

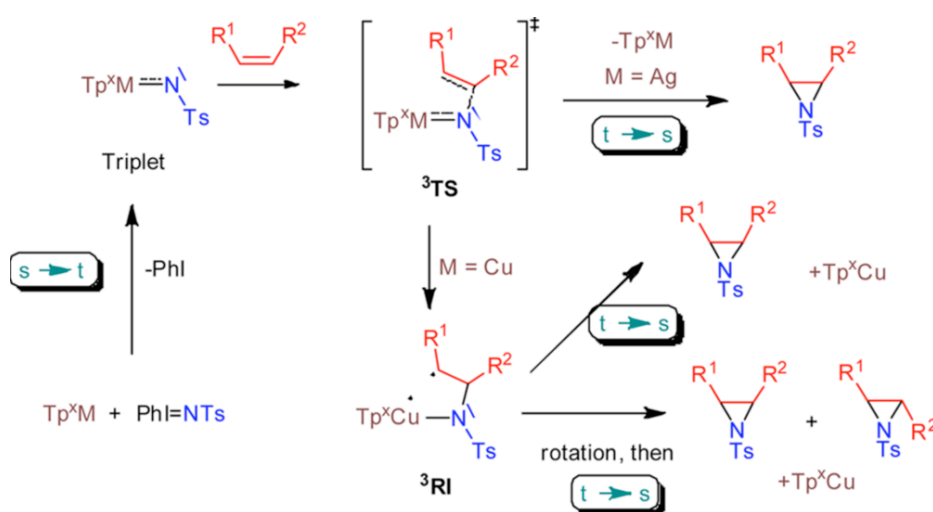
Spin tricks in the reactivity of transition metal nitrene complexes

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The conversion of olefins into aziridines by the metal-catalyzed addition of a nitrene NR group to the C=C bond constitutes a useful tool in the preparation of these three-member rings. The reaction is especially intriguing when dienes are used as reactant because the resulting vinylaziridines allow direct access to biologically relevant fragments. These systems have been explored experimentally by the groups of Pérez (Huelva) and Castellón (Tarragona), and we have been able to contribute to the clarification of the reaction mechanisms through DFT calculations.^{1,2}



In all cases, the reaction starts with the formation of a metal–nitrene species in the triplet state. The reaction product is a singlet, and therefore a crossing between the triplet and singlet spin surfaces must take place. The placement of the crossing point is different for copper- and silver-based systems, which explains the different level of stereochemical retention for both metals (see Figure). We were also able to reproduce the regio- and stereoselectivity in the silver-catalyzed aziridination of dienes.

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2. J. Llaveria, A. Beltrán, W. M. C. Sameera, A. Locati, M. M. Díaz-Requejo, M. I. Matheu, S. Castellón, F. Maseras, P. J. Pérez *J. Am. Chem. Soc.* in press, [dx.doi.org/10.1021/ja412547r](https://doi.org/10.1021/ja412547r)