SUPPORTING INFORMATION

Zwitterionic Alcoholic Solutions for Integrated CO₂ Capture and Hydrogenation.

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SUMARY

1. Ge	neral
1.1	NMR Analysis5
2. Syr	hthesis of Zwitterionic Bases (<i>ZB-p</i> and <i>ZB-m</i>)
2.1 salt ZB-p	Synthesis of the 1,3-dimethyl-2-(4-oxyphenyl) imidazolium inner 6
2.2 salt ZB-m	Synthesis of the 1,3-dimethyl-2-(3-oxyphenyl) imidazolium inner 8
3. Syr [Ru(dppm) ₂ Cl ₂])	hthesis of the <i>cis</i> -bis(dppm)dichloro-ruthenium(II) Complex (<i>cis</i> -
4. Inte	egrated CO ₂ capture and hydrogenation experiments
4.1	Experiments Using Ethylene Glycol as Solvent 10
4.1	.1 CO ₂ Capture
4.2	AKC hydrogenation reactions 12
4.3 using ZB-p .	Standard procedure for reactions in different alcohols and water 15
4.3	.1 CO ₂ Capture
4.3.2 Alcohols and	Standard Procedure for Hydrogenation Reactions of Different Water
4.4 Bases	Standard Procedure for Reactions in Isopropanol with Different 26
4.4	.1 CO ₂ Capture
4.4.2 bases in isop	Standard procedure for hydrogenation reactions of different ropanol
4.5	In-situ ¹ H NMR spectra of CO ₂ capture using MDEA34
4.6 variation of ca	Hydrogenations with fixed alkyl carbonate concentration and atalyst to AKC percentage
4.7 Using ZB-p	Procedure for Capture and Indirect Hydrogenation to Methanol 39
5. ZB	and Catalyst Recyclability Tests 47
5.1	Ion-Exchange Resin 47
5.2	Extraction of ZB.HCOOH adducts using water 47
6. Re	ferences

TABLES

Table S1: Sample preparation method for NMR and d1 used	16
Table S2: Relaxation delay and peak utilized in NMR	26
Table S3: Summary of carbon dioxide capture data	42

Table S4 Hydrogenation of alkyl carbonate using ZB-p dissolved in EG
Table S5: Data for catalytic hydrogenation of alkyl carbonates in isopropanol at 50 °C using <i>cis</i> -[Ru(dppm) ₂ Cl ₂]
Table 56: Results found the literature of ICCU by catalytic hydrogenation
Table S7: ZB and Catalyst reuse attempts
FIGURES
Figure S1: Ru complexes used as catalysts in this work
Figure S2: 'H NMR spectrum of the compound ZB-p
Figure S3: 'H NMR spectrum of the compound ZB-m
(Table 1) after CO ₂ capture 11
Figure S5: ¹ H NMR spectrum of the reaction mixture after AKC
hydrogenation in ethylene glycol
Figure S6: ¹³ C NMR spectrum of the reaction mixture after AKC
hydrogenation in ethylene glycol
Figure S7: HSQC heteronuclear correlation map of the reaction mixture
after AKC hydrogenation in ethylene glycol 14
Figure S8: HMBC heteronuclear correlation map of the reaction mixture
after AKC hydrogenation in ethylene glycol
Figure S9: 'H NMR spectrum of the CO_2 capture reaction using ZB-p in
Elianoi. Figure S10: ¹ H NMR spectrum of the CO ₂ capture reaction using 7 \mathbf{R}_{-} in
<i>n</i> -butanol n -butanol
Figure S11: inversed gate decoupling ¹³ C NMR spectrum of the of the
CO ₂ capture reaction using ZB - <i>p</i> in water
Figure S12: ¹ H NMR spectrum of the CO ₂ capture reaction using ZB - <i>p</i> in
isopropanol 19
Figure S13: Heteronuclear HSQC correlation map of the ZB-p sample
solution in isopropanol after CO_2 capture. Positive (CH ₃ and CH) are shown in
black, and negative (CH ₂) are shown in red
Figure 514: Helefonuclear HMBC correlation map of the $2B-p$ sample solution in isopropagol after CO ₂ capture 20
Figure S15: ¹ H NMR spectrum after bydrogenation of the 7B-n's AKC in
ethanol
Figure S16: ¹ H NMR spectrum after hydrogenation of the ZB - <i>p</i> 's AKC in
<i>n</i> -butanol. 22
Figure S17: ¹ H NMR spectrum after hydrogenation of the ZB-<i>p</i>'s AKC in
water
Figure S18: ¹ H NMR spectrum after hydrogenation of the ZB - <i>p</i> 's AKC in
isopropanol
Figure 519: HSQC neteronuclear correlation map of the <i>ZB-p</i> solution
sample in isopropation after ArC hydrogenation. Positive ($C\Pi_3$ and $C\Pi$) In DIaCK and negative ($C\Pi_2$) in red
Figure S20. HMBC heteronuclear correlation map of the 78-n solution
sample in isopropanol after AKC hydrogenation
Figure S21: ¹ H NMR spectrum of the ZB-m solution after CO ₂ capture in
isopropanol

Figure S22: ¹ H NMR spectrum of the 1.0 mol L ⁻¹ MDEA solution in
Figure S23: ¹ H NMR spectrum of the 1.0 mol L ⁻¹ TEA solution in
isopropanol during CO ₂ capture in DMSO-d ₆
Figure S24: ¹ H NMR spectrum of the 1.0 mol L ⁻¹ TMEDA solution in
isopropanol during CO ₂ capture in DMSO-d ₆
Figure S25: ¹ H NMR spectrum of the 1.0 mol L ⁻¹ DBU solution in
isopropanol during CO ₂ capture in DMSO-d ₆
Figure S26: ¹ H NMR spectrum of ZB - <i>m</i> solution in isopropanol after
hydrogenation in DMSO-d ₆
Figure S27: ¹ H NMR spectrum of MDEA solution in isopropanol after
hydrogenation in DMSO-d ₆
Figure S28: ¹ H NMR spectrum of DBU solution in isopropanol after
hydrogenation in DMSO-d ₆
Figure S29: ¹ H NMR spectrum at 500 MHz of the 1.0 mol L ⁻¹ MDEA
solution in isopropanol after 72 hours of reaction under 1.6 bar of CO_2 , with $d_1 =$
60s and 36 scans
Figure S30: Inversed gate decoupling ¹³ C NMR spectrum at 500 MHz of
the 1.0 mol L ⁻¹ MDEA solution in isopropanol after 72 hours of reaction under 1.6
bar of CO ₂ , d ₁ = 25s and 10240 scans
Figure S31: ¹ H NMR spectrum at 500 MHz of the 1.0 mol L ⁻¹ MDEA
solution in isopropanol after releasing CO_2 pressure, with $d_1 = 60s$ and 6 scans.
Figure S32: ¹³ C NMR at spectrum at 500 MHz of the 1.0 mol L ⁻¹ MDEA
solution in isopropanol after releasing CO ₂ pressure. The acquisition parameters
were d ₁ = 25s and 1024 scans
Figure S33: ¹ H NMR spectrum of the hydrogenation of alkyl carbonate
(AKC) to methanol in DMSO-d ₆
Figure S34: Hydrogenation reaction conversion and formate yield profile
at 5 bar of H ₂ . Conditions: ~0.5 mol L ⁻¹ ZB-p , 0.8% mol <i>cis</i> -[Ru(dppm) ₂ Cl ₂], 50°C.
Figure S35: Hydrogenation reaction conversion and formate yield profile
at 10 bar of H ₂ . Conditions: ~0.5 mol L ⁻¹ ZB-p , 0.8% mol cis-[Ru(dppm) ₂ Cl ₂],
50°C
Figure S36: Hydrogenation reaction conversion and formate yield profile
at 70 bar of H ₂ . Conditions: ~0.5 mol L ⁻¹ ZB-p , 0.8% mol <i>cis</i> -[Ru(dppm) ₂ Cl ₂],
50°C

