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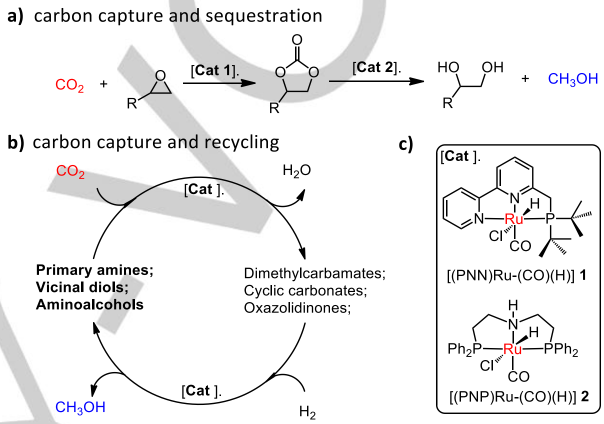
Synthesis, Characterization and Catalytic Application of Pyridine-bridged N-Heterocyclic Carbene Ruthenium Complexes in Hydrogenation of Carbonates

Jiangbo Chen,[a] Haibo Zhu,[a,b] Jinjin Chen,*[c] Zhang-Gao Le*[b] and Tao Tu*[a]

Dedication ((optional))

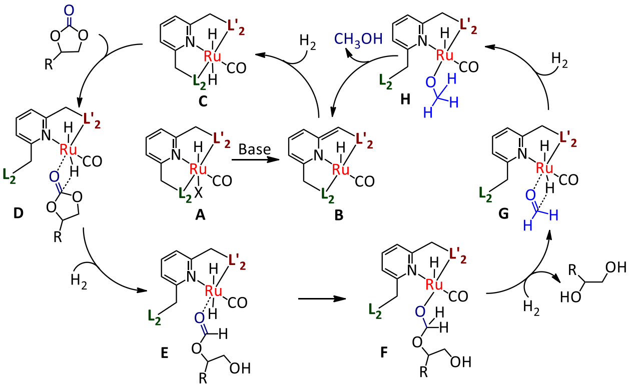
Abstract: A series of novel bulky pyridine-bridged NHC-Ru complexes have been rational designed and synthesized, which exhibited extremely high catalytic activity in the hydrogenation of cyclic and linear carbonates under mild reaction conditions. In the presence of catalytic amount of weak base, a broad range of substrates with different ring size and steric bulkiness were well tolerated providing methanol and corresponding diols in excellent yields with the catalyst loading as low as 0.5 mol %.

As a consequence of global climate change, the increasing emission of CO_2 has attracted many attentions.[1] Therefore, a variety of research focuses on the transformation of CO_2, a sustainable C1 source,[2] to value-added chemicals.[3] Among them, methanol constitute one of the most attractive products, because it can be directly used as a drop-in liquid fuel for internal combustion engines and fuel cells.[4] As an efficient hydrogen storage medium (12.5 wt% H_2), methanol is also a convenient chemical feedstock to produce a myriad of crucial fine chemicals and important platform molecules.[5] However, the direct transformation of CO_2 to methanol has been somewhat challenging at current stage, due to the chemical inertness of CO_2. Alternatively, the hydrogenation of formates, carbonates and carbamates, readily accessed from CO_2 in a large scale, is much more attractive and provides an indirect approach to produce methanol. Two strategies including “carbon capture and sequestration” (Scheme 1a) and “carbon capture and recycling” (Scheme 1b) are usually applied in these approaches, in which amines,[6] vicinal diols[7] or aminoalcohols[8] are utilized as CO_2 trapping agents. The resulting trapping intermediates, such as cyclic carbonates, dimethylcarbamates, oxazolidinones, are subsequently hydrogenated to produce desired methanol along with regeneration of trapping agents. By using PNN-Ru pincer complex **1** (Scheme 1c), Milstein and coworkers accomplished the hydrogenation of carbonates, carbamates and formates to efficiently produce methanol.[9] Subsequently, Ding and coworkers found that PNP-Ru pincer complex **2** (Scheme 1c) exhibited the highest activity in the hydrogenation of cyclic carbonates.[10]



Scheme 1. Indirect catalytic transformation of CO_2 to methanol and corresponding privileged catalysts.

