Ring Distortion,Å[c]	Ref.
10	*t*-Bu	Me	CH_2CF_3	69.4	2.362(2)	sym. boat		5
1	*t*-Bu	*t*-Bu	CH_2CF_3	64.5	2.504(3)	sym. boat		1
26	*t*-Bu	*t*-Bu	Ph	60.8	2.640(2)	twisted boat	1.05	3
25	*t*-Bu	Me	Ph	56.8	2.744(2)	twisted boat	1.16	3
24	Me	Me	Ph	44.1	2.880(1)	twisted boat	1.20	3
				% SP[e]				
27[d]				29	3.652(3)	twisted boat	1.62	6
					3.485(4)	twisted boat	1.55	
				% TBP[g]	Si–S,Å			
23[f]				53	3.04(1)	sym. boat		7
				43	3.11(1)	twisted boat	1.39	



27



23

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[a] Percent displacement from an ideal square pyramid to an octahedron.

[b] Symmetric is abbreviated "sym".

[c] Ring distortion, for example in **23**, is defined[7] as the sum of the displacements of O5 and C72 from the mean plane found for O7, C71, C51, and C52 for the ring containing Si2.

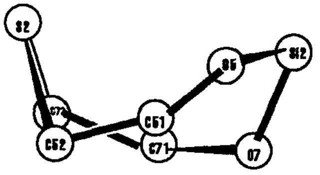


TABLE I. Continued

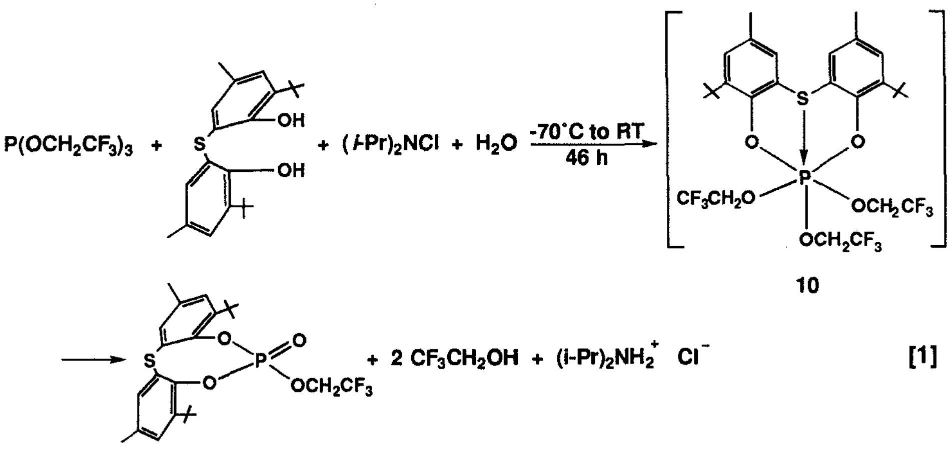
[d] The tetraoxyphosphorane shown above is TBP with no P–S interaction.

[e] The TBP for **27** is displaced 29% toward a square pyramid (SP).

[f] The headings of the entries for **23** remain the same as that for the oxyphosphoranes except where noted.

[g] The disiloxane **23** shown above has silicon atoms distorted from a tetrahedral geometry toward a TBP.

This hexacoordinated state has been proposed as an intermediate in hydrolysis processes where either cyclic or acyclic phosphates may form.[6] For example, the intermediate **10** is proposed[6] in the reaction of the phosphite $P(OCH_2CF_3)_3$ with a diol in the presence of water giving a cyclic phosphate, eq. 1.

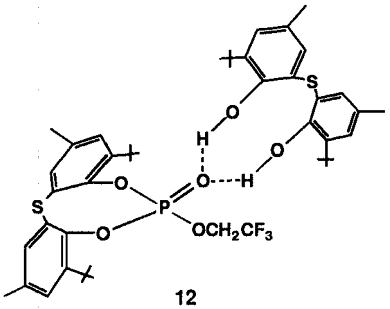


[1]

$^{31}P = -13.2$ ppm

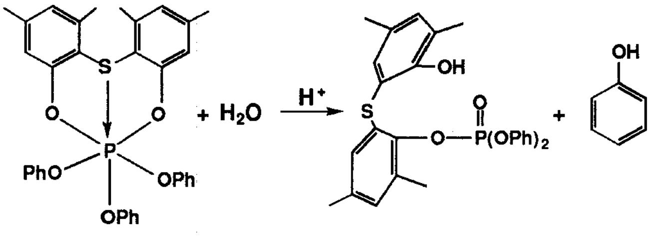
11

In the absence of water, the reactants of eq. 1 lead to oxidative addition yielding the hexacoordinated phosphorane **10** (^{31}P chemical shift of -82.2 ppm[6]). The X-ray structures of **10** and the cyclic phosphate **11** as well as a form containing a diol as a hydrogen bonded solvate (**12**) have been obtained.[5]



