P1.1 Synthesis, characterisation, and reactivity studies of mono- and bis-alkoxycarbonyl metal phosphine complexes, specifically based on Ru, Pd and Pt

Topic and overall goal. Bis-alkoxycarbonyl and related complexes of late transition metals constitute a largely overseen class of organometallic compounds, which have been only scarcely studied in the past, both with respect to their preparation as well as their general reactivity. While "simple" palladium alkoxycarbonyl complexes are known to be intermediates in industrially relevant large scale carbonylation reactions, the related bis-alkoxycarbonyl complexes remain unknown except for few specific cases.[1] On the other hand, such metal complexes should allow for a direct and straightforward synthesis of oxalates via the corresponding reductive elimination reactions. In this respect, bis-alkoxycarbonyl metal complexes can be viewed as central intermediates for the direct creation of C-C bonds from CO or CO_2. In previous projects, the Beller group has studied carbonylation reactions for more than two decades. As an example, a palladium-catalysed two-step synthesis of ethylene glycol via oxalates starting from CO has been developed.[2] In this project, the coordination chemistry, activation, and reductive coupling of CO_2 will be studied using late transition metal complexes. Organometallic studies will be complemented by catalytic, spectroscopic, and theoretical investigations to identify general reaction principles of CO_2 coupling to oxalate and thus realising C-C-bond forming reactions from CO_2 under mild conditions.

Specific aims and work plan. Initially, in this subproject, we plan to synthesise defined bis-methoxycarbonyl complexes of Ru, Pd, and Pt (Figure P1.1). As an alternative class of catalysts defined Mn, Fe, and Re pincer dicarbonyl complexes are envisioned, too and will be studied in P1.2. Once prepared, the corresponding methoxycarbonyl and if possible hydroxycarbonyl species will be investigated towards *reductive coupling reactions*. For the synthesis of the key intermediates, two synthetic routes will be explored: a) *Addition* of alcohol or amine nucleophiles to carbonyl complexes as a model reaction, and b) *insertion* of CO_2 into metal hydrides. For the latter reaction, the regioselectivity of the insertion process to give the M-CO_2H instead of the more common formyl complex M-OCHO must be controlled. To achieve this demanding step, detailed knowledge of ligand synthesis and the existence of a broad ligand library are essential. Furthermore, in situ spectroscopy and theory are expected to be helpful. After preparation of the complexes, their thermal stability and reactivity in the presence of CO and/or CO_2 will be studied. In parallel, catalytic investigations with H_2 as cost-efficient reductant will be performed.

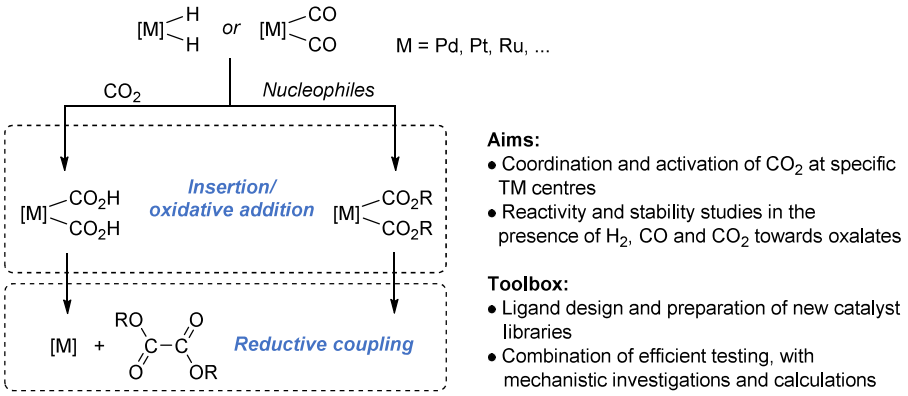

Figure P1.1 Reductive coupling of CO_2 at late TM complexes.

Within this project the PhD student will receive training in the rational synthesis of ligands and highly reactive (pre-)catalysts, reaction monitoring and high-pressure chemistry.

Connection within the RTG. This PhD project will be jointly supervised by Matthias Beller and Milica Feldt. Within the RTG there will be a close collaboration with the Brückner (operando spectroscopy), Ludwig (spectroscopy, calculations), Beweries (early TM chemistry) and Francke (electrochemical characterisation and electrocatalysis) groups.

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1 G. Vasapollo, L. Toniolo, G. Cavinato, F. Bigoli, M. Lanfranchi, M. A. Pellinghelli, *J. Organomet. Chem.* **1994**, *481*, 173-178.

2 K. Dong, S. Elangovan, R. Sang, A. Spannenberg, R. Jackstell, K. Junge, Y. Li, M. Beller, *Nat. Commun.* **2016**, *7*, 12075.