Electronic Supplementary Material (ESI) for New Journal of Chemistry.

New Ru(II)-N′NN′ Typed Pincer Complexes: Synthesis, Characterization and the Catalytic Hydrogenation of CO_2 or Bicarbonates to Formate Salts

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Electronic Supporting Information

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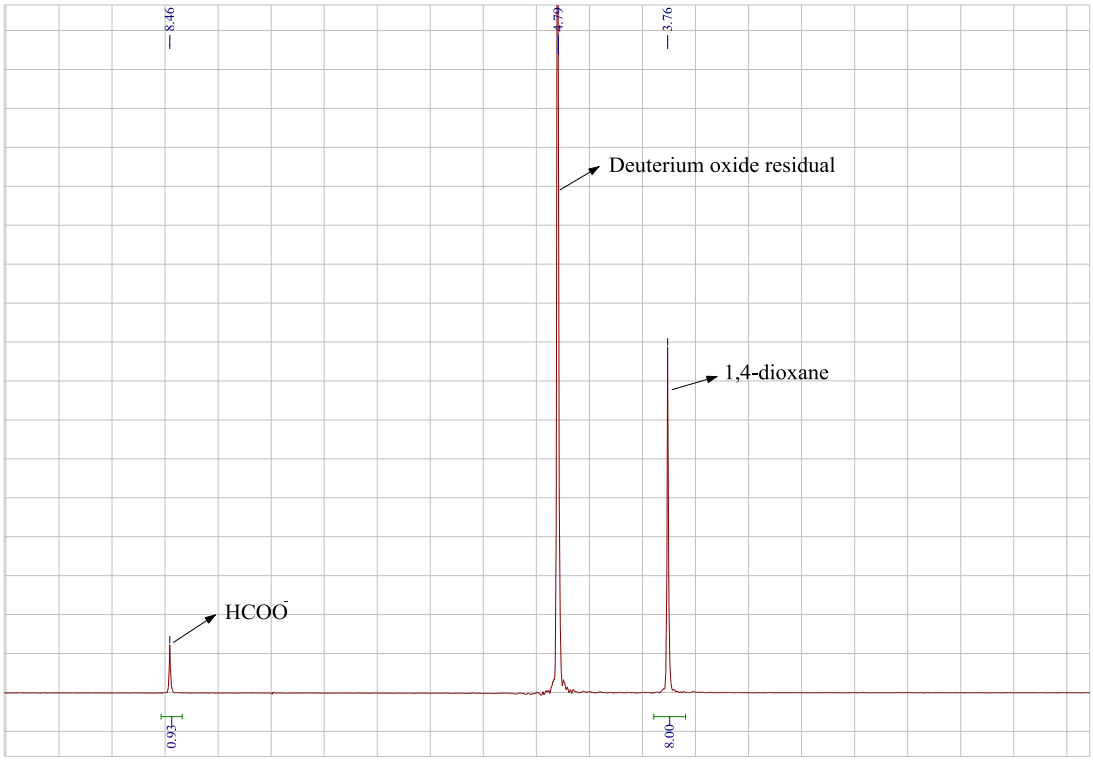
General Procedure for Catalytic Hydrogenation of CO_2

