

Si–O and P–O motifs in inorganic rings and clusters

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Abstract. This article presents a brief overview of different kinds of silanols and the important reactions of N-bonded silanetriols. The synthesis and characterization of silanediols containing Si–N and Si–C bonds, (2,4,6-Me₃C₆H₂)N(SiMe₃)Si(Me)(OH)₂ (**1e**) is described. **1e** shows a polymeric crinkled tape type of structure due to extensive intermolecular hydrogen bonding. We also describe the formation of a neutral copper(II) complex derived from the reaction of CuCl₂ with (O)P(3,5-Me₂Pz)₃ where the ligand undergoes a facile P–N bond cleavage and functions as an N₂O type of tridentate ligand.

Keywords. Silanols; metallasiloxanes; hydrogen bonding; phosphonates; metal clusters.

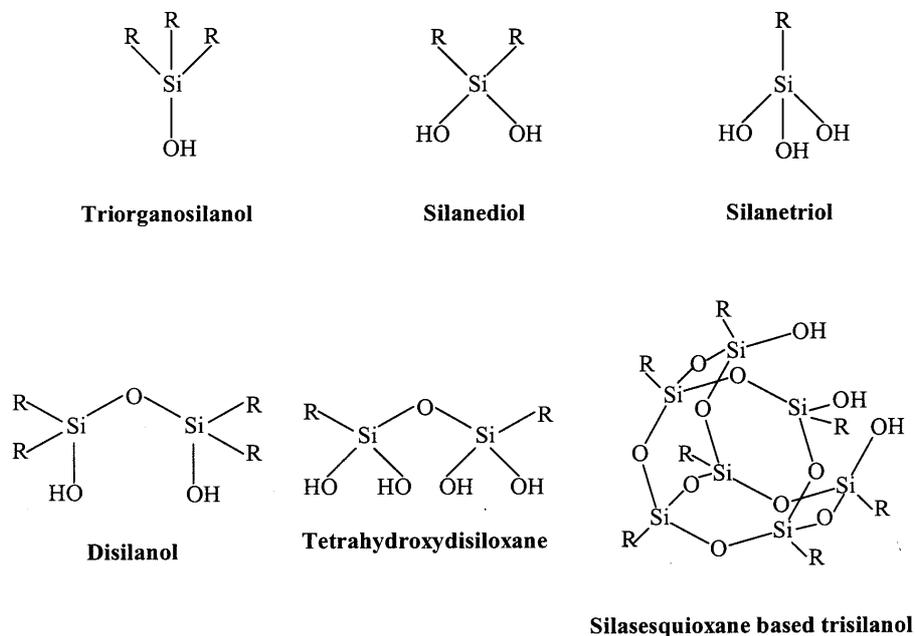
1. Introduction

The chemistry of silanols, compounds containing Si–OH groups have been receiving a lot of interest in recent years due to several reasons. Foremost is because these compounds can function as models for silica surface¹. Thus, appropriate metallasiloxanes can be good structural models for silica supported transition metal catalysts. Another reason for the widespread interest in this class of compounds is that they can function as excellent synthons for the preparation of a large variety of metallasiloxanes in acyclic and cyclic structural formulations^{2–3}. Also there is considerable structural diversity among silanols due to the presence of extensive intra and intermolecular hydrogen bonding⁴.

Several types of silanols are known. These include compounds of the type R₃SiOH, R₂Si(OH)₂, RSi(OH)₃, R₂Si(OH)(O)Si(OH)R₂, RSi(OH)₂OSi(OH)₂R and also silasesquioxane based trisilanols. Some of these are shown in scheme 1. All of these compounds can be used as synthons for the preparation of acyclic, cyclic or cage metallasiloxanes. Recently, Roesky and coworkers have synthesized N-bonded silanetriols containing a Si–N bond⁵. These compounds have excellent solubility and are soluble in a large variety of organic solvents including hexane. This attribute enables the use of the N-bonded silanetriols in a variety of reactions with metal alkoxides, metal alkyls, metal chlorides and metal hydrides. Some of these reactions and the products formed therein are shown in scheme 2^{2,6–9}.