1. General

All procedures involving air-sensitive compounds were carried out under atmosphere using Schlenk techniques. The reagents argon 4hydroxybenzaldehyde (98%), 3-hydroxybenzaldehyde (98%), methylamine (40% aqueous solution), and glyoxal (40% aqueous solution) used for the synthesis of zwitterionic bases were purchased from Sigma-Aldrich. The solvents methanol (Moderna, \geq 99.8%), acetonitrile (Vetec, \geq 99.5%), ethanol (Moderna, \geq 99.8%), ethyl acetate (Moderna, \geq 99.5%), dichloroethane (Moderna, \geq 99.5%), and hexane (Moderna, \geq 98.5%) used in the synthesis of the zwitterions and the *cis*bis(dppm)dichloro-ruthenium (II) complex were used as received.

The reagents RuCl₃.xH₂O (anhydrous trace metal basis, 99.98%) and 1,1-bis(diphenylphosphino)methane (dppm, 97%, Sigma-Aldrich), used for the synthesis of the *cis*-bis(dppm)dichloro-ruthenium (II) complex were used without prior purification.

The solvents and catalytic precursors for the hydrogenation reactions were: anhydrous ethylene glycol (EG, Sigma-Aldrich, \geq 99.8%), ethanol (EtOH, Panreac, \geq 99.9%), isopropanol (iPrOH, TEDIA, \geq 99.8%), and *n*-butanol (n-BuOH, Sigma-Aldrich, \geq 99.5%), all used without further purification. The complexes dichloro tris(triphenylphosphine)ruthenium (II) (97%), Ru-SNS (97%), Ru-MACHO-BH (\leq 100%), and Ru-MACHO (\leq 100%) were purchased from Sigma-Aldrich and used without additional purification. Deuterated dimethyl sulfoxide (DMSO-d₆, Sigma-Aldrich, 99.9% deuterated) was employed as the deuterated solvent.

The amines N-methyldiethanolamine (MDEA, Sigma-Aldrich, \geq 99%), triethylamine (TEA, VETEC, \geq 99%), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, Alfa Aesar, \geq 99%), and tetramethylethylenediamine (TMEDA, Sigma-Aldrich, \geq 99%) were dried with sodium hydroxide pellets (NaOH, Dinâmica, \geq 97%) and distilled under reduced pressure, except for TEA, which was distilled under atmospheric pressure.

The gases Argon 5.0, carbon dioxide 4.8, and hydrogen 5.0 were supplied and refilled by Air Liquide. The reactor used was a Parr Series 5000 multi-reactor system with a 45 mL volume. Heating for the alkoxy carbonate (AKC) hydrogenation towards formate was conducted using a silicone oil bath on IKA C-MAG HS 7 hotplates with and themperature was controlled by a thermocouple. Methanol formation reactions were heated using the resistances and controllers of the Parr Series 5000 multi-reactor system.



Figure S1: Ru complexes used as catalysts in this work.

1.1 NMR Analysis

The NMR experiments were conducted on the following spectrometers: Bruker Avance III-HD 400, Bruker Avance I 400, and Varian MR400, all equipped with a 5 mm probe with a Z-gradient capability, operating at 400 MHz for ¹H and 100 MHz for ¹³C. Additionally, an Agilent 500 DD2 spectrometer equipped with a 5 mm OneNMR probe was used, operating at 500 MHz for ¹H and 125 MHz for ¹³C. All spectra were recorded at 298 K. Chemical shifts were reported in ppm relative to the DMSO-d₆ solvent signals (δ 2.50 ppm for ¹H and 39.52 ppm for ¹³C). Abbreviations for signal multiplicities include: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), hep (heptet) and m (multiplet). Coupling constants were expressed in Hz, and chemical shifts were referenced to tetramethylsilane (TMS) or to the residual hydrogen signal of the deuterated solvent.¹ For quantitative assays, the T₁ relaxation times were measured for each combination of solvent, base, catalyst, and products. The ¹H NMR spectra for these combination were manually selected and integrated to ensure accuracy. ¹**H NMR**: Spectra were acquired with recycle delay (d_1) ranging from 1 to 50 s and 6 to 32 scans. The spectral window was set to 20 ppm with 32 k points for acquisition and 64 k for processing, providing a spectral resolution of 0.5 Hz for spectra acquired on 400 MHz spectrometers for ¹H and 0.5 Hz.

¹³**C NMR**: Spectra were acquired with recycle delay d_1 ranging from 1 to 75 s. The spectral window was set to 250 ppm with 64 k points for acquisition and 64 k for processing, resulting in a spectral resolution of 0.7 Hz for spectra acquired at 100 MHz for ¹³C and 0.7 Hz for spectra acquired at 125 MHz for ¹³C. For quantification spectra, the experiment used was ¹³C inverse gated decoupling (¹³C decoupled from hydrogens during acquisition – NOE, 90° pulse).

HMBC Correlation Maps (${}^{13}C-{}^{1}H$): These experiments were carried out with 512 points in the F₁ dimension and 8192 points in the F₂ dimension. Constant values (cnst13) of 8 Hz were applied to ${}^{n}J_{CH}$ values. The final data were processed using a sine function in both dimensions before Fourier transformation.

HSQC Correlation Maps (¹³C-¹H): These experiments were carried out with 512 points in the F₁ dimension and 4096 points in the F₂ dimension. A constant of 145 Hz was applied to ¹J_{CH} values. The final data were processed using a sine-squared function in both dimensions before Fourier transformation.

in situ NMR: The experiments were conducted using a high-pressure Daedalus cell equipped with an integrated needle valve and zirconia tube. Measurements were performed on a Varin 500 MHz spectrometer. For ¹H spectra, the window was set to 20 ppm, with 32 k points used for acquisition and 64 k points for processing. This provides a spectral resolution of 0.5 Hz. For ¹³C spectra, acquisition parameters included a recycle delay (d₁) ranging from 1 to 75 seconds. The spectral window was set 250 ppm, with 64 k points used for both acquisition and processing. This configuration achieved a spectral resolution of 0.7 Hz for spectra acquired at 125 MHz. For quantification, ¹³C inverse-gated decoupling experiments were employed. In this setup, ¹³C was decoupled from hydrogen during acquisition (NOE was suppressed).

2. Synthesis of Zwitterionic Bases (ZB-p and ZB-m)

The previously described three-step synthesis method² was slightly modified in the purification step of the iodide intermediate.

2.1 Synthesis of the 1,3-dimethyl-2-(4-oxyphenyl) imidazolium inner salt ZBp

Preparation of 1-methyl-2-(4-hydroxyphenyl) imidazole

A solution of methylamine (79.70 g, 1.02 mol) was added to a solution of 4-hydroxybenzaldehyde (117.22 g, 0.96 mol) dissolved in 450 mL of methanol. The resulting amber solution was stirred for 10 minutes. Then, ammonium carbonate (69.71 g, 0.72 mol) was added in a single portion, followed by the dropwise addition of glyoxal (139.3 g, 0.96 mol) dissolved in 100 mL of methanol under vigorous stirring while maintaining the reaction mixture at 40°C. CO₂ evolution was observed, and the desired imidazole starts precipitating. The reaction mixture was then stirred for more 120 minutes at 40°C. Then, 500 mL of cold water were added to the reaction flask, and the crystals were vacuum-filtered and washed with a 50% v/v methanol/cold water mixture. The resulting light amber crystals of 1-methyl-2-(4-hydroxyphenyl) imidazole were dried under reduced pressure. Yield: 45.7%; 76.27 g; 0.44 mol.