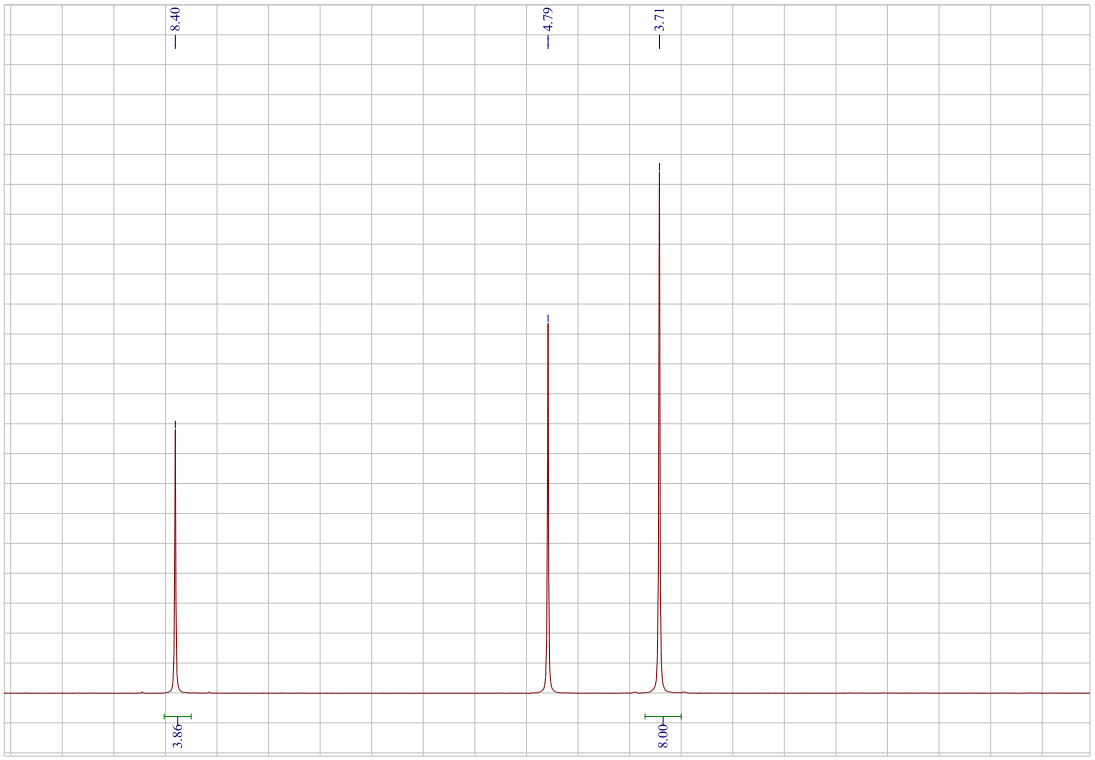
Table 1, entry 1 as the example. NaOH (60 mmol, 2.4g), complex **1** (0.05 mmol, 29.0 mg), 10 mL THF and 10 mL H_2O were placed in a 100 mL autoclave with argon bubble under stirring at room temperature. The autoclave was deoxygenated and filled with 10 atm H_2 and the mixture was stirred at room temperature for 1 h. Then the autoclave was filled with 15 atm H_2 and 15 atm CO_2 (~48 mmol CO_2). The reaction mixture was heated at 130 ℃ for 24 h. After cooling to room temperature, the residual pressure was slowly released. The residue was taken to dryness under vacuum to form 4.55 g grey solid, 0.050 g of solid was taken out from the crude product and dissolved in 0.5 mL D_2O with 11.0 mg (0.125 mmol) 1, 4-dioxane, 0.1 mL of sample was taken out from the solution and diluted to 0.5 mL. Integration of the ^1H NMR spectrum was used to determine the amount of formate and calculate TONs and yields.

