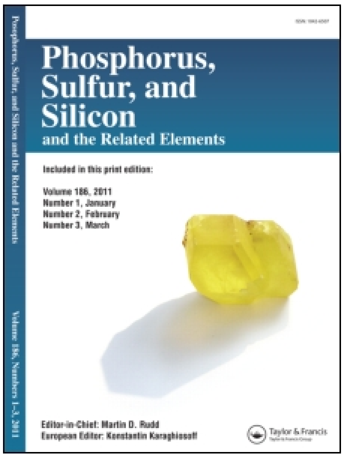

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AN APPLICATION OF LOW-COORDINATION PHOSPHORUS SPECIES: PHOSPHORYLATION OF OH GROUPS ON VARIOUS SOLIDS

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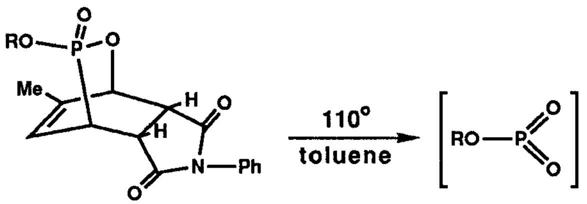
Abstract The 3-coordinate phosphoryl species RO-PO_2, R-PO_2, and RO-P(S)O and the 2-coordinate ArOP=O were generated in the presence of silica gel; alumina, titanium dioxide, Zeolites, and cellulose were also used with some of these reactants. Phosphorus functions were covalently bonded to the surface as revealed by CP-MAS ^{31}P and (for silica gel and Zeolites) by ^{29}Si NMR. Phosphorylated silica gel has potential value as an HPLC packing.

A valuable characteristic of low-coordination phosphoryl compounds is that they are highly reactive as electrophiles, and can serve as agents for attaching phosphate groups on substances containing OH, NH, or SH groups. As we have shown previously,[1] even OH groups on the surface of the solid silica gel are reactive to alkyl metaphosphates when generated in the presence of the suspended solid in an inert solvent. The metaphosphates were generated from thermolysis of bicyclic phosphonates of type **1** or from α-oxyiminophosphonates, and form alkyl phosphate groups on the surface as in **2**.



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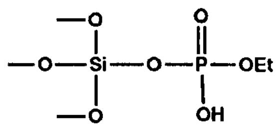

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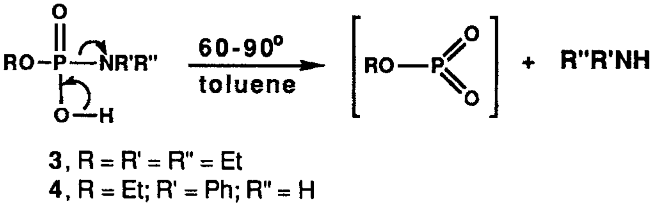
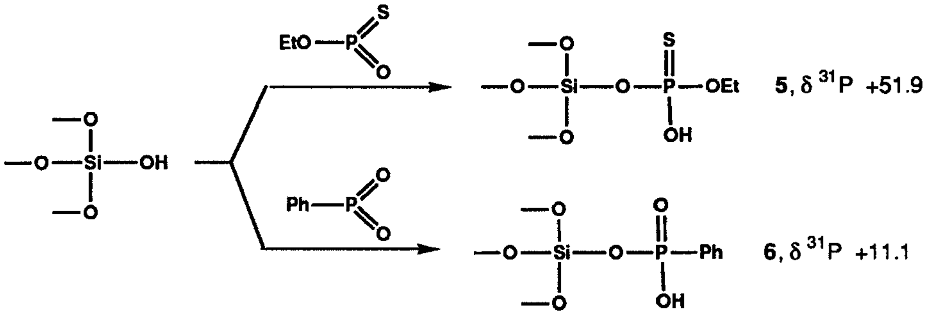
We have now extended the process to include other types of low-coordination phosphoryl compounds and other solid surfaces. Uses for the surface-modified solids are also being considered.

The structural feature on the silica surface was initially established by CP-MAS ^{31}P NMR spectroscopy, which for the ethyl phosphate group gave a signal at δ -10. The upfield shift of this magnitude was expected from model compounds: $(EtO)_2P(O)OH$, δ +1; $(EtO)_2P(O)OSiMe_3$, δ -9.1. Further proof that surface OH has been reacted was obtained by CP-MAS ^{29}Si NMR. Silica gel (Aldrich) gives two strong equal-intensity signals, one at δ -114 for Si containing no OH groups, the other at δ -104 for Si containing one OH.[2] After the phosphorylation, the signal at δ -104 is either gone or greatly diminished. The size of the δ -114 signal increases, and overlaps with that from phosphorylated Si (confirmed by a change in the relaxation time for the δ -114 signal).

