

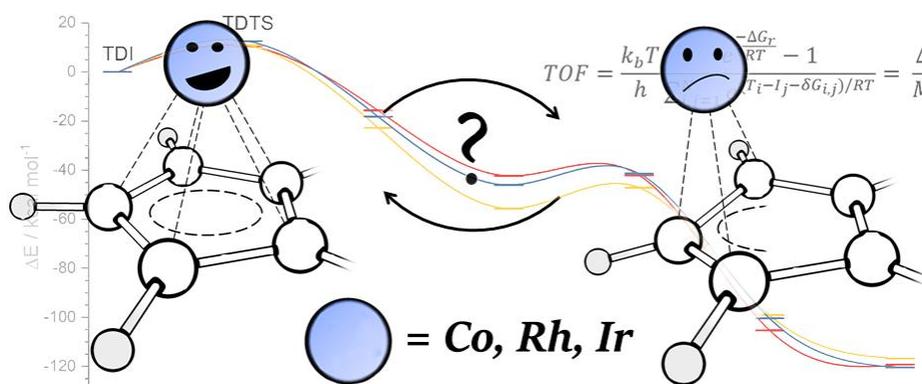
# Rational Design of Half-Sandwich Group 9 Catalysts for [2+2+2] Alkynes Cycloadditions

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Nowadays, modern computational facilities allow us to predict reactivity in *silico* and tackle molecular systems that are otherwise difficult to rationalize. In this work, state-of-the-art relativistic density functional (DFT) methodologies are employed to design catalytic fragments for the [2+2+2] alkynes/alkynes-nitriles cycloaddition to benzene/pyridine. The very good selectivity and the possibility to maintain a solvent-free environment make this type of reactions very attractive and justify the continuing investigations.<sup>1</sup> The catalyst's structure is Cp'M, where Cp' is the cyclopentadienyl ligand (Cp) or a more extended aromatic/heteroaromatic moiety, and M is a group 9 metal (Co, Rh, Ir). The singlet potential energy surface of the process is explored by locating all intermediates/transition states and the catalysts' performance is calculated in terms of turnover frequency (TOF), by implementing the equations of the energy span model.<sup>2,3</sup> The different bonding mode of the substrate to the catalyst, and, vicariously, the nature of Cp'-M coordination, is investigated using the activation strain model (ASA) and energy decomposition analysis (EDA) in order to follow the metal displacement (slippage) and connect structural information with the energy.<sup>4</sup> Commonly, the highly symmetric coordination of the metal to the aromatic ligand is never achieved, but the distortions during the cycle can be larger or smaller under different conditions (different metal center, changes in the aromatic ligand, presence of an additional ancillary ligand, etc.) and this fluxionality is found to significantly influence the overall efficiency.



## References:

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