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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### <sup>31</sup>P NMR Spectral Evidence for the Hexacoordinated Phosphorus Intermediates in the Reaction of Oxyphosphorochloridate With Amino Acids

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## <sup>31</sup>P NMR Spectral Evidence for the Hexacoordinated Phosphorus Intermediates in the Reaction of Oxyphosphorochloridate With Amino Acids

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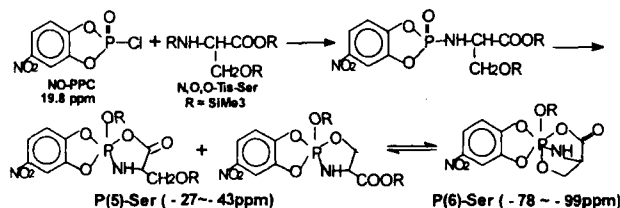
The nucleophilic groups on the side chain of amino acid can attack phosphoryl to form high-coordinated phosphorus intermediate, which was similar to the active sites of the cAMP-enzyme system.[1,2]

4-nitro-O,O-phenylene phosphorochloridate(NO-PPC) was synthesized, and used to interact with silanizing serine(Ser), threonine(Thr) and cysteine(Cys) respectively. The high-coordinated phosphorus compounds containing amino acid of penta- and hexa-coordinated intermediates(P(5)-AA) and (P(6)-AA) were observed by <sup>31</sup>P NMR spectra. Their chemical shifts were shown in an region of -25~ -45ppm and -78~ -100ppm respectively. However the unsubstituted similar compound(O-PPC) was carried out to the parallel reaction, not any <sup>31</sup>P NMR signal at upfield was observed.

TABLE 1 <sup>31</sup>P NMR Chemical shifts of (P(5)-AA) and (P(6)-AA)

PC	N,O-Tis-AA	(P(5)-AA)ppm	(P(6)-AA)ppm
O-PPC	Ser	-35.0 -36.2 -44.1 -44.5	
O-PPC	Thr	-42.7 -43.4 -44.3 -45.1	
O-PPC	Cys	-26.6 -26.9 -42.4 -42.8	
NO-PPC	Ser	-26.9 -27.6 -40.6 -42.5 -42.9 -43.4	-78.6 -84.4 -98.9 -99.7
NO-PPC	Thr	-27.8 -28.1 -43.0 -43.3 -43.8 -44.1	-99.1 -100.1
NO-PPC	Cys	-25.9 -26.1 -43.5 -43.8	-77.9 -78.1

The reaction process of NO-PPC and N,O-Tis-Ser was shown in following.



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- [2] R.R. Holmes, Chem., Rev., **96**, 927, (1996).