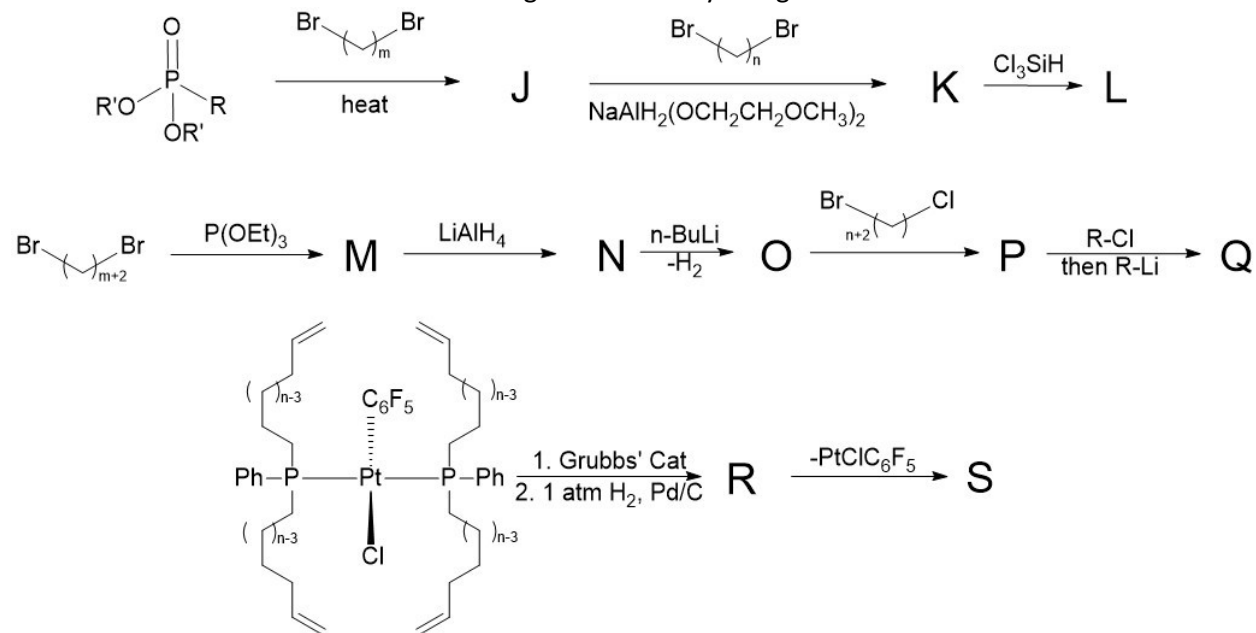


The Cummins Group at the Massachusetts Institute of Technology has been investigating methods to stereoselectively make macrocyclic diphosphine ligands. Previously, synthesis of macrocyclic diphosphine ligands either resulted in mixtures of stereoisomers or involved highly dangerous reagents. Three methods are shown below for making these macrocyclic ligands are outlined below:



Hint: **O** is an intermediate containing both a P-P bond and a P-Li bond.

Instead of these methods, the Cummins group stereoselectively synthesizes ligands with a key organophosphorus intermediate **A** with formula $C_{12}P_2H_{20}$ containing a P-P bond, which can be synthesized via reaction of 2,3-dimethyl-1,3-butadiene with white phosphorous upon irradiation with ultraviolet light.

This intermediate is very versatile and can be manipulated in a variety of ways. For example, upon reaction with $BnBr$, **A** forms an ionic compound with cation B^+ and anion Br^- . Treatment of this compound with $PhMgBr$ results in compound **C**.

Upon reaction of **A** with C_2Cl_6 , another ionic compound with cation D^+ and anion Cl^- can be formed. This intermediate is in equilibrium with covalent species **E**, which can be transformed back into a compound with cation D^+ upon action of $GaCl_3$. **E** can also be transformed into compound **F** under treatment of 2 equivalents of cyclohexyl magnesium chloride ($CyMgCl$).

F possesses a very rich coordination chemistry. Treatment with $CoCl_2$ produces **G**, which has formula $C_{24}P_2H_{30}CoCl_2$. Under action of SmI_2 , **G** transforms into an olive-green $Co(I)$ intermediate **H** with formula $C_{48}P_4H_{60}Co_2I_2$, which further transforms into a grass-green $Co(I)$ complex **I** upon treatment with two equivalents of ethylene. **I** contains only one cobalt atom.

1. Draw the intermediates **J** – **S** in the first routes. No stereochemistry is required. Which route(s) (1, 2, and/or 3) make these ligands stereospecifically, and what is the relative stereochemistry created?
2. Draw the intermediates **A** - **I**. Use relevant stereochemistry where appropriate.
3. Propose a simple method for the reversion of **I** back to **H**.