A new method for generating metaphosphates that we have developed and employed in our studies on solids phosphorylation consists of the thermal fragmentation of phosphoramidic acids in an inert solvent.[3] Since these reagents are made from simple substitution reactions starting with $POCl_3$, they are inexpensive and readily applicable as practical phosphorylating agents for silica gel. Thus, both compounds **3** and **4** led to silica gel with the same CP-MAS ^{31}P NMR shift (-10) as obtained with our other methods.[1]



Other types of 3-coordinate phosphoryl compounds were found to behave similarly. Ethyl metathiophosphate[4] gave a thiono ester grouping on the surface (**5**), while $Ph\text{-}PO_2$ [5] gave a phosphonate group on the surface (**6**). In each case the expected upfield shift of about 10 ppm from a simple alkoxy analog was observed.



Other solid surfaces have also been phosphorylated:

(1) Alumina (Brockman 1, acidic). Using the bicyclic precursor in both cases, alumina with ethyl metaphosphate gave a solid with a strong CP-MAS ^{31}P NMR signal at δ -9.6, and with Ph-PO_2 a signal at δ +10.9. The upfield shift from attachment of Al to the phosphate group was expected from the model $(EtO)_2P(O)OAlEt_2$,[6] δ -14.5.

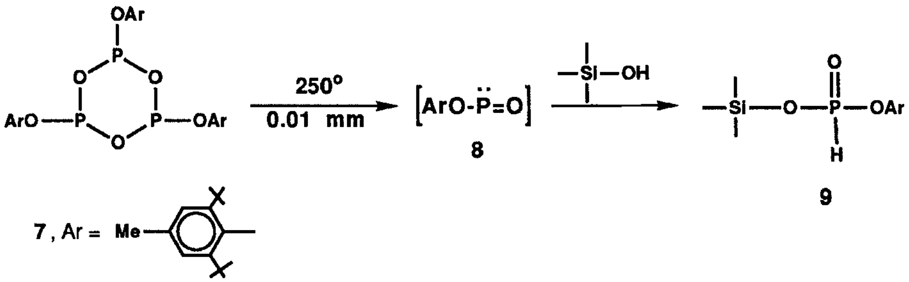
(2) Titanium Dioxide. A complex signal extending from δ 0 to -20 (peaks at -13 and -15) was obtained after phosphorylation with ethyl metaphosphate generated from phosphoramidic acid **4**.

(3) Zeolites. Using bicyclic phosphonate **1** as $EtOPO_2$ generator, ZSM-5 gave a complex, strong CP-MAS ^{31}P signal at δ +5 to -30. The signal from Zeolite Y was much sharper at δ -14.4. Zeolite Y had two equal intensity ^{29}Si NMR peaks at δ -101 and δ -106 but after phosphorylation the signal at δ -101 disappeared and was replaced by a new signal of equal intensity at δ -111. With phosphoramidic acid **4** as the generator for ethyl metaphosphate, the same results were obtained.

(4) Cellulose. Aldrich 20 micron cellulose was phosphorylated with ethyl metaphosphate made from **1**. After a 2-propanol wash, the CP-MAS ^{31}P NMR spectrum consisted of a strong signal at δ +1.4, as expected for a phosphate derivative, and a weak signal at δ -10. The spectrum for cellulose phosphorylated by the use of phosphoramidic acid **4** as the generator gave two nearly equal peaks with the same shifts. The signal at δ -10 is very likely due to a bonded pyrophosphate group.

We have included a 2-coordinate phosphoryl species in our studies, and found that it too reacts rapidly with the OH groups on silica gel. Trimer **7** was prepared[7] by partial hydrolysis of ArO-PCl_2 and heated at 250°

and 0.01 mm. Silica gel exposed to the vapor was found to give a strong CP-MAS ^{31}P NMR signal at δ -4, suggestive of the functionality **9** (cf. to δ +4 for the ethyl ester).



Preliminary studies have been made on the use of phosphorylated silica gel in HPLC applications. We found, for example, that some amino compounds in admixture are eluted in sharp, reasonably symmetrical peaks from Exsil 100 phosphorylated with ethyl metaphosphate while as is typical for silica gels, untreated Exsil 100 gives broad, asymmetrical peaks and is not useful for separations. We have also placed a chiral alkyl phosphate group on the surface of Exsil 100, by reacting it with (+)-menthyl-O-P(O)(OH)NHPh to generate (+)-menthyl-O-PO_2. The new packing has given some preliminary indications of utility in the resolution of racemic mixtures.

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