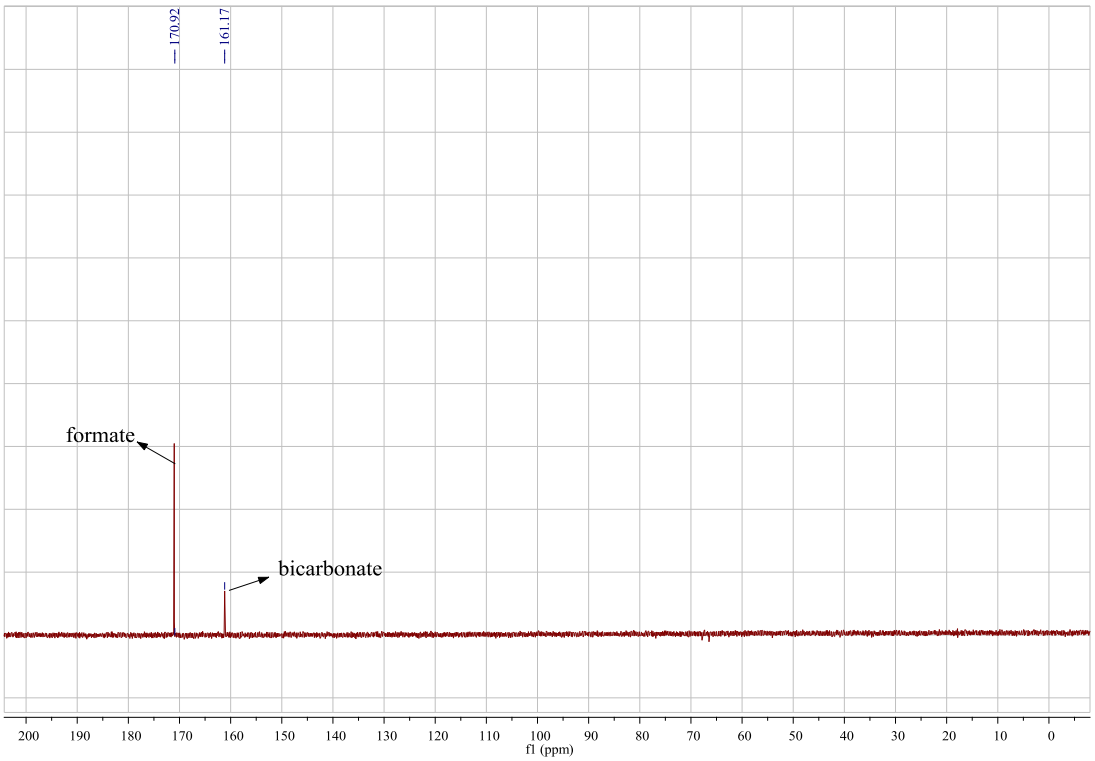


General Procedure for Catalytic Hydrogenation of Alkali Bicarbonate

Table 2, entry 1 as the example. $NaHCO_3$ (10 mmol, 0.84 g), complex **1** (0.005 mmol, 2.9 mg), 10 mL THF and 10 mL H_2O were placed in a 100 mL autoclave with argon bubble under stirring at room temperature. The autoclave was deoxygenated and filled with 10 atm

H_2 and the mixture was stirred at room temperature for 1 h. Then the autoclave was filled with 30 atm H_2. The reaction mixture was heated at 130 ℃ for 24 h. After cooling to room temperature, the residual pressure was slowly released. The residue was taken to dryness under vacuum to form 0.71 g white solid, 0.051 g of solid was taken out from the crude product and dissolved in 0.5 mL D_2O with 11.0 mg (0.125 mmol) 1, 4-dioxane, 0.1 mL of sample was taken out from the solution and diluted to 0.5 mL. Integration of the ^1H NMR spectrum was used to determine the amount of formate and calculate TONs and yields.

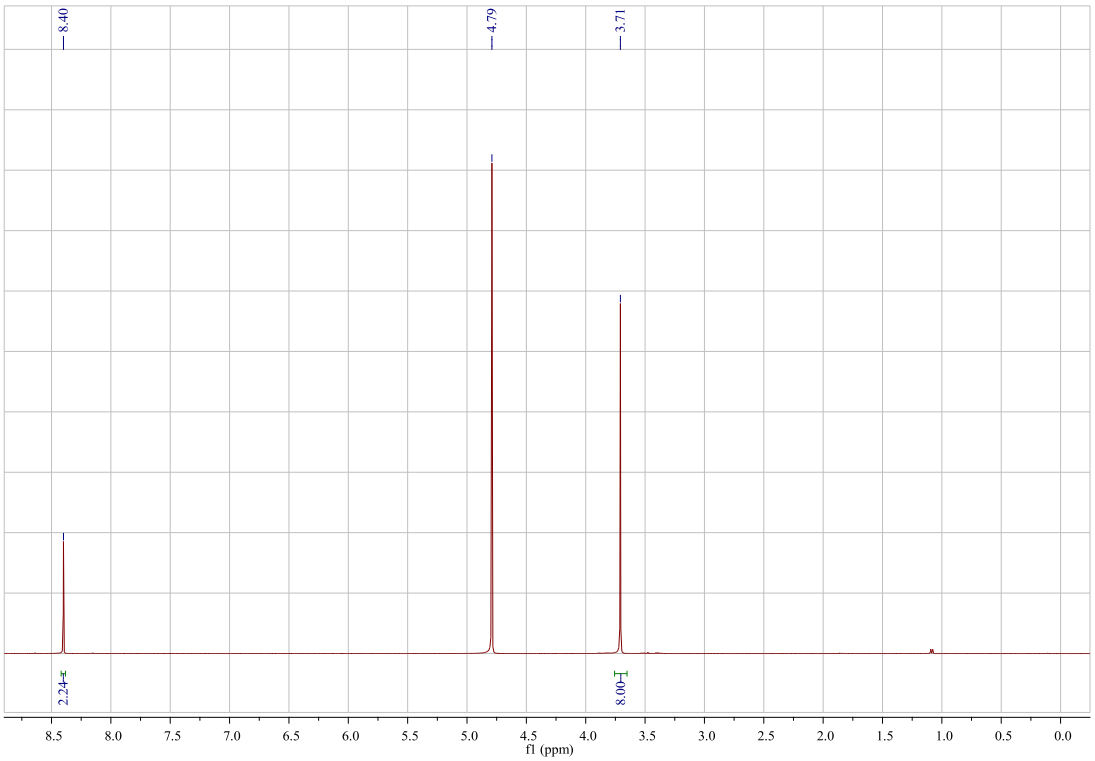




^{13}C NMR of the product(s) (in D_2O)

