Ru-nitrosyl complex salts as efficient catalysts for the reversible CO_2 hydrogenation/FA dehydrogenation in ionic liquids

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ABSTRACT: We demonstrate that bench-stable ruthenium-PNP nitrosyl complex salts with different counteranions (Cl^-, BF_4^-, BPh_4^-, PF_6^-, and OTs^-) and a ruthenium-POP nitrosyl complex are competent (pre-)catalysts for the CO_2 hydrogenation to formic acid (FA) at low temperature in ionic liquids. Only little effect of variation of the counteranion was observed and weakly basic ionic liquids such as EMIM OAc, BMIM OAc, and EMIM HCO_2 were suitable for this transformation, affording conversions up to 94 mol% formic acid compared to the ionic liquid (FA/IL) and turnover numbers (TONs) up to 1305. Importantly, the same catalytic system was also efficient for the dehydrogenation of formic acid back to CO_2 and H_2, affording conversions up to >95% (949 TON) after 3 h at 95 °C. To investigate the application of such protocol for hydrogen storage and transportation purposes, hydrogenation/dehydrogenation cycles were

performed, showing that this new catalytic system can promote up to 10 reversible CO_2 hydrogenation/FA dehydrogenation cycles before losing its activity.

Introduction

Carbon capture and utilization (CCU) technologies consist of a set of strategies that allow for the capture and use of CO_2 from gas stream feedstock for making industrially relevant products such as commodity chemicals, fuels, and building materials. Such technologies aim at reducing the world´s dependency on fossil resources and, at the same time, complement the large-scale efforts to prevent greenhouse gas emissions.[1] Despite its main role in the rapid and severe climate changes observed over the last century, CO_2 is an abundant, renewable, nontoxic, and economical carbon source.[1,2] It can be converted into a set of highly valuable chemicals, such as carbonates, carboxylic acids, amides, formic acid and methanol.[2] Among them, formic acid (FA) stands out as a promising candidate for the long-term, safe, and practical storage of hydrogen (4.4 wt% H), connecting renewable energy and hydrogen fuel cells, and potentially closing an ideal carbon-free energy cycle.[3] The majority of already reported catalytic protocols for the reversible CO_2/FA interconversion rely on the use of additives and volatile solvents, or high pressures of H_2, rendering these systems impractical for application and scaling up for, for example, rechargeable hydrogen storage and release purposes. Other drawbacks are harsh reaction conditions often used and the necessity of an inert atmosphere, due to the intrinsic nature of the catalysts employed (Chart 1a-e).[4] Aiming to overcome such limitations, our group recently developed a protocol employing a Ru-PNP pincer catalyst in ionic liquids (IL) for the additive- and volatile solvent-free, reversible CO_2/FA interconversion under very mild conditions showing high compatibility with continuous-flow conditions (Chart 1f).[5] Driven by the achievements in this first work, we embarked on a

search for even more practical and applicable systems, which include the screening for more reactive and stable (preferentially bench-stable) catalysts.

Widely known by their medicinal application as nitric oxide donors,[6] nitrosyl complexes have been found suitable for catalytic applications over the last two decades.[7] In catalysis, the nitrosyl ligand remains bonded to the metal center, acting as a stronger electron-withdrawing ancillary ligand than the carbonyl, or as a non-innocent ligand, changing the oxidation state of the metal center through its characteristic bent/linear interconversion.[6a]

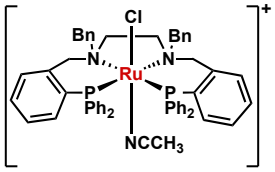
Although the synthesis and characterization of a variety of nitrosyl complexes of base- and precious metals have appeared in literature, most catalytic protocols described to date focus on the hydrogenation,[7a-c] hydrosilylation,[7h] or transfer hydrogenation[7d,e] of carbonyls and alkenes, and on dehydrogenative couplings.[7g] The only exception to this trend are the works from Plietker and co-workers, who employ the iron nitrosyl complex $[Bu_4N][Fe(CO)_3(NO)]$ and its derivative $[Bu_4N][Fe(CO)(PPh_3)_2(NO)]$ as efficient catalysts for a large number of organic transformations, such as allylic substitutions, Michael additions, C-H aminations and cyclotrimerizations.[8] Narrowing down to pincer nitrosyl complexes exhibiting catalytic activity, there are very few examples reported in literature, all of them in the aforementioned categories.[9]