Preparation of 1,3-dimethyl-2-(4-hydroxyphenyl) imidazolium iodide

1-methyl-2-(4-hydroxyphenyl) imidazole (76.27 g, 0.44 mol) was mixed with 500 mL of acetonitrile in a 1 L two-necked round bottom flask equipped with a reflux condenser and an addition funnel. CH₃I (41.5 mL, 0.67 mol) dissolved in 50 mL of acetonitrile was then added dropwise over 45 minutes through the addition funnel, while maintaining the reaction mixture at 70°C under stirring. After stirring for an additional 2 hours, the system was cooled, and 200 mL of ethyl acetate were added to precipitate the product. The resulting light amber crystals were vacuum-filtered, washed with ethyl acetate, and dried under reduced pressure. The solid obtained was recrystallized twice from an ethanol/water mixture (94:6) at a ratio of 1 g of solid to approximately 8.5 mL of solvent. The obtained solid was washed with ethyl acetate and dried in vacuum affording 111.8 g (81.3%; 0.36 mol) of white needle-like crystals.

Ion Exchange

Amberlyst 26 OH ion-exchange resin (510 mL, 0.8 meq OH⁻/mL, 408 meq OH⁻) was placed in a 1 L beaker and washed three times with distilled water. A solution of 1,3-dimethyl-2-(4-hydroxyphenyl) imidazolium iodide (111.8 g, 0.36 mol dissolved in 360 mL of water) was added to the resin, and the resulting suspension was stirred at room temperature for 20 minutes. The I⁻/OH⁻ exchange was confirmed by a negative qualitative iodide test (nitrite/sulfuric acid). The solution was vacuum-filtered, and water was evaporated under reduced pressure, yielding a white solid. Yield: 98.0%; 65.9 g; 0.35 mol. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.60 (s, 2H), 7.03 (dd, *J* = 8.8 Hz, 3.2 Hz, 2H), 6.23 (dd, *J* = 8.8 Hz, 3.2 Hz, 2H), 3.67 (s, 6H).



2.2 Synthesis of the 1,3-dimethyl-2-(3-oxyphenyl) imidazolium inner salt ZBm

Preparation of 1-methyl-2-(3-hydroxyphenyl)imidazole

A solution of methylamine (43.73 g; 0.56 mol) was added to a solution of 3-hydroxybenzaldehyde (64.73 g; 0.53 mol) dissolved in 300 mL of methanol. The resulting amber solution was stirred for an additional 10 minutes. Ammonium carbonate (38.16 g; 0.40 mol) was then added in one portion, followed by the dropwise addition of glyoxal (76.85 g; 0.53 mol) dissolved in 50 mL of methanol under vigorous stirring, maintaining the reaction mixture at 40°C. CO_2 evolution was observed, and the desired imidazole starts precipitating. The reaction mixture was then stirred for more 120 minutes at 40°C. Then, 250 mL of cold water were added to the reaction flask, and the crystals were vacuum-filtered and washed with a 50% v/v methanol/cold water mixture. The 1-methyl-2-(3-hydroxyphenyl) imidazole was obtained as light amber crystals, which were dried under reduced pressure. Yield: 42.4%; 0.22 mol; 39.17 g.

Preparation of 1,3-dimethyl-2-(3-hydroxyphenyl) imidazolium iodide

1-methyl-2-(3-hydroxyphenyl) imidazole (39.17 g; 0.22 mol) was mixed with 340 mL of acetonitrile in a 1 L two-necked round bottom flask equipped with a reflux condenser and an addition funnel. CH_3I (21 mL; 0.34 mol) dissolved in 50 mL of acetonitrile was then added dropwise over 45 minutes through the addition funnel, while maintaining the reaction mixture at 70°C under stirring. The

imidazole reactant was slightly soluble in acetonitrile but reacted in solution at 70°C. After stirring for an additional 2 hours, the system was cooled, and 100 mL of ethyl acetate was added to precipitate the product. The resulting light amber crystals were vacuum-filtered, washed with ethyl acetate, and dried under reduced pressure. The solid obtained was recrystallized twice from an ethanol/water mixture (98:2), at a ratio of 1 g of solid to approximately 8.5 mL of solvent. The obtained solid was washed with ethyl acetate and dried in vacuum affording 54.36 g (78.7%; 0.17 mol) of highly hygroscopic white needle-like crystals.

Ion Exchange

Amberlyst 26 OH ion-exchange resin (260 mL, 0.8 meg OH⁻/mL, 208 meg OH⁻) was placed in a 1 L beaker and washed three times with distilled water. A solution of 1,3-dimethyl-2-(3-hydroxyphenyl) imidazolium iodide (54.36 g; 0.17 mol, dissolved in 250 mL of water) was added to the resin, and the resulting suspension was stirred at room temperature for 20 minutes. The I⁻/OH⁻ exchange was confirmed by performing a negative gualitative iodide test (nitrite/sulfuric acid). The solution was vacuum-filtered, and the water was evaporated under reduced pressure. resulting white solid. in а Yield: 95.0%; 30.12 g; 0.16 mol. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.74 (s, 2H), 7.01-6.93 (m,1H), 6.36 (dd, J = 8.5, 2.5 Hz, 1H), 6.16 (t,J = 2.2 Hz 1H), 6.06-6.00 (m, 1H), 3.64 (s, 6H).



3. Synthesis of the *cis*-bis(dppm)dichloro-ruthenium(II) Complex (*cis*-[Ru(dppm)₂Cl₂])

The *cis*-[Ru(dppm)₂Cl₂] was prepared according to a previously published method^{3, 4}. Initially, the *trans*-[Ru(dppm)₂Cl₂] complex was synthesized, followed by isomerization.

0.30 g (1.44 mmol) of RuCl₃·nH₂O and 1.15 g (2.99 mmol) of dppm were dissolved in 30 mL of ethanol. The reaction mixture was refluxed under an inert atmosphere for 3 h, resulting in the formation of a yellow precipitate. The obtained solid was separated by filtration, washed with hot ethanol and ethyl ether, both degassed solvents.

Next, 0.50 g (0.53 mmol) of the *trans*-[Ru(dppm)₂Cl₂] complex was refluxed in 30 mL of dichloroethane for 10 hours. The solvent volume was reduced, and 30 mL of hexane was added. The *cis*-[Ru(dppm)₂Cl₂] solid obtained was collected by filtration and dried under vacuum. Yield: 80%.