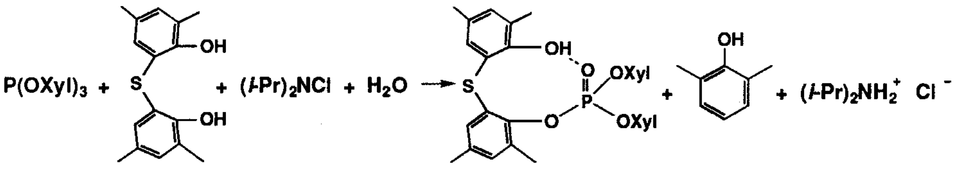
12

To establish that this type of sulfur-induced hexacoordinated state does hydrolyze to a phosphate, the acid hydrolysis of **13** was carried out, eq. 2. The principal product, identified from its ^{31}P chemical shift of -16.38 ppm, was the acyclic phosphate **14A**.[33]



13 14A [2]

Following the reaction scheme in eq. 1 with the xylyloxy containing phosphite $P(OXyl)_3$ in place of $P(OCH_2CF_3)_3$, an acyclic phosphate results[6] rather than a cyclic phosphate. The implication is that the presence of the poorer departing groups, OXyl in eq. 3 and OPh in eq. 2, are responsible for the formation of acyclic vs. cyclic phosphates.



14B [3]

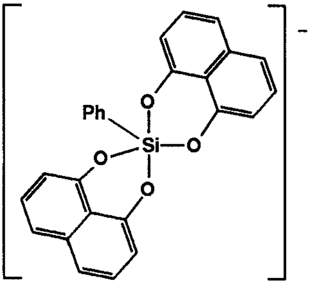
The presence of a P–S interaction in **10**[5] and related members of this series seems to increase the P–O bond distances in general and presumably makes them more reactive. For the hexacoordinated form **10** proposed as an intermediate in the hydrolysis reaction of eq. 1, the P–O ring distances are 1.698(5)Å and 1.694(4)Å.[5] These are compared with the considerably shorter distances present in **9**[1] which has a similar eight-membered ring but where the sulfur atom is replaced by a methylene group, and consequently incapable of a bridge donor to phosphorus interaction. Here the P–O_{ax} ring bond length is

1.660(3)Å and the P–O_{eq} ring value is 1.602(4)Å. Comparison of P–O bond distances for the acyclic OCH_2CF_3 groups in **10**[5] shows values of 1.638(4)Å and 1.656(5)Å for groups *cis* to P–S and 1.615(4)Å for the OCH_2CF_3 group *trans* to the P–S interaction. These P–O values are again larger than those for **9**.[1] Here a P–O_{ax} distance of 1.654(4)Å is obtained while the P–O_{eq} values are 1.592(4)Å and 1.594(4)Å. With the general increase in P–O distances accompanying increased coordination, support for a catalytic role for sulfur-induced hexacoordinated phosphorus in hydrolysis and perhaps other solvolysis reactions seems reasonable.

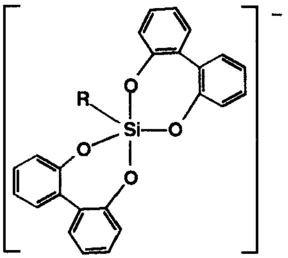
CYCLIC SILICATES

Structural Aspects

In studies designed to compare pentaoxyphosphoranes with corresponding silicon chemistry, we prepared the first anionic five-coordinated silicates with six- and seven-membered oxygen-containing rings, **15-17**, as K^+, 18-crown-6 salts.[34]



15

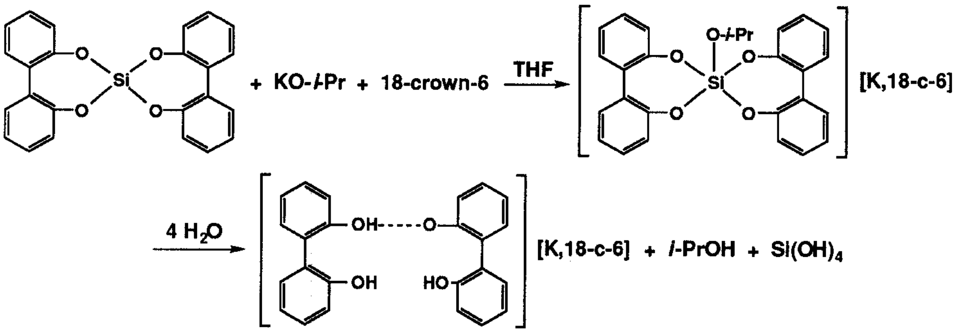


16 (R = O-*t*-Bu)
17 (R = F)

