

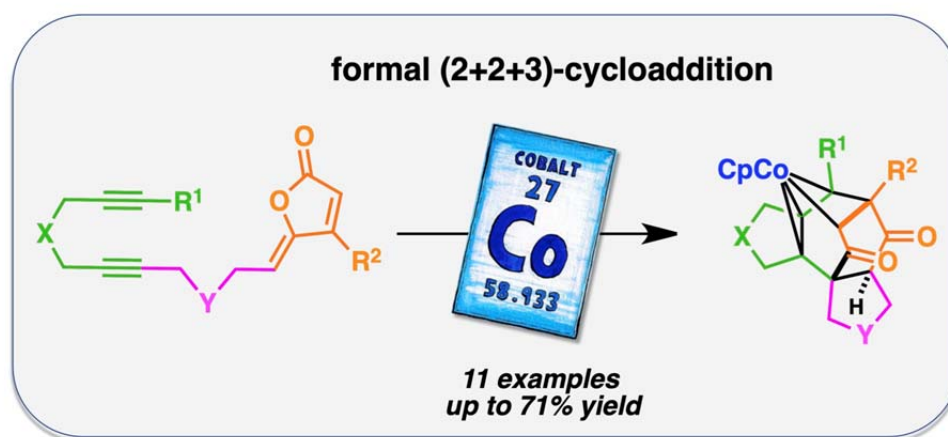
## DIVERGENT COBALT-MEDIATED FORMAL (2+2+3) CYCLOADDITION OF ENEDIYNES: EXPERIMENTAL AND THEORETICAL INSIGHTS

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The discovery of new chemical tools and the development of new methodologies that would allow for a rapid, straightforward and stereo-controlled synthetic access to tailored targets, from simple and achiral substrates, is a topical issue for both industrial and fundamental research. Among all the transformations to access functionalized polycyclic compounds, purely atom-economy couplings are rare and only cycloaddition reactions appear as the most suited approaches. In this context, we propose to explore the reactivity of the captodative *exo*-cyclic double bond of  $\gamma$ -alkylidenebutenolides towards [2+2+2] cycloaddition reactions.<sup>1</sup> Compared to the standard [2+2+2] cycloaddition reaction outcomes of diyne/ene, the cobalt-mediated cycloaddition diverges dramatically leading to unprecedented cobalt(III) polycyclic scaffolds. The mechanism of this reaction has been studied by DFT calculations involving an open-shell potential energy surfaces and an unusual fragmentation of the  $\gamma$ -alkylidenebutenolide moiety to form a  $\beta$ -oxo-ketene as a key intermediate.<sup>2</sup>



[1] Domínguez, G.; Pérez-Castells, J. *Chem. Eur. J.* **2016**, *22*, 6720-6739.

[2] Delorme, M.; Punter, A.; Aubert, C.; Oliveira, R.; Carissan, Y.; Parrain, J.-L.; Amatore, M.; Nava, P.; Commeiras, L. *Organometallics*, **2019**, submitted.