Recently, in a search for alternative catalysts to the well-established Ru-MACHO and its derivatives,[10] our group embarked on the synthesis and characterization of a set of bench-stable Ru-PNP-nitrosyl complex salts (PNP = $(^{i}Pr_2PCH_2CH_2)_2NH$), and their application as (pre-)catalysts in hydrogen-involving reactions. The promising catalytic activity observed in our preliminary investigation prompted us to test such family of catalysts in the CO_2 hydrogenation and FA dehydrogenation, adapting our recently described approach. Besides developing a more efficient and practical protocol, our investigation also aimed to study in which extension the nature

of the (pre-)catalyst´s counteranion affects the reaction outcome, which might be particularly relevant since the reaction medium is a salt as well. Herein, we present the first application of a nitrosyl complex for the mild, additive- and volatile-solvent-free, reversible CO_2/FA interconversion (Chart 1g).

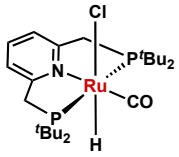
Chart 1. Previously reported catalytic systems for the CO_2/FA interconversion that do not require pH adjustment or any other additional step.

(a) 2014, Plietker et al.[4a]



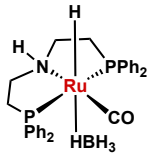
Hydrogenation: Dry ice/70 bar H_2, DBU/Toluene, 100 ºC, 2 h
Dehydrogenation: 100 ºC, 2 h
5 cycles

(b) 2014, Pidko et al[4b]



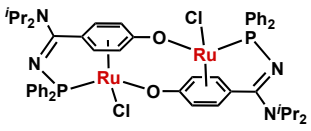
Hydrogenation: 40 bar H_2/CO_2 (1:1), DMF/DBU (30/5 mL), 65 ºC, up to 3 h
Dehydrogenation: 90 ºC, up to 1 h
5 cycles

(c) 2015, Czaun, Prakash, Olah et al[4c]



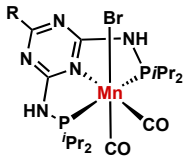
Hydrogenation: 75 bar H_2/CO_2 (3:1), Dioxane/H_2O (20/10 mL), NaOH (20 mmol), 70 ºC, 5 h
Dehydrogenation: 70 ºC, 5 h
5 cycles

(d) 2023, Igau, Fischmeister et al[4d]



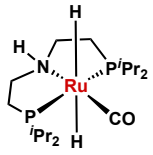
Hydrogenation: 60 bar H_2/CO_2 (1:1), DMSO (3 mL), 60 ºC, 16-21 h
Dehydrogenation: 90 ºC, up to 2.5 h
4 cycles

(e) 2023, Junge, Sponholz, Beller et al[4e]



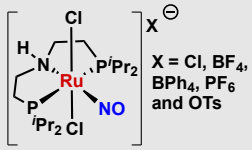
Dehydrogenation: FA/Lys (1:1), THF/H_2O (5/5 mL), 90 ºC, 12 h
Capture: CO_2 (20 bar for 0.5 h or 2 bar for 6 h)
Hydrogenation: H_2 (80 bar), 85ºC, 12 h
10 cycles

(f) 2023, Das, Nielsen et al[5]



Hydrogenation: 20 bar H_2/CO_2 (20:10), EMIM OAc (2 mL), 25 ºC, 18 h or 72 h
Dehydrogenation: 95 ºC, 4 h
13 cycles

(g) This work



X = Cl, BF_4, BPh_4, PF_6 and OTs

Hydrogenation: 20 bar H_2/CO_2 (20:10), EMIM OAc (1 mL), 30 ºC, 18 h or 72 h
Dehydrogenation: 95 ºC, 4 h
10-12 cycles

First report of a reversible CO_2 hydrogenation catalyzed by pincer nitrosyl complexes

