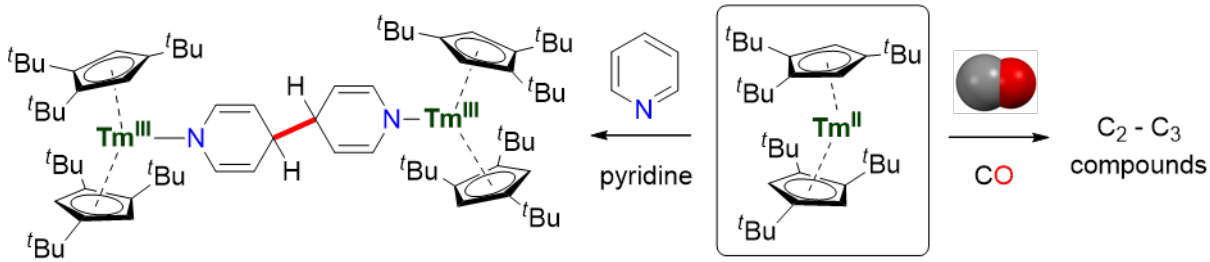
Carbon Monoxide Transformations by Low-Valent Lanthanide Complexes

Short description of the research topic:

Carbon monoxide is an inexpensive and readily available raw material used in the production of value-added organic molecules such as methanol, acetic acid or hydrocarbons. It is also a strong greenhouse gas, which transformation is relevant in green chemistry. The breakdown of the CO triple bond is the key step in the Fischer-Tropsch process. This important industrial process typically operates under harsch conditions involving high energy consumptions. In this context, a renewed interest in the **activation of CO under mild conditions by low-valent metal complexes and main-group compounds** has recently been witnessed.[1]

Lanthanide complexes, especially in their +II oxidation state, are interesting candidates for CO activation. Notably, **samarium(II) and thulium(II) complexes are very reactive single-electron reductants**. As such, they can transfer one electron per metal centre to various substrates leading to the activation of N_2, CO, CO_2 or pyridine under mild conditions (Scheme 1).[2-5] The aim of this project is to further **explore the promising reactivity of lanthanide(II) complexes in the context of small molecule activation.**



Scheme 1. Reactivity of highly reducing Tm^{II} complexes

The objectives will be to synthesize Sm^{II} and Tm^{II} complexes supported by different cyclopentadienyl ligands and study their reactivity towards small molecules and especially CO. All complexes will be handled under inert atmosphere using Schlenk techniques and gloveboxes. The different compounds will be characterized using various spectroscopic methods including NMR, IR, X-ray crystallography and magnetism studies.

Required background of the student: Chemistry student with good knowledge of synthetic chemistry. The knowledge of the specific techniques of inert atmosphere synthesis or magnetism is best but not mandatory.

References:

[1] R. Y. Kong, M. R. Crimmin, *Dalton Trans.* **2020**, DOI: 10.1039/D0DT01564D.

[2] W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 3728-3730.

[3] **G. Nocton**, L. Ricard, *Chem. Commun.*, **2015**, *51*, 3578-3581.

[4] M. Xémard, V. Goudy, A. Braun, M. Tricoire, M. Cordier, L. Ricard, L. Castro, E. Louyriac, C. E. Kefalidis, C. Clavaguéra, L. Maron, **G. Nocton**, *Organometallics* **2017**, *36*, 4660-4668

[5] M. Xémard, M. Cordier, E. Louyriac, L. Maron, C. Clavaguéra, **G. Nocton**, *Dalton Trans.* **2018**, *47*, 9226-9230.