Reactivity of Acceptor Diazo Derivatives and Corresponding Metal Carbene Leveraging Strain Heterocycles

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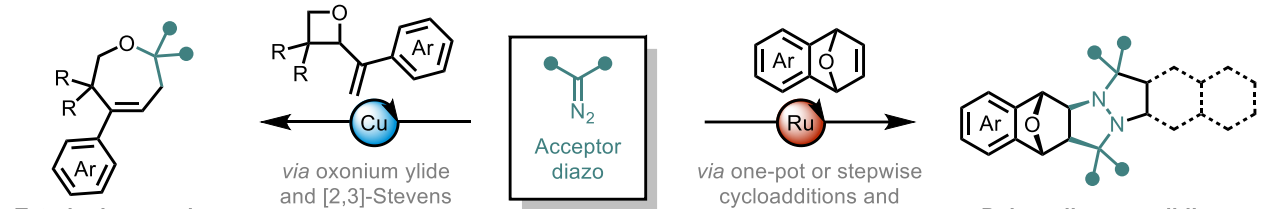
Metal carbene reactivity has been extensively investigated in the field of organic synthesis,[1] affording C-C or X-C bond *via* different transformations.[2] To generate these species, decomposition of diazo reagents is an efficient strategy, in which their stability and reactivity could be modulated by the electronic properties of the α-substituents.[3] The resulting electrophilic metal carbenes can be trapped by various *Lewis* bases such as cyclic ethers leading to medium sized rings and macrocycles formations.[4]

In this context, direct methods have been developed for the synthesis of oxepines and pyrazolidines derivatives, valuable scaffolds present in natural and medicinal products.[5] First, owing to an unprecedented *gem*-dialkyl substituent effect, a large scope of 2-vinyl oxetanes and either diazo mono or diester reagents gave access to a series of functionalized oxepines under copper-catalysis.[6] Furthermore, complex spiro and bridged bicycles were obtained by late-stage functionalization. On the other hand, a fully-diastereoselective one-step synthesis of diaza polycycles *via* a series of cascade reactions has been investigated.[7] More interestingly, this reaction can be done stepwise, and each intermediate, cycloadduct and azomethine imine, can be isolated in high yields. The unusual bench stable ylide, resulting from carbene addition catalyzed by [CpRu] complexes, can further react with various dipolarophiles to access symmetrical on non-symmetrical polycyclic pyrazolidines.



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