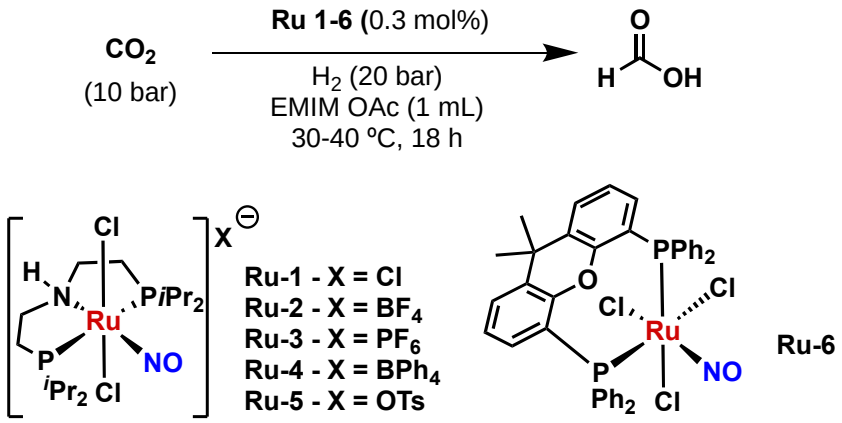
Results and discussion

CO_2 Hydrogenation

We started our investigation testing the activity of the PNP-Ru-NO salts **Ru-1** and **Ru-2**, using 1-ethyl-3-methylimidazolium acetate (EMIM OAc) as solvent, due to its well-known capability of

chemisorbing CO_2 (Table 1).[11] To our delight, both complexes (0.02 M in 1 mL of EMIM OAc, 0.3 mol% loading based on the amount of loaded CO_2) promoted the desired transformation, affording 85 mol% and 87 mol%, respectively, of FA in IL (85% and 87% FA/IL) when subjected to 30 bar of CO_2/H_2 (10:20 bar) at 40 °C for 18 h (Table 1, entries 1-2). This corresponds to 75% and 77% yields, respectively, calculated from the amount of CO_2 available under the given conditions (see Supporting Information for details). Lowering the temperature to 30 °C does not substantially affect the catalytic activity of the system (Table 1, entries 3-4) and we therefore decided to continue the screening at this temperature. We then tested PNP-Ru-NO salts **Ru-3**, **Ru-4**, and **Ru-5**, which all performed very similar to **Ru-2**, affording up to 94 mol% FA/IL (Table 1, entries 5-7). A POP-Ru-NO complex (**Ru-6**) showed much inferior reactivity (52 mol% FA/IL) under the same conditions employed to the PNP analogues (Table 1, entry 8). However, a significant increase in the formic acid formation (70 mol% FA/IL) was observed when the reaction temperature was increased to 40 °C (Table 1, entry 9). A control experiment using the precursor of all the pincer Ru-NO complexes, $RuCl_3(NO)\cdot H_2O$, did not show any reactivity under the optimal conditions established at this stage of the study (Table 1, entry 10).

Table 1. Initial temperature and catalyst screening for CO_2 Hydrogenation to FA.[a]



Entry	Catalyst [mol%][b]	T [°C]	FA/IL [mol%][c]	Yield [%][b]	TON
1	**Ru-1**	40	85	75	268
2	**Ru-2**	40	87	77	275
3	**Ru-1**	30	78	69	247
4	**Ru-2**	30	88	79	282
5	**Ru-3**	30	93	82	293
6	**Ru-4**	30	87	77	275
7	**Ru-5**	30	94	83	297
8	**Ru-6**	30	52	46	164
9	**Ru-6**	40	70	62	222
10	$RuCl_3(NO)\cdot H_2O$[d]	30	-	-	-

[a] Standard reaction conditions: **Ru-1** – **Ru-6** (0.02 mmol), EMIM OAc (1 mL), 10:20 bar CO_2/H_2, 18 h. [b] Based on the amount of CO_2. [c] Determined by ^{1}H-NMR. [d] 0.6 mol%.