4. Integrated CO₂ capture and hydrogenation experiments

4.1 Experiments Using Ethylene Glycol as Solvent

4.1.1 CO₂ Capture

A total of 1.32 g (7.0 mmol) of **ZB-p** was dissolved in 14 mL of anhydrous ethylene glycol in a Schlenk flask under an inert argon atmosphere, using a magnetic stir bar for mixing. The flask was subjected to vacuum-argon cycles to remove residual gases, and the system was maintained under vacuum with its mass being determined. CO₂ was introduced into the system under vigorous stirring (1200 rpm), with the CO₂ pressure controlled at 1.6 bar using a gas reservoir and a pressure regulator. The reaction was considered complete when no further pressure change was observed in the reservoir, which occurred after approximately 45 minutes. The system was then connected to the Schlenk line, evacuated until no bubbling was observed for approximately 5 minutes, and kept under vacuum for a second mass measurement. Following this, the Schlenk flask was refilled with 1 bar of CO₂ and stored for subsequent catalytic hydrogenation reactions. The amount of chemisorbed CO₂ was determined through gravimetric analysis, comparing the system's mass before and after capture, and corroborated by ¹H NMR spectroscopy. For NMR analysis, a 400 µL aliquot of the solution was diluted with 300 μ L of DMSO- d_6 . The ¹H NMR experiment was performed using a recycle delay of 26 s, determined from prior measurements of the T1 relaxation time (recycle delay being equivalent to 5 times T1).

Assignment of the ¹H NMR signals were confirmed through a combined analysis of ¹H, ¹³C, HSQC, and HMBC spectra obtained after an incomplete AKC hydrogenation reaction. The spectra are provided in Figures S4-S8.

The observed peaks were assigned as follows:

Peaks at 3.42 and 4.87 ppm: Solvent signals;

Doublets at 7.32 and 6.86 ppm: CH groups of the para-substituted aromatic ring; Singlet at 7.52 ppm: CH of the imidazole ring.

Singlet at 3.62 ppm: CH₃ group of **ZB-p**.

Triplet at 3.75 ppm: Alkyl carbonate anion derived from ethylene glycol.



(Table 1) after CO_2 capture.

The CO_2 capture percentage, or the base conversion, by any system can be obtained using equation 1.

$$CO_2 \ capture \ (\%) = \left(\frac{A_{0AKC}*nH_B}{A_B*nH_{AKC}}\right) * \ 100 \tag{1}$$

Where $A_{o}AKC$ is the area of one of the ¹H NMR peaks of the alkyl carbonate, nH_{AKC} is the number of hydrogens of the corresponding peak of the alkyl carbonate molecule, A_B is the area of a ¹H NMR peak of the base, and nH_B is the number of hydrogens of the corresponding peak of the base. In the case of the reaction between **ZB-p** and CO₂, the following peaks were integrated: the triplet at 3.75 ppm corresponding to 2 H atoms of the AKC and the singlet at 7.52 ppm corresponding to the two hydrogens of **ZB-p** imidazolium ring. Thus, the conversion of **ZB-p** to carbonate in EG can be calculated using the following equation:

$$CO_2 \ capture \ (\%) = \left(\frac{A_{0AKC}}{A_{ZB-p}}\right) * \ 100 \tag{2}$$

Where:

 A_{0AKC} = peak area at 3.75 ppm corresponding to the AKC formed by CO₂ capture A_{0ZB-p} = peak area at 7.52 ppm corresponding to **ZB-p**

4.2 AKC hydrogenation reactions

10 µmol of the Ru catalytic precursor ([RuCl₂(PPh₃)₃]/Ru-MACHO-BH/Ru-SNS/*cis*-[Ru(dppm)₂Cl₂]/Ru-MACHO) were placed in the glass liner of the high-pressure reactor. The autoclave was closed, and 4 mL of the CO₂-captured solution were transferred into the reactor using a syringe through a ball valve under Ar flow. The reactor was then purged with vacuum-argon cycles and kept under vacuum, and then the reactor was pressurized with H₂ to the desired pressure. The reactor was placed in a preheated silicon oil bath at a temperature such that the internal equilibrium temperature of the solution inside the reactor reached 50 °C and continuously stirred at 600 rpm with a PTFE-coated magnetic bar. After the reaction period, the reactor was removed from the oil bath, and the H₂ pressure released. The reactor was cooled in an ice bath for 30 minutes. A 400 µL aliquot of the reaction was diluted with 300 µL of DMSO-d₆ and analysed by ¹H NMR.

NMR analyses after hydrogenation showed that there was no decomposition of the zwitterionic bases. Additionally, the ZBs do not volatilize during the process and, therefore, can be used as an internal standard for quantifying the conversion of AKC and the yield of the products. These reaction parameters can be calculated quantifying the ¹H NMR spectra obtained after CO₂ capture (Section 4.1.1) and after the hydrogenation reaction. **Both spectra must be acquired with d₁ = 26 s, and the integrals should be normalized relative to the same peak of the base.** With these conditions, the conversion of AKC and the product yield can be calculated using the general equations below.

$$Conversion (\%) = \left(1 - \frac{A_{AKC}}{A_{0_{AKC}}}\right) * 100$$
(3)

$$Yield (\%) = \left(\frac{A_{Product} * nH_{0AKC}}{A_{0_{AKC}} * nH_{Product}}\right) * 100$$
(4)

Where:

 A_{AKC} = area of the AKC peak after the hydrogenation reaction A_{OAKC} = area of the AKC peak after CO₂ capture nH_{OAKC} = number of hydrogens corresponding to the integrated signal of

AKC .

 $A_{product}$ = area of the product peak

 $nH_{product}$ = number of hydrogens corresponding to the integrated signal of the reaction product

For the reactions in ethylene glycol, the conversion was determined by integrating the signals at 3.75 ppm for A_{AKC} and A_{OAKC} . The yield for the formate was then obtained using the equation below:

$$Yield (\%) = \left(\frac{2*A_{Formate}}{A_{0_{AKC}}}\right) * 100$$
(5)

 A_{0AKC} = Peak area at 3.75 ppm refers to the formation of AKC after CO₂ Capture.





Figure S5: ¹H NMR spectrum of the reaction mixture after AKC hydrogenation in ethylene glycol.



Figure S6: ¹³C NMR spectrum of the reaction mixture after AKC hydrogenation in ethylene glycol.



Figure S7: HSQC heteronuclear correlation map of the reaction mixture after AKC hydrogenation in ethylene glycol.



Figure S8: HMBC heteronuclear correlation map of the reaction mixture after AKC hydrogenation in ethylene glycol.

- 4.3 Standard procedure for reactions in different alcohols and water using **ZB-p**.
 - 4.3.1 CO₂ Capture

1.32 g (7.0 mmol) of **ZB-p** were dissolved in 14 mL of the respective alcohol in a Schlenk flask under an inert argon atmosphere. The gases were removed by cycles of argon and the flask maintained under an argon atmosphere. CO₂ was then added under vigorous stirring with a PTFE-coated magnetic stirring bar (1200 rpm). The CO₂ partial pressure was kept constant at 0.6 bar using a gas reservoir and pressure regulator. The reaction was considered complete when no further pressure change was observed in the reservoir, which occurred after approximately 45 minutes. After this period, the system was transferred to the Schlenk line, purged with argon, and an aliquot was taken for ¹H NMR analysis. The system was then refilled with 1 bar of CO₂ and stored for subsequent catalytic hydrogenation reactions. The amount of CO₂ captured was quantified by ¹H NMR for the alcohols and ¹³C NMR for the water. The ¹H NMR analysis required the preparation of the samples in different ways, depending on the solvent used, as well as different d₁ values. Table S1 summarizes the methodology used for each solvent and which signals from the spectrum were used for the calculation according to equation 1 (section 4.1.1).

