The efficient transformation of CO₂ into chemicals and fuels is a key challenge for the decarbonisation of the synthetic production chain. Formic acid (FA) represents the first product of CO₂ hydrogenation and can be a precursor of higher added value products or employed as a hydrogen storage vector. Bases are typically required to overcome thermodynamic barriers in the synthesis of FA, generating waste and requiring post-processing of the formate salts. The employment of buffers can overcome these limitations, but their catalytic performance has so far been modest. Here, we present a methodology utilising IL as buffers to catalytically transform CO₂ into FA with very high efficiency and comparable performance to the base-assisted systems. The combination of multifunctional basic ionic liquids and catalyst design enables the synthesis of FA with very high catalytic efficiency in TONs of >8*10⁵ and TOFs > 2.1*10⁴ h⁻¹.
Formic acid (FA) is an important basic chemical, is currently being discussed as a promising candidate for hydrogen storage and can potentially be upgraded to higher added value CO₂ synthetic products. Unfortunately, to date its synthesis is based on the indirect water carbonylation, using CO generated from fossil fuels. Without a doubt a system using the greenhouse gas CO₂ as a carbon source would be environmentally preferential, if the hydrogen used for these transformations is generated from renewable resources. However, the direct hydrogenation of CO₂ is thermodynamically unfavourable. Bases are commonly added to reaction mixture to shift the thermodynamic equilibrium by the consecutive consumption of FA in an acid–base reaction to the product side.

However, an important limitation of these approaches is the formation of formate adducts and salts, which would need to be tediously purified in the consecutive steps with acids, which adds to the cost and the amount of waste generated. Therefore, the direct hydrogenation of CO₂ would be preferential. Unfortunately, the hydrogenation is in gas phase thermodynamically unfeasible. Alternatively, the reaction can be undertaken in the absence of bases utilising basic properties of solvents applied during the hydrogenation. However, in the absence of strong bases the reaction is thermodynamically and kinetically difficult to operate. As a consequence, considerably fewer systems have been reported for the hydrogenation of CO₂ to FA under base-free conditions. Furthermore, these systems typically operate under very high pressures and the catalytic activity and concentration of FA achieved are significantly lower than under basic conditions.

We have recently demonstrated that basic ionic liquids can effectively buffer the reaction, therefore acting as very mild bases that shift the thermodynamic equilibrium to the product side, whilst stabilising the catalytically active species at low partial pressure of H₂ and CO₂. Furthermore, we have demonstrated that buffering ILs can be immobilised onto supported phases, thus facilitating the separation of the FA at the end of the process following a supported ionic liquid approach. In our previous studies we have established the thermodynamic parameters for this transformation employing basic ILs, and therefore we can understand the maximum concentration of FA achievable as a function of the reaction conditions. Furthermore, we previously studied the effect of ligand modifications onto the hydrogenation of CO₂ in the presence of ILs. Key parameters effecting the catalytic activity and stability were associated with the electron density at the metal centre and the resistance of the catalyst towards protonation.

Here, we present a catalytic system for the hydrogenation of CO₂ under buffering conditions specifically designed to work under a wide range of temperatures. This enables optimising the catalyst performance by pushing the conditions to the thermodynamic limitations imposed by the reaction and consequently balancing kinetic and thermodynamic performance and achieving high catalytic efficiency. The robustness of the catalyst enables the addition of Lewis acids, which increases the performance of the catalyst in terms of activity and stability. The results obtained here are comparable to those reported with systems containing stronger bases and represents an important leap forward towards sustainable systems to transform CO₂.

Results and discussion

Synthesis of catalyst. The design of the catalysts plays a key role in the development of efficient catalytic systems. Very recently, it has been demonstrated that basic ionic liquids provide a buffering environment that enables the efficient synthesis of FA, but with much lower enthalpy than when a base (leading to a salt formation) is employed. Under these conditions, optimal electron-donation properties of the ligand are key to balance reactivity and the resistance to deactivation via protonation of the catalyst. Furthermore, complexes with high chemical and thermal stability lead to catalysts with large operational windows and an increased compatibility with other components, such as co-catalysts. NH2-based pincer architectures fulfil all these criteria, hence being ideal candidates for this transformation.

Consequently, a suitable catalyst should prevent the coordination of substrates in undesired positions. In this study, this was achieved by a direct connection of the aromatic pyridine with the imidazole side arms.

