



Computational  
Chemistry  
Group

# Bimolecular Nucleophilic Substitution Reactions of Organophosphorus Compounds

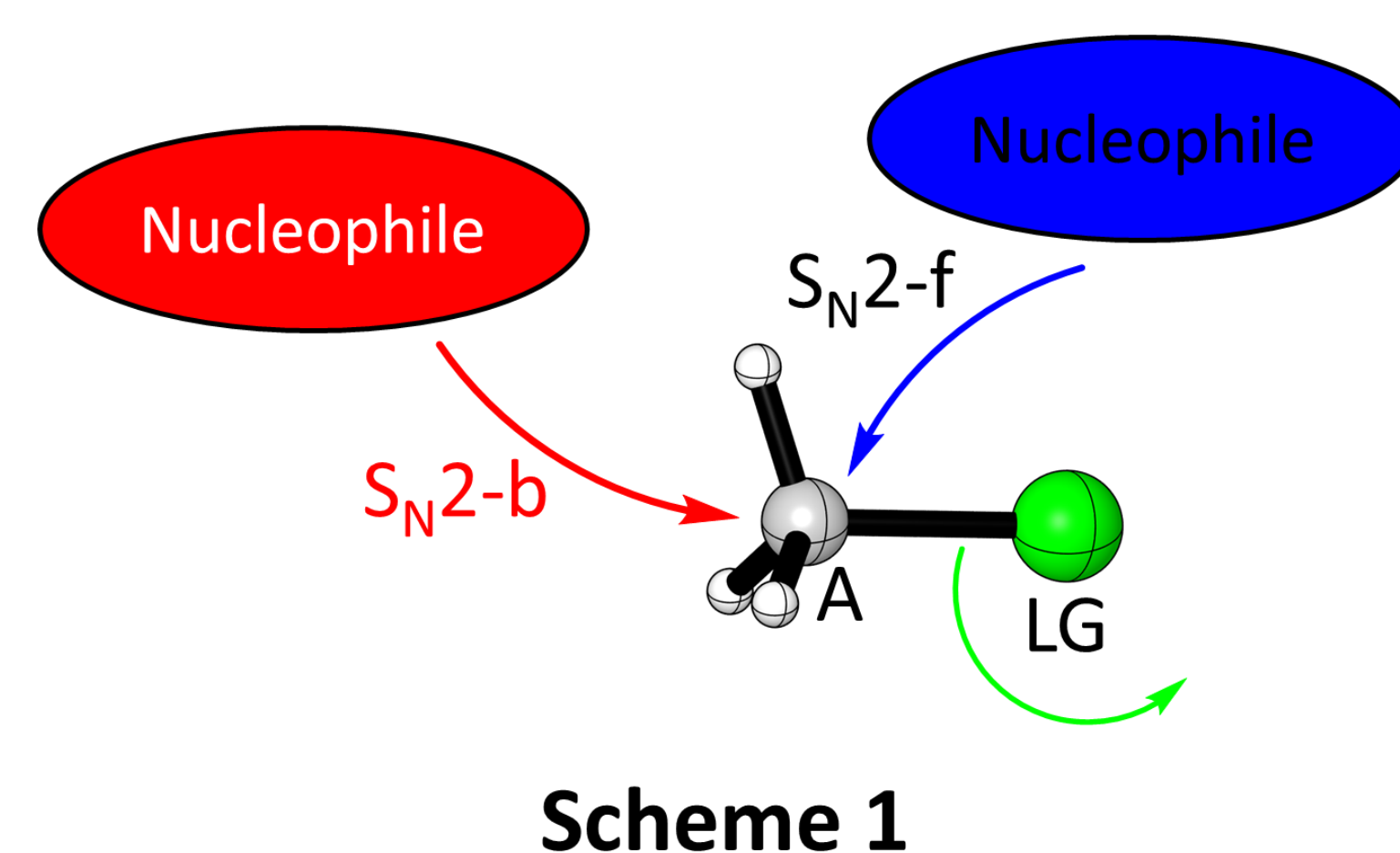
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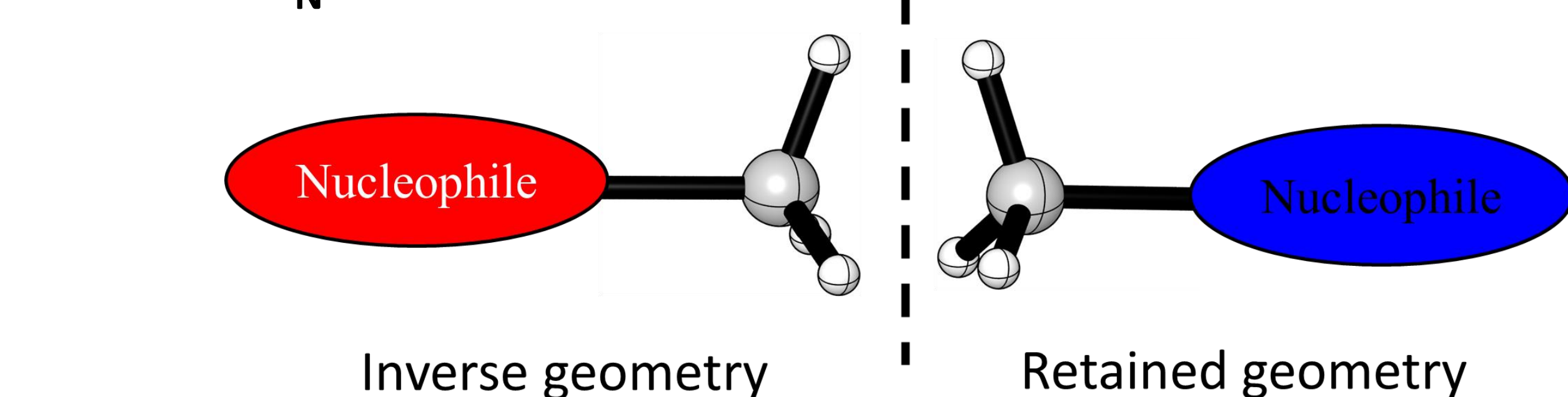
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## What are bimolecular substitution ( $S_N2$ ) reactions?



