

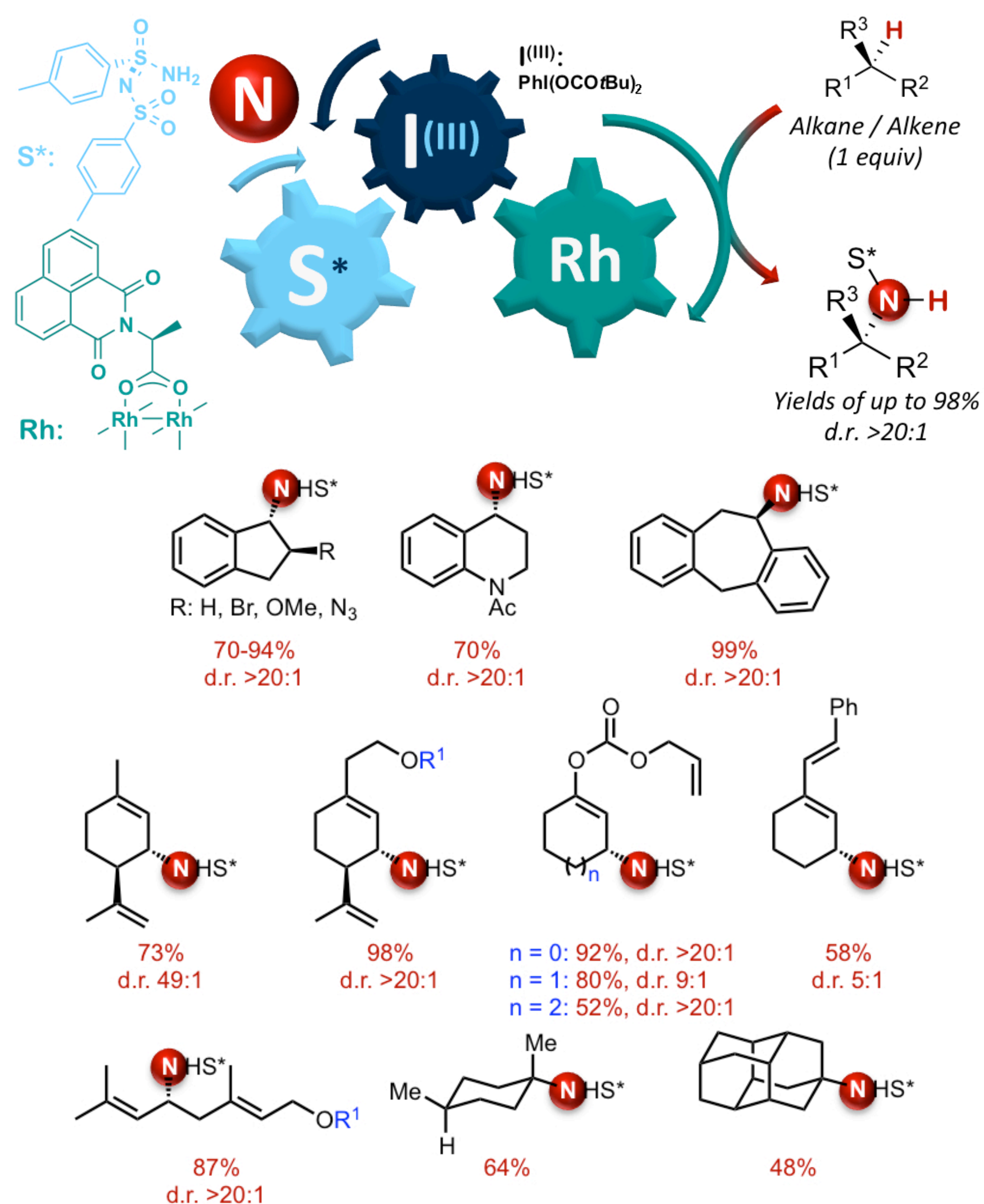
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### Aims of the project

There is a clear evidence that the development of reactions allowing the direct conversion of C-H bonds to C-X bonds (X: C, N, O,...) will streamline the synthesis of organic compounds and enhance the synthetic value of alkanes.<sup>1</sup> The search for an efficient process requires to address the issues of reactivity – C-H bonds of alkanes are inert – and selectivity – C-H bonds are ubiquitous in organic compounds. Whereas elegant solutions have been found through chelation-controlled additions or intramolecular reactions, intermolecular C-H functionalization remains challenging. This project that combines synthetic and theoretical studies, was aimed at developing efficient catalytic nitrene and carbene transfers for the selective functionalization of hydrocarbons (alkanes, alkenes).

