

Sciforum-195145: Ru-tris(pyrazolyl)methane Complexes as Active Catalysts for the Homogeneous Hydrogenation of CO₂ to Formate

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Over the past ten years, there has been a renewed focus on using CO₂ as a readily available, renewable, and economical starting material for the synthesis of C1 chemicals. The environmentally sustainable production of formic acid through CO₂ hydrogenation is particularly noteworthy, given its diverse applications in fields such as agriculture (for silage), food preservation, and wood pulping. In this context, a series of cationic Ru(κ^3 -tpm) piano-stool complexes [where tpm = tris(pyrazolyl)methane], with various auxiliary ligands, were evaluated in our laboratories for their ability to catalyze the hydrogenation of CO₂ to formate in homogeneous phase. These reactions were performed both with and without a Lewis acid co-catalyst, achieving high product yields (>99%) and turnover numbers (TONs) exceeding 54,000 under mild conditions. Finally, proof-of-concept experiments demonstrated that the catalyst solution can be efficiently recycled for consecutive runs without significant loss of activity. The presented results showcase the potential of tris(pyrazolyl)methane complexes in catalytic reactions of high current interest that have previously been neglected, and they pave the way for further studies in other CO₂ reduction processes. Key findings, along with mechanistic insights derived from NMR analysis and DFT calculations, will be discussed. This research was supported by Project POR H2 AdP funded by the European Union – NextGeneration EU through the Italian Ministry of Environment and Energy Security, PNRR - Mission 2, Component 2, Investment 3.5 "Ricerca e sviluppo sull'idrogeno".



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