Formic acid dehydrogenation catalyzed using ruthenium complexes bearing carboxamide ligands: Structural diversity, and mechanistic insights

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Introduction

Due to the urgent need to replace fossil fuel-based energy systems with sustainable alternatives, the use of hydrogen (H_2) as an energy medium is gaining increasing recognition.[1] Hydrogen is a valuable energy source because of its high energy content and clean combustion.[2] Significant research efforts have been geared towards developing efficient hydrogen carriers. Formic acid (FA) is one of the so-called liquid organic hydrogen carriers (LOHCs), and has recently attracted significant attention as a chemical hydrogen storage medium because of its favourable properties. Formic acid contains 4.4 wt% of hydrogen, and it is liquid under ambient conditions, allowing it to be handled, stored, and transported easily and safely.[3] In this work, focuses on the development of Ru complexes for the formic acid dehydrogenation.

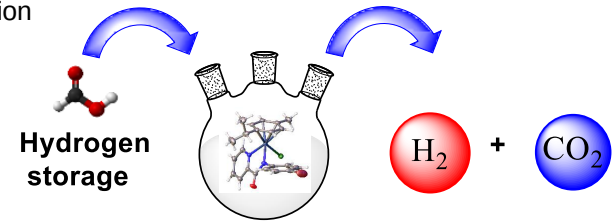
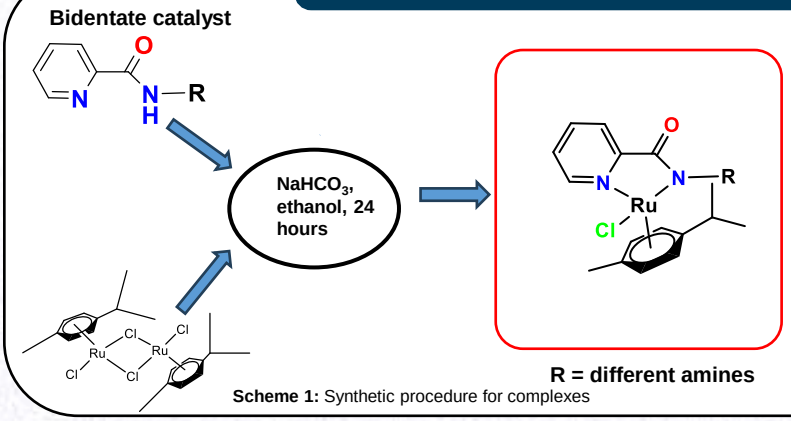
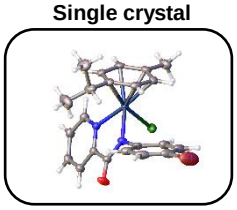


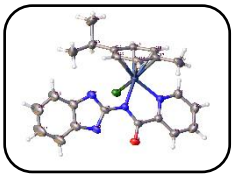
Figure 1: Graphical abstract

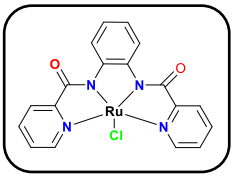
Synthesis and Characterization



Scheme 1: Synthetic procedure for complexes



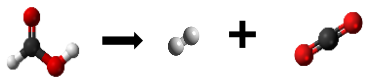




Ligands and complexes were characterized by:

- FTIR- and NMR spectroscopy
- Single crystal diffraction analysis

Formic Acid Dehydrogenation



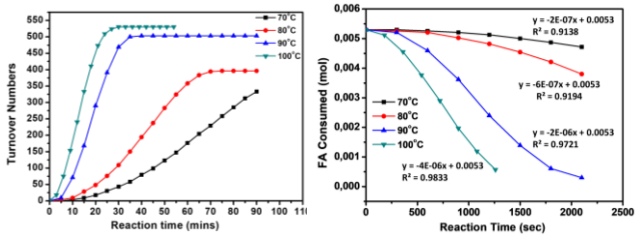
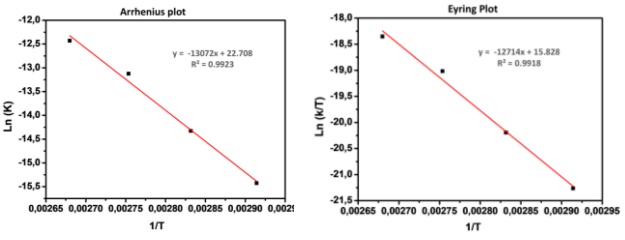


Figure 2: Influence of temperature on the reactivity of complex **C1**. Reaction condition: 0.01 mmol catalyst loading, HCOOK = 3 mmol, FA = 5 mmol, DMSO = 2 mL.

Formic Acid Dehydrogenation



- Activation energy (E_A): = **108 kJ/mol**
- Entropy of activation: = -65 **kJ/mol**
- Enthalpy of activation: = **-105 kJ/mol**

Summary

- Ruthenium complexes (**C1** and **C3**) have been successfully synthesized and characterized.
- Preliminary studies have been performed for the formic acid dehydrogenation using complex **C1**.

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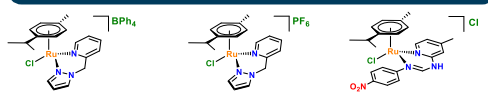

References

[1] J. Skea, Energy Environ. Sci., 2014, 7, 21–24.

[2] N. Armaroli and V. Balzani, ChemSusChem, 2011, 4, 21–36.

[3] Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Chem. Soc. Rev. 2016, 45, 3954-3988.

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