Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Homogeneous CO_2 Hydrogenation to Methanol - A Highly Productive Tandem Catalytic Approach via Amide Intermediates

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Experimental

General considerations

All procedures were carried out under an inert atmosphere (N_2) using standard Schlenk line techniques or in an inert atmosphere glovebox (Ar). Chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Solvents were purified using an anhydrous Engineering Grubbs-type solvent system except anhydrous ethanol and methanol which were purchased from Sigma-Aldrich and used as received. Complexes **1**,[1] **2**,[2] **3**,[3] **4**[4] and **5**[5] were synthesised by literature methods. NMR spectra were recorded on a Jeol ECS300 or ECS400 spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were referenced relative to the residual solvent resonances in the deuterated solvent. $^{31}P\{^{1}H\}$ NMR spectra were referenced relative to 85% H3PO4 external standard. Mass spectra (ESI) were recorded on a Bruker Daltonics micrOTOF II. All catalytic samples were analysed by GC-FID, using an Agilent 7820A GC, fitted with a DB-WAX capillary column, 30 m x 0.32 mm, I.D. 0.25 µm. Method: starting oven temp 30 °C, heat to 50 °C at 15 °C min^{-1}, hold at 50 °C for 2 min, heat to 250 °C at 75 °C min^{-1}. Flow rate: 2.5 mL min^{-1}.

Synthesis

Preparation of Complex **6**

A solution of 2-(diphenylphosphino)-N-pyrrolidine (0.51 g, 2.1 mmol) in toluene (10 mL) was added to a stirred solution of tris(triphenylphosphine)ruthenium(II) dichloride (1.00 g, 1.04 mmol) in toluene (30 mL). The mixture was stirred at 100 °C for 6 h, after which time the resulting suspension was allowed to cool and then filtered. The solid was washed with toluene (4 × 20 mL), until the filtrate was colourless, and dried under reduced pressure to give complex **6** (0.41 g, 60%) as an orange solid; 1H NMR (300 MHz, CD_2Cl_2) δ 7.25-6.97 (m, 20H, Ar*H*), 3.41-3.18 (m, 8H, C*H*$_2$), 2.92-2.68 (m, 8H, C*H*$_2$), 2.04-1.74 (m, 8H, C*H*$_2$). ^{31}P NMR (122 MHz, CD_2Cl_2): δ 58.7 ppm.

Catalysis

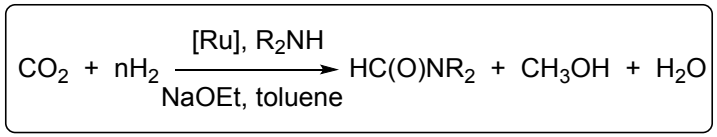
Catalytic reactions were carried out either in a 100 mL Parr stainless steel autoclave with aluminium heating mantle and using magnetic stirring, or in an 8 x 62 mL HEL CHEMScan II stainless steel multicell autoclave. A typical procedure for both is shown below. Full catalytic results are shown in Table S1.

Typical Catalytic Run

In a glove box, *trans*-[$RuCl_2(dppea)_2$] (3.2 mg, 5.1 µmol) and sodium ethoxide (10 mg, 0.16 mmol) were weighed into a clean and oven dried PTFE insert. The insert was then sealed inside an autoclave, which was then evacuated and refilled with N_2 3 times. Toluene (10 mL) and amine (2 mL) were then injected into the autoclave through a septum. The autoclave was then pressurised with CO_2 (10 bar) and H_2 (30 bar), then placed in a pre-heated (180 °C) aluminium heating mantle for 20 h.

After the reaction time, the autoclave was cooled rapidly in an ice-water bath, then vented. 1 mL of reaction mixture was then analysed by gas chromatography (25 µL hexadecane standard). The GC peaks were then integrated against the standard and then compared to the appropriate calibration plots.

Table S1. Ruthenium catalysed conversion of carbon dioxide to amide and methanol.



