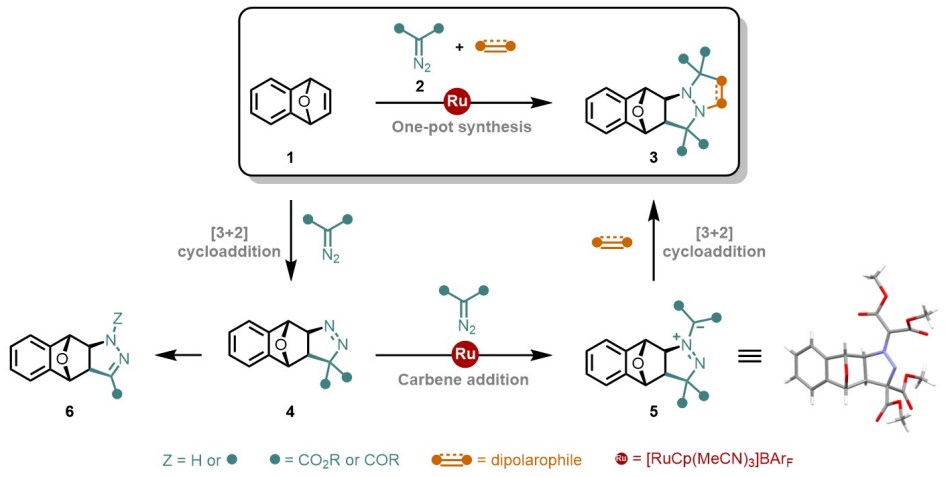
CpRu-Catalyzed Multicomponent Synthesis of Polyheterocycles Pyrazolidines Through Cycloadditions and Metal-Carbene Addition

C. Montagnon[1], J. Bultel[1], C. Besnard[1], J. Lacour[1]*

[1]Department of Organic Chemistry and Laboratory of Crystallography, University of Geneva, Switzerland

Cyclopentadienyl-Ruthenium (II) complexes are known to efficiently promote the decomposition of diazo malonates and α-diazo-β-ketoesters to generate *Fischer*-type carbenes. These electrophilic intermediates form ylides in presence of various *Lewis* bases, such as cyclic ethers,[1] ketones,[2] and lactams,[3] among others. Subsequently, the reactive zwitterions can undergo different rearrangement or insertion reactions to obtain different classes of functionalized heterocycles.

Based on previous reactivities developed in our lab with oxonium[1] and ammonium[4] ylides, and in divergence with recently reported studies using 2,2,2-trifluorodiazoethane,[5] the reactivity of bicyclic ether **1** and diazomalonate **2** under ruthenium (II) catalysis was investigated. Herein, a fully-diastereoselective one-step synthesis of diaza polycyclic compounds **3** *via a* series of cascade reactions is obtained. More interestingly, this reaction can also be done stepwise, and each intermediate **4** and **5** can be isolated in high yields. Moreover, ylides **5** showed unusual stability, as they can be stored at room temperature under air conditions and can further react with various dipolarophiles to access symmetrical on non-symmetrical polycyclic pyrazolidines. In addition, the cycloadduct **4** can undergo rearrangements such as a 1,3-ester shift or a decarboxylation to afford corresponding pyrazolines scaffolds **6**. We thus report a direct methodology to access valuable N−N bond-containing heterocycles, which are presented in many natural products and bioactive molecules.[6]



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