With these promising results in hand, we further investigated different parameters such as catalyst loading, overall pressure, CO_2/H_2 pressure ratio and the nature of IL. The system was found to be highly responsive to the variation of the reaction parameters, as shown in Table 2. Decreasing the catalyst loading of **Ru-2** from 0.3 mol% (Table 2, entry 1) to 0.15 mol% and further to 0.06 mol% resulted in a significant decrease of conversion, affording merely 65 mol% and 30 mol% FA/IL, respectively, after 18 h (Table 2, entries 2-3). As expected, the catalytic activity was restored by increasing the temperature from 30 °C to 60 °C, providing 82 mol% FA/IL with 0.06 mol% **Ru-2** (Table 2, entry 4). Keeping the catalyst loading at 0.3 mol%, a screening of ILs showed that BMIM OAc performs similarly to EMIM OAc (92 mol % FA/IL, entry 5, Table 2), while the ILs containing other counterions such as carbonate, formate, and diethylphosphate afforded lower conversions (Table 2, entries 6–8). These results indicate that the anion of the IL must be basic enough to promote the CO_2 chemisorption *via* NHC carbene formation, catalyst activation, and/or

to favor the equilibrium towards FA by its deprotonation upon formation. Decreasing the partial pressure of H_2 to 10 bar led to only 47 mol% FA/IL (42% NMR yield, Table 2, entry 9), showing that 20 bar of H_2 is necessary to afford FA in higher conversions when 10 bar of CO_2 is employed. The catalytic activity of the **Ru-2** in EMIM OAc was also tested under 5:10 bar of CO_2/H_2 (Table 2, entry 10). Under such conditions, 57 mol% FA/IL was obtained, which corresponds to >95% yield with respect to CO_2, highlighting that the system can be potentially productive in reactors with lower pressure limit.

Table 2. Screening of catalyst loading, CO_2/H_2 pressure ratio, overall pressure and ILs for CO_2 Hydrogenation to FA.[a]

Entry	Catalyst [mol%]	CO_2/H_2 [bar]:[bar]	IL	FA/IL [mol%][c]	Yield [%][b]	TON
1	**Ru-2** [0.3]	10:20	EMIM OAc	88	79	282
2	**Ru-2** [0.15]	10:20	EMIM OAc	65	58	387
3	**Ru-2** [0.06]	10:20	EMIM OAc	30	27	483
4[d]	**Ru-2** [0.06]	10:20	EMIM OAc	82	73	1305
5	**Ru-2** [0.3]	10:20	BMIM OAc	92	81	270
6	**Ru-2** [0.3]	10:20	EMIM $MeCO_3$	74	66	220
7	**Ru-2** [0.3]	10:20	BMIM HCO_2	66	58	193
8	**Ru-2** [0.3]	10:20	EMIM $(EtO)_2PO_2$	38	34	113
9	**Ru-2** [0.3]	10:10	EMIM OAc	47	42	140
10	**Ru-2** [0.6]	5:10	EMIM OAc	57	>95	170

[a] Standard reaction conditions: **Ru-2** (0.004 – 0.04 mmol), IL (1 mL), CO_2/H_2, 18 h, 30 °C. [b] Based on the amount of CO_2. [c] Determined by ^{1}H-NMR. [d] Reaction carried out at 60 °C.

We also monitored the conversion over the time. The reaction reaches a plateau after 15 hours at 30 °C, having already promoted the hydrogenation of CO_2 to FA in good conversion (up to 87% FA/IL, corresponding to 77% yield, Figure 1). After 48 h, the FA is formed in practically 100% FA/IL (89% yield).

