Phosphorus(III)-Containing Silicates via a New Aprotic Building-Block Approach to Multicomponent Silicates

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Water is an important component in virtually all "sol-gel" routes to multicomponent silicates.[1] It is the source of oxygen in most metal oxides, and it is normally a reactant or product in most steps leading to the formation and growth of a metallosilicate network. In principle, each of the many reactions involving water presents an opportunity to fine-tune the structure and properties of a silicate, but in practice the rates of these reactions differ by several orders of magnitidue and product formation invariably occurs under kinetically "controlled" conditions which are inherently difficult to control. The result from most attempts to prepare multicomponent silicates via sol-gel techniques is a material that does not have uniform incorporation of metal oxide and silica at the molecular level.

We have been examining the possibility of preparing multicomponent silicates under rigorously aprotic conditions. The salient feature of our approach is that (initial) product formation occurs via a single condensation reaction, which is simultaneously responsible for incorporating the metal into the Si/O network. In principle, this approach allows much greater control over the stoichiometry, homogeneity, and properties of multicomponent silicates than is normally possible with conventional sol-gel techniques.

In this paper we report the results from our initial efforts to prepare multicomponent silicates from aprotic condensation reactions of active metal halides with labile spherosilicates.[2,3] The focus of the present work is the reaction of PCl_3 with $(Me_3SnO)_8(Si_8O_{12})$ (**1**),[3,4] which affords an interesting new phosphorus(III)-containing silicate. The synthesis, characterization, and properties of this material will be discussed, as well as the implications of our work for the future utility of labile spherosilicates as building blocks for multicomponent silicates.

As reported previously, spherosilicate **1** can be prepared in excellent yield by the reaction of $H_8Si_8O_{12}$ with $Me_3SnOSnMe_3$.[3,5] This aprotic, hydrocarbon-soluble source of $[Si_8O_{20}]^{8-}$ reacts rapidly with a variety of active metal

$$\underset{\mathbf{1}}{3(\mathrm{Me_3SnO})_8(\mathrm{Si_8O_{12}})} \xrightarrow[-n\mathrm{Me_3SnCl}]{+8\mathrm{PCl_3}} [(\mathrm{Si_8O_{12}})(\mathrm{OSnMe_3})_{8-n}(\mathrm{OPCl_2})_p(\mathrm{O_2PCl})_q]_m \quad (1)$$

$$n = 2q + p$$

halides (e.g., Me_3SiCl) to afford trimethyltin halide (e.g., Me_3SnCl) and high yields of octafunctional spherosilicates (e.g., $(Me_3SiO)_8(Si_8O_{12})$). High yields of trimethyltin halide are also observed when **1** reacts with multifunctional halide complexes (e.g., PCl_3, $AlCl_3$, BBr_3, $TiCl_4$, $ZrCl_4$, Me_2SiCl_2). In most cases, both the multifunctional halide and **1** are completely consumed to produce insoluble metallosilicate networks.

The addition of PCl_3 to a benzene solution of **1** produced a gelatinous suspension within 15 min of mixing at 25 °C. Subsequent heating for 14 h at 80 °C afforded a thick slurry, from which a dusty white powder was isolated after filtration and drying.[6] For three separate reactions performed using enough PCl_3 to stoichiometrically liberate all Me_3Sn groups from **1** as Me_3SnCl (i.e., Sn/Cl = 1:1), an ^{1}H NMR spectrum of the crude reaction mixture indicated that approximately 60-75% of the available tin was liberated as Me_3SnCl.[7] This result, which suggested that a surprisingly large percentage of available reactive groups had produced Si-O-P linkages, was qualitatively corroborated by elemental analysis (C, H, Cl, and P). However, elemental analysis clearly indicates that the fraction of unreacted (O_3SiO)-$SnMe_3$ and P-Cl groups remaining in the solid obtained after filtration and drying is somewhat higher than the fraction estimated on the basis of ^{1}H NMR integrations of Me_3SnCl produced in the reaction.[8] The surface area measured by BET (nitrogen) was 500 m^2/g, and the pore volume and pore diameter were calculated to be 0.3 cm^3/g and 24 Å, respectively. This is quite similar to the results obtained by Klemperer for the sol-gel polymerization of $(MeO)_8Si_8O_{12}$ under acidic conditions.[2d]

The ^{29}Si CPMAS NMR spectrum of the solid obtained from a typical reaction exhibits two resonances at δ -110 and -105, corresponding to O_3Si-O-P and O_3Si-O-$SnMe_3$ groups, relatively. The line widths of both resonances are relatively narrow (~330-340 Hz), and there is no evidence for the formation of products derived from cleavage or degradation of individual Si_8O_{12} frameworks. This contrasts with the aqueous sol-gel chemistry of $(MeO)_8Si_8O_{12}$, where initial hydrolysis and condensation reactions appear

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(1) For an excellent overview of sol-gel routes to silicates see: Brinker, C. J.; Scherer, G. W. *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*; Academic Press: New York, 1990.

