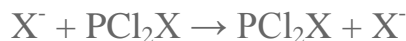
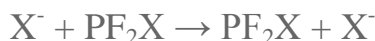
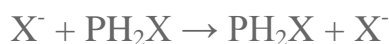


NUCLEOPHILIC SUBSTITUTION AT PHOSPHORUS

We discuss nucleophilic substitution at heteroatoms. Unlike the paradigmatic case for substitution at carbon, which proceeds via the S_N2 mechanism. Nucleophilic substitution at second-row atoms (S, Si, P) appears to follow an addition-elimination pathway. Bickelhaupt¹ now adds a more thorough computational examination of nucleophilic substitution at phosphorus. He looked at a few identity reactions involving tricoordinate P, namely



where X is chloride or hydroxide. In all cases the only critical point located on the potential energy surface is for a tetracoordinate intermediate. Shown in Figure 1 are the intermediates for the reaction $OH^- + PH_2OH$ and $Cl^- + PCl_3$. This result is consistent with the studies of nucleophilic substitution at sulfur and silicon.

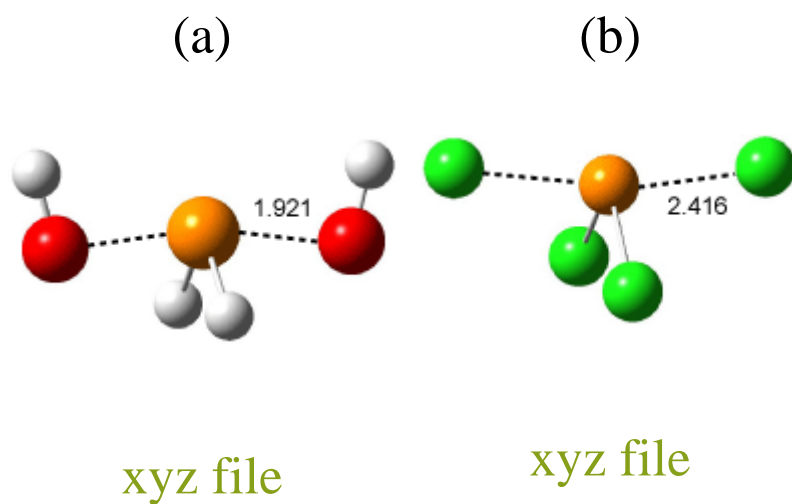


Figure 1. OLYP/TZ2P optimized intermediate for the reaction (a) $\text{OH}^- + \text{PH}_2\text{OH}$ and (b) $\text{Cl}^- + \text{PCl}_3$.

Source: <http://comporgchem.com/blog/?p=25>