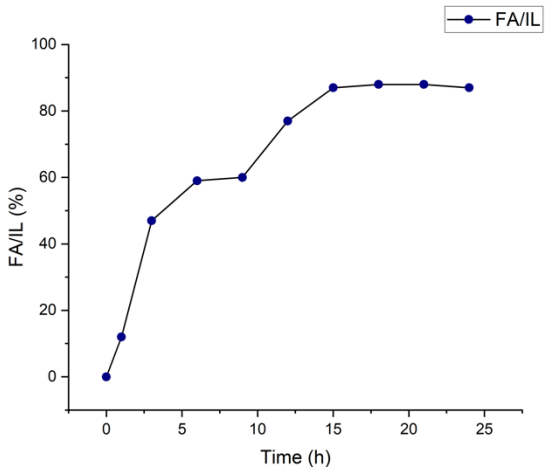


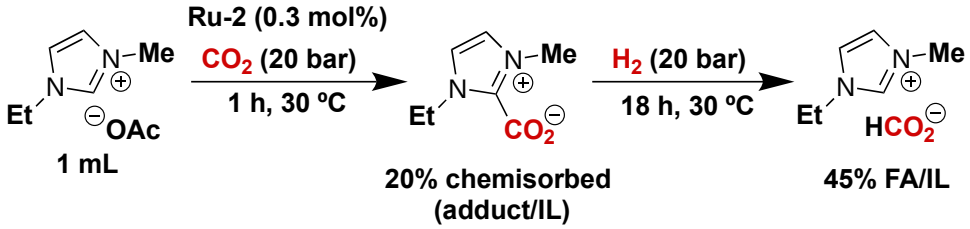
Figure 1. Conversion of CO_2 to FA *vs* time. Reaction conditions: **Ru-2** (0.004 mmol, 0.03 mol%), IL (1 mL), CO_2/H_2 (10:20 bar), 30 °C

To gather more knowledge about the catalysts and our new catalytic system, we also tested a two-step approach where the CO_2 was captured by the IL, followed by a subsequent atmosphere exchange to H_2 for the catalytic hydrogenation process (Scheme 1). It is of paramount importance for the development of future CCU systems to demonstrate both steps of carbon capture and utilization in sequence one-pot under benign conditions, even as a proof of concept from a source of pure CO_2.

Initially, the system was charged with 20 bar CO_2 to EMIM OAc (1 mL) and **Ru-2** (0.02 M) for 1 h at 30 °C, which resulted in 20 mol% CO_2/IL as determined by the amount of chemisorbed CO_2 measured by NMR. Subsequent release of the CO_2 pressure and addition of 20 bar of H_2 afforded

45 mol% FA/IL after 18 h at 30 °C. As observed in our previous study,[5] the FA/IL ratio was higher than the chemisorbed CO_2/IL ratio. This discrepancy can be explained by an amount of physisorbed gaseous CO_2 in the IL, which stays in the IL during the gas change.

Scheme 1. CO_2 capture and subsequent hydrogenation experiment



In a first approach to measuring the reusability of the catalytic system and the maximum amount of FA it can sustain, the reaction mixture (**Ru-2** in 1 mL of EMIM OAc) was subjected to consecutive hydrogenation steps, in which the system was refilled with 30 bars (10:20 bar) of CO_2/H_2 mixture every 18 h (Figure 2). We observed a significant increment of the FA/IL ratio after the first refilling step (112%) and it reached a maximum of 117% at the third refiling step (4th reaction). The maximum amount was relatively constant over two more refilling steps, after which it started to decrease, indicating that dehydrogenation was taking place even with the maintenance of the CO_2/H_2 atmosphere.

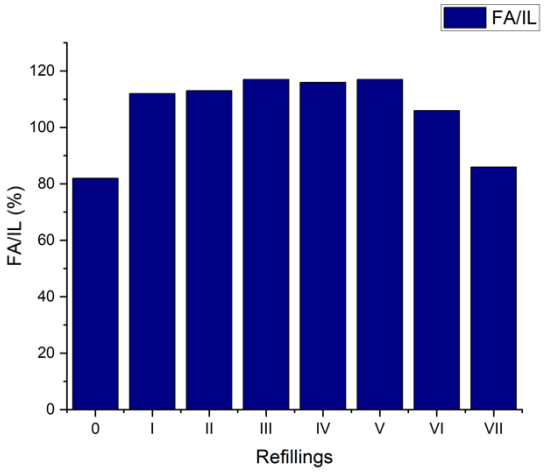


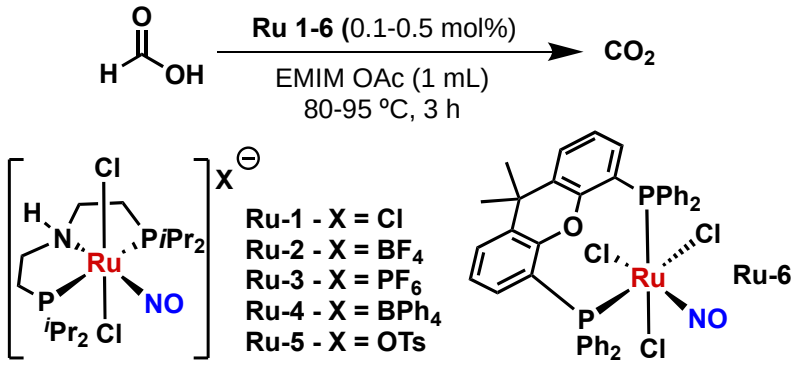
Figure 2. Refilling experiments showing the maximum amount of FA that can be formed after successive hydrogenation steps using the same reaction mixture. Reaction conditions: **Ru-2** (0.004 mmol, 0.03 mol%), IL (1 mL), CO_2/H_2 (10:20 bar), 18 h, 30 °C.