(2) Reports of other efforts to prepare siliceous material from spherosilicates: (a) Brevett, C. S.; Cagle, P. C.; Klemperer, W. G.; Millar, D. M.; Ruben, G. C. *J. Inorg. Organomet. Polym.* **1992**, *1*, 335-42. (b) Agaskar, P. A. *Colloids Surf.* **1992**, *63*, 131-8. (c) Agaskar, P. A. *J. Chem. Soc., Chem. Commun.* **1992**, 1024-6. (d) Cagle, P. C.; Klemperer, W. G.; Simmons, C. A. *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 29-37. (e) Agaskar, P. A. *Inorg. Chem.* **1990**, *29*, 1603. (f) Agaskar, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 6858-9. (g) Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 3-13. (h) Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 15-25. (i) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262-4.

(3) Feher, F. J.; Weller, K. J. *Inorg. Chem.* **1991**, *30*, 880.

(4) For other attempts to prepare P-containing silicates see: (a) Szu, S.-P.; Klein, L. C.; Greenblatt, M. *J. Non-Cryst. Solids* **1992**, *143*, 21-30. (b) Prabakar, S.; Rao, K. J.; Rao, C. N. R. *J. Mater. Res.* **1991**, *6*, 592.

(5) Spherosilicate **1** can also be prepared by the reaction of H_8T_8 with Me_3SnOH.[2a]

(6) In a typical experiment, PCl_3 (432 mg, 3.14 mmol) in C_6H_6 (5 mL) was added to a solution of **1** (2.185 g, 1.178 mmol) in C_6H_6 (40 mL) in a 250-mL round-bottomed flask. Cyclohexane (764 μL) was added as an internal standard for the determination of Me_3SnCl.[7] After freeze (-196 °C)-pump-thaw degassing, the solution was heated at 80 °C for 14 h. Upon cooling the product was collected by vacuum filtration, washed with C_6H_6 (3 × 10 mL), and dried in vacuo (80 °C, 0.01 Torr, 10 h). Yield: 1.117 g of white powder.

(7) The amount of Me_3SnCl was determined from the integrated intensity of its ^{1}H NMR resonances relative to cyclohexane:[6] a small aliquot of solution was removed, several drops of C_6D_6 were added, and the ^{1}H NMR spectrum was recorded after presaturating the resonance for C_6H_6.

(8) (a) For a reaction[6] in which ^{1}H NMR spectroscopy indicated that 72(±5)% of the theoretical maximum of Me_3SnCl was evolved, the following analytical data[8b] were obtained for the isolated product: C, 6.84-7.01; H, 1.49-1.61, P, 4.53-4.88; Cl 9.30. The C, H, and P data are consistent with the evolution of ~60% of the available tin as Me_3SnCl. The total halide analysis was, however, ~25% higher than expected. (b) Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37950.

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to occur without disrupting Si_8O_{12} frameworks,[2a,d,g] but the later stages of gelation and/or drying often lead to extensive framework cleavage.[2h] Upon exposure to air,[9] a new resonance assignable to O_3Si-OH groups (δ −101) gradually appeared at the expense of the resonance for $O_3Si-O-SnMe_3$ groups. This change was accompanied by the formation of Me_3SnCl, which was identified on the basis of mass spectrometry (as well as its distinctive odor[10]).

The ^{31}P CPMAS NMR spectrum of the initial product obtained from a typical reaction revealed a complex set of resonances spanning a 250 ppm range centered at approximately δ 150. Upon exposure to small amounts of air,[9] this set of resonances was gradually replaced by a new set centered at approximately δ 0. The complexity of these spectra is due to the large chemical shift anisotropy for ^{31}P, which produces several overlapping series of large spinning sidebands when molecular motion about ^{31}P is severely restricted.[4,11] To gain information about the environment around phosphorus centers in the material, it was necessary to eliminate these sidebands using the TOSS (total suppression of sidebands) pulse sequence, which relies on a series of 180° pulses administered during a single rotation of the sample to suppress all but the central resonance.[12]

A ^{31}P TOSS NMR spectrum of a typical product obtained from the reaction of **1** with PCl_3 exhibits two resonances at δ 184 and 145 (Figure 1A). On the basis of the amount of Me_3SnCl produced in the reaction, elemental analysis of the solid product (C, H, Cl, P), and comparison to the chemical shifts estimated for $(Me_3SiO)PCl_2$ (δ 165) and $(Me_3SiO)_2PCl$ (δ 145),[13] these resonances can be assigned to $(O_3SiO)PCl_2$ and $(O_3SiO)_2PCl$ groups, respectively. As might have been anticipated, the line width for the resonance attributable to $(O_3SiO)PCl_2$ "end groups" (δ 184) is significantly narrower due to greater rotational freedom around phosphorus. Quite surprisingly, there is no evidence for the formation of $(O_3SiO)_3P$ groups, which would be expected to produce a ^{31}P resonance at 100–120 ppm.[13]

Upon exposure to air, the ^{31}P TOSS spectrum showed a gradual disappearance of resonances at δ 184 and 145 and the appearance of two new resonances at δ 8 and −18 (Figure 1B). Upon prolonged exposure to air, two resonances with very narrow line widths were observed at δ 4.4 and −5.4, and TOSS was no longer necessary (Figure 1C).