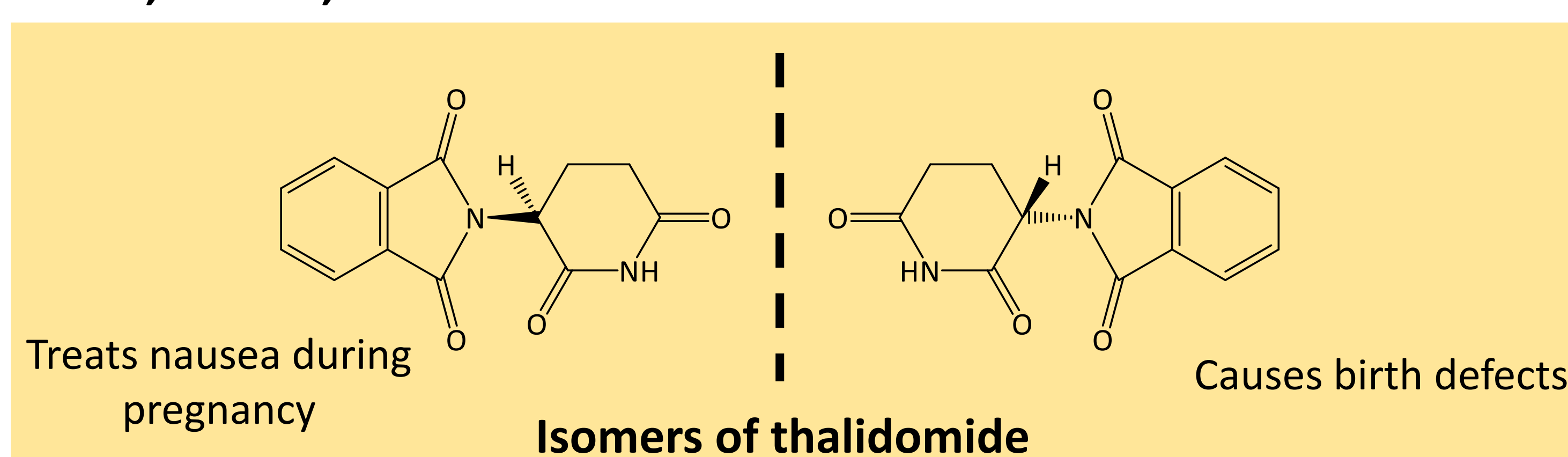
$S_N2$  reactions occur when an electron-rich species (nucleophile) bonds to a reactive atom centre (A in Scheme 1) in a molecule and causes part of the molecule (leaving group; LG) to depart simultaneously.