FA Dehydrogenation

Aiming at exploiting the system as a promising candidate for an energy storage technology based on CO_2–FA interconversion, we turned our investigation towards the FA dehydrogenation. Given their distinct pincer ligand frameworks, we started studying the reactivity of **Ru-2** and **Ru-6**, adapting the optimized reaction conditions for FA dehydrogenation previously reported by our group (i.e., EMIM OAc, 0.5 mol% catalyst, 80 °C). To our delight, both reactions showed very high conversions after 3 hours (Table 3, entries 1 and 2). To identify the best reaction conditions, we screened different parameters, such as catalyst loading, temperature, the other pre-catalysts (**Ru-1** and **Ru-3**–**5**) and different ILs (Table 3, entries 3-14). Lowering the catalyst loading from 0.5 mol% to 0.1 mol% caused a decrease in conversion for both **Ru-2** and **Ru-6** (Table 3, entries 3 and 4).

Maintaining the catalyst loading at 0.1 mol% and increasing the temperature to 95 °C led to the recovery of the excellent conversions observed in the initial experiments (Table 3, entries 5 and 6). Under such conditions, **Ru-1** and **Ru-3**–**5** all afforded very high FA conversions within 3 h (Table 3, entries 7–10). The same behavior was observed when BMIM OAc was used instead of EMIM OAc (Table 3, entry 11), while no FA dehydrogenation was observed when using BMIM HCO_2 and EMIM $(EtO)_2PO_2$ (Table 3, entries 12 and 13). In a control experiment, the precursor of both PNP- and POP-Ru-NO complexes, $RuCl_3(NO)\cdot H_2O$, only afforded 41% conversion although the catalyst loading was 10 times higher than the optimized conditions (Table 3, entry 14).

Table 3. FA dehydrogenation optimization.[a]



Entry	Catalyst [mol%]	T [°C]	IL	Conv. [%][b]	TON
1	**Ru-2** [0.5]	80	EMIM OAc	93	202
2	**Ru-6** [0.5]	80	EMIM OAc	94	189
3	**Ru-2** [0.1]	80	EMIM OAc	67	683
4	**Ru-6** [0.1]	80	EMIM OAc	25	255
5	**Ru-2** [0.1]	95	EMIM OAc	94	958
6	**Ru-6** [0.1]	95	EMIM OAc	>95	>968

7	**Ru-1** [0.1]	95	EMIM OAc	>95	>968
8	**Ru-3** [0.1]	95	EMIM OAc	>95	>968
9	**Ru-4** [0.1]	95	EMIM OAc	90	917
10	**Ru-5** [0.1]	95	EMIM OAc	93	948
11	**Ru-1** [0.1]	95	BMIM OAc	>95	>968
12	**Ru-1** [0.1]	95	BMIM HCO_2	<5	-
13	**Ru-1** [0.1]	95	EMIM $(EtO)_2PO_2$	<5	-
14	$RuNOCl_3H_2O$ [1.0]	95	EMIM OAc	41	41

[a] Standard reaction conditions: **Ru-1** – **Ru-6** (0.013 - 0.066 mmol), EMIM OAc (1 mL), FA (0.5 mL, 13.25 mmol), 3 h under gentle flow of Ar. Gas composition is analyzed by GC-TCD. [b] Determined by ^{1}H-NMR.

To gather more information about the system under study, the progress of the FA dehydrogenation employing **Ru-2** and **Ru-6** was monitored at different time points over 3 hours (Figure 3). The data shows that the overall behavior of both catalysts is very similar over this period.