According to previous study,[11] the plausible catalytic mechanism of pyridine-bridged Ru complex catalyzed hydrogenation of cyclic carbonates was proposed (Scheme 2). At first, dihydrogen is added to the dearomatic complex **B** to form the aromatic active catalytic species **C**. Then decoordination of the “hemilabile site” (L) provides the blank site for ketone coordination. The resulting intermediate **D** could be further converted to **E** after intramoleculer hydride transfer and the second H_2 addition. After ester C-O bond cleavage, formaldehyde coordinated intermediate **G** is formed along with diols generation. Further hydrogenation of formaldehyde via similar intramoleculer hydride transfer and the H_2 addition leads complex **H** formation, which is further liberating the final product MeOH and regenerating the dearomatc species **B**.



Scheme 2. Plausible catalytic mechanism of hydrogenation of cyclic carbonates with pyridine-bridged Ru catalysts (X = Cl, PPh_3 and etc.).

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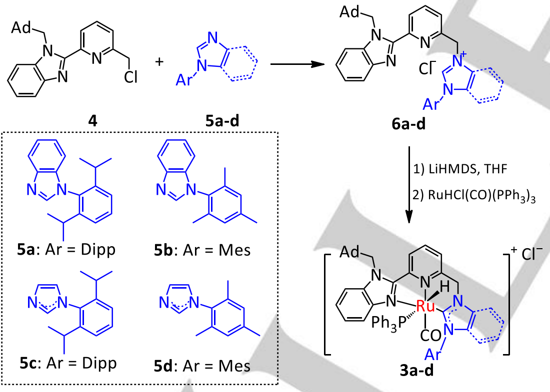
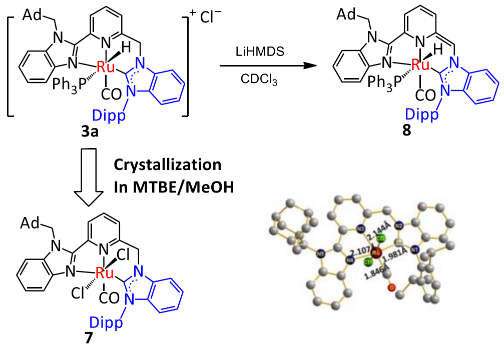
From the plausible mechanism, three issues are found crucial for this catalytic cycle to produce methanol from cyclic carbonates. The first is the σ-donor ability of L′. When ligand with strong σ-donor and weak π-acceptor properties, the active dihydride intermediate **C** is readily formed. The second is the hemilabile property of the "arm" (L), which is favor to coordinate to the metal center and is readily dissociated in the presence of suitable substrate. The third is the bulkiness around the metal center. Bulky enviroment helps the elimination steps to generate biols and methanol. Therefore, the rational design of ligands and corresponding catalysts may not only help us to further increasing the catalytic efficiency for methanol production, but also support the plausible mechanism. In comparison with air-sensitive phosphines, robust N-heterocyclic carbenes (NHCs) with strong σ-donor and weak π-acceptor properties represent a class of privileged ligands,[12] which exhibit promising potential activity in the hydrogenation reactions.[13] In addition, the coordination topologies NHCs are bulky than phosphine, due to the substituents on NHCs readily forming a pocket surrounding to the metal center. Furthermore, imidazolines with similar skeletons of NHCs may function as a new type of hemilabile ligands, in which the bulkiness and coordination ability may be easily tunning. To our best knowledge, the combination of NHCs and imidazolines to fabricate new pyridine-bridged ligands is rarely studied, especially, in the hydrogenation reactions. Following our recent research interests in exploring novel NHC metal complexes and their potential applications,[14] herein, new pyridine-bridged Ru complexes **3** containing bulky benzimidazoline and NHC fragments have been successfully developed and exhibited high catalytic activity towards the hydrogenation of cyclic carbonates under mild reaction conditions.