Although silanediols are among the simplest of the silanols, only two examples, viz. Ph₂Si(OH)₂ and *t*-Bu₂Si(OH)₂ have been studied in detail³, while several compounds have been studied by X-ray crystallography^{4,10–14}. In view of the successful assembly of

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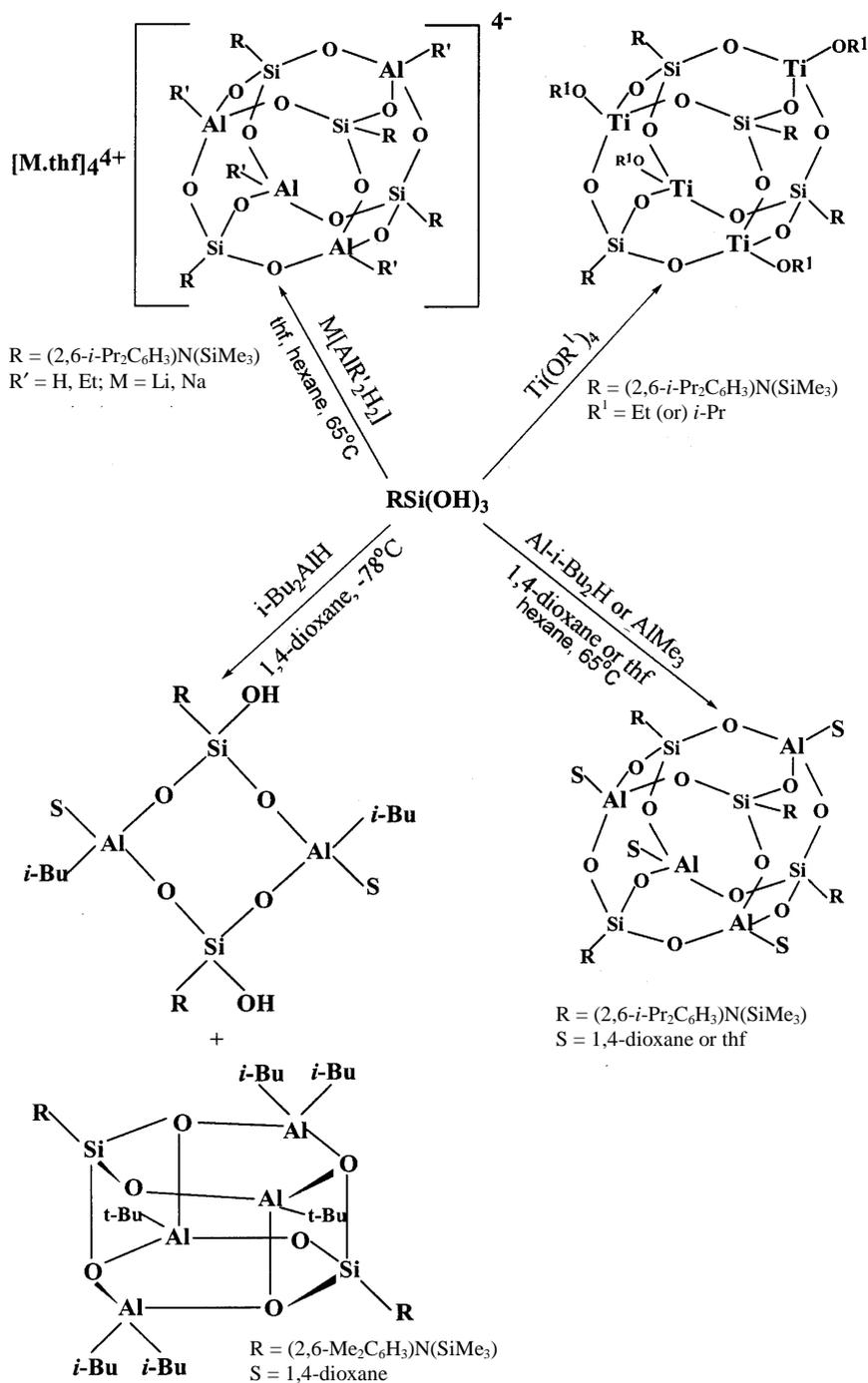
Scheme 1. Representative examples of silanols.

N-bonded silanetriols, it seemed logical to apply the same synthetic strategy for the preparation of silanediols containing a Si–N bond. This presentation summarizes the synthesis and X-ray structural characterization of the silanediol, (2,4,6-Me₃C₆H₂)N(SiMe₃)Si(Me)(OH)₂, **1e**. A detailed account on this topic has appeared elsewhere¹⁵. We also report in this presentation some of our recent findings on the assembly of P–O–M compounds generated by an *in situ* hydrolysis of P–N bonds.