## How do $S_N2$ reactions occur?



- $S_N2$  reactions may occur through the backside ( $S_N2$ -b) or the frontside ( $S_N2$ -f) pathways.
- This leads to two different isomers (mirror images) with two different geometries.

## What is the significance of synthesising a compound in a pure state, that is, without its isomer?

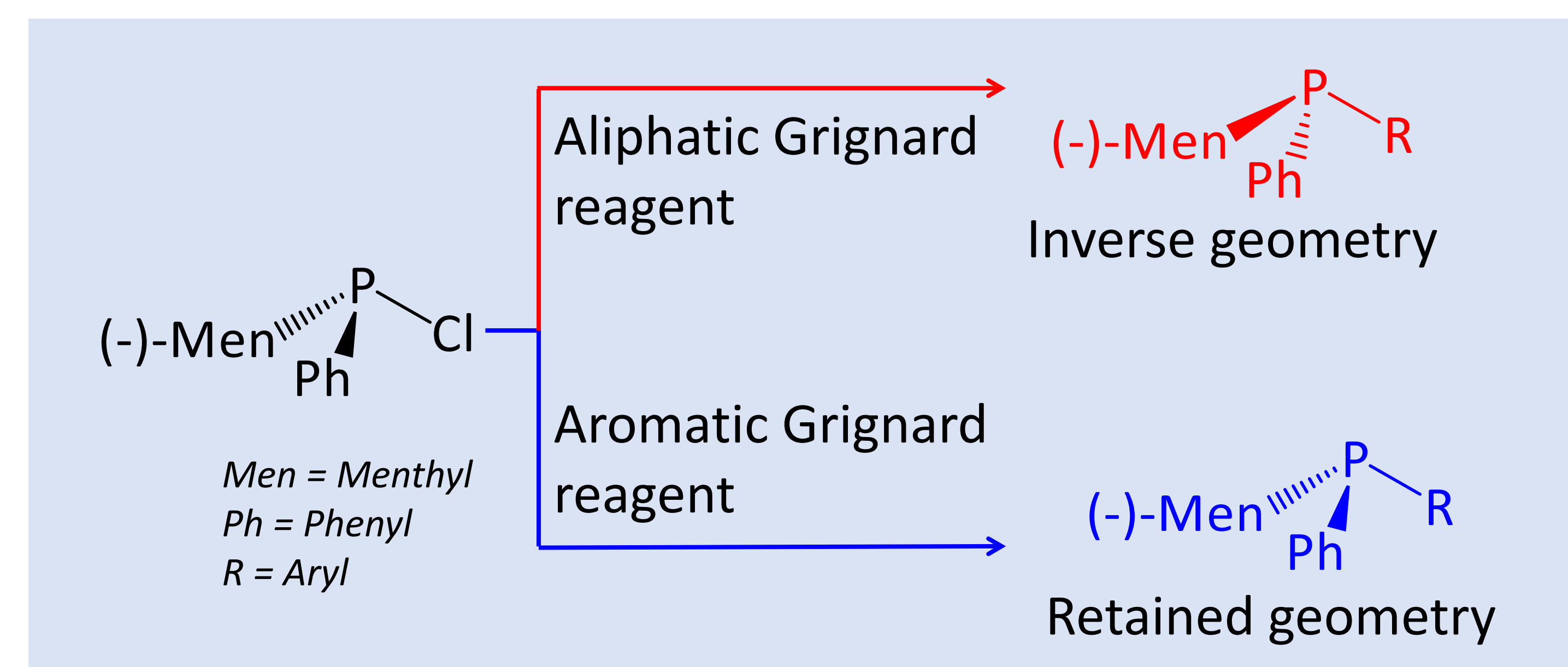


## Research question ?

Investigate the mechanism of organophosphorus  $S_N2$  reactions reported by experimentalists\*

