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Fixation of atmospheric carbon dioxide by ruthenium complexes bearing an NHC-based pincer ligand: formation of a methylcarbonato complex and its methylation†

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A methylcarbonato ruthenium complex was prepared by capture of CO₂ from air using the (CNC)(bpy)Ru scaffold. The methylcarbonato complex was relatively inert to decarboxylation. Treatments with methylating reagents released dimethylcarbonate.

Chemists are facing the energy/resource depletion problems that should be solved. One of the clues to the solution is utilization of abundant and ubiquitous carbon dioxide (CO₂) as a C1 feedstock. Although attractive conversion/incorporation of CO₂ has been reported recently,¹ preparations of carbonates are currently more practical, since organic carbonates are useful for engineering plastics (polycarbonates), electrolyte solvents for lithium ion batteries, organic solvents, and so on. Organic carbonates are roughly categorized into cyclic and acyclic (linear) carbonates. The former can be easily synthesized by reaction of CO₂ with epoxides and have been investigated a lot,² but little has been reported on the latter. More convenient synthetic strategy for the synthesis of the linear carbonate is direct synthesis from CO₂ and ROH (CO₂ + 2ROH → (RO)₂CO + H₂O). Sakakura *et al.* have reported catalytic synthesis of dimethylcarbonate using stannanes,^{2c} and some transition-metal mediated catalytic preparations have been reported.³ However, in both systems, the reaction conditions of high pressure CO₂ and relatively high reaction temperature are required. The formation mechanism should involve CO₂ insertion into a metal-alkoxide, generating a metallacarbonate (M-OC(O)OR), followed by elimination of the linear carbonate. To find more efficient catalysts, mechanistic studies, in particular reactivity of the metallacarbonate (M-OC(O)OR), are significant, but these studies are scarce.

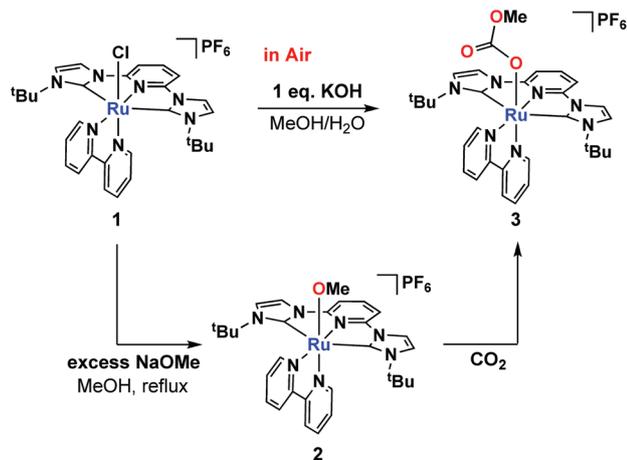
In this paper, we report the preparation of a carbonato ruthenium complex and its reactivity. Preparations of carbonato complexes through insertion of CO₂ into M-OR have been mainly reported in Zn,⁴ Cu,⁵ Pt,⁶ Ir,⁷ Ln,⁸ U⁹ complexes, and group 6¹⁰ and 7¹¹ complexes. However, facile their decarboxylation, hydrolysis, and low reactivity impede often development to the catalytic reactions. We are interested in metal complexes with a pincer ligand containing NHC (N-heterocyclic carbene) ligands, because a number of pincer complexes have exhibited interesting reactivities, and the strong σ -donating ability of the NHC ligand can enhance the reactivity of the metal center. A ruthenium(II) complex bearing a pincer ligand 2,6-bis(*tert*-butylimidazol-2-ylidene)pyridine (CNC) and a bipyridine (bpy) was prepared from the reaction of H[Ru(bpy)Cl₄] with the carbene precursor (pyridine-bridged bis(imidazolium) chloride), according to a literature method¹² with slight modifications. From this reaction, [(CNC)Ru(bpy)Cl]PF₆ (**1**) was isolated in 40% yield, along with a trace amount of [(CNC)₂Ru](PF₆)₂. Interestingly, in the course of preparing potent reducible complexes based on the (CNC)(bpy)Ru scaffold, fixation of atmospheric CO₂, yielding the carbonato complex, was found.