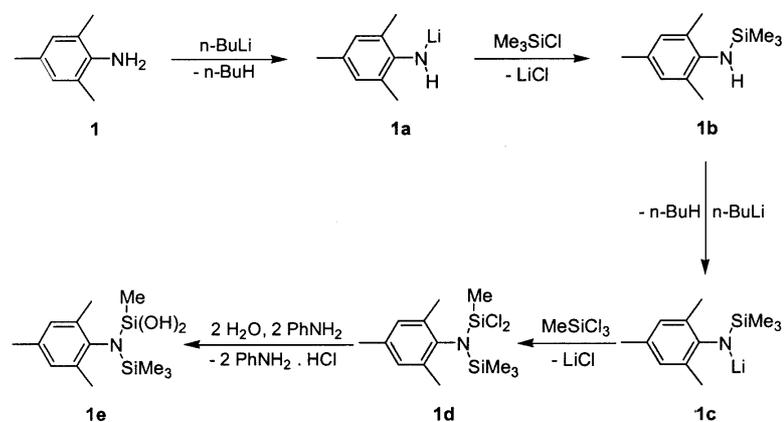
2. Experimental

2.1 Synthesis and X-ray structural characterization of (2,4,6-Me₃C₆H₂)N(SiMe₃)Si(Me)(OH)₂

The synthesis of the above silanediol has been accomplished by following the strategy shown in scheme 3. A sterically hindered aromatic amine 2,4,6-trimethylaniline (**1**) was used as the starting material. Deprotonation of (**1**) by *n*-butyllithium followed by reaction with trimethylsilylchloride afforded the trimethylsilyl substituted amine, **1b**. Further deprotonation of **1b** by *n*-butyllithium followed by reaction with methyl trichlorosilane gave the organosilicon dichloride, **1d**. Hydrolysis of the silicon dichloride using aniline as the hydrogen chloride acceptor afforded the silanediol **1e** in about 60% yield. The silanediol **1e** is a free-flowing white powder with excellent solubility properties in a large variety of organic solvents including hexane. The ²⁹Si NMR chemical shift of Si(OH)₂ in **1e** appears at –29.2 ppm. In comparison, the corresponding resonance for an Si(OH)₃



Scheme 2. Representative reactions of silanetriols.



Scheme 3. Synthesis of an N-bonded silanediol.

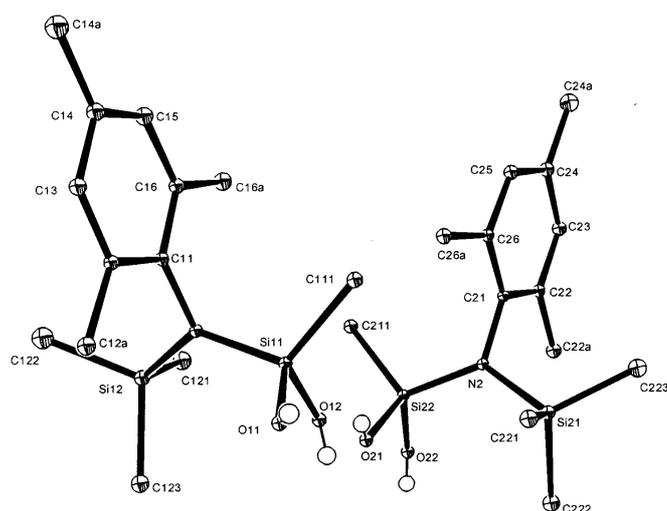


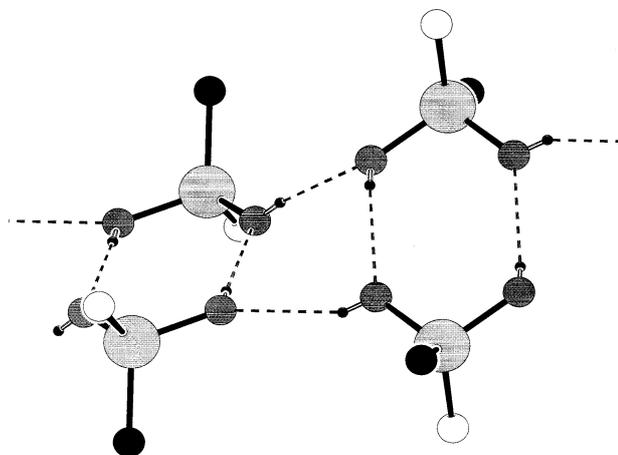
Figure 1. Molecular structure of 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{N}(\text{SiMe}_3)\text{Si}(\text{Me})(\text{OH})_2$.

group in the N-bonded silanetriol (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{N}(\text{SiMe}_3)\text{Si}(\text{OH})_3$) appears considerably upfield at -65.8 ppm. It may be noted that the SiCl_2 resonance in **1d** appears at -1.2 ppm, which moves upfield upon hydrolysis. A similar trend has also been observed in the case of N-bonded silicontrichlorides and N-bonded silanetriols.

