Organic Soluble Silicophosphonate $[RSi(OH)\{OP(O)(H)(OH)\}]_2O$ ($R = (2,6\text{-}i\text{-}Pr_2C_6H_3)NSiMe_3$): The First Silicophosphonate Containing Free Si−OH and P−OH Groups[†]

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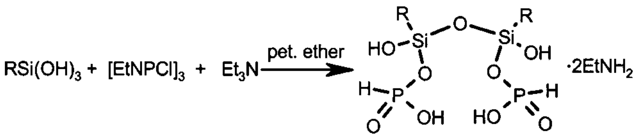
The syntheses and reactions of organosilanols $R_nSi(OH)_{4-n}$ ($n = 1-3$),[1] alkylphosphonic acids $RP(O)(OH)_2$,[2] dialkylphosphinic acids $R_2P(O)(OH)$,[3] and dialkyl phosphates $(RO)_2P(O)(OH)$[4a,b] have attracted considerable attention in recent years in view of their direct relevance in the preparation of metal containing silicate and phosphate assemblies for applications in catalysis and materials science.[1] It has now been well documented that the presence of a greater number of hydroxyl groups on silicon/phosphorus in these compounds leads to cage or polymeric structures in their subsequent reactions with suitable metal precursors.[1,2] While silanols containing three −OH groups on silicon (e.g., $t\text{-}BuSi(OH)_3$) and alkylphosphonic acids containing two −OH groups and a phosphoryl oxygen atom (e.g., $t\text{-}BuP(O)(OH)_2$) have recently been used for the synthesis of soluble molecular silicate and phosphate cages,[1a,2] there are no known examples of compounds which simultaneously contain Si−OH and P−OH moieties along with a silicophosphate Si−O−P linkage. Apart from the synthetic challenges these kinds of molecules can offer, they will also be useful in the synthesis of metal containing soluble silicophosphate materials which could be eventually converted in solid-state materials under mild conditions (e.g., sol−gel routes).

Continuing our interest in synthesizing model compounds for silicate and phosphate materials, we have now investigated the reactions of $RSi(OH)_3$ ($R = (2,6\text{-}i\text{-}Pr_2C_6H_3)NSiMe_3$)[5] with phosphorus halides. The preliminary results of this investigation, reporting the successful synthesis of an unusual and hitherto unknown *hydrocarbon-soluble* molecular silicophosphonate containing *two* Si−O−H, *two* P−O−H, *one* Si−O−Si, and *two* Si−O−P linkages, are described in this communication.

The title compound $[RSi(OH)\{OP(O)(H)(OH)\}]_2O\cdot 2EtNH_2$ ($R = (2,6\text{-}i\text{-}Pr_2C_6H_3)NSiMe_3$) (**1**) is obtained in 35% yield from a direct reaction between $RSi(OH)_3$ and the λ^3-cyclotriphosphazane $[EtNPCl]_3$[6] in the presence of Et_3N (Scheme 1). Analytically pure **1**, recrystallized from dichloromethane/petroleum ether (1:1), was characterized by elemental analysis, EI-MS, IR, and NMR spectroscopic techniques.[7] The strong absorption observed in the IR spectrum at 2407 cm^{-1} is characteristic of P−H stretching vibrations.[8] The resonance due to the P−H proton in the ^1H NMR spectrum appears at δ 5.73 ppm with a large $^1J_{PH}$ (670 Hz). The proton-coupled ^{31}P NMR spectrum shows a doublet centered at δ −9.4 ppm ($^1J_{PH} = 670$ Hz). The high-field ^{29}Si NMR spectrum shows a doublet centered at δ −82.9 ($^2J_{SiP} = 5.5$ Hz) and a singlet at δ 8.1 ppm for the siloxide and the trimethylsilyl centers, respectively.

Scheme 1. Synthesis of **1**



A single-crystal X-ray diffraction study reveals that the molecule is built around a HO−P−O−Si(OH)−O−Si(OH)-O−P−OH inorganic backbone (Figure 1).[9] Each of the phosphorus atoms has a (SiO)P(O)(H)(OH) local geometry, and hence each end of the molecule can be regarded as a monosilyl ester of H_3PO_3. The only organic residue on each silicon ($Ar(SiMe_3)N-$ group) accounts for the high solubility of **1** in a variety of organic solvents apart from also imparting necessary kinetic stability to the heterocatenated inorganic chain. A space-filling model of **1** indicates that the inorganic core is completely enclosed in an organic sheath provided by this organic group.