(All K^+, 18-c-6 salts)

An X-ray structure of **15** was obtained, however, both **16** and **17** rapidly degraded during data collection preventing their structural elucidation.[34]

In related reactions to that used to obtain **15-17** using ligands such as O-*i*Pr and $Bu_4N^+F^-$, less stability was encountered and only the formation of anionic organic systems was established.[34] It was postulated that these reactions initially yielded five-coordinated cyclic anionic silicates that then underwent rapid hydrolytic cleavage, e.g., formation of **18** in eq. 4.

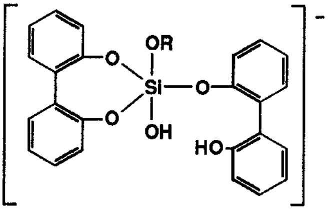


18

[4]

An X-ray structure of **18** isolated as the $(n\text{-Bu})_4N^+$ salt established its structure.

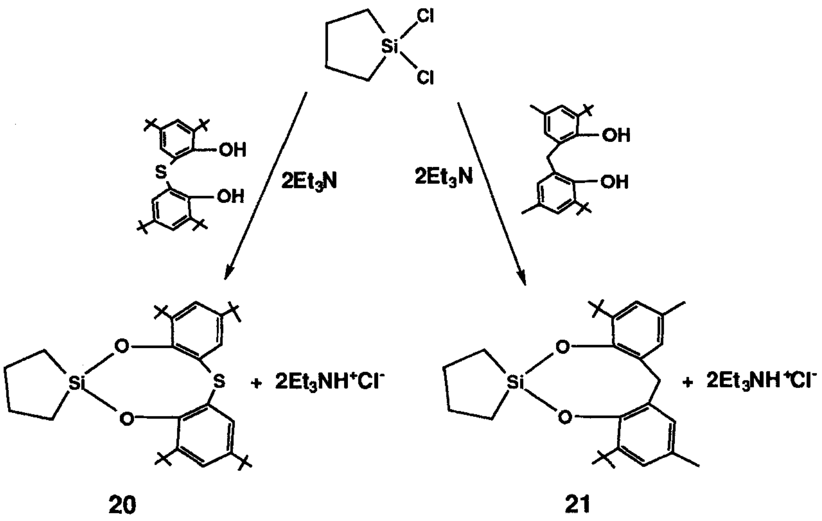
The hydrolysis presumably is initiated by attack at silicon by a water molecule resulting in the formation of a hexacoordinated activated state which undergoes Si–O bond cleavage and yields a postulated intermediate of the type, **19**. Repetition of the process is envisioned to lead to the organic products. The instability of five-coordinate anionic silicates compared to their four-coordinate silane precursors provided another example of enhanced reactivity[35-43] for this class of substances.