### Catalytic intermolecular C-H amination

A rhodium(II)-catalyzed nitrene C-H insertion involving chiral sulfonylimidamides allows the chemo-, regio-, and stereoselective C-H amination of alkanes, allylic and benzylic systems. The methodology has been scaled up to 10 mmol scale.<sup>2</sup>

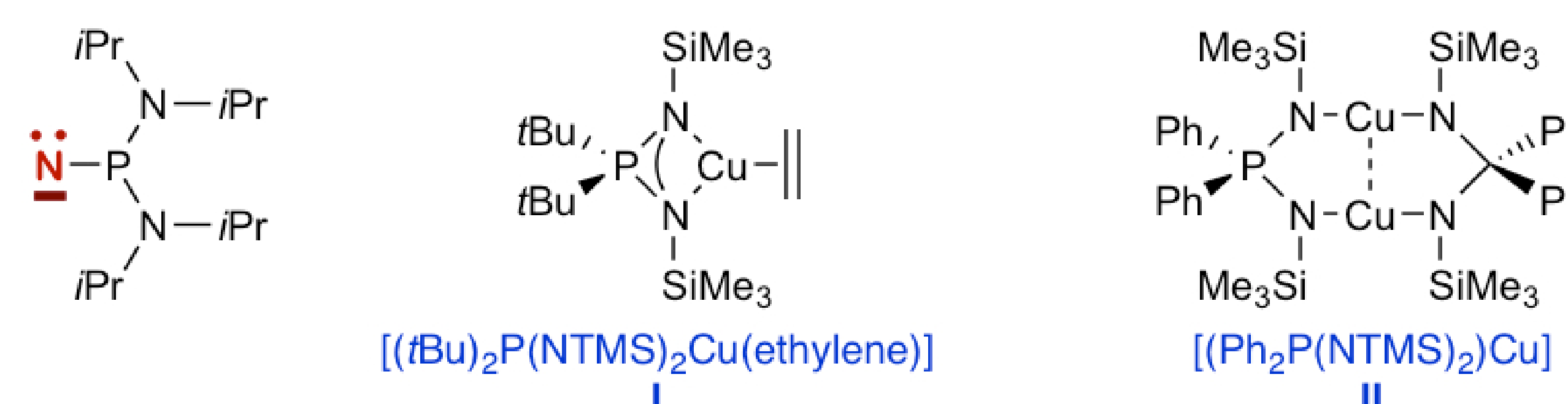


### References

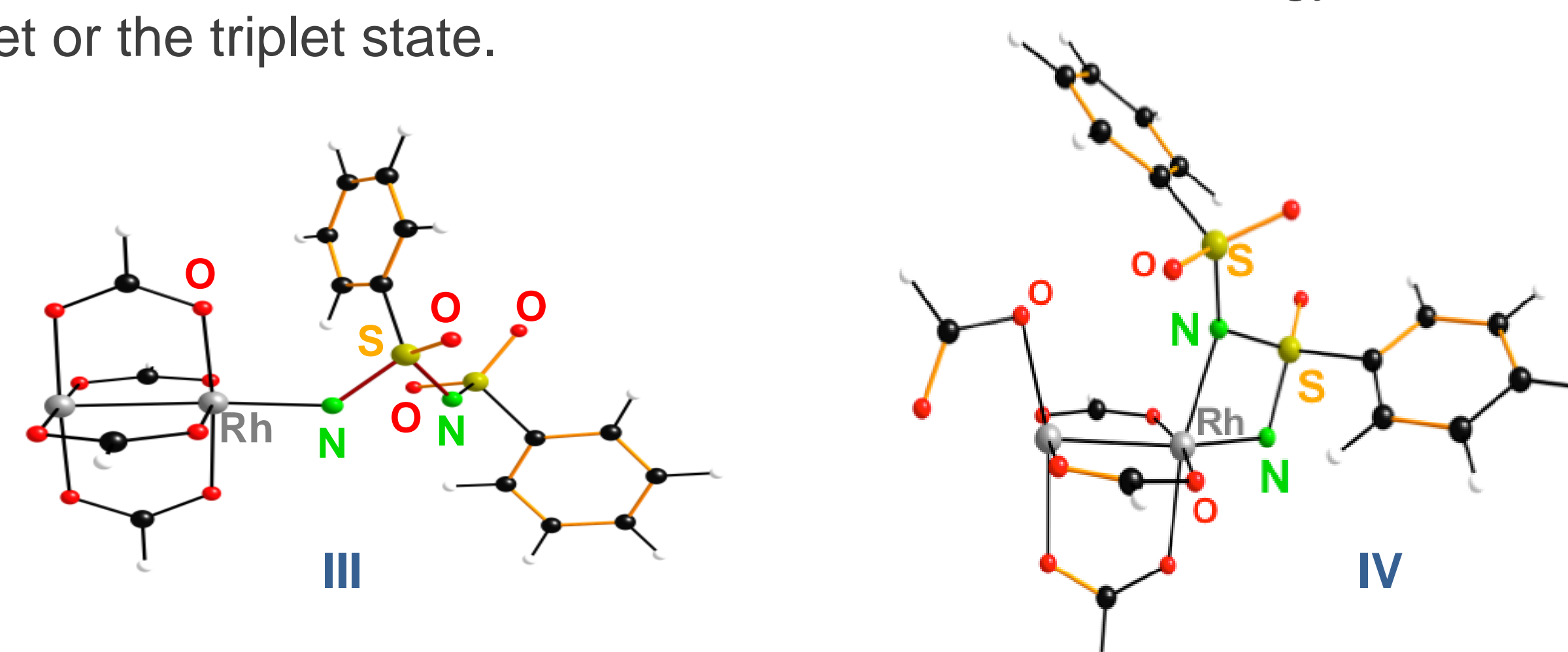
- (a) „C-H Activation“ *Top. Curr. Chem.* **2010**, 292, pp 1-384. (b) F. Collet, R. Dodd, P. Dauban, *Chem. Commun.* **2009**, 5061. (c) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, 16, 2654.
- (a) F. Collet, C. Lescot, C. Liang, P. Dauban, *Dalton Trans.* **2010**, 39, 10401. (b) C. Lescot, B. Darses, F. Collet, P. Retailleau, P. Dauban, *J. Org. Chem.* DOI: 10.1021/jo301563j.
- N. Nebra, C. Lescot, P. Dauban, B. Martin-Vaca, D. Bourissou, *Chem. Eur. J.*, submitted.

