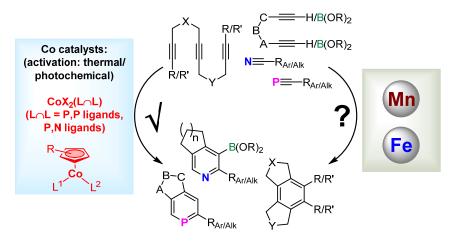
CYCLOADDITION REACTIONS WITH MANGANESE AND COBALT PRECATALYSTS: CATALYTIC TWINS?

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Transition metal-catalyzed cycloaddition reactions have become particularly successful examples for high versatile and atom-efficient transformations with [2+2+2]cycloaddition reactions as a particular versatile representative [1]. While many metals catalyze this reaction, the late 3d metals have been among the first, from which successful examples of catalytic cyclotrimerizations have been reported [2]. Systematic studies on cobalt complexes revealed the possibilities of reactivity fine-tuning with neutral ligands [3]. Most recently our studies led to the discovery of an unique Co(II)based catalytic process for the synthesis of phosphinines from diynes and phosphaalkynes, featuring a large substrate scope including even tolerance to nitrile groups in the substrates [4]. While our interest is focusing on developing new catalysts and exploiting different oxidation states, we are also interested in discovering the catalytic features of other 3d metals like iron and especially manganese. Except for a few (formal) examples, manganese complexes were not known to catalyze cyclotrimerization reactions so far, although the Cp (cyclopentadienyl) and CO complexes share structural similarities to those of cobalt. The presentation will discuss the development of novel cobalt and manganese and exemplary low-valent iron precatalysts for cycloaddition reactions, their catalytic features and scope of substrates as well as their evolution to master new substrate challenges.



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- [2] Gläsel, T.; Baumann, B. N.; Hapke, M. Cobalt Catalysts for [2+2+2] Cycloaddition Reactions: Isolated Precatalysts and in situ Generated Catalysts. *Chem. Rec.* **2021**, *21*, 3727-3745.
- [3] Fischer, F.; Pientka, T.; Jiao, H.; Spannenberg, A.; Hapke, M. CpCo(I) precatalysts for [2+2+2] cycloaddition reactions: synthesis and reactivity. *Catal. Sci. Technol.* **2020**, *10*, 8005-8014.
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