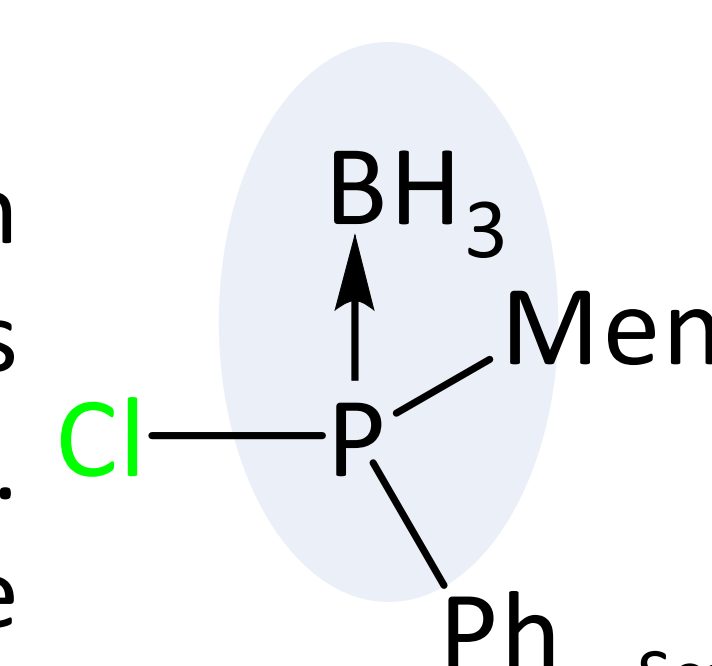


\*Scan to read the experimental paper



## How was the reaction investigated?

In the experimental paper, the reaction was performed with  $BH_3$ -THF as solvent. Hence, in this study, the reaction was modelled with a dative bond between the P and B atoms. The reaction was investigated in THF, using the polarisable continuum model.



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## $S_N2$ reaction with the aliphatic nucleophile

- The aliphatic nucleophile,  $EtMgBr$ , prefers the  $S_N2$ -b pathway with a lower activation energy.
- The product has inverse geometry, as reported in the experimental paper.

