

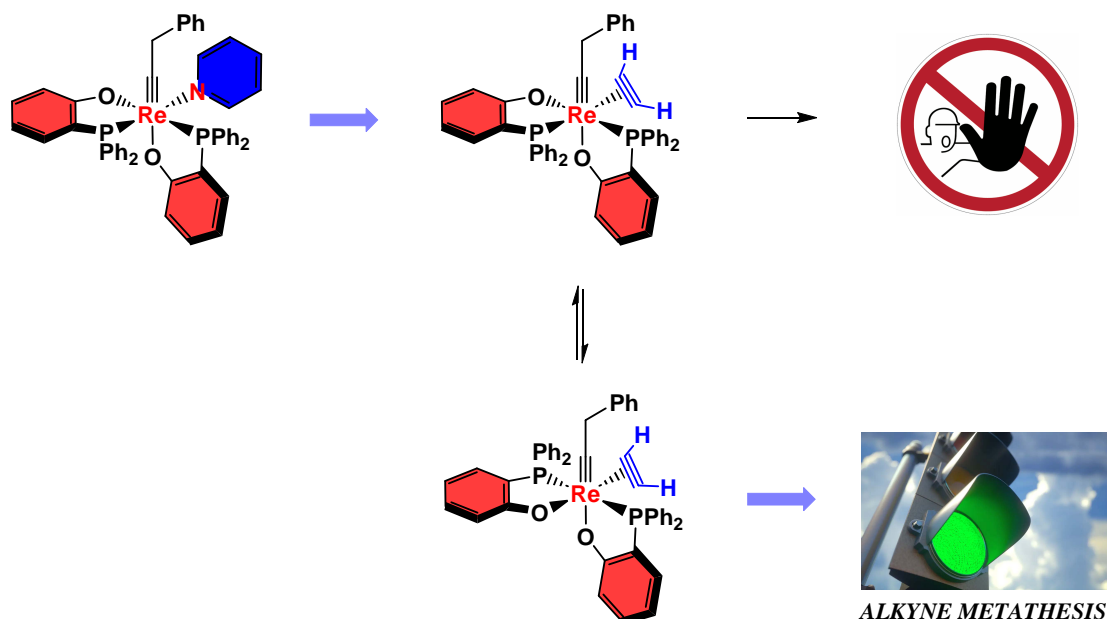
BE CAREFUL TO ISOMERIZATION! - A RHENIUM CATALYSIS CASE STUDY

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In 2022, Mingxu Cui *et al.* [1] designed a family of d^2 Re(V) alkylidyne complexes able to catalyze alkyne metathesis after releasing a pyridine into solution and bearing phosphino-phenolate ligands. In the following study, we performed Density Functional Theory (DFT) calculations to unveil the reaction mechanism finding out that the simple substitution of the pyridine with an alkyne cannot promote the desired metathesis due to the high energies involved. However, the alkyne metathesis has been found to be efficiently catalyzed by one of its isomers, the one bearing the phosphine groups in *trans* and therefore, the isomerization process has been analyzed in detail. The latter analysis helped to understand when the isomerization occurs. Indeed, even if the presence of a pyridine as a ligand disfavors this step, once the alkyne took the position of the pyridine the two isomers can be easily interconverted. Finally, the alkyne metathesis can start.



[1] M. Cui, H. H. Y. Sung, I. D. Williams*, G. Jia, Alkyne Metathesis with d^2 Re(V) Alkylidyne Complexes Supported by Phosphino-Phenolates: Ligand Effect on Catalytic Activity and Applications in Ring-Closing Alkyne Metathesis, *J. Am. Chem. Soc.* **2022**, *144*, 14, 6349–6360.