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Communication

Conversion of CO_2 from Air into Formate Using Amines and Phosphorus-Nitrogen PN^3P-Ru(II) Pincer Complexes

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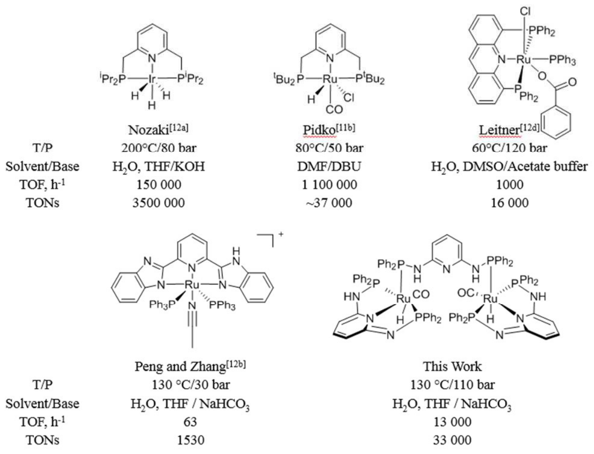
Abstract: Well-defined ruthenium (II) PN^3P pincer complexes were developed for the hydrogenation of carbon dioxide. Excellent product selectivity and catalytic activity with TOF (turnover frenquency) and TON (turnover number) up to 13,000 h^{-1} and 33,000, respectively, in a THF/H_2O biphasic system were achieved. Notably, effective conversion of carbon dioxide from air into formate was conducted in the presence of an amine, allowing easy product separation and catalyst recycling.

Meeting increasing global energy demands by comsuming carbon-based fossil fuels has led to the carbon dioxide (CO_2) levels in the atmosphere rising from the preindustrial 280 ppm to the current 409 ppm.[1] One attractive approach to reducing CO_2 levels is carbon capture and recycling (CCR), which utilizes CO_2 as an important C1 source for the synthesis of value-added chemicals or liquid fuels.[2] Several important products, such as formic acid (FA) or formate,[3] methane,[4] formate esters,[5] methanol,[6] or gasoline,[7] can be obtained from hydrogenation of CO_2. Of these, FA is considered a promising energy carrier with an energy density of 1.77kW·h/L.[8]

On this basis, the catalytic hydrogenation of CO_2 into FA/formate has gained significant interest in recent years and a variety of transition-metal complexes have been employed, such as those based on iron,[9] cobalt,[10] ruthenium,[11] iridium[12] and rhodium.[13] Nozaki et al. set the record for CO_2 hydrogenation activity in 2009 using a PNP-pincer iridium complex [2,6-$(PiPr_2)_2C_5H_3N]IrH_3$ in a THF/H_2O binary solvent medium. This catalyst gave a turnover frequency (TOF) of up to 150,000 h^{-1} at 200 °C and 80 bar. However, this result was obtained in a very dilute concentration of catalyst with a low conversion.[12a] In 2014, Pidko et al. demonstrated that a Ru-PNP pincer complex could hydrogenate CO_2 in DMF in the presence of a DBU base with a remarkable TOF of up to 1,100,000 h^{-1} in 2 min.[11b] In 2016, Leitner et al. reported a Ru complex, $[Ru(Acriphos)(PPh_3)(Cl)(PhCO_2)]$, for the CO_2 hydrogenation to FA, affording an average TOF of 1,000 h^{-1} in the presence of DMSO/H_2O at 60 °C and 120 bar of H_2/CO_2 (2:1).[12d] Later, Peng and Zhang et al. reported a rigid N,N,N-pincer Ru complex for CO_2 hydrogenation with TOF of 63 h^{-1} at 130 °C and 30 bar of H_2.[12b] However, the synthesis of most of these compounds involves the use of costly ligands (Fig. 1).[8e] Very few examples have been reported to convert a low concentration of CO_2 into formate. Olah, Prakash, and coworkers have demonstrated hydrogenation of CO_2 from air to methanol and formate using a commercial catalyst.[14] However, there is still a need for more economical and efficient approaches for such processes for future practical applications. To realize this goal, diversified approaches to offer more examples for the better understanding on the catalyst structure/activity correlation will be invaluable. Our group has recently developed a series of complexes based on a new class of PN^3-pincer ligands, and demonstrated that these complexes show enhanced stability in the presence of water and air and reactivities towards hydrogenation and dehydrogenation reactions.[15] Herein, we report the synthesis of an economical PN^3P-pincer ruthenium complex to convert CO_2 captured from air (409 ppm) with excellent product selectivity and catalytic activity to formate.