Solvent	Sample preparation method	d ₁ (s)	Peaks Used in Quantification
EtOH	300 μL of DMSO + 400 μL of Solution	33	AKC = 3.74 ppm (2H) ZB-p = 7.33 ppm (2H) Formate = 8.47 ppm (1H)
BuOH	600 μL of Solution + capillary of DMSO-d ₆	31	AKC = 3.62 ppm (2H) ZB-p = 7.46 ppm (2H) Formate = 8.48 ppm (1H)
iPrOH	300 μL of DMSO + 400 μL of Solution	36	AKC = 4.47 ppm (1H) ZB-p = 7.74 ppm (2H) Formate = 8.50 ppm (1H)
H ₂ O*	300 μL of DMSO + 400 μL of Solution	50	AKC = 159.46 ppm (1C) ZB-p = 35.67 ppm (2C) Formate = 8.30 ppm (1H)

Table S1: Sample preparation method for NMR and d1 used.

* The spectra for determining the percentage of CO₂ capture as bicarbonate were carried out using inversed gate decoupling ¹³C NMR spectra.



The observed peaks were assigned as follows:

Peaks at 1.05 (t), 3.46 (q) and 4.80 (s) ppm: Solvent signals;

Doublets at 7.33 and 6.87 ppm: CH groups of the para-substituted aromatic ring; Singlet at 7.67 ppm:CH of the imidazole ring.

Singlet at 3.69 ppm: CH₃ group of **ZB-p**.

Triplet at 3.74 ppm: Alkyl carbonate anion derived from ethanol.



The observed peaks were assigned as follows:

Peaks at 0.70 (q), 1.15 (m), 1.23 (m), 3.32 (t) and 5.38 (s) ppm Solvent signals; Doublets at 7.01 (dd) and 6.74 ppm (dd) correspond to the CH of the *para*-substituted aromatic ring;

Singlet at 7.46 ppm:CH of the imidazole ring.

Singlet at 3.52 ppm: CH₃ group of **ZB-p**.

Triplet at 3.62 ppm: Alkyl carbonate anion derived from *n*-butanol.



capture reaction using **ZB**-*p* in water.

No Solvent signals from water, only 39.52 ppm from DMSO-D₆;

Peaks at 107.77 ppm: C quaternary of the *para*-substituted aromatic ring: Peaks at: 118.16 and 132.08 ppm CH groups of the para-substituted aromatic ring;

Peak at 122.55 ppm: CH of the imidazole ring

Peak at 145.78 ppm: C quaternary of the imidazole ring.

Peak at 35.66 ppm: CH₃ group of **ZB-p**.

Peak at 165.57 ppm: C-O of the *para*-substituted aromatic ring Bicarbonate peak at 159.46 ppm.



isopropanol.

The observed peaks were assigned as follows:

Peaks at 1.03 (d) and 3.80 (hep) and 5.03 (s) ppm: Solvent signals;

Doublets at 7.31 (dd) and 6.86 (dd) ppm correspond to the CH of the *para*-substituted aromatic ring;

Singlet at 7.74 ppm: CH of the imidazole ring.

Singlet at 3.69ppm: CH₃ group of **ZB-p**.

Heptet at 4.46 ppm: Alkyl carbonate anion derived from isopropanol.



Figure S13: Heteronuclear HSQC correlation map of the **ZB**-*p* sample solution in isopropanol after CO₂ capture. Positive (CH₃ and CH) are shown in black, and negative (CH₂) are shown in red.



Figure S14: Heteronuclear HMBC correlation map of the *ZB-p* sample solution in isopropanol after CO_2 capture.

4.3.2 Standard Procedure for Hydrogenation Reactions of Different Alcohols and Water

6.32 mg (10 µmol) of the *cis*-[Ru(dppm)₂Cl₂] were placed in the glass liner of the high-pressure reactor. The autoclave was closed, and 4 mL of the CO₂-captured solution were transferred into the reactor using a syringe through a ball valve. The reactor was then filled with 10 bar of H₂. The reactor was placed in a pre-heated silicon oil bath at a temperature such that the internal equilibrium temperature of the solution inside the reactor reached 50 °C and continuously stirred at 600 rpm with a PTFE-coated magnetic bar. After the reaction period, the reactor was removed from the oil bath, and the H₂ pressure was released and the reactor was cooled in an ice bath for 30 minutes. Conversion and yield were determined from the ¹H NMR spectra, with d₁ and the signals reported in Table S1, following the assumptions and equations (3 and 4) described in section 4.1.2.









isopropanol.

•



Figure S19: HSQC heteronuclear correlation map of the **ZB-**p solution sample in isopropanol after AKC hydrogenation. Positive (CH₃ and CH) in black and negative (CH₂) in red.



Figure S20: HMBC heteronuclear correlation map of the **ZB-***p* solution sample in isopropanol after AKC hydrogenation.

4.4 Standard Procedure for Reactions in Isopropanol with Different Bases 4.4.1 CO_2 Capture

14.0 mmol of base were dissolved in 14 mL of isopropanol in a Schlenk flask under flask under an inert argon atmosphere. The gases were removed by cycles of argon and the flask maintained under an argon atmosphere. CO_2 was then added under vigorous stirring with a PTFE-coated magnetic stirring bar (1200 rpm). The CO_2 partial pressure was kept constant at 0.6 bar using a gas reservoir and pressure regulator. The reaction was considered complete when no further pressure change was observed in the reservoir, which occurred after approximately 45 minutes. After this period, the system was transferred to the Schlenk line, purged with argon, and a 400 µL aliquot of the reaction was diluted with 300 µL of DMSO-*d6* for ¹H NMR analysis. The system was then refilled with 1 bar of CO_2 and stored for subsequent catalytic hydrogenation reactions. The amount of CO_2 captured was quantified by ¹H NMR using equation (1) from section 4.1.1, and the d1 and signals used for quantification are outlined in Table S2.

Base	d ₁ (s)	Picos Utilizados na Quantificação
		AKC = 4.45 ppm (2H)
ZB-m	50	ZB- <i>m</i> = 7.79 ppm (2H)
		Formate = 8.54 ppm (1H)
		AKC = 4.45 ppm (2H)
DBU	30	CH ₂ = 1.89 ppm (2H)
		Formate = 8.48 ppm (1H)
		AKC = 4.45 ppm (2H)
TEA	1	CH ₂ = 2.40 ppm (6H)
		Formate = Not detected
		AKC = 4.45 ppm (2H)
MDEA	1	CH ₂ = 2.43 ppm (4H)
		Formate = Not detected
		AKC = 4.45 ppm (2H)
TMEDA	1	CH ₃ = 2.12 ppm (12H)
		Formate = Not detected

Table S2: Relaxation delay and peak utilized in NMR



isopropanol.

The observed peaks were assigned as follows:

Peaks at 1.03 (d), 3.80 (hep) and 5.03 (s) ppm: Solvent signals;

Peaks at 7.17 (t), 6.81 ppm (d), 6.71 ppm (s), and 6.52 ppm (d) correspond to the CH of the meta-substituted aromatic ring;

Singlet at 7.80 ppm: CH of the imidazole ring.

Singlet at 3.70 ppm: CH₃ group of **ZB-m**.

Heptet at 4.45 ppm: Alkyl carbonate anion derived from isopropanol.



isopropanol during CO₂ capture in DMSO-d₆.

The observed peaks were assigned as follows: Peaks at 1.03 (d), 3.80 (hep) and 4.58 (br s) ppm: Solvent signals; Singlet at 2.28: CH₃, Peaks at 2.43 ppm (t): CH₂-N and 3.47 ppm (t): CH₂-OH There no peak from Alkyl carbonate anion derived from isopropanol near 4.50 ppm.



isopropanol during CO₂ capture in DMSO-d₆.