In spite of the poor quality of the X-ray diffraction data,[9] the bond distances and bond angles obtained for **1** are consistent with the values reported for simple silanols and phosphonic acids in

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[†] Dedicated to Professor V. Krishnan on the occasion of his 63rd birthday.

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(7) $[EtNPCl]_3$ (2 mmol) was slowly added to a solution of $RSi(OH)_3$ (2 mmol) and Et_3N (6 mmol) in petroleum ether (100 mL) at 0 °C, and the reaction mixture was slowly brought to room temperature and stirred for 24 h. Removal of the hydrochloride salt by filtration and the solvent under reduced pressure yielded a greasy white solid, which was recrystallized from CH_2Cl_2/petroleum ether (5:1) at −18 °C to yield **1** (yield: 35 %). Mp: 139−141 °C. Anal. Calcd for $C_{34}H_{72}N_4O_9P_2Si_4$ (855.3): C, 47.75; H, 8.49; N, 6.55. Found: C, 47.9; H, 8.2; N, 6.8. Spectral data: ^1H NMR (300 MHz; $CDCl_3$) δ 0.15 (18H, s, $SiMe_3$), 1.1 (6H, t, $CH_3CH_2NH_2$), 1.18 (24H, $(CH_3)_2CH$), 1.7 (4H, NH_2), 2.7 (4H, q, $CH_3CH_2NH_2$), 3.5, 3.7 (4H, m, $(CH_3)_2CH$), 5.7 (2H, d, PH, $^1J_{PH} = 670$ Hz), 7.1 (2H, Ar), 7.3 (4H, Ar), 8.2 (OH); ^{29}Si NMR (99 MHz; C_6D_6) 8.1 (s, $SiMe_3$), −82.9 (d, $NSiO_3$, $^2J_{PSi} = 5.5$ Hz); ^{31}P NMR (202 MHz; C_6D_6) δ −9.4 (d, $^1J_{PH} = 670$ Hz). EI-MS (70 eV): m/z 855 (4%, M^+).

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(9) Crystal data: $C_{34}H_{72}N_4O_9P_2Si_4$, fw = 855.3, $T = 293$ K, λ(Mo Kα) = 0.71073, triclinic, $P\bar{1}$, $a = 9.908(2)$ Å, $b = 15.265(2)$ Å, $c = 18.321(2)$ Å, $\alpha = 112.8(2)°$, $\beta = 94.18(2)°$, $\gamma = 95.15(2)°$, $V = 2526$ Å^3, $Z = 2$, $d_c = 1.124$ mg/m^3, $F(000) = 925$, 2θ range 2.9−40.0°, unique reflections 4713, parameters = 463, R1 ($I > 2\sigma(I)$) = 0.083, wR2 ($I > 2\sigma(I)$) = 0.1850. GOF = 0.9. The intensity data for a 0.1 × 0.05 × 0.2 mm^3 sized crystal were collected on a Nonius MACH-3 four-circle diffractometer. The structure was solved by direct methods and refined using SHELXL-97. Owing to the very small size of the crystal, the quality of the diffraction data was very poor. Also no intensities were found for reflections above $\theta = 20°$.

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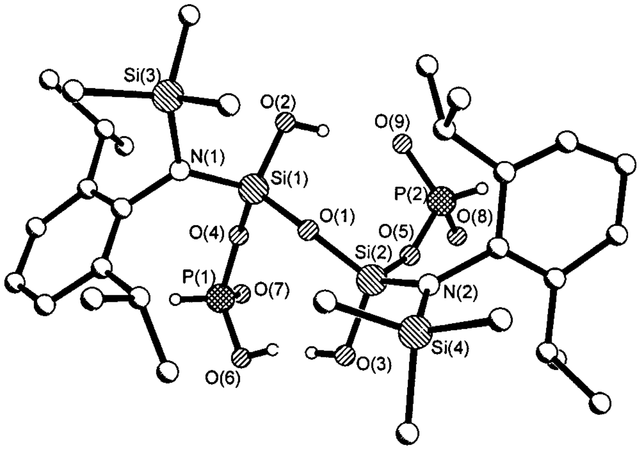
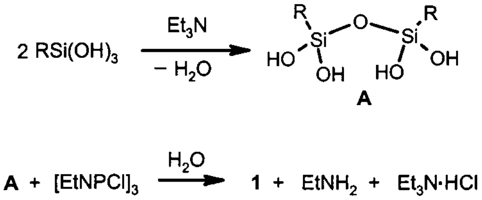


Figure 1. Molecular structure of **1**. Average bond distances and bond angles: Si−O 1.614(8) Å, P−O 1.535(8) Å, P=O 1.465(8) Å; Si−O−Si 142.2(5)°, Si−O−P 151.7(6)°.