The silver transmetalation route employing [Ru(CO)₂(Cl)₂]₁₆ as the Ru source, and L₁ as the ligand was chosen to synthesise the desired Ru–CNC complex (Fig. 1). The reaction was followed by the disappearance signal for the C₂ – H in the 1H-NMR spectra and the appearance of a new peak at 181 ppm in the 13C spectra (see Supplementary Figs. 1 and 2). In the IR spectra two significant bands at 1993 and 2051 cm⁻¹ (see Supplementary Fig. 3), corresponding to two asymmetric CO stretching vibrations can be observed. The general structure was confirmed with single X-ray crystal analysis. Minor scrambling is observed with Cl⁻ bond to Ru, i.e. replacement of Br⁻. In a similar fashion the counterion distributed 1:1 (Br:Cl), giving an overall molecular sum formula of C₂₁H₁₁Br₆N₅O₂Ru. The major halide bond to the metal centre was chloride, as confirmed with ESI-MS. The analysis gave a mass of 516m/z and a minor product with 562m/z (see Supplementary Fig. 4). The analogous complex consisting solely of Cl counterions was synthesised as a control experiment to rule out the influence of multiple halides. The exchange of counterions in L₁ to Cl employing an ion exchange resin yielded the ligand L₁(Cl) (Supplementary Fig. 5), though at significantly reduced yields compared to 1 (see “Methods” section for more details). The formation of the carbene complex following the same procedure employed for the synthesis of 1, yields 1-Cl at significantly lower yield. The complex was characterised by ESI-MS, where 1-Cl displayed a sole peak at 516m/z (see Supplementary Fig. 6), whereas identical NMR shifts were observed compared to 1.

The single crystal analysis of 1 (Supplementary Fig. 7) indicated an average molecular mass of 578.11 g/mol, distributing...
to complexes with the sum formulas of C21H25Cl2N5O2Ru and C21H25BrClN5O2Ru. This in bromide to chloride ratio of 30:70. Indeed, the observed mass peaks for the M-Cl$$^{+}$$ to M-Br$$^{+}$$ of ca. 73:27 indicate that the ratio determined by single crystal analysis is valid. Further evidence for this ratio was found by ICP-OES analysis. Here a Ru content of 19.2 mg L$$^{-1}$$ was found in a 0.199 mM solution (for 100% Cl expected Ru content is 20.8 mg L$$^{-1}$$ and for 100% Br expected Ru content is 18.2 mg L$$^{-1}$$), which indicate a molar ratio between Br$$^{-}$$:Cl$$^{-}$$ of 70:30. In this way a molecular mass of 578.11 g/mol was used to determine the amount of catalyst in solution. Furthermore, neither the addition of Cl$$^{-}$$ or Br$$^{-}$$ showed a difference in catalytic activity or stability in comparison to the non-modified system, indicating that the halide plays an insignificant role onto the catalytic activity.

Catalytic efficiency evaluation. In an initial screening of catalytic activity, it was observed that 1 (0.28 mM) achieves a concentration of 0.5 M solution of FA at 80 °C in DMSO:water (5 v/v% water) in the presence of 1-butyl-2,3-dimethylimidazolium acetate (BMMI.OAc) under 60 bar pressure (H2:CO2 = 1:1). Furthermore, in the absence of catalyst we do not observe any conversion under elsewise identical reaction conditions (6 mL DMSO:H2O, 3.3 mmol BMMI.OAc, with P$_{H2}$ = P$_{CO2}$ = 30 bar at 80 °C). According to the thermodynamic parameters previously calculated for this system16, the concentration of FA observed is close to the thermodynamic equilibrium at ~120 °C (see Supplementary Fig. 8). Above 80 °C the decomposition of DMSO was observed. Fortunately, when BMMI.OAc is employed as an additive the reaction can be performed in a broad range of solvents16. In dioxane:H2O the catalytic system achieves similar concentration of FA at 80 and 100 °C as in DMSO at 80 °C (0.5 M at 100 °C in dioxane:H2O and 0.5 M in DMSO:H2O). Note also that the temperature range employed did not lead to a decomposition of the IL, as evidenced by NMR spectroscopy provided in Supplementary Fig. 9.