The observed peaks were assigned as follows: Peaks at 1.03 (d), 3.80 (hep) and 4.52 (br s) ppm: Solvent signals; Triplet at 0.92 ppm: CH_3 ,

Quadruplet at 2.41 ppm: CH₂-N

There no peak from Alkyl carbonate anion derived from isopropanol near 4.50 ppm.



isopropanol during CO₂ capture in DMSO-d₆.

The observed peaks were assigned as follows:

Peaks at 1.03 (d), 3.80 (hep) and 4.52 (br s) ppm: Solvent signals;

Singlet at 2.11 ppm: Four CH₃,

Singlet at 2.29 ppm: CH₂-N

There no peak from Alkyl carbonate anion derived from isopropanol near 4.50 ppm.



Figure S25: ¹H NMR spectrum of the 1.0 mol L⁻¹ DBU solution in isopropanol during CO_2 capture in DMSO-d₆.

4.4.2 Standard procedure for hydrogenation reactions of different bases in isopropanol

12.6 mg (20 µmol) of the catalytic precursor *cis*-[Ru(dppm)₂Cl₂] were placed in the glass liner of the high-pressure reactor. The autoclave was closed, and 4 mL of the CO₂-captured solution were transferred into the reactor using a syringe through a ball valve. The reactor was then filled with 10 bar of H₂. The reactor was placed in a pre-heated silicon oil bath at a temperature such that the internal equilibrium temperature of the solution inside the reactor reached 50 °C and continuously stirred at 600 rpm with a PTFE-coated magnetic bar. After the reaction period, the reactor was removed from the oil bath, and the H₂ pressure was released and the reactor was cooled in an ice bath for 30 minutes. Conversion and yield were determined from the ¹H NMR spectra, with d₁ and the signals reported in Table S2, following the assumptions and equations (3 and 4) described in section 4.1.2.



Figure S26: ¹H NMR spectrum of **ZB**-*m* solution in isopropanol after hydrogenation in DMSO-d₆.

The observed peaks were assigned as follows:

Peaks at 1.03 (d), 3.80 (hep) and 5.03 (s) ppm: Solvent signals;

Peaks at 7.17 (t), 6.81 ppm (d), 6.71 ppm (s), and 6.52 ppm (d) correspond to the CH of the *meta*-substituted aromatic ring;

Singlet at 7.80 ppm: CH of the imidazole ring.

Singlet at 3.70 ppm: CH₃ group of **ZB-m**.

Heptet at 4.45 ppm: Alkyl carbonate anion derived from isopropanol.

Singlet at 8.54 ppm: H of formate specie.



Figure S27: ¹H NMR spectrum of MDEA solution in isopropanol after hydrogenation in DMSO-d $_{6}$.

The observed peaks were assigned as follows:

Peaks at 1.03 (d), 3.80 (hep) and 4.58 (br s) ppm: Solvent signals; Singlet at 2.28: CH₃, Peaks at 2.43 ppm (t): CH₂-N and 3.47 ppm (t): CH₂-OH There no peak from Alkyl carbonate anion derived from isopropanol near 4.50 ppm.

Peak at 8.44 ppm (s) corresponds to the proton of the formate species.



hydrogenation in DMSO-d₆.

4.5 *In-situ* ¹H NMR spectra of CO₂ capture using MDEA.

In a high-pressure cell with an integrated needle valve and zirconia tube, 450 μ L of a 1.0 mol L⁻¹ MDEA solution was placed along with a capillary of DMSO-*d*₆. The cell was purged and pressurized with 1.6 bar of CO₂, and the pressure was maintained constant for 72 hours. The experiments were conducted on a Varian 500 MHz spectrometer. After the experiments, the pressure was released from the cell, and the solution was transferred to a glass NMR tube, to which 300 μ L of DMSO-d₆ was added.



solution in isopropanol after 72 hours of reaction under 1.6 bar of CO_2 , with $d_1 = 60s$ and 36 scans.

The observed peaks were assigned as follows: Peaks at 1.03 (d), 3.80 (hep) and 4.58 (br s) ppm: Solvent signals; Singlet at 2.28 (s): CH₃, Peaks at 2.43 ppm (t): CH₂-N and 3.47 ppm (t): CH₂-OH; Heptet from Alkyl carbonate anion derived from isopropanol at 4.48 ppm.



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm Figure S30: Inversed gate decoupling ¹³C NMR spectrum at 500 MHz of the 1.0 mol L⁻¹ MDEA solution in isopropanol after 72 hours of reaction under 1.6 bar of CO₂, d₁ = 25s and 10240 scans..

The observed peaks were assigned as follows: Peaks at 1.03 (d), 3.80 (hep) and 4.58 (br s) ppm: Solvent signals; Peak at 124.27 ppm: CO₂; Peak at 41.48 ppm: CH₃; Peaks at 58.08 ppm: CH₂-N and 59.06 ppm: CH₂-OH; Peak from Alkyl carbonate anion derived from isopropanol at 158.42 ppm.



Figure S31: ¹H NMR spectrum at 500 MHz of the 1.0 mol L⁻¹ MDEA solution in isopropanol after releasing CO₂ pressure, with $d_1 = 60s$ and 6 scans.

The observed peaks were assigned as follows:

Peaks at 1.03 (d), 3.80 (hep) and 4.58 (br s) ppm: Solvent signals; Singlet at 2.28 (s): CH₃, Peaks at 2.43 ppm (t): CH₂-N and 3.47 ppm (t): CH₂-OH; There no peak from Alkyl carbonate anion derived from isopropanol near 4.48 ppm.



Figure S32: ¹³C NMR at spectrum at 500 MHz of the 1.0 mol L⁻¹ MDEA solution in isopropanol after releasing CO₂ pressure. The acquisition parameters were $d_1 = 25s$ and 1024 scans.

The observed peaks were assigned as follows: Peaks at 1.03 (d), 3.80 (hep) and 4.58 (br s) ppm: Solvent signals; Peak at 41.48 ppm: CH_3 ; Peaks at 58.08 ppm: CH_2 -N and 59.06 ppm: CH_2 -OH; There no peak at 124.27 ppm and 158.42 ppm of CO₂ and Alkyl carbonate anion derived from isopropanol.

4.6 Hydrogenations with fixed alkyl carbonate concentration and variation of catalyst to AKC percentage.

The amount of alkyl carbonate for the reactions was fixed at 5.3 mmol dissolved in 14 mL of solvent. 14.0 mmol (**ZB-***p*), 10.5 mmol (**ZB-***m*), or 8.82 mmol (DBU) were dissolved in 14 mL of isopropanol in a Schlenk flask under an inert argon atmosphere. The gases were removed by cycles of argon and the flask maintained under an argon atmosphere. CO_2 was then added under vigorous stirring with a PTFE-coated magnetic stirring bar (1200 rpm). The CO_2 partial pressure was kept constant at 1.6 bar using a gas reservoir and pressure regulator. The reaction was considered complete when no further pressure change was observed in the reservoir, which occurred after approximately 45

minutes. After this period, the system was transferred to the Schlenk line, purged with argon, and a 400 μ L aliquot of the reaction was diluted with 300 μ L of DMSO*d6* for ¹H NMR analysis. The system was then refilled with 1 bar of CO₂ and stored for subsequent catalytic hydrogenation reactions. The amount of CO₂ captured was quantified by ¹H NMR using equation (1) from section 4.1.1, and the d1 and signals used for quantification are outlined in Table S1 and S2.

