SUPPORTING INFORMATION

Mechanism of CO_2 Hydrogenation to Formates by Homogeneous Ru-PNP Pincer Catalyst: from a Theoretical Description to Performance Optimization

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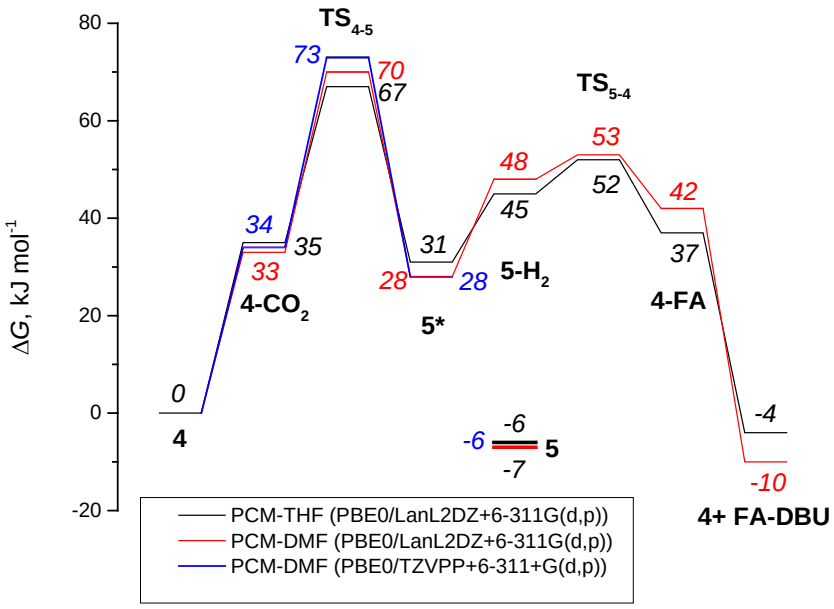

Figure S1. A comparison of Gibbs free energy diagrams for catalytic cycle **I** calculated using PCM model for THF and DMF solvents using standard basis sets and extended basis set combination for the PCM-DMF solvent system (these methodologies were employed for the full geometry optimization and normal mode analysis of all reaction intermediates and transition states, relative Gibbs free energy values are given in italic in kJ mol^{-1}).

Table S1. Summary of the small-scale CO2 hydrogenation experiments with **1** ($p(H_2/CO_2 = 1/1)$ = 40 bar).[a]

Solvent	Base	TON	Formic acid-to-base ratio
THF	DBU	12829	0.381
THF	KO^tBu	728	0.217
DMF	DBU	38642	1.147
DMF	KO^tBu	649	0.194

[a] - Conditions: 70°C, 2h, 40 bar equimolar H_2/CO_2, 0.1 mkmol catalyst, 3ml solvent.

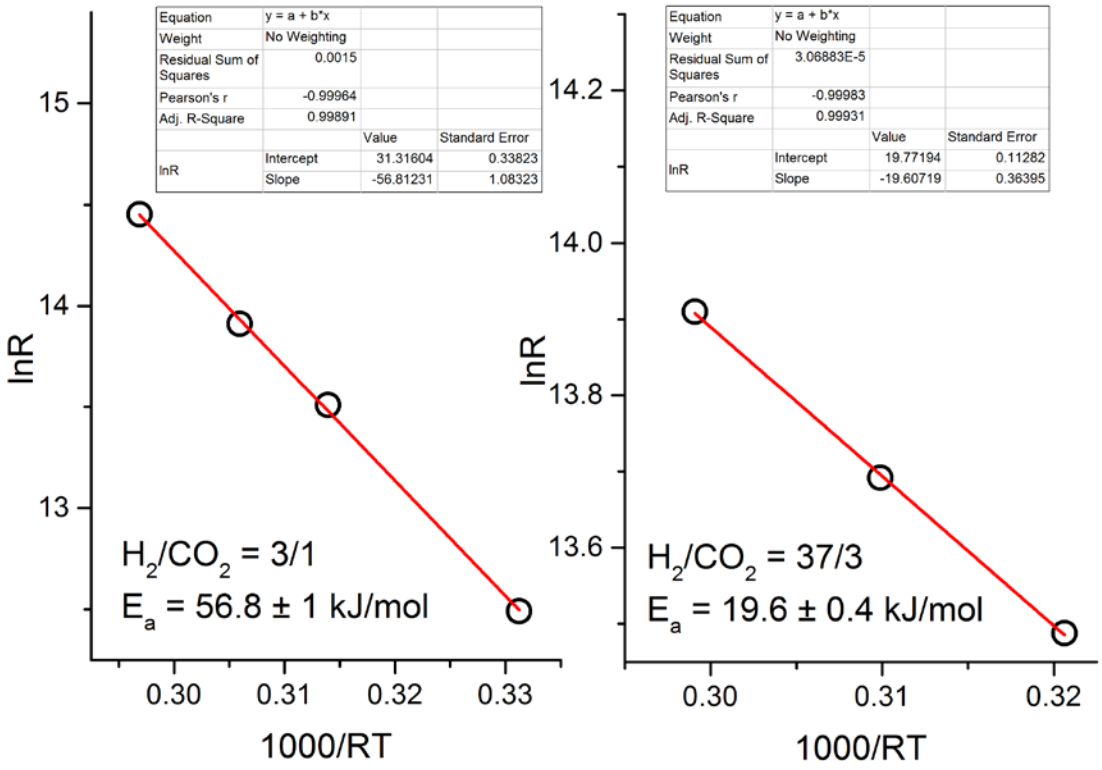

Figure S2. Arrhenius plots for hydrogenation of CO_2 over **1** at different H_2 partial pressures.

Initial rates were used for determination of E_a. Since the rate law was not known, the pre-exponential values could not be determined accurately.