Scheme 3. Synthesis of pyridine-bridged NHC-Ru complexes **3a-d**.

A series of pyridine-bridged NHC-Ru complexes **3a-d** (Scheme 3) were designed according to our aforementioned strategy, in which benzimidazoline with bulky adamantyl was selected as hemilabile moiety. Due to the bulkiness of ligand may also accelerate the elimination steps in the catalytic cycles, several imidazoles and benzimidazoles **5a-d** with bulky substitutes groups (2,6-diisopropylphenyl: Dipp and 2,4,6-trimethylphenyl: Mes) were selected for N-alkylation with benzyl chloride **4** to synthesize desired (benz)imidazolium salts **6a-d** (see the supporting information). After deprotonation by lithium hexamethyldisilazide (LiHDMS) in dry THF, the respective free carbenes further react with $RuHCl(CO)(PPh_3)_3$ to produce the desired pyridine-bridged NHC-Ru complexes **3a-d** in moderate to good yields, which were further fully characterized by NMR, MS, and IR studies. For instance, in the case of NHC-Ru complex **3a**, a singlet signal at 22.96 ppm in the ^{31}P NMR spectrum and a doublet signal originated from the hydride ligand at -7.97 ppm (J_{PH} = 104 Hz) in the ^{1}H NMR spectrum were observed. In addition, NHC carbon at 185.21 ppm was a broad singlet, the carbonyl carbon at 206.92 ppm was a doublet signal (J_{PC} = 6.2 Hz) in the ^{13}C NMR spectra. All aforementioned information clearly indicates that PPh_3 coordinates to the Ru(II) center. The C-O stretch at 1910 cm^{-1} is observed in the IR spectrum, which was slightly greater than what observed for pincer complex **1** (1906 cm^{-1})[11]. The rest NHC-Ru complexes **3b-d** all exhibited similar spectra and properties (see the supporting information). To our delight, cubic crystals, which are suitable for X-ray diffraction analysis, could be slowly formed from the solution of complex **3a** in the mixture of MTBE (methyl *tert*-butyl ether) and MeOH. However, PPh_3 ligand is not observed. Instead, a neutral dichlorides pincer complex **7** was obtained (Scheme 4), which probably caused by the congested environment around the Ru center formed by the bulky pocket NHC ligand with both Ad- and *i*-Pr groups. Therefore, the PPh_3 ligand was easily dissociated from Ru center even under ambient condition. The X-ray structure of complex **7** revealed a distorted octahedral geometry around the Ru center, in which the CO ligand coordinated trans to the nitrogen atom of pyridine ring. The distances of Ru-C_{NHC} and Ru-C_{CO} are 1.846 and 1.981 Å, respectively, which clearly indicate the strong coordination of NHC to Ru(II) center. In addition, the two important coordination-bonds Ru-N_3 and Ru-N_4 are 2.144 Å and 2.107 Å, and the difference is 0.037Å, which supported our strategy for ligand design by using strong coordination benzimidazoline as the hemilabile arm to construct the pincer ligands.

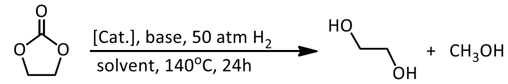


Scheme 4. Deprotonation and crystallization of complex **3a**; and X-ray structure of complex **7** (hydrogen atoms were omitted for clarity).

Deprotonation of complex **3a** with LiHMDS in $CDCl_3$ resulted in formation of the dearomatized complex **8** (Scheme 4), which was somewhat unstable at room temperature and hard to get satisfactory ^{1}H NMR data. However, it still tells us important information from ^{31}P NMR spectrum that a new singlet at -5.48

ppm further confirmed the formation of complex **8** under the basic condition (see the Supporting Information, Figure S21).