To determine the reason for the changes observed in the NMR spectra upon exposure to air, freshly prepared samples were reacted separately with O_2 and H_2O under carefully controlled conditions.[14] After exposure to dry O_2, the ^{31}P and ^{29}Si CPMAS NMR spectra were still unchanged after several hours, but upon exposure to humid nitrogen, the ^{31}P and ^{29}Si NMR spectra were identical to spectra obtained previously for samples exposed to air. Since Si–O–Sn linkages are only slowly hydrolyzed by water, it appears that the air sensitivity of our samples is due to the reaction of atmospheric moisture with P–Cl and/or P–O–Si linkages.

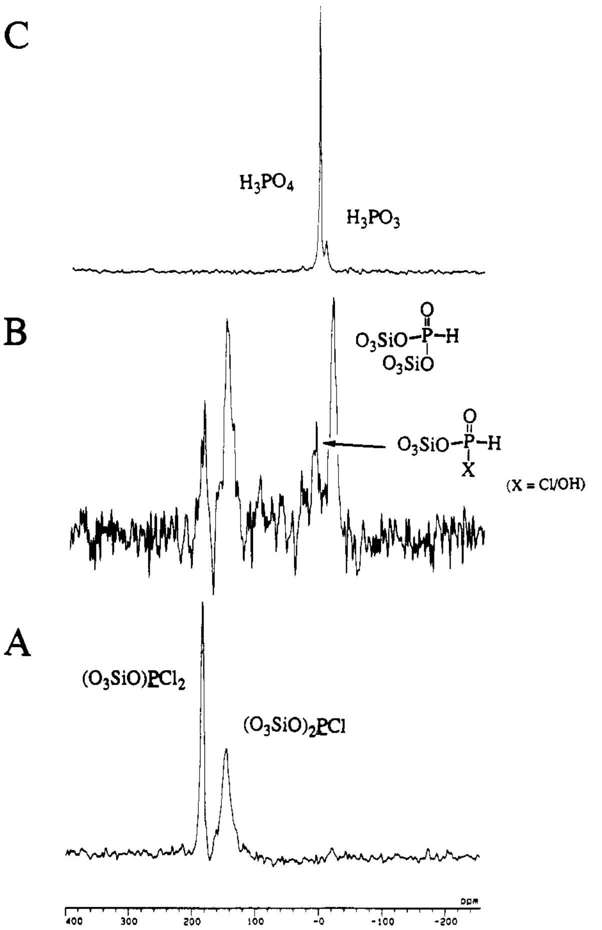

Figure 1. The 80.96-MHz ^{31}P CPMAS NMR spectra of the product obtained from the reaction of PCl_3 with $(Me_3SnO)_8(Si_8O_{12})$ (**1**). Spectra A and B were recorded using the TOSS pulse sequence with a contact time of 1 ms and a spinning rate of 1009 Hz.[12] (A) Freshly prepared sample.[14c] (B) After brief exposure to air (<5 min) or a few hours in a commercial "airtight" rotor.[9] (C) After exposure to water vapor (30 min)[14b] or several hours in a commercial "airtight" rotor.[9]

The hydrolysis of P–O–Si linkages is quite facile for solution complexes,[15] and it appears to occur with our samples upon prolonged exposure to water, but the major reaction pathway during the early stages of hydrolysis appears to be hydrolysis of unreacted P–Cl groups. This initial reaction produces HCl, which rapidly reacts with Si–O–Sn groups to produce Me_3SnCl and O_3Si-OH groups. Only after prolonged exposure to air does the ^{29}Si resonance for $O_3Si-O-P$ groups (δ −110) begin to disappear as P–O–Si linkages are hydrolyzed.

The hydrolysis of P–Cl groups also produces P–OH groups, which can tautomerize to give phosphorus(V) centers. In the case of $(O_3SiO)_2PCl$ groups, the species resulting after tautomerization would be $(O_3SiO)_2P(O)H$, which we assign to the ^{31}P resonance at δ −18. This

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(9) The "airtight" 7-mm sample rotors supplied by ChemMagnetics admitted enough air over a few hours to react with all P–Cl and $(O_3SiO)-SnMe_3$ groups.[14c]

(10) Me_3SnCl is both highly volatile and highly toxic; it should not be inhaled.