Scheme 2. Suggested Pathway for the Formation of **1**



the literature.[1,2] The two phosphonate moieties in the molecule adopt an approximate trans orientation on the central siloxane unit. The silicon and phosphorus atoms in the molecule are approximately tetrahedral. The Si−O−Si bond angle (142.2(5)°) is in very good agreement with the value obtained for the [RSi(OH)$_2$]O (R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$) (140.7(2)°).[10] The observed Si−OH distances in **1** (average 1.600(8) Å) are signifcantly shorter than the corresponding values observed for disilanols of the type [R$_2$Si(OH)]$_2$O (R = Me 1.642(5); *i*-Pr 1.640(2); Ph 1.620(3)−1.647(3) Å).[11] However, there are no considerable variations in the observed P=O and P−OH distances in **1** compared to the several earlier reported phosphorus acids as well as orothophoshate and phosphonate esters.[12]

Although, at a first glance, the isolation of **1** from the above reaction may seem somewhat unexpected, Scheme 2 provides a possible pathway for the formation of **1**. Step 1 is consistent with the recent observation that the silanetriol can undergo a facile self-condensation reaction to yield the tetrahydroxydisiloxane intermediate **A** during the course of its reactions with metal substrates such as Cp*TaMe$_4$[13] or NaInMe$_4$[14] or in the presence of acidic or basic impurities.[10] It appears that the water liberated during this step is utilized in step 2 to hydrolyze the moisture-sensitive λ^3-cyclotriphosphazane[6] and eventually result in the formation of the final product, presumably via a phosphonic acid intermediate. If the above mechanism is really operative, product **1** should also be obtained as the product even if PCl$_3$ is used in place of [EtNPCl]$_3$. Indeed, when silanetriol was reacted directly with PCl$_3$, silicophosphonate **1** was isolated, however in very poor and varying yields (2−10%). Hence the use of the more reactive PCl$_3$ in place of [EtNPCl]$_3$ does not appear to be a good alternative route for the synthesis of **1**.

The preliminary investigations indicate that **1** would be useful as a molecular precursor for the synthesis of soluble models for silicoaluminophosphate materials (SAPO). For example, treatment of 2 equiv of AlMe$_3$ with **1** revealed interesting spectral changes in ^{31}P and ^{29}Si NMR chemical shifts.[15] The ^{31}P NMR signal for **1** at −9.4 ppm completely disappears with the appearance of several new upfield signals between −12 and −18 ppm. Many of these new signals disappear with time, and the spectra recorded after 7 days revealed the presence of only three very closely spaced signals at δ −14.1, −14.5, and −14.9 ppm. Similarly, the original doublet ^{29}Si NMR spectrum due to the siloxide of **1** completely disappears with the appearance of two new upfield doublets at −86.0 and −88.3 ppm. These spectral changes are consistent with the formation of P−O−Al and Si−O−Al linkages,[1,2] indicating the existence of molecular SAPO species in solution. Our attempts to obtain single crystals of these species have so far not been successful.

Thus, it has been demonstrated here that the reaction between a kinetically stabilized organosilanetriol and a highly reactive λ^3-cyclotriphosphazane offers an easy route to a unique molecular silicophosphonate with abundant acidic hydroxyl groups. Further possibilities exist for the conversion of the silicophosphonate **1** into the corresponding silicophosphate (by oxidation of the P−H group), which would contain six free hydroxyl groups. Reactions of such hydroxyl rich silicophosphates with metal alkyls, alkoxides, and amides are likely to open up new possibilities in synthesizing tailored silicometallophosphate (SMPO) materials through molecular routes. Work in this direction is currently underway in our laboratories.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles, and the details of NMR spectral investigations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) To a C$_6$D$_6$ solution of **1** in a NMR tube was added AlMe$_3$ in hexane (1.6 M solution, 2 equiv) dropwise. After the mixture was shaken well and the methane gas evolution was allowed to cease, the ^{31}P and ^{29}Si NMR spectrum were recorded. After the solution was stored for 7 days, the spectra were again recorded.