Run	Autoclave used	Complex (μmol)	Co-catalyst (mmol)	Base (mmol)	mmol amide (TON) [TOF]	mmol methanol (TON) [TOF]
1	HEL Multicell	**1** (5)	Me_2NH	NaOEt (0.15)	72(14000)[700]	0.0(0)[0]
2	HEL Multicell	**2** (5)	Me_2NH	NaOEt (0.15)	6.5(1300)[65]	0.0(0)[0]
3	HEL Multicell	**2** (5)	Me_2NH	NaOEt (0.15)	52(10000)[500]	0.0(0)[0]
4	HEL Multicell	**2** (5)	Et_2NH	NaOEt (0.15)	3.8(760)[38]	0.0(0)[0]
5	HEL Multicell	**2** (5)	$^{i}Pr_2NH$	NaOEt (0.15)	0.038(7.5)[0.38]	0.0(0)[0]
6	HEL Multicell	**2** (5)	$^{n}Pr_2NH$	NaOEt (0.15)	0.071(14)[0.7]	0.0(0)[0]
7	HEL Multicell	**2** (5)	Pyrrolidine	NaOEt (0.15)	0.75(150)[7.5]	0.0(0)[0]
8	HEL Multicell	**2** (5)	Et_3N	NaOEt (0.15)	0.0(0)[0]	0.0(0)[0]
9	HEL Multicell	**3** (5)	Me_2NH	NaOEt (0.15)	0.62(120)[60]	0.55(110)[5.5]
10	HEL Multicell	**3** (5)	Me_2NH	NaOEt (0.15)	2.8(550)[28]	1.9(370)[18]
11	HEL Multicell	**3** (5)	Et_2NH	NaOEt (0.15)	1.3(260)[13]	1.0(200)[10]
12	HEL Multicell	**3** (5)	Pr_2NH	NaOEt (0.15)	0.0(0)[0]	1.1(220)[11]
13	HEL Multicell	**3** (5)	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	12(2300)[120]
14	HEL Multicell	**3** (5)	Pyrrolidine	NaOEt (0.15)	0.0(0)[0]	3.0(590)[30]
15	HEL Multicell	**2/3** (5)	Me_2NH	NaOEt (0.15)	3.7(730)[37]	0.23(46)[2.3]
16	HEL Multicell	**3** (5)	DMF	NaOEt (0.15)	-	0.12(23)[1.2]
17	HEL Multicell	**3** (5)	DEF	NaOEt (0.15)	-	0.75(150)[7.5]
18	HEL Multicell	**3** (5)	DIPF	NaOEt (0.15)	-	1.1(210)[11]
19	HEL Multicell	**3** (5)	Me_2NH	NaOEt (0.15)	1.6(320)[16]	1.2(240)[22]
20	HEL Multicell	**4** (5)	Me_2NH	NaOEt (0.15)	1.7(330)[17]	9.1(1800)[90]
21	HEL Multicell	**5** (5)	Me_2NH	NaOEt (0.15)	2.2(430)[22]	0.0(0)[0]
22	HEL Multicell	**6** (5)	Me_2NH	NaOEt (0.15)	0.39(77)[39]	0.0(0)[0]
23	HEL Multicell	**3** (5)	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	12(2300)[120]
24*	HEL Multicell	**4** (5)	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	21(4000)[2000]
25	HEL Multicell	**5** (5)	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	0.0(0)[0]

26	HEL Multicell	**6** (5)	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	0.0(0)[0]
27	100 mL Parr	**3** (0.05)	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	0.25(5100)[260]
28*	100 mL Parr	**4** (0.05)	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	0.44(8900)[4500]
29	100 mL Parr	none	Me_2NH	NaOEt (0.15)	0.0(0)[0]	0.0(0)[0]
30	100 mL Parr	none	$^{i}Pr_2NH$	NaOEt (0.15)	0.0(0)[0]	0.0(0)[0]
31	100 mL Parr	**3** (5)	none	NaOEt (0.15)	0.0(0)[0]	0.0(0)[0]
32	100 mL Parr	**3** (5)	Me_2NH	none	0.0(0)[0]	0.0(0)[0]
33	100 mL Parr	**3** (5)	Me_2NH	NaOEt (15)	0.0(0)[0]	0.0(0)[0]

*2 h catalytic run.

