

Abstract

The conversion of CO₂ into valuable chemicals has been of major interest because it is cheap and readily available. The concept of reducing CO₂ pollution *via* its utilization into valuable products has inspired us to synthesise novel 4,4'-((1Z)-butane-2,3-diylidenebis(azanylylidene))dibenzoic acid (**L**) metal complexes {[**(L)Ru^{III}**] (**C1**), [**(L)Rh^{III}**] (**C2**), [**(L)Ir^{III}**] (**C3**)} complexes for catalytic hydrogenation of CO₂. The α -diimine metal complexes (**C1–C3**) were characterised using several analytical techniques, including: NMR spectroscopy and single crystal X-ray crystallography. In a mixture of THF/H₂O and a base, all three catalyst precursors were able to hydrogenate CO₂ cleanly to formate as a product. However, the best combination of catalyst precursor and a base was **C1** and DBU that selectively produced formate at a moderate temperature of 120 °C and at 60 bar. The best productivity under these conditions is TOF of 35 h⁻¹ within 2 h and a TON of 322. This work is significant because it provides a one-step synthesis for formate from CO₂ using α -diimine-based complexes which can be synthesised in a one-step reaction. The density functional theory calculations on **C1** supports that Ru–H is the active species in the process of CO₂ hydrogenation to formate with the insertion of the CO₂ to Ru–H being the rate determining step.