

## New Insights in Cobalt-Mediated Cycloaddition Reactions

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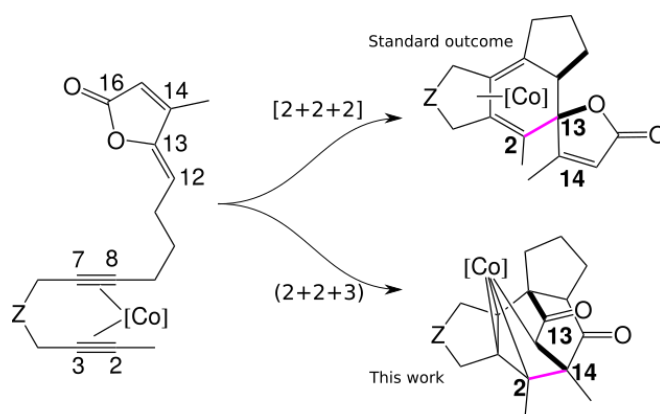
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The chemistry of cobalt(I)-mediated reactions is very rich and challenging from a computational point of view, as cobalt complexes can easily access open-shell (triplet) potential energy surfaces, as in the well established [2+2+2] cobalt-mediated cycloadditions.

The reaction of  $\text{CpCo}(\text{CO})_2$  with an enediyne substrate, where the double bond is a  $\gamma$ -alkylidenebutenolide, diverges dramatically from the expected behavior: it results in a formal (2+2+3) cycloaddition reaction, leading to a cobalt(III) system with a highly increased molecular complexity. This fascinating transformation is not straightforward to rationalize. However, we are able to suggest a reaction pathway based on a computational approach that discloses unusual, low-energy intermediates. Through this study, we explore the role of the cobalt center, the role of the organic link that connects the diyne to the lactone, and the unicity of the lactone moiety, which might be exploited in other transformations. Finally, this new reactivity and its understanding extend the possibilities of the cobalt-mediated cyclization processes.



**Figure 1** Possible outcomes of the cobalt-mediated reaction,  $[\text{Co}] = \text{CpCo}$ .