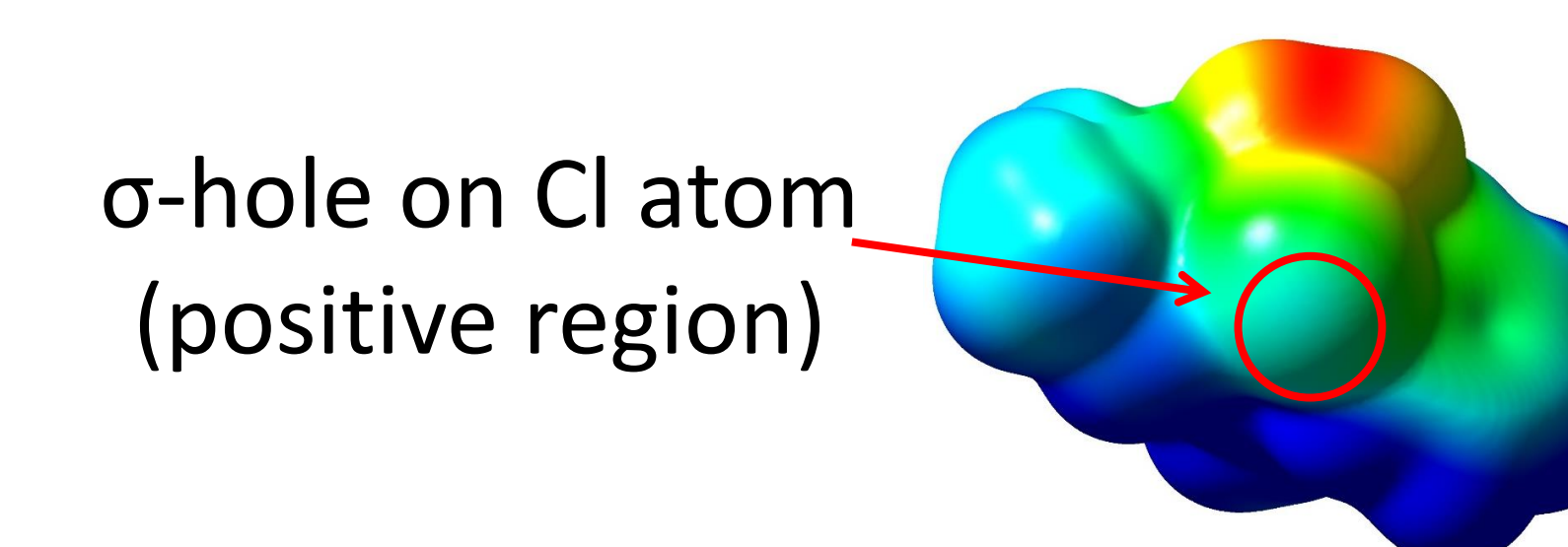


## $S_N2$ reaction with the aromatic nucleophile

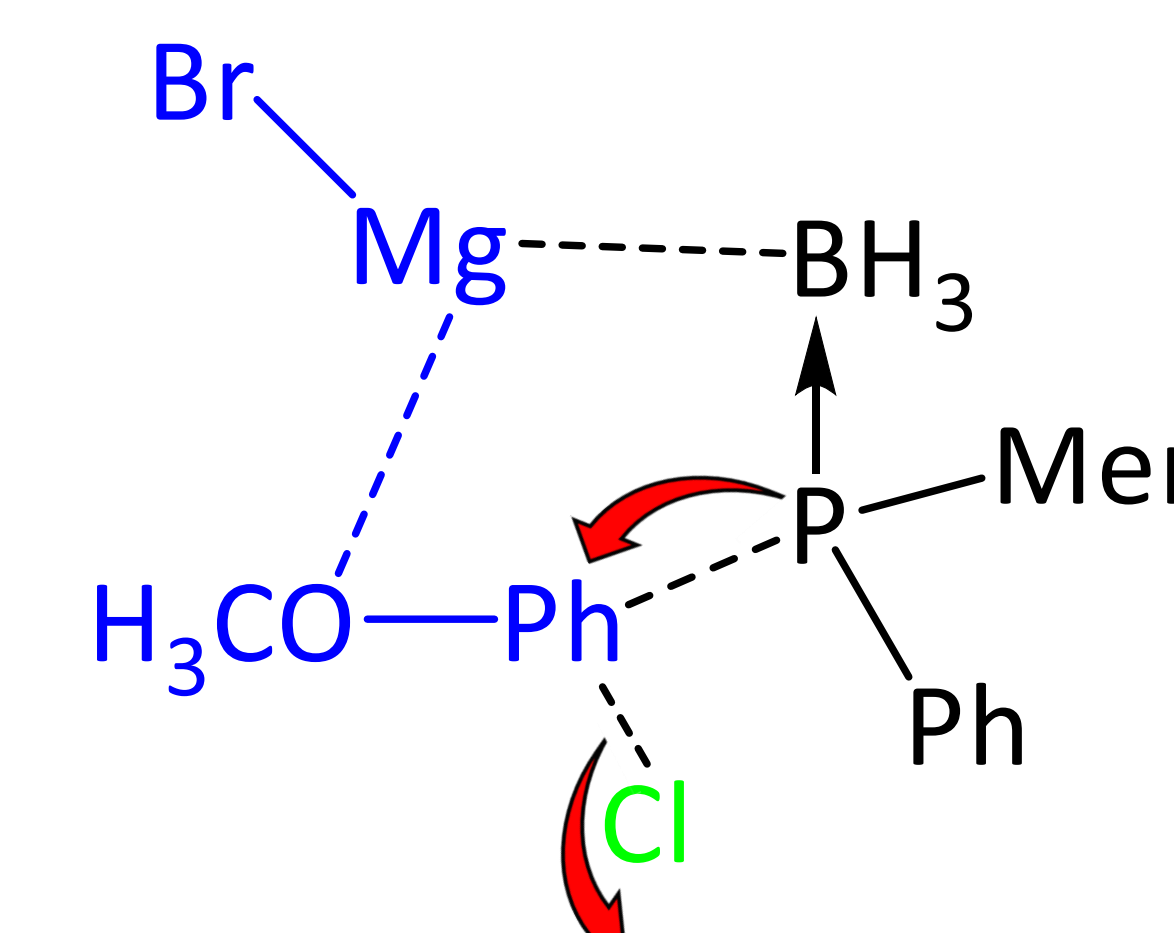
- The aromatic nucleophile,  $MeOPhMgBr$ , also has a preference for the  $S_N2$ -b pathway.
- This is contrary to the observations made in the experimental paper.



