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Phosphorus, Sulfur, and Silicon and the Related Elements

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Sulfur Induced Coordination at Phosphorus and Silicon

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SULFUR INDUCED COORDINATION AT PHOSPHORUS AND SILICON

ROBERT R. HOLMES, T. K. PRAKASHA, SRIKANTH SRINIVASAN, AND ROBERTA O. DAY

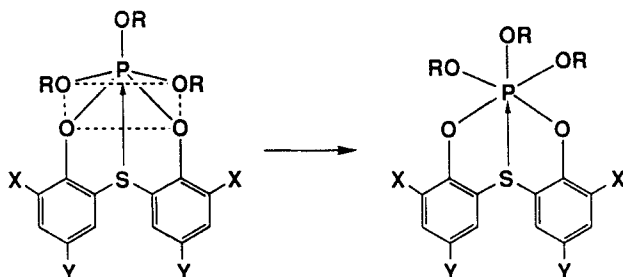
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Abstract Recent work has shown that a sulfur atom is capable of inducing higher coordination geometries for both phosphorus and silicon. These geometries serve as models for activated states in nucleophilic substitution reactions.

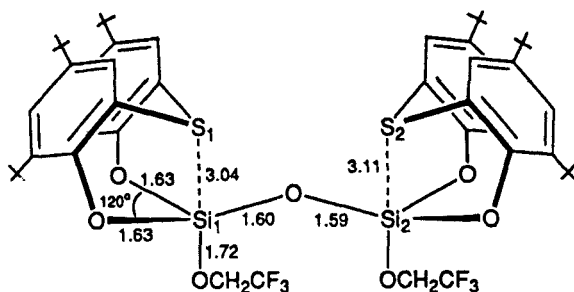
INTRODUCTION

With the use of cyclic components containing sulfur-bridged aryl groups, a series of pentaoxyphosphoranes has been formed that exhibits structures extending from square pyramidal to octahedral.¹⁻⁴ In the case of silicon, employment of the same type of ring system has resulted in the formation of the first cyclic disiloxane whose structure is between a tetrahedron and a trigonal bipyramid.⁵ Recent work reported here reveals additional examples of higher coordinate geometries. Their role as models in nucleophilic substitution reactions are illustrated with phosphorus.

Square Pyramidal to Octahedral Geometry



Tetrahedral to Trigonal Bipyramidal Geometry



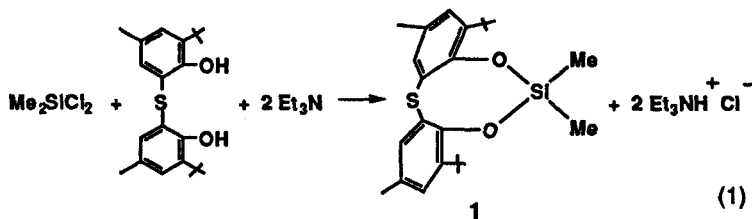
Si-S (covalent) = 2.20 Å
 Si-S (Van der Waals) = 3.90 Å

²⁹Si, ppm (solid)

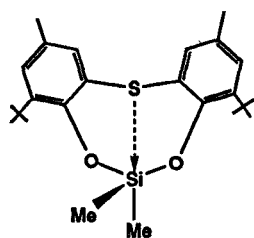
Si₁ -107.8
 Si₂ -99.4

RESULTS AND DISCUSSION

Reaction of Me_2SiCl_2 with 2,2'-thiobis(4,6-di-*t*-butylphenol) in the presence of *N*-chlorodiisopropylamine yielded the cyclic silane **1** (eq 1) whose X-ray structure resulted in a Si-S distance of 3.1 Å. This value supports the angles at silicon giving a geometry about halfway between a tetrahedron and a trigonal bipyramid.

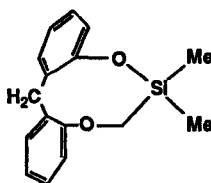


A similar reaction produced **2** having a methylene group in place of the ring sulfur atom. The sulfur-silicon coordination present in **1** compares with recent work of Edema et al.⁶ on **3** showing nitrogen coordination to silicon.

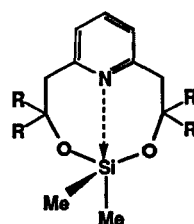


Si...S = 3.1 Å

1



2



(RR = Adamantyl)

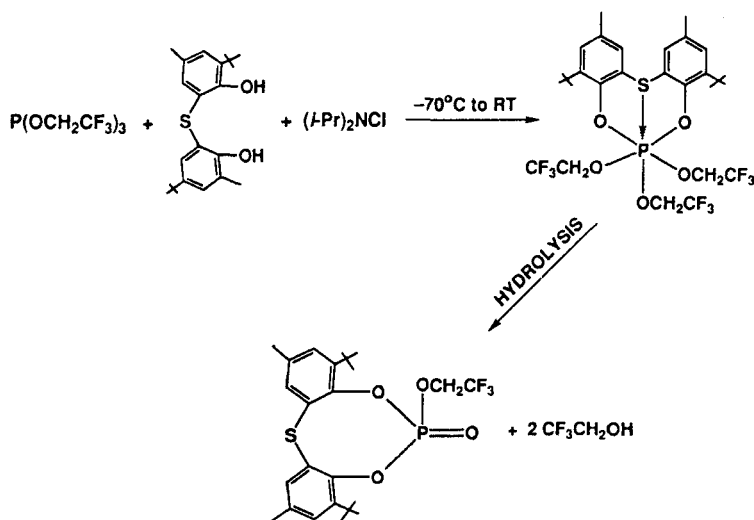
Si...N = 2.727(2) Å

3

Model Intermediates

In the case of hydrolysis processes of pentaalkoxyphosphoranes, evidence⁶ suggests that sulfur induced coordination appears in an active state intermediate accompanying the hydrolysis process yielding cyclic or acyclic phosphates. This is illustrated in eq 2 leading to A.⁷

Hydrolysis Leading to A (Cleavage of Two Acyclic Groups)

A $\delta P = -13.2$ ppm

30% yield

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