	Nozaki[12a]	Pidko[11b]	Leitner[12d]
T/P	200°C/80 bar	80°C/50 bar	60°C/120 bar
Solvent/Base	H_2O, THF/KOH	DMF/DBU	H_2O, DMSO/Acetate buffer
TOF, h^{-1}	150 000	1 100 000	1000
TONs	3500 000	~37 000	16 000

	Peng and Zhang[12b]	This Work
T/P	130 °C/30 bar	130 °C/110 bar
Solvent/Base	H_2O, THF / $NaHCO_3$	H_2O, THF / $NaHCO_3$
TOF, h^{-1}	63	13 000
TONs	1530	33 000

Figure 1. State-of-the-art catalytic systems for CO_2 hydrogenation.

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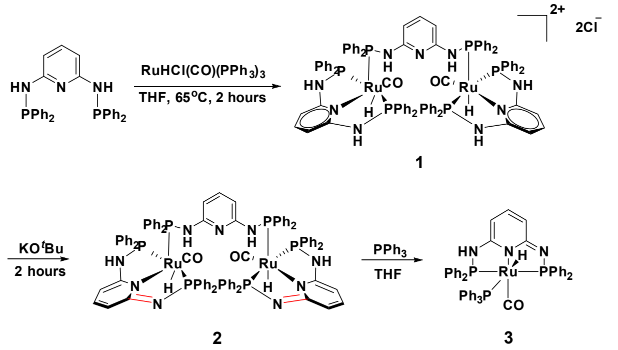
Complex **1** was synthesized using the Ru metal precursor $RuHCl(CO)(PPh_3)_3$ and a PN^3P ligand derived from 2,6-diaminopyridine and chlorodiphenylphosphine (N,N'-bis(diphenylphosphino)-2,6-diaminopyridine) (Scheme 1). By slow evaporation, colorless single crystals of **1'** (Fig. 2), suitable for X-ray crystallography, were obtained from the solution. The molecular structure of **1** (M·Cl·Cl) contains two Ru(II) centers and three PN^3P ligands. As indicated in **1'** ($M·Cl·HCO_3$), during crystal growth one of the chloride ions was readily replaced by a bicarbonate ion, presumably due to the absorption of CO_2 and moisture from air. The other chloride ion was held in the crystal cell by the formation of N-H···Cl hydrogen bonds (Fig. 2).



Scheme 1. Preparation of complex **1**, **2** and **3**.

Each Ru center of **1'** was symmetric with respect to the plane of the pyridine ring in the pincer ligand to which it was coordinated, indicated by the almost equal C1-N1 (1.378(6) Å) and C2-N3 (1.375(6) Å) bond lengths of the two pincer arms. Moreover, the P1-N1-C1 angle (120.1(3) °) and P2-N3-C2 angle (121.4(3) °) were almost the same, revealing the aromatized nature of **1'** (Fig. 2).

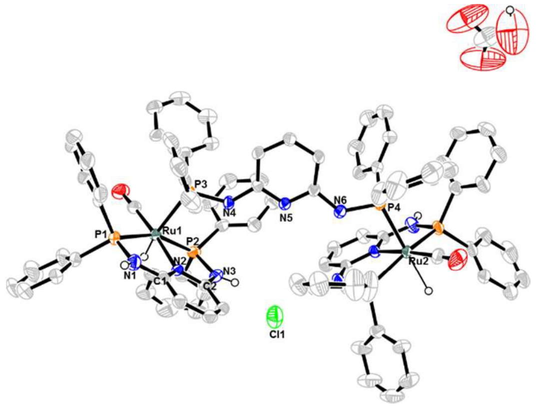


Figure 2. Molecular structure of **1'** ($M·Cl·HCO_3$) with thermal ellipsoids set at 50% probability. The H atoms were omitted for clarity. Selected bond lengths (Å): Ru1–P2 2.2961(12) Ru1–P1 2.2821(12), Ru1–P3 2.4232(10), C1-N1 (1.378(6), C2-N3 (1.375(6), Selected bond angles (°): P1-N1-C1 120.1(3), P2-N3-C2 121.4(3).