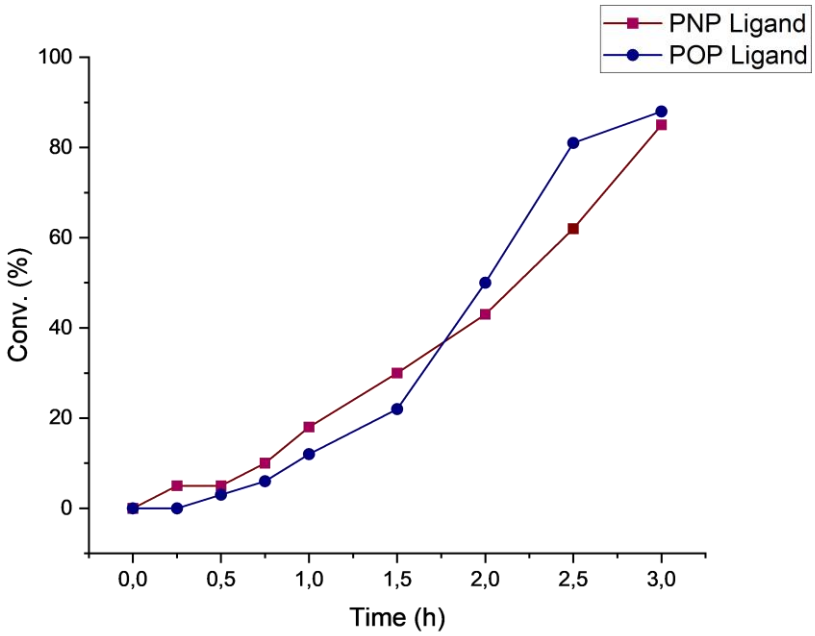


Figure 3. Dehydrogenation of FA *vs* time at 95 °C. Reactivity comparison between **Ru-2** and **Ru-6** 0.1 mol%.

CO_2 Hydrogenation/FA Dehydrogenation Cycles

With the optimal conditions of both hydrogenation and dehydrogenation protocols in hand we challenged our system in the reversible CO_2 hydrogenation/FA dehydrogenation process (Figure 4). **Ru-2** in EMIM OAc was chosen for the first set of experiments, in which each cycle was composed of an 18 h (dark blue bars) or 72 h (light blue bars) hydrogenation step followed by a 4 h dehydrogenation step (dark red bars). As displayed in figure 4a, the system was able to maintain its hydrogenation efficiency over 8 cycles, losing a significant part of it (lower than 50% FA/IL ration) from the 9th cycle onwards. On the other hand, the dehydrogenation process was kept close to completion over the whole study. Performing the same investigation with **Ru-1**, it was observed

that a significant loss of hydrogenation efficiency was observed only after the 11th cycle (Figure 4b).