In order to investigate the thermal stability of the catalyst we investigated the reaction mixture towards the formation of nanoparticles during the reaction. It is important to note that no evidence of nanoparticle formation was observed under the reaction conditions assayed, even when a relatively high concentration of catalyst (0.28 mM) was employed. Even at high temperatures and pressures (120 °C, 60 bar (P$_{H2}$ = P$_{CO2}$)), TEM and DLS analysis showed no evidence of nanoparticles (see ESI for more details). Furthermore, the catalyst was not active in a reaction typically catalysed by Ru nanoparticles27-31, such as the hydrogenation of benzene at 120 °C under 50 bar H2 in the presence of BMMI.OAc even when high catalyst loadings are used, see SI for more details.

Table 1 Temperature-dependant results obtained with catalyst 1.

| Entry | Catalyst | T (°C) | [FA] (M) | TON$^a$ | TOF$_{ini}^b$ (h$^{-1}$) |
|-------|----------|--------|----------|--------|-------------------|
| 1     | 1        | 100    | 0.22 (0.01) ± 0.005 | 77,550 ± 1600 | 1080 ± 400 |
| 2     | 1        | 110    | 0.29 (0.02) ± 0.005 | 100,580 ± 1600 | 1750 ± 400 |
| 3     | 1        | 120    | 0.49 (0.05) ± 0.005 | 162,900 ± 1600 | 4360 ± 400 |
| 4     | 1        | 130    | 0.40 (0.12) ± 0.005 | 141,000 ± 1600 | 10,620 ± 400 |
| 5     | 1        | 140    | 0.29 (0.19) ± 0.005 | 100,862 ± 1600 | 16,500 ± 400 |
| 6     | 1-Cl     | 120    | 0.49 (0.05) ± 0.005 | 163,000 ± 1600 | 4200 ± 400 |

Reaction conditions: 6 mL dioxane:water (5 v/v% water), 3.3 mmol BMMI.OAc, 2.8 µM catalyst.

$^a$Determined after 72 h.

$^b$Determined after 4 h of reaction time.

$^c$Data reproduced two times, error values within the error margin of the NMR determination, which were used as the standard deviation.
Our previous report shows the thermodynamic equilibrium curve calculated employing Van’t Hoff plots for the CO2 hydrogenation to FA employing BMMI.OAc as a buffering system (see Supplementary Fig. 8)16.

In the next step the effect of pressure was investigated. Here a linear correlation in between the achieved concentration of FA and pressure can be observed (Fig. 3b). This is in consistence with the Henry’s law, which predicts a linear relationship between the amount of dissolved gas and the pressure.

Mechanistically, the hydrogenation of CO2 to FA can be divided into two main steps. In the first step, a hydride is transferred onto CO2. In the second step, H2 is activated releasing a proton and formate, with a simultaneous regeneration of the active hydride (Fig. 4a). In order to determine the rate-determining step, various gas compositions were tested (maintaining constant the total pressure). The observed reaction rate decreased significantly at low partial pressure of CO2 (Fig. 4b). Indeed, at 20 bar CO2 and 40 bar H2 a TOFini of 2700 h⁻¹ was obtained. On the contrary an increased partial pressure of CO2 led to increased rates, i.e. at 45 bar CO2 and 15 bar H2 a TOFini of 9700 h⁻¹ is determined, (cf. 4360 h⁻¹ at P_{CO2} = P_{H2} = 30 bar). These experiments clearly show a strong dependence on CO2, thus indicating the CO2 insertion to be the rate-determining step.

An activation energy of 93 ± 7 kJ mol⁻¹ was determined from the Arrhenius plot (Fig. 4c). The activation energy can either be decreased by increasing the electron donation onto the metal, leading to a more nucleophilic hydride, thus decreasing the hydricity (ΔG°H)32. Based on our recent study21, a low hydricity will ultimately lead to a more nucleophilic/basic hydride, rendering the catalyst prone protonation and hence deactivation.