Table 1. Hydrogenation of ethylene carbonate in the presence of **3a-d**.[a]



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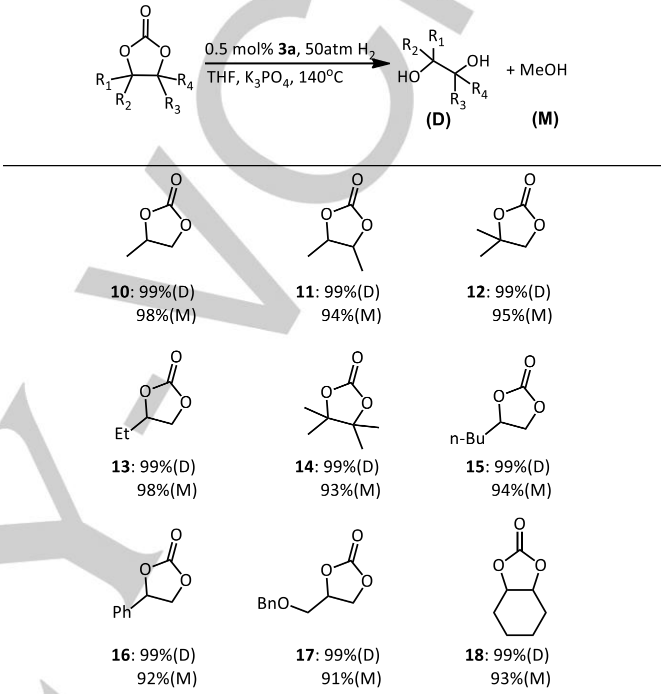
Entry	[Cat.] (mol %)	Base	Solvent	Conv.[b]	Yield (%)[b]	
					EG	MeOH
1	**3a** (0.5)	K_3PO_4	THF	>99%	99	90
2	**3b** (0.5)	K_3PO_4	THF	93%	93	92
3	**3c** (0.5)	K_3PO_4	THF	92%	92	91
4	**3d** (0.5)	K_3PO_4	THF	85%	84	84
5	**3a** (0.5)	KO^tBu	THF	>99%	93	80
6	**3a** (0.5)	K_2CO_3	THF	>99%	99	60
7	**3a** (0.5)	KHMDS	THF	25%	22	20
8	**3a** (0.5)	K_3PO_4	MeCN	/	/	/
9	**3a** (0.5)	K_3PO_4	Toluene	15%	12	10
10	**3a** (0.5)	K_3PO_4	Dioxane	87%	80	62
11	**3a** (0.5)	K_3PO_4	DCE	/	/	/
12[c]	**3a** (0.05)	K_3PO_4	THF	90%	85	51
13[d]	**3a** (0.05)	K_3PO_4	THF	>99%	99	67

[a] Reaction was carried out with 10 mmol ethylene carbonate in 10 mL solvent and 1 mol% base in the presence of pyridine-bridged NHC-Ru complexes **3**; [b] The conversion and yield was determined by GC-MS with *p*-xylene (50 μL) as the internal standard; [c] with 0.1 mol% base for 24 h; [d] with 0.1 mol% base for 45 h.