Spectral Data

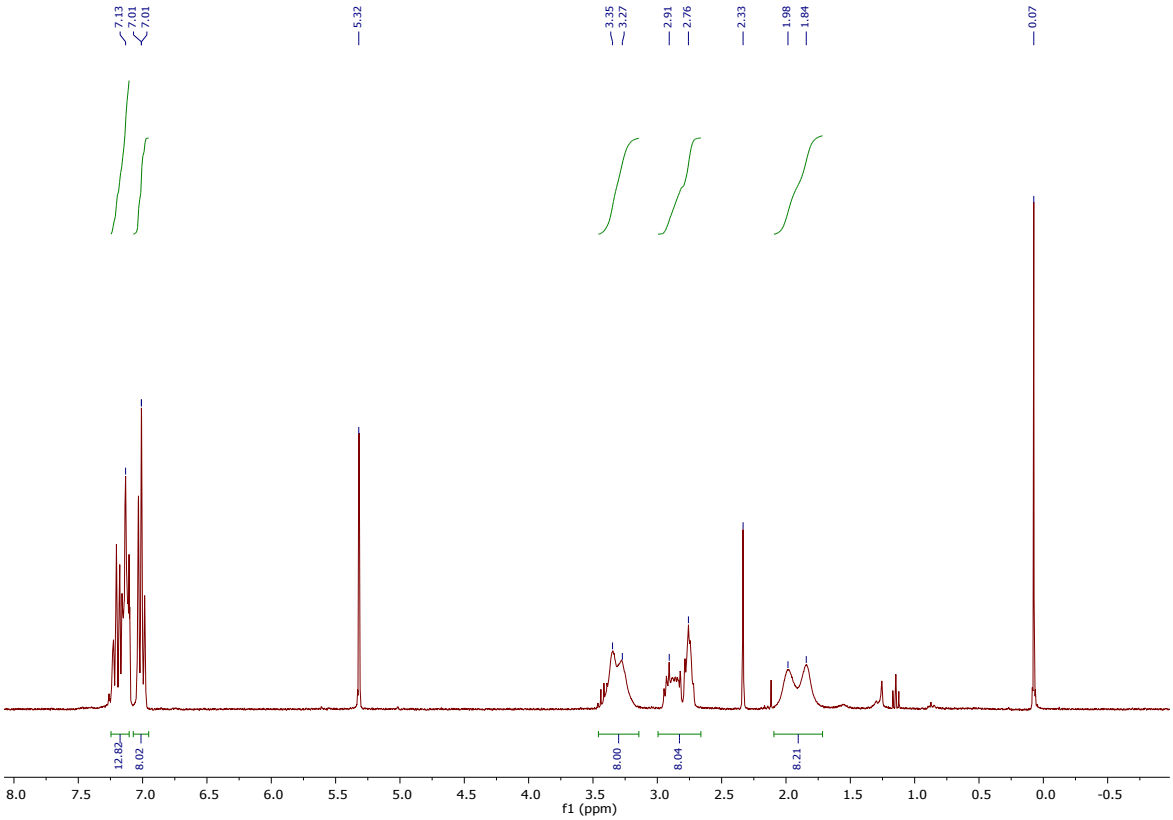


Figure S2. ^{1}H NMR spectrum of $[RuCl_2(Ph_2P(CH_2)_2N(C_4H_8))_2]$, **6** in CD_2Cl_2.

$^{31}P\{^{1}H\}$ NMR spectrum (122 MHz)

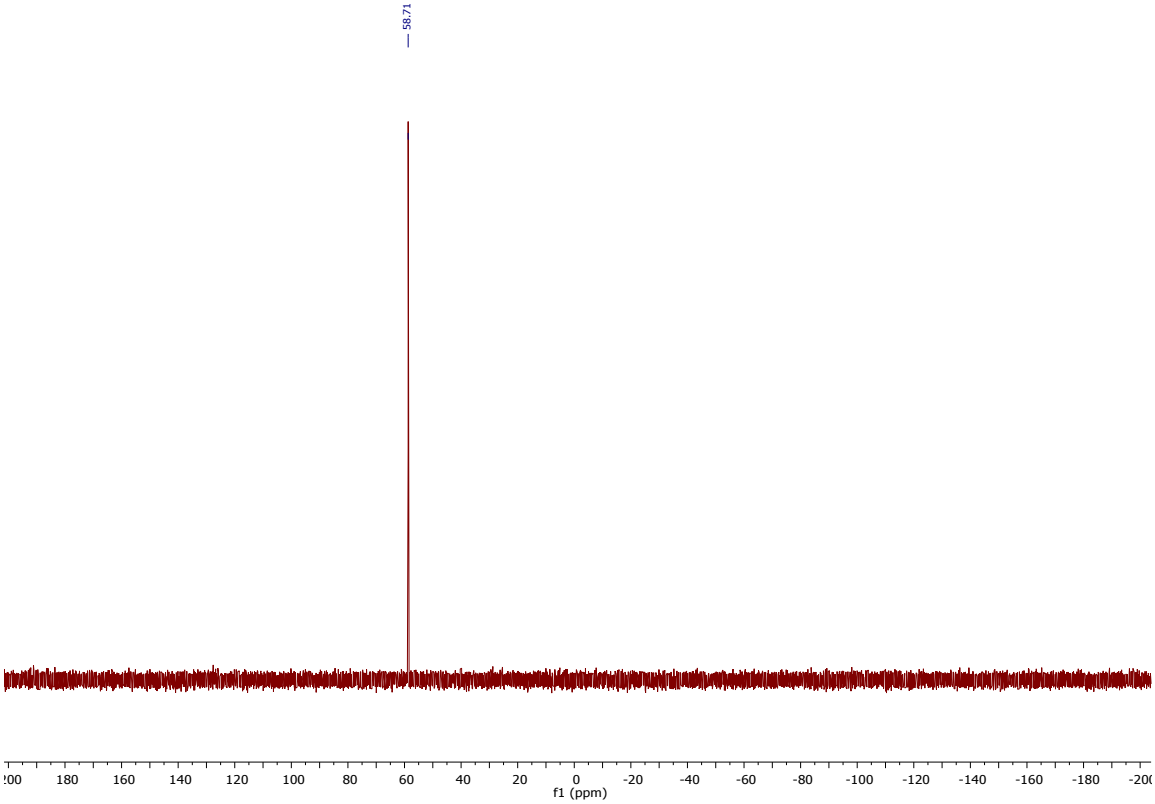


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of $[RuCl_2(Ph_2P(CH_2)_2N(C_4H_8))_2]$, **6** in CD_2Cl_2.

References

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