The dearomatized complex **2** was achieved by the treatment of complex **1** with potassium *t*-butoxide in THF according to a similar procedure previously reported by us (Scheme 1).[16] Upon coordination of **2** with a neutral PPh_3 ligand, a dearomatized monometallic species **3** was obtained. Pale yellow crystals of **3**, suitable for X-ray crystallography, were obtained from a concentrated THF solution in a glovebox. The structure of **3** was characterized by a PPh_3 coordinated to the Ru center with a CO, hydride and pincer-type PN^3P ligand (Fig. 3). In contrast to **1'**, the C1-N1(1.377(5) Å) and C2-N3 (1.341(5) Å) bond lengths of the two arms in the pincer ligand were very different in **3**, as were the P1-N1-C1 angle (121.2(3) °) and the P2-N3-C2 angle (115.7(3) °), indicating that the pyridine ring in **3** underwent dearomatization (Fig. 3). Consistently, the different chemical shifts in the $^{31}P\{^1H\}$ NMR of **3** corresponded to the different chemical environments of phosphine at the two arms of the pincer ligand (Fig. S10).

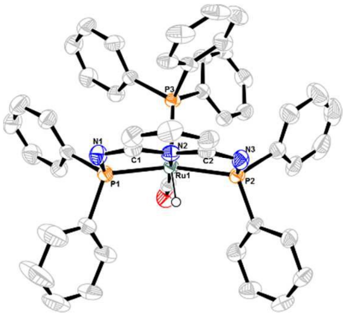


Figure 3. (a) Molecular structure of **3** with thermal ellipsoids set at 50% probability. The H atoms were omitted for clarity. Selected bond lengths (Å): Ru1–P2 2.3156(11) Ru1–P1 2.3153(11), C1-N1(1.377(5) C2-N3 (1.341(5). Selected bond angles (°): P1-N1-C1 121.2(3), P2-N3-C2 115.7(3).

The catalytic activity of the dearomatized Ru-PN^3P pincer complex **2** was tested for CO_2 hydrogenation in a THF/H_2O solution at 110 °C (Table 1). Under the base-free condition, very low reactivity was observed even after a prolonged reaction time (Entry 1). Subsequently, various bases were used, including NaOH, Na_2CO_3 and $NaHCO_3$. Compared to the base-free results, the catalytic performance of **2** was greatly improved in the presence of a base (Entry 2-5). These observations suggest that the base played an important role in the catalytic activity. A maximum average TOF of 740 h^{-1} was achieved using Na_2CO_3 as the base and excess CO_2 (Entry 3). When the reaction was carried out under the same conditions in the absence of CO_2, a negligible amount of formate product was obtained[17] (Entry 4), indicating the importance of CO_2 as the source of the formate production. In all cases, the liquid composition of the product was confirmed by ^1H NMR and ^{13}C NMR (Fig. S12-S13), and GC analysis of gas mixture after reaction showed no detectable amount of CO. To our delight, the catalyst showed excellent selectivity for CO_2 hydrogenation to formate. Interestingly, when $NaHCO_3$ was used instead, only H_2 was needed to produce formate, indicating that $NaHCO_3$ can serve as both the source of CO_2 and the base; the catalyst also afforded a moderate TOF and TON (Entry 5). In general, however, higher catalytic activity was obtained when both CO_2 and H_2 were present (Entry 2-3), since a bicarbonate makes the hydrogenation process more efficient to carry out.[18] Hence, in subsequent studies, hydrogenation of bicarbonates were further examined.

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Table 1. Hydrogenation of CO_2, carbonate and bicarbonate in the presence of complex **2***.

Entry	Base	$P(H_2)/P(CO_2)$ (psi)	Time (h)	Formate (mmol)	NMR yield (%)	TON	TOF (h^{-1})
1	/	400/400	17	0.089	/	12	0.7
2	NaOH	400/400	2.25	9.9	/	1338	600
3	Na_2CO_3	400/200	2.25	12.3	/	1662	740
4	Na_2CO_3	400/0	2.25	trace	/	/	/
5	$NaHCO_3$	400/0	2.25	7.14	69	965	430

*General conditions: T=110 °C, base (10.4 mmol), THF/H_2O (1:1, 20 mL). n(**2**)=3.7 µmol, internal standard DMSO (1.4 mmol). TOF is an average value and calculated according to the reaction time.