A quantity of 3.2 mg (5 μ mol, 0.25% mol percent) of the *cis*-[Ru(dppm)₂Cl₂] was placed in the glass liner of the high-pressure reactor. The autoclave was closed, and 4 mL of the CO₂-captured solution were transferred into the reactor using a syringe through a ball valve, and the reactor was purged with argon. For the 0.1% mol percent experiments, 4.7 mg (7.4 μ mol) of *cis*-[Ru(dppm)₂Cl₂] were dissolved in 14 mL of the alkyl carbonate solution containing 0.53 mol per mL of solvent in an amber Schlenk. Then 4 mL of the solution were transferred into the reactor using a syringe through a ball valve, and purged with Ar.

The reactor was then filled with 10 bar of H_2 , and was placed in a pre-heated silicon oil bath at a temperature such that the internal equilibrium temperature of the solution inside the reactor reached 50 °C and continuously stirred at 600 rpm with a PTFE-coated magnetic bar. After the reaction period, the reactor was removed from the oil bath, the H_2 pressure was released, and the reactor was cooled in an ice bath for 30 minutes. Conversion and yield were determined from the ¹H NMR spectra, with d₁ and the signals reported in Table S2, following the assumptions and equations (3 and 4) described in section 4.1.2.

4.7 Procedure for Capture and Indirect Hydrogenation to Methanol Using ZBp

4.71 g (25 mmol) of **ZB-p** were dissolved in 50 mL of anhydrous ethylene glycol in a Schlenk flask under an inert argon atmosphere, using a magnetic stir bar for mixing. The flask was subjected to vacuum-argon cycles to remove residual gases, and the system was maintained under vacuum with its mass being determined. CO₂ was introduced into the system under vigorous stirring (1200 rpm), with the CO₂ pressure controlled at 1.6 bar using a gas reservoir and a pressure regulator. The reaction was considered complete when no further pressure change was observed in the reservoir, which occurred after approximately 45 minutes. The system was then connected to the Schlenk line, evacuated until no bubbling was observed for approximately 5 minutes, and kept under vacuum for a second mass measurement. Following this, the Schlenk flask was refilled with 1 bar of CO₂ and stored for subsequent catalytic hydrogenation reactions. The amount of chemisorbed CO₂ was determined through gravimetric analysis, comparing the system's mass before and after capture, and corroborated by ¹H NMR spectroscopy. For NMR analysis, a 400 µL aliquot of the solution was diluted with 300 μ L of DMSO- d_6 .

For the hydrogenation, the 24.62 mg (42 μ mol) Ru-MACHO-BH was charged in the reactor inside an Ar filled glove box. Outside the glovebox, 15 mL of the CO₂-captured solution were transferred to the reactor under an inert atmosphere. The reactor was pressurized with 70 bar of H₂. The reaction mixture was stirred with a magnetic bar at approximately 800 rpm, and heating was initiated in a Parr Multi-Reactor Series 5000. After 20 hours, the reactor was cooled in an ice bath for 30 minutes, and then the pressure was slowly released.

The conversion and yield were calculated from the ¹H NMR spectra using the assumptions described in section 4.1.2. The equation used to calculate the methanol yield was:

$$Yield (\%) = \left(\frac{2*A_{Methanol}}{3*A_{0AKC}}\right) * 100$$
(6)

 A_{0AKC} = The peak area at 3.75 ppm corresponds to the formation of alkyl carbonate (AKC) post-capture

 $A_{methanol}$ = peak area at 3.19 ppm corresponding to the CH₃ of methanol.





The observed peaks were assigned as follows: Peaks at 3.42 and 4.87 ppm: Solvent signals; Doublets at 7.32 and 6.86 ppm: CH groups of the para-substituted aromatic ring; Singlet at 7.52 ppm: CH of the imidazole ring. Singlet at 3.62 ppm: CH₃ group of **ZB-p**. Triplet at 3.75 ppm: Alkyl carbonate anion derived from ethylene glycol. Singlet at 8.36 ppm: H of formate specie and singlet at 3.17 ppm: CH₃ of MeOH.



Figure S34: Hydrogenation reaction conversion and formate yield profile at 5 bar of H₂. Conditions: ~0.5 mol L⁻¹ **ZB-p**, 0.8% mol *cis*-[Ru(dppm)₂Cl₂], 50°C.



Figure S35: Hydrogenation reaction conversion and formate yield profile at 10 bar of H₂. Conditions: ~0.5 mol L⁻¹ **ZB-p**, 0.8% mol *cis*-[Ru(dppm)₂Cl₂], 50°C.



Figure S36: Hydrogenation reaction conversion and formate yield profile at 70 bar of H₂. Conditions: ~0.5 mol L⁻¹ **ZB-p**, 0.8% mol *cis*-[Ru(dppm)₂Cl₂], 50°C.

Entry	Base	CO ₂ capture (%) ^a	mmol CO₂ captured (¹ H RMN)	mmol CO ₂ capturaed (Gravimetric) ^c	Solvent
1	ZB-p⁵	70	4,9	4,7	EG
2	ZB-p⁵	71	5,0	-	EtOH
3	ZB-p	53	7,4	-	iPrOH
4	ZB-p⁵	70	4,9	-	BuOH
5	ZB-p⁵	70	4,9 ^d	-	H ₂ O
6	ZB-m	70	9,8	-	iPrOH
7	MDEA	Not detected	-	-	iPrOH
8	TEA	Not detected	-	-	iPrOH
9	TMEDA	Not detected	-	-	iPrOH
10	DBU	86	12,0	-	iPrOH

Table S3: Summary of carbon dioxide capture data.

Capture conditions: 14.0 mmol of base dissolved in 14 mL of solvent, 1.6 bar of CO₂, stirring at 1200 rpm, 45 minutes, ambient temperature. ^a Calculated by NMR, ^b 7.0 mmol of **ZB-p**. CO₂ pressure of 1.6 bar. ^c The only solvent that could be determined gravimetrically was EG, as it does not evaporate under high vacuum. ^d Determined by quantitative ¹³C NMR.

Entry	Catalyst (mol %)	Time (h)	T (°C)	Conversion ^a (%)	Formate Yield ^a (%)
1	-	1	50	6	0
2	<i>cis</i> -[Ru(dppm) ₂ Cl ₂] (0.80)	20	70	100 ± 0	100 ± 5
3	<i>cis</i> -[Ru(dppm) ₂ Cl ₂] (0.80)	16	70	100 ± 1	87 ± 1
4	<i>cis</i> -[Ru(dppm) ₂ Cl ₂] (0.80)	1	70	100 ± 7	81 ± 7
5	<i>cis</i> -[Ru(dppm) ₂ Cl ₂] (0.80)	1	50	52 ± 5	37 ± 5
6	cis-[Ru(dppm) ₂ Cl ₂] (0.80)	2	50	61 ± 9	45 ± 7
7	<i>cis</i> -[Ru(dppm) ₂ Cl ₂] (0.80)	1	40	53 ± 4	39 ± 9
8	Ru-SNS (0.80%)	2	50	34 ± 5	7 ± 3
9	Ru-MACHO-BH (0.8)	20	140	100 ± 0	66 ± 2 ^b

Table S4 Hydrogenation of alkyl carbonate using **ZB-p** dissolved in EG

General conditions: ~0.5 mol L^{-1} *ZB-p* in ethylene glycol, 70 bar H_2 pressure, 600 rpm stirring. ^aCalculated by ¹H NMR. ^bMethanol yield.

