P2.1 Cathodic activation of transition metal complexes

Topic and overall goal. Electrochemical approaches toward CO_2-to-oxalate conversion will be investigated building on the strategy described in TP1.[1] In contrast to the classical homogeneous catalytic approach, electrochemistry allows for continuous adjustment of the driving force (electrode potential vs. redox potential of the stoichiometric reductant).[2,3] Aside from a more precise control of the selectivity of the reductive processes, alternative pathways may thus become accessible. With the aim of establishing an electrocatalytic process (Figure A), the cathodic activation of TM catalysts for subsequent reaction with CO_2 will be explored.

Specific aims and work plan. The project will start with investigation of the key steps of targeted catalytic schemes. Two strategies will be pursued: First, the cathodic activation of TM catalysts will be analysed (Figure B, top), which may subsequently be converted with CO_2. For this purpose, suitable candidates from TP1 as well as from existing libraries at our institutions will be used. Second, cathodic conversion of bis(alkoxycarbonyl) and bis(hydroxycarbonyl) model intermediates toward intramolecular C-C bond formation (Figure 1B, bottom) will serve as another starting point. In a similar fashion, an alternative pathway via the binuclear intermediate depicted in Figure 1B may be probed by conversion of pre-formed adducts. The studies are intended to gather knowledge about the involved (electro)chemical steps, which will later be useful in the development and optimization of electrocatalytic processes (P2.2). Comprehensive mechanistic analysis of the individual steps will be conducted using electroanalytical techniques and controlled potential electrolysis. Promising pre-catalysts and pre-formed intermediates will be subjected to cyclic voltammetry (CV) and UV-Vis and FTIR SEC for reaction monitoring (the latter in collaboration with P2.4 and 2.5). Based on these findings, controlled potential electrolysis with *ex situ* product analysis (mass spectrometry, NMR and EPR spectroscopy) will be carried out to complement the mechanistic picture.

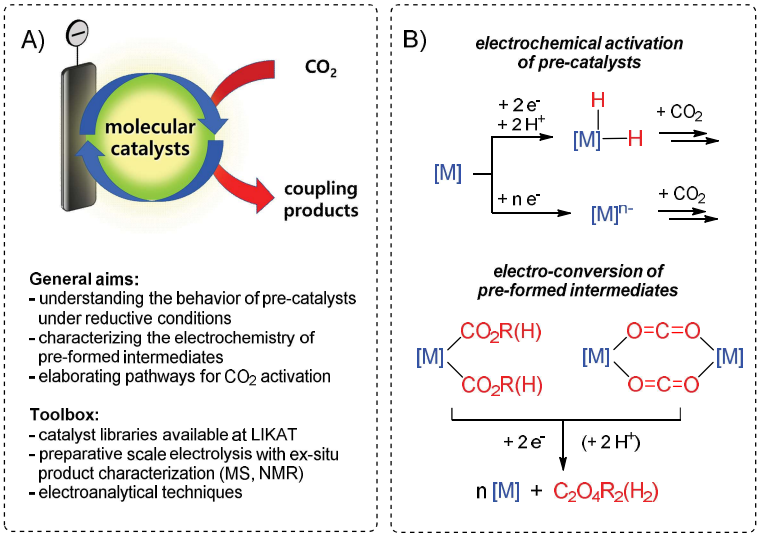

Figure P2.1. Summary of the electrochemical studies on catalyst activation and intermediates.

Connection within the RTG. Synthesis and characterization of organometallic compounds and catalytic intermediates is planned in close collaboration with TP1. Since the studies on thermochemical approaches (TP1) and electrochemical systems will be carried out in parallel, synergy effects can be generated for both approaches by designing and carrying out mechanistic control experiments together. Spectroscopic analysis of the electrochemical processes will be conducted in close collaboration with P2.4 (FTIR SEC and UV-Vis SEC), P2.5 (TR-UV-Vis SEC). The electrocatalytic and spectroelectrochemical studies will be complemented by quantum chemical modelling (P2.3) and chemometric analysis of the spectroscopic data (TP4). Furthermore, P2.1 and P2.2 are closely interlinked, as information gathered in this project can be utilized for development of catalytic processes in P2.2.

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1 H. Liang, T. Beweries, R. Francke, M. Beller, *Angew. Chem. Int. Ed.* **2022**, e202200723.

2 R. Francke, B. Schille, M. Roemelt, *Chem. Rev.* **2018**, *118*, 4631–4701.

3 R. Francke, P. Enders, "Methods and Materials Applied in Electrosynthesis" in *Science of Synthesis: Electrochemistry in Organic Synthesis* (Ed.: L. Ackermann), Thieme, Stuttgart, **2022**, 33-72.