To illustrate the possible macro-process taking place during bicarbonate hydrogenation, an image of the reaction with three phases, gas, liquid 1 (THF) and liquid 2 (THF/H_2O), is shown in Fig. 4. It was rationalized that complex **2** (or the active catalytic species derived from **2**) would prefer to stay in the organic THF phase where the catalytic reaction occurred, because of the presence of phenyl groups that made it relatively hydrophobic. Hydrogen and bicarbonate then diffused into the THF phase to react to yield formate, which was desolved back into the THF/H_2O phase.

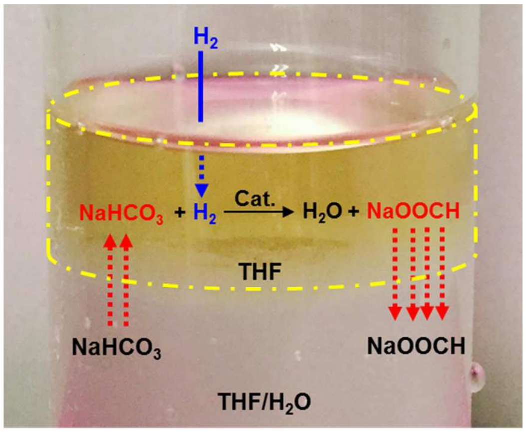

Figure 4. The macro-process of bicarbonate hydrogenation.

The catalytic performance of **2** was also optimized by varying different parameters, such as the reaction temperature, catalyst loading, bicarbonate concentration and pressure of H_2 (Fig. S14-17). The relationship between TON and the reaction time for the bicarbonate hydrogenation under the optimized reaction conditions (130 °C, catalyst loading of 0.1µmol, 1600 psi H_2) is shown in Fig. S18. TON increased as a function of the reaction time, and a maximum TON of 33,000 was achieved after approximately 50 hours.

Based on the feature of aromatization-dearomatization of complex **2** and our previous mechanistic studies of ^{t}Bu-PN^{3}P Ru-catalyzed FA dehydrogenation[16a], we proposed a plausible mechanism involving metal-ligand cooperation[19] (Figure 5). The initial dissociation of a PN^{3}P ligand from the bimetallic ruthenium complex **2**, gives two coordinately unsaturated 16-electron complex **A** as the catalytically active species. Upon hydrogenation, **A** undergoes rearomatization of the pyridine ring and a bihydride species **B** is formed. HCO_3^- could dissociate into CO_2 and OH^-,[20] serving as the CO_2 source. Insertion of CO_2 into the Ru-H bond of **B** then affords a Ru-formate complex **C**, similar to the intermediate formed in the ^{t}Bu case. Finally, elimination of the formate product in the presence of OH^- can regenerate the catalytically active **A**. To support **A** is a plausible active species, further investigation was carried out using the monometallic **3** in the reaction. In the presence of additional PPh_3, there was indeed a significant drop in catalytic activity (Fig. S19), strongly suggesting that the dissociation of the phosphine ligand is needed to achieve a catalytically active species, i.e. **A**.

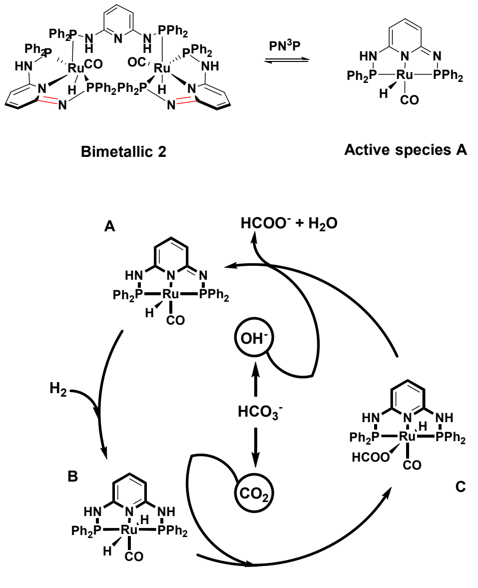

Figure 5. Proposed mechanism for hydrogenation of bicarbonate using complex **2**.