### Tracking the intermediate M-nitrene

Theoretical studies have shown an energy gap > 10 kcal.mol<sup>-1</sup> between the singlet and triplet states for copper phosphonitrene (iPr<sub>2</sub>N)<sub>2</sub>P-N complex. They have helped to identify copper(I) complexes **I** and **II** as potential species likely to provide stabilisation of the corresponding metallanitrene. Mono- and dinuclear complexes **I** and **II** have thus been prepared but the expected nitrene intermediate has not been characterized.

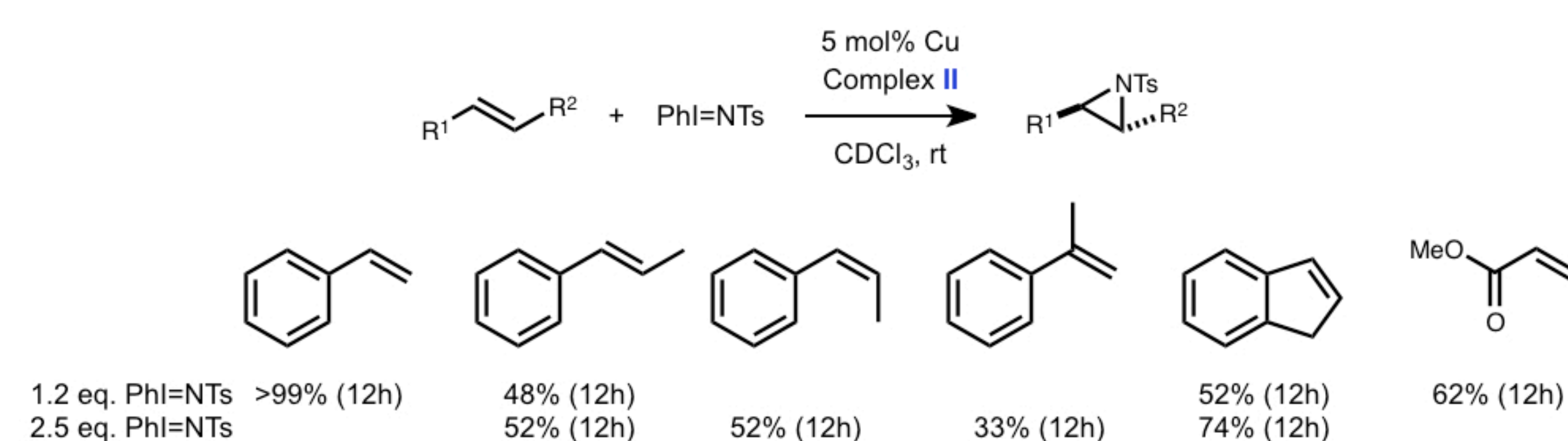


DFT calculations have revealed the possible involvement of unexpected intermediates of type **IV** for rhodium-catalyzed C-H amination in addition to the classical species **III**. Decoordination of one of the O of the acetate ligand would allow a strong N→Rh interaction confirmed by NBO analysis. These are favored intermediates close in energy either in the singlet or the triplet state.



### Catalytic activity of Cu-complex II

The Cu-complex **II** is one of the first dinuclear copper(I) complex able to catalyze efficiently the aziridination of alkenes used as the limiting agent (yields of up to 99%).<sup>3</sup> No catalytic activity, however, has been found for the analogous nitrene C-H insertion.



### Conclusion

Catalytic C-H amination of hydrocarbons can be efficiently performed with high levels of selectivity. This new transformation thus allows expanding the toolbox of the synthetic chemist. However, the analogous carbene transfer with sulfoximines has not been found possible so far. Characterisation of the nitrene intermediate remains highly challenging though necessary to better understand their behavior and enhance their scope in organic synthesis.

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