(11) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983.

(12) (a) Dixon, W. T. *J. Chem. Phys.* **1982**, *77*, 1800. (b) Raleigh, D. P.; Olejniczak, E. T.; Vega, S.; Griffin, R. G. *J. Magn. Reson.* **1987**, *72*, 238–250. (c) Raleigh, D. P.; Kolbert, A. C.; Griffin, R. G. *J. Magn. Reson.* **1990**, *890*, 1–9. (d) Hagemeyer, A.; van der Putten, D.; Spiess, H. W. *J. Magn. Reson.* **1991**, *92*, 628–630.

(13) Methods used to estimate chemical shifts are described in the supplementary material.

(14) (a) Oxygen was dried using freshly activated molecular sieves. (b) Water was added via a stream of N_2 which was bubbled through water. (c) The "airtight" sample rotor[9] was made truely airtight by sealing its top with a small amount of hot paraffin wax. (Excess wax was removed with a razor blade.) No noticeable decomposition was observed over 8 h at spinning rates as high as 3000 Hz.

(15) Voronkov, M. G.; Maletina, E. A.; Roman, V. K. *Heterosiloxanes, Volume 2: Derivatives of Nitrogen and Phosphorus*; Harwood Academic Publishers: New York, 1991.

assignment is based on (i) the ^{31}P chemical shift reported for $(Me_3SiO)_2P(O)H$ (−15 ppm),[16] (ii) Morrow's identification of a stoichiometrically similar $(SiO)_2P(O)H$ species (δ −5) on the surface of PCl_3-treated silica,[17] and (iii) the appearance of an absorption at 2400 cm^{-1} in IR spectrum attributable to P–H stretching. The hydrolysis of $(O_3SiO)PCl_2$ groups should proceed similarly, but the initial hydrolysis product in this case would be $(O_3SiO)P(O)(Cl)H$, which could react further with water to produce $(O_3SiO)P(O)(OH)H$ and HCl. There are no reports of stoichiometrically similar complexes in the literature, but on the basis of trends in ^{31}P NMR data,[13] it seems likely that the chemical shifts for $(O_3SiO)P(O)(Cl)H$ and $(O_3SiO)P(O)(OH)H$ would be similar and that both would appear downfield from the resonance for $(O_3SiO)_2P(O)H$ (δ −18). We have therefore assigned the ^{31}P resonance at δ 8 in Figure 1B to $(O_3SiO)P(O)(Cl)H$ and/or $(O_3SiO)P(O)(OH)H$.

Prolonged exposure to air or the intentional addition of water completely hydrolyzes the P–O–Si linkages, as evidenced by the appearance of two sharp ^{31}P resonances due to adsorbed $(HO)_2P(O)H$ (δ −5.4) and $(HO)_3P(O)$ (δ 4.4, Figure 1C).[18] At this point the material has a somewhat wet appearance and neither TOSS nor rapid sample rotation is necessary to observe these resonances by ^{31}P NMR spectroscopy. We suspect that the (Si_8O_{12}) cages condense to form a phosphorus-free, silica-like material similar to that prepared by Klemperer from $(MeO)_8Si_8O_{12}$,[2] but this has not yet been examined in detail.

In conclusion, we have described an interesting new approach for the preparation of multicomponent silicates. The salient feature of this approach is that the (initial) product is assembled under rigorously aprotic conditions from molecular "building blocks" via a single bond-forming reaction. The utility of this approach has been demonstrated by preparing a P(III)-containing silicate which could not be prepared via traditional sol–gel methods because of its hydrolytic instability. The results from our efforts to prepare other metallosilicates derived from 1 will be described in due course.

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Supplementary Material Available: Solid-state ^{29}Si and ^{31}P NMR spectra (without TOSS) of phosphorus(III)-containing silicates and a table and plot of ^{31}P chemical shifts used to estimate chemical shifts for $(O_3SiO)_2PCl$, $(O_3SiO)PCl_2$, and $(O_3SiO)_3P$ groups (4 pages). Ordering information is given on any current masthead page.

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(16) Livantsov, M. V.; Prishchenko, A. A.; Lutsenko, I. F. *J. Gen. Chem. USSR* **1985**, *55*, 1976.

(17) Morrow, B. A.; McFarlan, A. J.; Gay, I. D. *J. Phys. Chem.* **1991**, *95*, 1360–1368.

(18) (a) H_3PO_4 is formed by the air oxidation of H_3PO_3;[18b] the presence of H_3PO_4 was confirmed by adding H_3PO_4. (b) Ohashi, in *Topics in Phosphorus Chemistry*; Grayson, M., Griffith, E. J., Eds.; Interscience: New York, 1964; Vol. 1, pp 113–87.