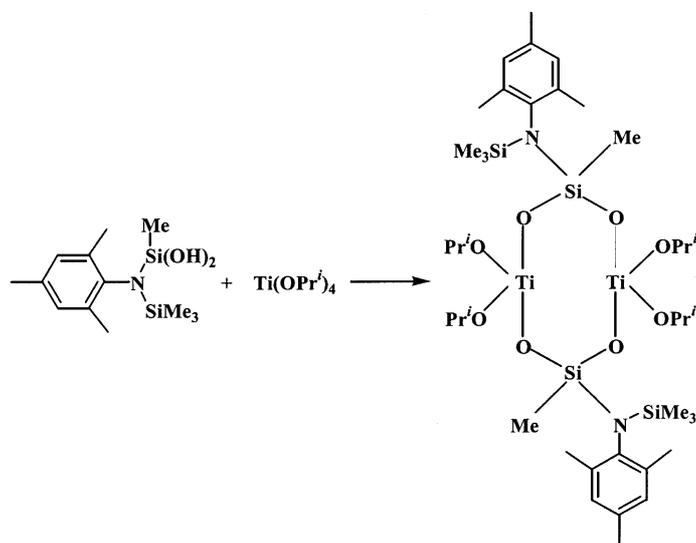
The X-ray crystal structure of **1e** is shown in figure 1. There are two crystallographically independent molecules in the unit cell. The metric parameters are summarized in table 1. The important points of note are that two kinds of Si–N bonds

Table 1. Selected bond lengths (Å) and bond angles (°) for **1e**.

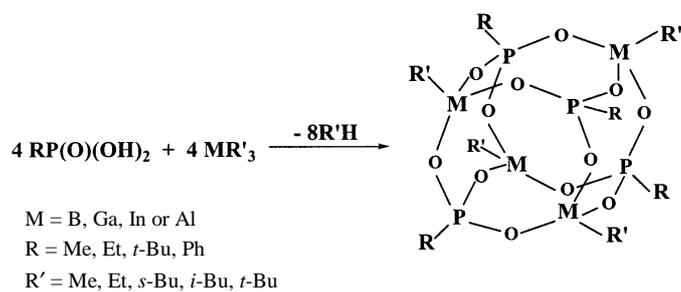
Molecule 1			Molecule 2		
<i>Bond distances (Å)</i>					
Si(11)–N(1)	1.7140(18)		Si(21)–N(2)	1.7586(18)	
Si(12)–N(1)	1.7510(18)		Si(22)–N(2)	1.7125(18)	
Si(11)–O(11)	1.6379(18)		Si(22)–O(21)	1.6373(18)	
Si(11)–O(12)	1.6336(18)		Si(22)–O(22)	1.636(2)	
<i>Bond angles (°)</i>					
Si(11)–N(1)–Si(12)	125.48(10)		Si(22)–N(2)–Si(21)	124.64(10)	
C(11)–N(1)–Si(11)	116.30(13)		C(21)–N(2)–Si(21)	116.28(14)	
C(11)–N(1)–Si(12)	118.01(14)		C(21)–N(2)–Si(22)	119.02(13)	
O(12)–Si(11)–O(11)	104.42(10)		O(22)–Si(21)–O(21)	102.01(11)	
<i>Hydrogen bonding</i>					
H-bond	O–H	O···O	H···O	O–H···O	Symmetry
O11A–H11D···O22B	0.642	2.810	2.176	169.6	$x, 1 + y, z$
O12–H12···O11A	0.650	2.769	2.124	172.0	$-x, 1 - y, 1 - z$
O21–H21···O12	0.638	2.782	2.208	150.6	x, y, z
O22–H22···O21B	0.645	2.801	2.198	156.3	$-x, -y, 1 - z$