## How is retained geometry achieved in the product with the aromatic nucleophile?



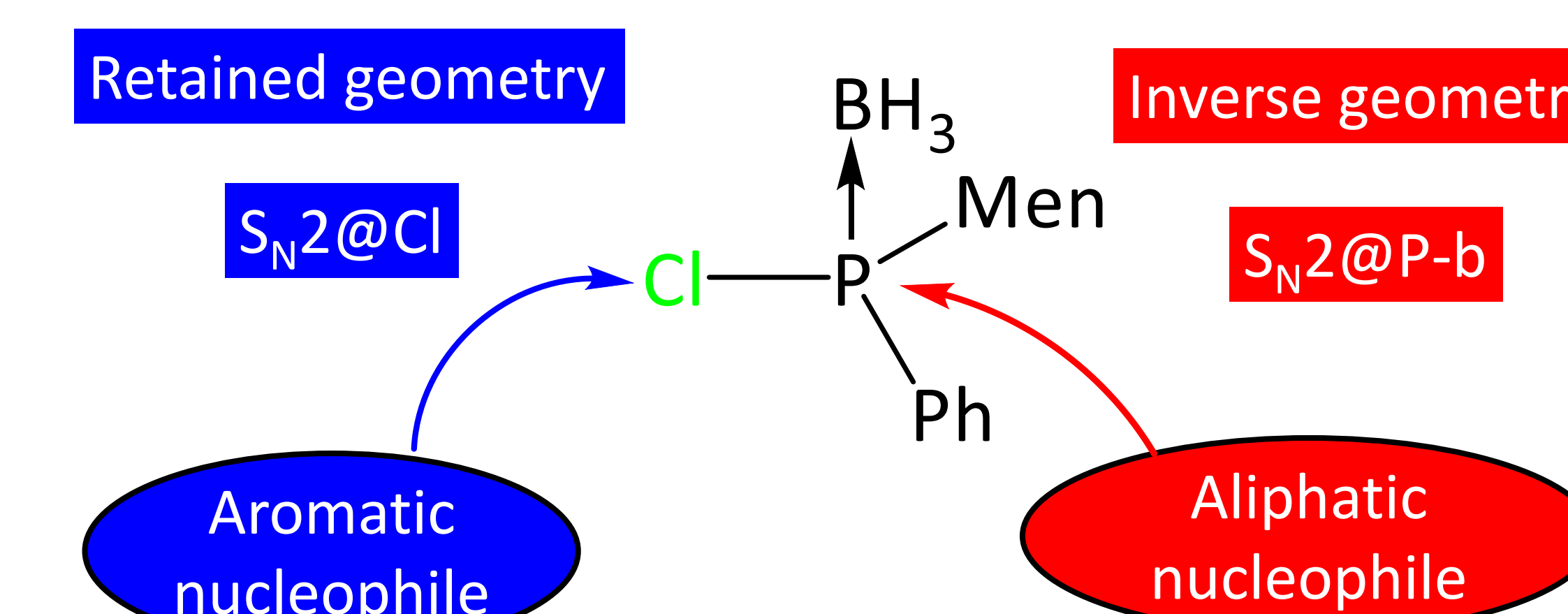
- A  $\sigma$ -hole is located on the Cl atom on the electrostatic potential map of the reactant.
- This  $\sigma$ -hole attracts the nucleophile, which leads to a novel  $S_N2$  attack on the Cl atom, instead of on the P atom.



- The reaction then proceeds by an  $S_N2$ -f attack by P atom on the C atom of Ph.
- Since this is a frontside attack, the geometry of the product is retained.

## Importance of this work !

These results will help in the synthesis of organophosphorus compounds in terms of the stereoselectivity.



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