With these novel pincer NHC-Ru complexes (**3a-d**) in hand, their catalytic activity was then investigated by the hydrogenation of cyclic carbonates, which are readily prepared from CO_2 and corresponding epoxides according to the previous reports.[15] Initially, ethylene carbonate(**9**) was selected as the model substrate to evaluate their performance (Table 1). Even in the presence of 0.5 mol% catalyst loading, all these pincer complexes exhibited high catalytic activity and resulted in satisfactory to quantitative outcomes (Table 1, entries 1-4), when the reaction was carried out in THF with K_3PO_4 under 50 atm of H_2 at 140 ºC. Among them, the most steric hindered complex **3a** gave out the best yields of ethylene glycol (EG) (>99%) and methanol (90%) after 24 h (Table 1, entry 1). Therefore, less-hindered complexes **3b-d** gave slightly inferior conversions (Table 1, entry 2-4), in which methyl formate was detected by GC-MS analysis in the reaction process, leading to the worse yield of methanol versus EG. In contrast with strong base,[10] relatively weaker base K_2CO_3 also gave a good methanol yield with full conversion of ethylene carbonate (Table 1, entry 6). However, when steric hindered strong base LiHMDS was employed, unsatisfied conversion was observed, which might due to the hard formation of dearomatized complex **8** (Table 1, entry 7). When other solvents, such as acetonitrile, dioxane, toluene and 1,2-dichloroethylane(DCE) were applied, inferior outcomes were obtained (Table 1, entries 8-11). In addition, when the catalyst loading of complex **3a** was decreased to 0.05 mol%, the conversion only suffered slightly reducing (Table 1 entry 12). Prolonging reaction time to 45 h, a full conversion could also be achieved (Table 1, entry 13).

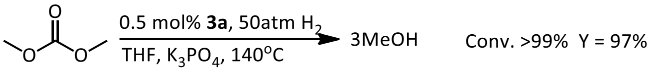
Table 2: Hydrogenation of diverse cyclic carbonates with complex **3a.**[a]



10: 99%(D) 98%(M)
11: 99%(D) 94%(M)
12: 99%(D) 95%(M)
13: 99%(D) 98%(M)
14: 99%(D) 93%(M)
15: 99%(D) 94%(M)
16: 99%(D) 92%(M)
17: 99%(D) 91%(M)
18: 99%(D) 93%(M)

[a] Reaction was carried out with 10 mmol cyclic carbonate in 10 mL THF and 1 mol% K_3PO_4 in the presence of 0.5 mol % complex **3a,** in which yields of diol **(D)** and methanol **(M)** were determined by GC analysis using *p*-xylene (50 μL) as the internal standard.

With the optimized reaction conditions in hand, we subsequently focused on the substrate scope of the newly developed catalytic system (Table 2). Pleasingly, all selected cyclic carbonates are able to fully convert to the corresponding diol and methnol under the optimized reaction conditions. Remarkably the carbonates with mono- (**10**,**13**,**15-17**), di-(**11**,**12**,**18**), and even tetra-(**14**) substituents are fully compatible, up to quantitative yields for methanol and corresponding diol were obtained.



Scheme 5. Hydrogenation of Dimethyl carbonate with complex **3a.**.

Besides the high catalytic activity observed with cyclic substrates, the liner dimethyl carbonate is also considered as a suitable substrate under the identical reaction conditions, providing methanol in quantitative yield (Scheme 5). The good compatibility of both cyclic and liner carbonates may highlight a potential alternation approach of “carbon capture and recycling” by using methanol directly.

In conclusion, a series of rational designed bulky pyridine-bridged NHC-Ru complexes were successfully synthesized, which exhibited extremely high catalytic activity in the hydrogenation of various cyclic and liner carbonates under mild reaction conditions. Even with low catalyst loading and catalytic amount of weak base, a broad range of substrates with different ring size and steric hindered cyclic carbonates were well tolerated providing methanol and their corresponding diols in excellent yields, which not only highlights our strategy efficiency of catalyst design but also provide an indirect and practical protocol to produce methanol from CO_2.

Acknowledgements

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Keywords: carbonates, hydrogenation, methanol, N-heterocyclic carbene, ruthenium pincer complex

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COMMUNICATION

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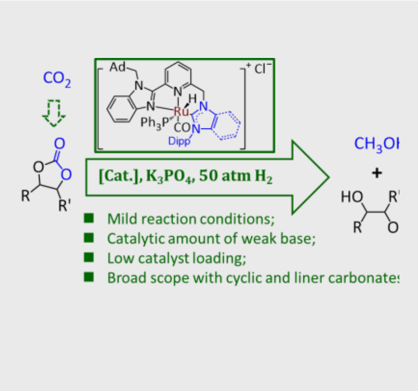

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