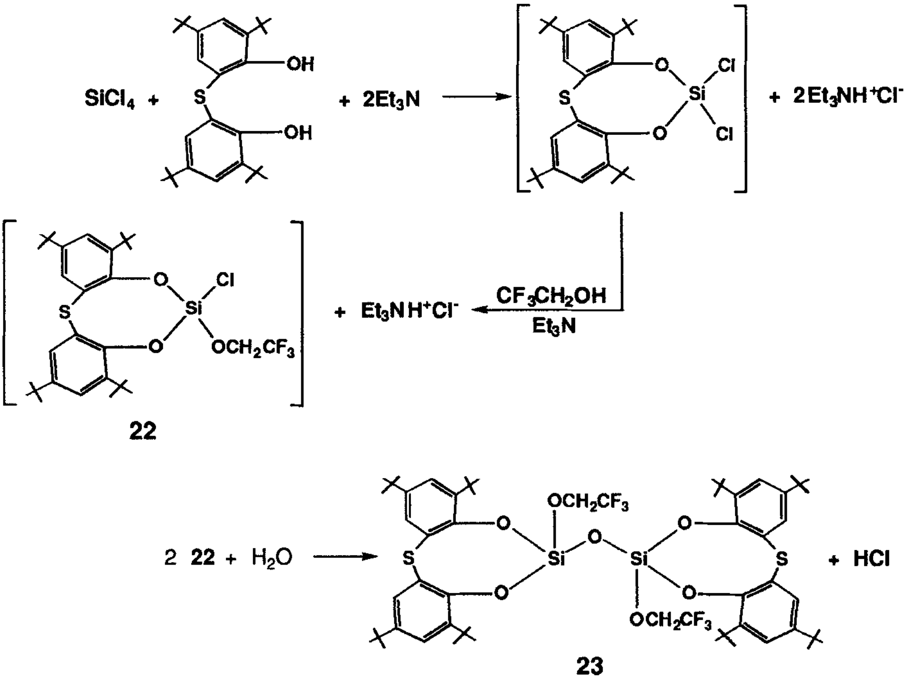
19

In more recent work[7] reactions of chlorosilanes with sulfur- and methylene-bridged diols lead to cyclic silicon compounds containing the same type of eight-membered ring system as that formed with the pentaoxyphosphoranes. This is shown in Scheme 1 for the formation of **20** and **21**.[7] Yields of 85–95% were obtained. A similar reaction was carried out with $SiCl_4$ in an attempt to prepare **22**. However, hydrolysis occurred leading to the disiloxane **23** isolated in 62% yield.[7] The proposed intermediates in Scheme 2 containing reactive Si–Cl bonds apparently gave preference to the hydrolytic process.

SCHEME 1



SCHEME 2



Structural analysis of both **21** and **23** proved possible but not that for **20**.[7] The geometry at the two silicon atoms of the cyclic disiloxane **23** is different with the expected tetrahedral orientation at each silicon modified by the nearness of the ring sulfur atoms resulting in a tendency toward trigonal bipyramidal formation. Each sulfur atom is positioned axially opposite a OCH_2CF_3 group. The structure of the cyclic silane **21** with a ring methylene group in place of a sulfur atom more nearly approaches the tetrahedral geometry. Analysis[7] of the bond parameters indicates the extent of the Si–S interaction for **23**. Here the Si(1)–Si(1) distance is 3.04(1)Å. This compares with the van der Waals' sum of 3.90Å[44] and the sum of covalent radii of 2.20Å.[45] For Si1–S1, a displacement from the tetrahedron toward the trigonal bipyramid, $T_d \rightarrow$ TBP, is calculated to be 53%. In a similar manner by making use of the sum of angles at silicon S1 that constitute the trigonal plane of the partially formed TBP (345°) relative to the sum for a tetrahedron (325.45°) and a TBP (360°), a displacement $T_d \rightarrow$ TBP of 57% is computed.[7] These same calculations performed for the silicon atom S2 give a 47% displacement ($T_d \rightarrow$ TBP) from the Si2–S2 distance and 39% from the bond angles.

An average of the two values for each silicon atom gives $T_d \rightarrow$ TBP of 53% at S1 and 43% at S2 for **23**. This conclusion is further supported by the longer Si1–O2 bond length (1.72(3)Å) which is an axial bond opposite the incoming sulfur atom that is approaching in line in the forming TBP. The other three Si–O bond lengths at Si1 range from 1.60(2) to 1.63(2)Å, about 0.1Å shorter as expected for equatorial bonds.

Ring Conformations

Ring conformations provide another measure of the extent of sulfur induced coordination. In oxyphosphoranes having sulfur containing eight-membered rings, all members that show P–S interactions and hexacoordination have either symmetrical or twisted tub (boat-like) ring conformations while a symmetrical chair conformation was obtained for **7**.[1] Here the geometry is trigonal bipyramidal with the ring occupying diequatorial positions.

In the disiloxane **23**,[7] the ring containing Si1 and S1, which has the shortest of the two Si–S distances, is in a symmetrical boat-like conformation. However, the ring containing Si2 and S2 is in a twisted boat-like conformation. By making use of the atom displacements from mean planes of the eight-membered rings, an approximate relation is obtained[7] between the extent of the P–S interaction and ring distortion. For example, Table I shows that the symmetrical boat conformations, **1** and **10**, have the shortest P–S distances, whereas as the degree of distortion of the twisted boat conformations increases, without paying attention to small differences, the P–S distance increases and accordingly the degree of displacement from a square pyramid to an octahedron decreases.

Similarly, as is apparent in Table I for the disiloxane **23**, the shortest silicon–sulfur distance (at Si1) is associated with the ring that is a symmetrical boat while the longer silicon–sulfur interaction (at Si2) accompanies the ring with a twisted boat-like conformation. The displacement from the tetrahedron toward the trigonal bipyramid for these two silicon centers is 53% and 43%, respectively.

ACKNOWLEDGMENT

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