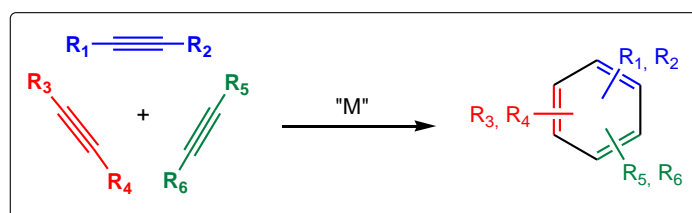


**“Rh(I)-catalyzed [2+2+2] cycloaddition reactions:
methodological and mechanistic studies”**

Magda Parera Briansó

One of the main goals of modern organic synthesis is to develop new reactions in which molecular complexity is rapidly increased. Processes that enable the construction of multiple bonds and/or stereogenic centres in a single reaction step offer significant advantages in the development of economical, greener syntheses of complex synthetic targets. One of these processes is the transition metal-catalyzed [2+2+2] cycloaddition reaction (Scheme 1), a transformation in which three new bonds are formed in a single reaction step with total atom economy, providing an effective route for the synthesis of polysubstituted hetero- and carbocycles.



Scheme 1. Transition metal-catalyzed [2+2+2] cycloaddition reaction of alkynes.

Among the different metals that are able to catalyze the [2+2+2] cycloaddition reaction, my thesis work has been focused on the use of rhodium(I). The main aims of the methodological part of the work have been to search for new chiral catalysts for the intramolecular cycloaddition of enediyne¹ and to determine how new unsaturated substrates have been involved.

Moreover, a full mechanistic study of the Rh(I)-catalyzed [2+2+2] cycloaddition of alkynes has been performed through ESI-MS(MS) technique and DFT calculations.² Key intermediates have been detected experimentally for the first time. Computer model studies supported the structural proposal made for the reaction intermediates. The collective studies provided new insight into the reactivity of cationic rhodacyclopentadienes, which should facilitate the design of related rhodium-catalyzed C-C couplings.

¹ a) Brun, S.; Parera, M.; Pla-Quintana, A.; Roglans, A. León, T.; Achard, T.; Solà, J.; Verdaguer, X.; Riera, A. *Tetrahedron* **2010**, *66*, 9032. b) León, T.; Parera, M.; Roglans, A.; Riera, A.; Verdaguer, X. *Angew. Chem. Int. Ed.* **2012**, *51*, 6951.

² Parera, M.; Dachs, A.; Solà, M.; Pla-Quintana, A.; Roglans, A. *Chem. Eur. J.* **2012**, *18*, 13097.