It has been demonstrated that charged intermediates and transition state formed during the CO2 insertion can be stabilised with Lewis acids (see Supplementary Fig. 10 for a suggested mechanism)33–36. Therefore Sc(OTf)3 was tested due to its high solubility in organic solvents, tolerance towards water and due to its relatively weak acidic nature37. It was found that Sc(OTf)3 significantly increased the reaction rate. However, smaller amounts have only a minor effect on the rate (Fig. 4d). An optimal concentration of 20 μM for Sc(OTf)3 was found a TOFini of 21,200 h⁻¹, which corresponds to 4.9 times the activity without using the Lewis acid. Above this concentration a drop in rate was observed, presumably due to catalyst poisoning as already observed in previous studies38. However, in the presence of Sc (OTf)3 the concentration of FA generated decreased slightly to 0.32 M, yielding a TON of 114,400 (Table 2, entry 2). Increasing the hydrogen to carbon dioxide ratio did not show any pronounced effects on activity nor stability (Table 2, entry 3).

Under these conditions, the amount of catalyst was reduced to 1.7 mmol, which led to an unprecedented TON of 833,800, while the TOFini was maintained at 20,600 h⁻¹ (Table 3, entry 4). In this case, there is no conversion without BMMI.OAc or with Sc (OTf)3 only as catalyst.

It is worth noting the remarkable activity and stability of our catalytic system, which shows ca. 50 times higher value in TON and 23 times higher value in TOFini in the hydrogenation of CO2 to FA under buffering conditions than the best reported to date9–11,14,16. Furthermore, the TON and TOFini towards FA are comparable to values obtained under basic conditions39–41. Interestingly, the CNC–Ru pincer reported here outperforms its previously reported analogue with a six-membered bite angle ring, even though the previous complex was reported to operate under basic conditions42.

To conclude, we have presented a catalytic system capable of highly efficiently transform CO2 into FA under buffering conditions. The combination of basic ionic liquids, highly robust catalysts based on Ru pincer N-heterocyclic carbenes and Lewis...
Fig. 4 Analysis of rate determining step and conditions on catalytic activity observed. a Simplified reaction mechanism with the rate-determining step (CO$_2$ insertion) highlighted. b Kinetic dependence of transformation on the partial pressure of CO$_2$. c Arrhenius plot for the IL-buffered FA synthesis. d Effect of Sc(OTf)$_3$ on observed catalyst activity.

Table 2 Optimised conditions for the hydrogenation of CO$_2$ to FA.

| Entry | 1 (µM) | $P_{\text{H}_2}$:$P_{\text{CO}_2}$ (bar:bar) | [Sc(OTf)$_3$] (mM) | [FA] (M) | TON | TOF$_{\text{ini}}$ (h$^{-1}$) |
|-------|--------|-------------------------------|----------------|----------|-----|-------------------|
| 1     | 2.83   | 30:30                         | 0              | 0.46 ± 0.005 | 162,900 ± 1600 | 4360 ± 400 |
| 2     | 2.83   | 30:30                         | 20             | 0.32 ± 0.005 | 114,400 ± 1600 | 21,200 ± 400 |
| 3     | 2.83   | 45:15                         | 20             | 0.36 ± 0.005 | 126,000 ± 1600 | 22,000 ± 400 |
| 4*    | 0.28   | 45:15                         | 20             | 0.26 ± 0.005 | 833,800 ± 1600 | 20,600 ± 400 |

Reaction conditions: 2.83 µM catalyst, $T = 120$ °C in 6 mL 1,4-dioxane:$H_2$O (5 v/v%) $H_2$O in the presence of 3.3 mmol BMMI.OAc; TON and [FA] determined after 72 h using BMMI.OAc as an internal standard, TOF$_{\text{ini}}$ determined after 4 h.

*0.28 µM, TON and [FA] determined after 5 days using BMMI.OAc as an internal standard, TOF$_{\text{ini}}$ determined after 18 h.
acid catalysts showed high efficiency at elevated temperatures, balancing kinetic and thermodynamic performance. The catalytic activity observed is the highest observed to date for base-free hydrogenation from formic acid and its derivatives: useful hydrogen storage materials. 

**Methods**

**General information.** The ionic liquids 1,2-dimethyl-3-butylimidazolium acetate (BMIM.OAc) were prepared from literature methods43. 

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Author contributions
A.W. and V.S. envisioned the work, develop the relevant hypotheses, and designed the experiments. A.W. did all the experimental work. S.P.A. resolved and interpreted the crystal structure. A.W. and V.S. analysed and interpreted the data and co-wrote the manuscript.

Competing interests
The authors declare no competing interests.

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