With the possible macro-process involving three phases and the plausible mechanism of bicarbonate hydrogenation in hand, we further developed a model for CO_2 capture and utilization.[21] First, we sought to capture CO_2 from air using various bases to create bicarbonate, which could then be hydrogenated into formate using our Ru-PN^{3}P pincer complex **2**. A series of commercially available bases were screened to evaluate their capacity for CO_2 capture by bubbling air through their aqueous solution (Table S1, Fig. S20). It was observed that the CO_2 absorption abilities of the inorganic bases were too low even after a prolonged period of time (over 50 hours), except for NaOH (Table S1, Entry 1). However, a quantitative ^{13}C NMR spectroscopy analysis of the salt formed in the aqueous NaOH solution after CO_2 absorption showed that only carbonate had formed, not suitable for our intended hydrogenation

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conditions (Table 1, Entry 4). Gratifyingly, the organic bases, such as amines, showed much better CO_2 absorption potential.[22] All the amines chosen for this study captured CO_2 from air or a gas cylinder (1 bar) to give carbamate, bicarbonate or both (Table S1, Entry 4-9, Fig. S21).[22c] Among the monoamines (Table S1, Entry 4-6), MEA, which has been used industrially as a CO_2 absorber[23], exhibited the highest absorption efficiency (17%), which was more than or almost double that of AMP (7%) and MDEA (9%). When the CO_2 absorption time was shortened to 24 hours, TEPA, NTEA and PMDTA still showed outstanding CO_2 absorption potential with absorption efficiencies of 38%, 59% and 39%, respectively, when the source of CO_2 was from a gas cylinder (1 bar) instead of air. It is noteworthy that only tertiary amine PMDTA (efficiency 39% (1.16 eq)) and MDEA (9%) captured and converted CO_2 into solely bicarbonate (Table S1; Fig. S22).[22a] Hence, PMDTA amine was the optimal choice for CO_2.

The final aqueous solution of the PMDTA amine, obtained after CO_2 capture from air and salt formation, was then subjected to hydrogenation in the presence of our Ru-PN^{3}P pincer complex **2**.[21] An average TOF of 990 h^{-1} (yield 71%) was achieved at 130 °C with a H_2 pressure of 1600 psi. (Fig. S23). In addition, recyclability studies were also performed in a 2-MeTHF/H_2O biphasic system using PMDTA as the CO_2 absorber. The low miscibility of 2-MeTHF with water allows a clean organic-water phase separation.[24] In this way, both product separation and catalyst recovery could be easily realized since the formate formed in the aqueous phase and the catalyst was in the organic phase. In the recyclability test, the organic layer, containing the catalyst, could be reused for five consecutive cycles in the hydrogenation of CO_2 captured from air in the presence of PMDTA without a significant reduction in catalytic activity (Figure 6). After five consecutive cycles, the resting state of the catalyst is confirmed to be complex **2** (Fig. S24) and only 4.1 % of the catalyst was leached into the aqueous phase as confirmed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Moreover, GC analysis of gas mixture and the ^{1}H NMR results indicated that the product consisted solely of formate, without any by-products (Fig. S23) to evidence that our catalyst demonstrated excellent product selectivity. Such a catalytic system shows not only the excellent selectivity and catalytic activity of a homogeneous catalyst, but also separability and reusability similar to those of a heterogeneous catalyst, due to the biphasic nature of the reaction mixture.

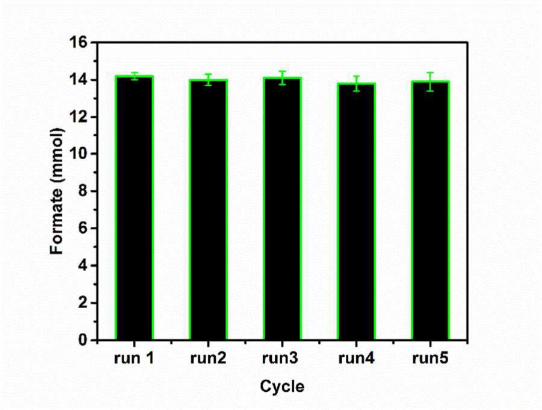

Figure 6. Recyclability test of complex **2**. Reaction conditions: 13 mmol PMDTA+ 10 mL H_2O (CO_2 captured in each cycle = 15 mmol), 10 mL 2-MeTHF, T=130 °C, Time=12 h, n(2)=20 µmol.

Conclusions

In summary, the PN^{3}P bimetallic Ru complex **2** serves as a catalyst precusor with excellent selectivity and catalytic activity with TOF and TON up to 13,000 h^{-1} and 33,000, respectively. Our catalytic system allowed both product separation and catalyst recycling, offering the advantages of both homogeneous and heterogeneous systems.

Conflicts of interest

There are no conflicts to declare.

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