Mercury test

$NaHCO_3$ (10 mmol, 0.84 g), complex **3** (0.005 mmol, 4.2 mg), 10 mL THF and 10 mL H_2O were placed in a 100 mL autoclave with argon bubble under stirring at room temperature, then a drop of mercury (0.58g, 2.9 mmol, 580 folds to the catalyst) was added. The autoclave was deoxygenated and filled with 10 atm H_2 and the mixture was stirred at room temperature for 1 h. Then the autoclave was filled with 30 atm H_2. The reaction mixture was heated at 130 ℃ for 24 h. After cooling to room temperature, the residual pressure was slowly released and the mercury was carefully collected. The residue was taken to dryness under vacuum to form 0.74 g white solid, 0.043 g of solid was taken out from the crude product and dissolved in 0.5 mL D_2O with 11.0 mg (0.125 mmol) 1, 4-dioxane, 0.1 mL of sample was taken out from the solution and diluted to 0.5 mL. Integration of the ^1H NMR spectrum was used to determine the amount of formate and calculate TONs and yield.



Single Crystal

Table 1 The crystal data and the structure refinement summary for complex **4**

Formula	$C_{30}H_{131}F_6N_{12}O_{13}P_4N_3Ru2S2$
Mr	2573.60 g/mol
Space group	*P21/n*
Crystal system	monoclinic
a/Å	19.8753(12)
b/Å	13.6546(8)
c/Å	23.5872(14)
α/°	90.00
β/°	108.782(1)
γ/°	90.00
V/Å^3	6060.4(6)

Z	2
T/K	100(2)
ρ_{calc},g/cm^{-3}	1.410
μ/mm^{-1}	0.413
No. reflections measured	15755
*R*1[I≥2σ(I)]	0.0402
*wR*2(all data)	0.1113

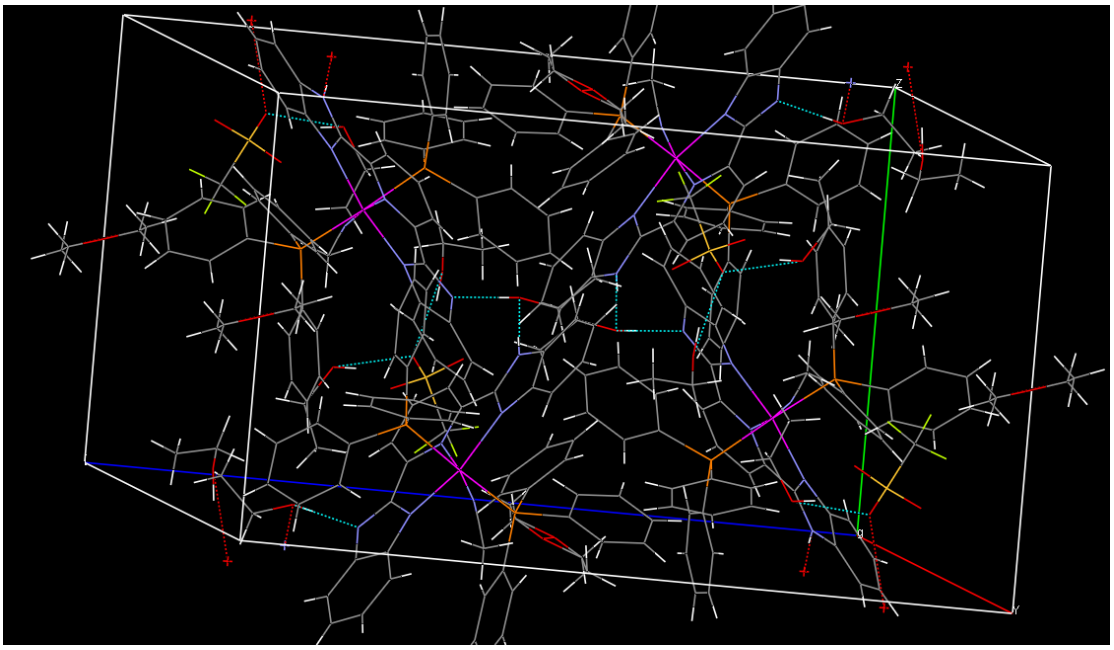


Fig. 1 The packing of complex **4** in the solid state showing the hydrogen bonds between complex **4** and three ethanol molecules.