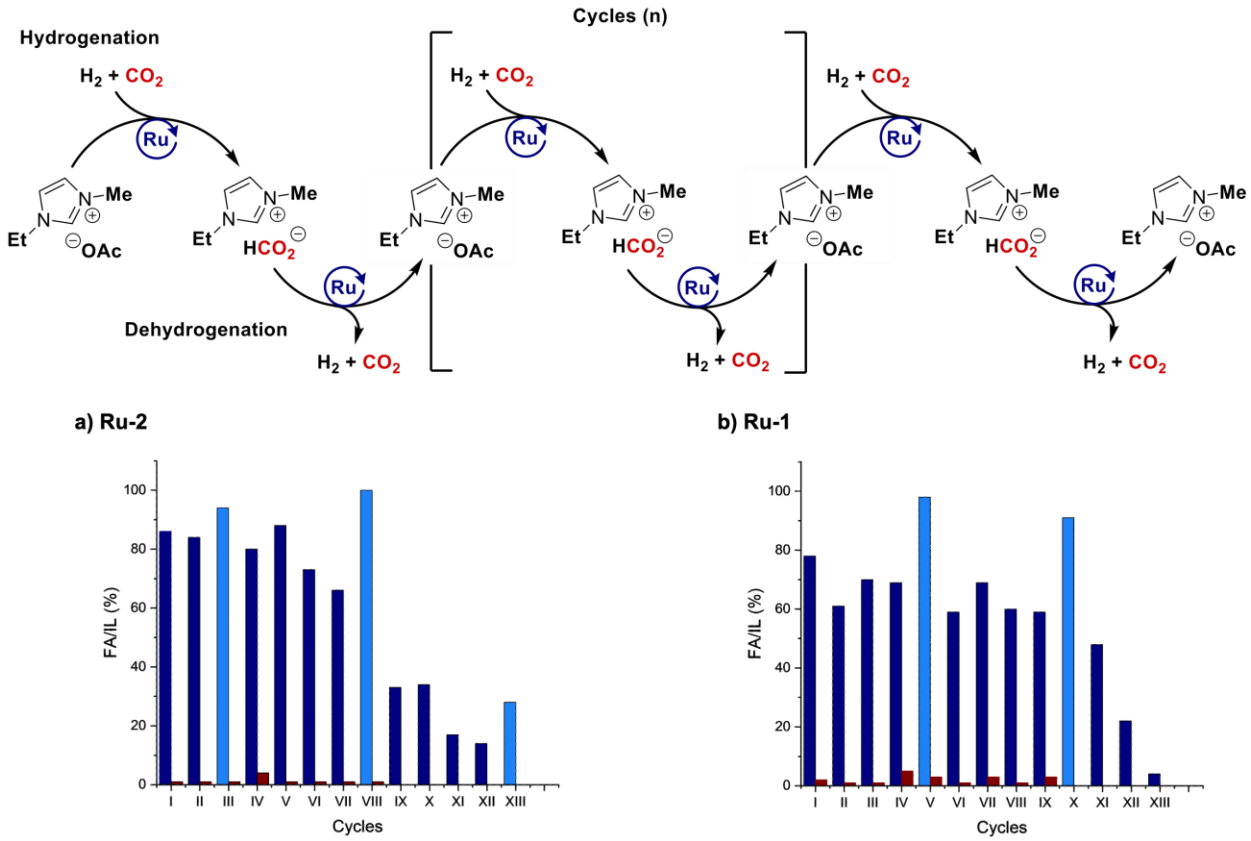


Figure 4. Reversible CO_2 hydrogenation / FA dehydrogenation studies: a) CO_2 hydrogenation/FA dehydrogenation cycles performed with **Ru-2**; b) CO_2 hydrogenation/FA dehydrogenation cycles performed with **Ru-1**. General conditions: Hydrogenation (dark blue bars = 18 h, light blue bars= 72 h): Ru (0.004 mmol, 0.03 mol%), IL (1 mL), CO_2/H_2 (10:20 bar), 30 °C; Dehydrogenation (red bars): **Ru-2** (0.004 mmol, 0.03 mol%), IL (1 mL), 4 h, 95 °C.

Conclusions

In summary, this work describes the use of PNP-Ru-NO and POP-Ru-NO complexes as catalysts for the reversible hydrogenation of CO_2 to formic acid using ionic liquids as solvents. Such

protocols are the first examples of the use of nitrosyl complexes in the contexts of CO_2 capture and valorization and hydrogen storage and transportation.

Under the optimized conditions, the catalytic system was able to afford up to >95% yield of FA using EMIM OAc or BMIM OAc and could be subjected to several refilling steps reaching a maximum of 117% FA/IL. Importantly, we demonstrate that CO_2 can be first captured and then converted to FA in a sequence of two independent steps in one pot. The same system was also capable of promoting the dehydrogenation of FA at elevated temperatures, in which maximum conversion was achieved using both EMIM OAc and BMIM OAc at 95 °C for 3 h. Hydrogenation/dehydrogenation cycles could be performed. The protocol described here offers, as the main advantage, more flexibility in terms of catalyst storage and manipulation, not requiring moisture avoidance and inert atmosphere during both hydrogenation/dehydrogenation processes.

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MN and JTMC conceptualized the project. MN, JTMC and VN conceived and designed the project. MSBJ and ATN developed the complex salts. JTMC and VN carried out the catalysis optimization. JTMC, VN, MSBJ, ATN carried out the data curation. JT and VN wrote the original manuscript. All authors revised the manuscript. MN did project administration and funding acquisition. All authors have given approval to the final version of the manuscript.

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Notes

Any additional relevant notes should be placed here.

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