**Figure 2.** Intermolecular hydrogen-bonding in 2,4,6-Me₃C₆H₂N(SiMe₃)Si(Me)(OH)₂.

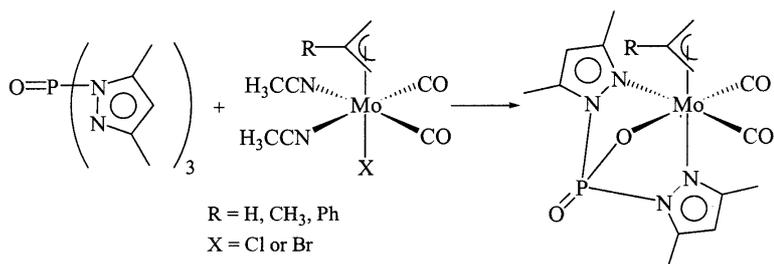
viz. Si(11)–N(1) of 1.7140(18) and Si(12)–N(2) of 1.7510(18) are observed, consistent with the change of the electronegativity of the substituents around the two silicon atoms Si(11) and Si(12). Also the average O–Si–O bond angles of 103.21(10)° are comparable to silanediols containing sterically hindered substituents.



Scheme 4. Reactions of N-bonded silanediol with titanium isopropoxide.



Scheme 5. Reactions of organophosphonic acids with group 13 metal alkyls.



Scheme 6. Reactions of *tris* (3,5-dimethyl pyrazolyl)phosphine oxide with organomolybdenum precursor.

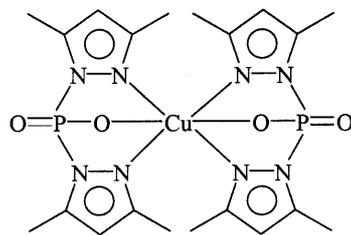


Figure 3. Cu(II) complex formed by the reaction of $(3,5\text{-Me}_2\text{Pz})_3\text{PO}$ with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

In keeping with the expectations for compounds of this type, the silanediol **1e** is involved in extensive intermolecular hydrogen bonding. This can be viewed as taking place in a sequential manner. First a dimeric planar eight-membered ring is formed by hydrogen bonding between two silanediols. The eight-membered rings are subsequently involved in an extensive crinkled ribbon-like arrangement by further hydrogen bonding between them (figure 2). It is interesting to compare the hydrogen bonding of **1e** with the situation present in the N-bonded silanetriol $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si}(\text{OH})_3$. In the latter, the presence of the additional hydroxyl group allows the molecule to arrange itself in a tubular, column-like arrangement.

The reactivity of **1e** with titanium isopropoxide has been investigated with a view to prepare cyclic metallasiloxanes. A 1:1 reaction of **1e** with $\text{Ti}(\text{OPr}^i)_4$ in a mixture of hexane and THF proceeds smoothly with the elimination of isopropanol to afford an eight-membered titanasiloxane (scheme 4). Other reactions of **1e** with main group and transition metal substrates are in progress.

2.2 Synthesis and characterization of compounds with a P–O–M framework

Reaction of *t*-butyl phosphonic acid with various group 13 metal alkyls has been reported recently to afford neutral cubic molecular phosphonates containing a P–O–M framework¹⁶ (scheme 5). Other types of gallophosphonates containing alkali metal ions have also been synthesized and characterized¹⁷. In a different approach to the assembly of compounds containing P–O–M linkages, *in situ* hydrolysis of P–N bonds has been investigated. The sensitivity of the P–N bonds in pyrazolyl-substituted phosphorus compounds particularly upon interaction with transition metals has been the subject of recent study. Sarkar and coworkers have shown that the reaction of *tris*(3,5-dimethyl)pyrazolyl phosphine oxide, $(3,5\text{-Me}_2\text{Pz})_3\text{PO}$ (**2**) with a molybdenum carbonyl compound proceeds with an *in situ* hydrolysis of one of the pyrazolyl groups attached to phosphorus and the ligand functions as a tridentate N_2O donor¹⁸ (scheme 6). In order to test the general applicability of this reaction we reacted **2** with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a 2:1 reaction in dichloromethane. The product isolated showed that a similar hydrolysis of the P–N bonds occurs and the ligand functions as N_2O coordinating ligand (figure 3). A neutral compound is obtained as a result of the involvement of the two anionic ligands. Currently we are investigating the scope of this reaction to other transition metal ions.

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