Entry	Base	Catalyst (%)	Conversion (%) ^a	Yield (%) ^a	TON	TOF (h ⁻¹)
1	ZB-p ^a	-	35 ± 4	-	-	-
2	ZB-p	0,1	46 ± 2	14 ± 2	135	232
3	ZB-p	0,25	92 ± 2	97 ± 2	386	662
4	ZB-p	0,5	95 ± 2	97 ± 4	194	332
5	ZB-mª	-	11 ± 2	-	-	-
6	ZB-m	0,1	54 ± 0	9 ± 3	90	155
7	ZB-m	0,25	87± 2	87 ± 2	349	599
8	ZB-m	0,5	90 ± 2	96 ± 2	192	329
9	DBUª	-	5 ± 2	-	-	-
10	DBU	0,1	34 ± 4	16 ± 3	159	273
11	DBU	0,25	81 ± 3	79± 7	315	540
12	DBU	0,5	88 ± 3	90 ± 2	180	309

Table S5: Data for catalytic hydrogenation of alkyl carbonates in isopropanol at 50 °C using *cis*-[Ru(dppm)₂Cl₂].

Reaction conditions: 0.53 mol of alkyl carbonate (AKC) per mL of isopropanol, 10 bar H_2 , 50 °C, 35 min, and agitation at 600 rpm. ^a Experiment without H_2 pressure.

Entry	Sorbent	Sorbent×CO ₂	P H ₂ (bar)	Product	Solvent	T (°C)	Catalyst	TON	TOF (h ⁻¹)	Recycling	Ref
1			40	Formate	MeOH	60	RhCl ₃ .3H ₂ O + CyPPh ₂	726	45,4	No	5
2		$\begin{array}{c} H_{N+} (0) \\ N \\ H_{N+} (0) \\ H_{N+} $	40	Formate	MeOH	60	RhCl₃.3H₂O + DPEphos	323	20,2	Base	6
3	DBU	[DBUH]⁺ MeOCO₂⁻	20	Formate and methyl formate	MeOH	140	RuCl ₂ (PPh ₃) 3	5100	127,5	No	7
4	0 N ⁻ K ⁺ 0		40	Formate	PEG 150	80	RhCl ₃ .3H ₂ O + PPh ₃	67,3	2,8	Base	8
5	H N OH		60	MeOH	THF	135	RuHCI(CO)(BPy- ^t PNN)	140	7,4	No	9
6	(CH₃)₂NH	[(CH ₃) ₂ NH ₂][OOC N(CH ₃) ₂]	50	MeOH, DMF and [(CH ₃) ₂ NH ₂][H COO]	THF	95 to 155	Ru- MACHO-BH + K3PO4	306 +270	8,5 (MeOH)	No	10
7	H_2N (N) H_1NH_2	Carbamate of PEHA	70	Formate, formamide and MeOH	2-MeTHF	145	Ru- MACHO-BH	520	7,2	Complete	11
8		CsHCO3	90	Formate	H ₂ O	100	[lr(cod)(emi m)(mtppms) +mtppts-Na ₃	80	1,3 x 10 ⁴	No	12

Table S6: Results found the literature of ICCU by catalytic hydrogenation to formate or methanol using molecular catalysts.

9	H ₂ N NH ₂ OH	Mixture of carbamate:bicarb onate (1:4)	80	Formate	H ₂ O/THF 1:1 V/V	145	Ru- MACHO-BH	54998	4583,2	No	13
10		NH2 N N I HCO3-/CO3 ²⁻	50	Formate	H ₂ O	120	[lr] ^{IMD}	19171	1598	Complete	14
11	[TBA][OH]	[TBA][HCO₃]	30	Formate	THF/H ₂ O	100	Ru Nanoparticle s	157	6,5	Catalyst	15
12	кон		70	MeOH	EG	140	Ru- MACHO-BH	200	10,0	No	16
13	$H_2 N \frown \begin{pmatrix} H \\ N \\ \end{pmatrix}_4 N H_2$	Carbamate of PEHA	50	MeOH	Triglyme	155	Ru- MACHO-BH	213	3,9	Complete	17
14		/N N _F H HCO ₃ -/CO ₃ ²⁻	50	Formate	H₂O/2- MeTHF	55	Ru- MACHO-BH	1440	685	Complete	18
15			70	MeOH	EG	140	Ru- MACHO-BH	184	2,6	Base	19
16	кон	KHCO ₃	50	Formate	H ₂ O/2- MeTHF	80	RuHCIPNP ^t Bu(CO)	2710	>5420	Complete	20
17	(PO)		60	MeOH	THF	140	Ru-MACHO	8148	509,3	No	21

18	PEHA functionaliz ed with PO	Carbamate of PEHA-1PO	80	MeOH and formate	Triglyme	145	Ru- MACHO-BH	158	7,9	No	22
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[CyPPh₂] = Cyclohexyldiphenylphosphine; [DPEphos] = Bis(2-diphenylphosphino)phenyl)ether; PEG-150 = polyethylene glycol 150; PEHA = pentaethylenehexamine, [Ir(cod)(emim)(mtppms)]+ mtppts-Na₃ as cod = 1,5 cyclooctadiene; emim = 1-ethyl-3methylimidazol-2-ylidene); mtppms = diphenyl phosphinobenzene-3-sulfonate; mtppts-Na₃ = tris(meta-sulfonatophenyl)phosphine trisodium salt. [TBA][OH] = Tetrabutylammonium hydroxide.

5. ZB and Catalyst Recyclability Tests

5.1 Ion-Exchange Resin

The test was performed using the reaction mixture obtained after a standard hydrogenation reaction (see Section 4.4.2 for details) in isopropanol, with *cis*- $[Ru(dppm)_2Cl_2]$ as the catalyst and ZB-p. Working under reduced light conditions and using amber flasks, 10 mL of the solution containing dissolved formate were passed through an Amberlyst 26 OH ion-exchange resin column, which had been previously thoroughly washed with isopropanol (10 mL, 0.8 meq OH⁻/mL, 10 meq OH⁻). The resulting suspension was stirred at room temperature for 20 minutes, and the HCOO⁻/OH⁻ exchange was confirmed by ¹H NMR.

Afterward, the solution was filtered via cannula and transferred into an amber Schlenk flask. CO₂ was captured using the standard procedure described in SI Section 4.4. Hydrogenation was then conducted using the standard procedure, without adding any additional catalyst.

5.2 Extraction of ZB.HCOOH adducts using water.

10 mL of the reaction mixture obtained after a standard hydrogenation (section 4.4.2) in *n*-butanol using *cis*-[Ru(dppm)₂Cl₂] as the catalyst and ZB-p as the base were extracted three times with 5 mL of water. Next, 10 mmol (1.88 g) of regenerated ZB-p were dissolved in the *n*-butanol phase, and the standard CO₂ capture and hydrogenation reactions were carried out as described in sections 4.4.1 and 4.4.2 with *n*-butanol as solvent.

Entry	Catalyst	Base Recovery	Solvent	1 st CO ₂ Capture (%)	HCOO ⁻ Yield 1 st run (%)	2 nd CO ₂ Capture (%)	HCOO ⁻ Yield 2 nd run (%)
1	<i>cis-</i> [Ru(dppm) ₂ Cl ₂]	lon Exchange Resin	<i>i</i> -PrOH	52	97	52	1 ≤
2	<i>cis-</i> [Ru(dppm) ₂ Cl ₂]	Extraction	<i>n</i> -BuOH	70	78	70	1 ≤

Table S7: ZB and Catalyst reuse attempts.

6. References

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