At first, to prepare a hydrido ruthenium complex, we run the reaction of [(CNC)Ru(bpy)Cl]PF₆ (**1**) with NaBH₄ in reflux MeOH under N₂. After stirring for 24 h, the ¹H NMR spectrum of the residue shows two sets of signals assignable to the starting complex **1** and a new complex without a hydride signal. The ESI-MS spectrum indicates the formation of a methoxido complex [(CNC)Ru(bpy)(OMe)]PF₆ (**2**), along with unreacted complex **1**. Preparation of the hydride complex was unsuccessful under these reaction conditions. To prepare the methoxido complex **2** quantitatively, the reaction of **1** with KOH–MeOH in air was conducted to afford a red-brown powder (Scheme 1). However, the ¹H NMR spectrum indicates the formation of a new complex, which is different from complex **2**. The ESI-MS spectrum exhibits the parent molecular ion signal at *m/z* 656.4, indicating the formation of a methylcarbonato complex [(CNC)Ru(bpy){OC(O)OMe}]PF₆ (**3**). The reaction conditions (atmospheric CO₂ and 1 eq. KOH) using MeOH/H₂O as the

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† Electronic supplementary information (ESI) available: Experimental details and characterization data, including crystallographic data for **1**, [(CNC)₂Ru](PF₆)₂·Et₂O, 2-MeCOMe·0.5Et₂O, 3-Et₂O, and 4-MeCN. CCDC 1039531–1039535. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00476d



Scheme 1 Synthesis of complex 3.

reaction solvent resulted in isolation of 3 in 56% yield. The IR spectrum of 3 shows a band at 1649 cm^{-1} , suggesting the formation of the carbonato complex. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3, two low-field resonances at δ 191.5 and 160.1 ppm are assignable to carbene and carbonate carbons, respectively, where the latter is similar to that of the previously reported carbonato complexes.^{4,6b,7c,8a,10,11} Finally, the structure of 3 was unambiguously determined by single-crystal X-ray diffraction analysis (Fig. 1). The κ^1 -coordinated methylcarbonato ligand is revealed, and the Ru–O bond length is 2.116(4) Å. The O1–C30 and O2–C30 bond distances (1.258(6) and 1.227(7) Å) are similar to those of alkylcarbonato rhenium complexes.^{11e} The planarity of the alkylcarbonato moiety is confirmed by the mean deviation (0.002 Å) from the least-squares plane (O1, C30, O2, O3, and C31). The NHC-based pincer and the bipyridine ligands complete the octahedral coordination sphere around the metal.

The methoxido complex 2 would be the intermediate for the formation of 3. Complex 2 was prepared in 65% yield from

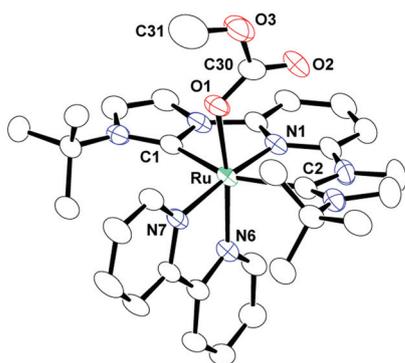
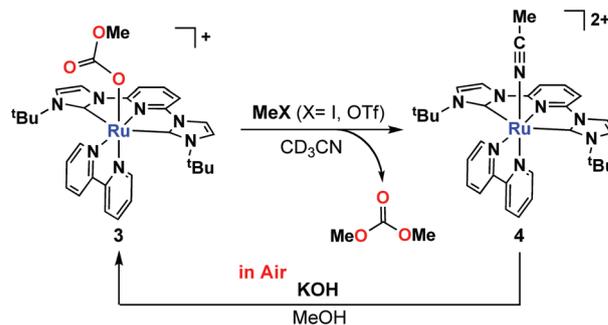


Fig. 1 An ORTEP diagram of the cation part of 3 with thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ru–O1 2.116(4), Ru–N1 2.007(5), Ru–N6 2.048(4), Ru–N7 2.064(4), Ru–C1 2.128(5), Ru–C2 2.131(6), O1–C30 1.258(6), O2–C30 1.227(7), O3–C30 1.358(7), O3–C31 1.420(11); O1–C30–O2 130.1(5), O1–C30–O3 115.9(5), O2–C30–O3 114.1(5).



Scheme 2 Release of dimethylcarbonate from treatments of 3 with methylating reagents.

the reaction of 1 with NaOMe in deaerated MeOH under Ar (Scheme 1). The NMR and ESI-MS data support its formation. Finally, the structure of 2 was confirmed by an X-ray diffraction analysis. When a 1 : 1 mixture of 1 and 2 in MeOH was stirred in air or with bubbling CO_2 , the ^1H NMR shows that signals of 2 are cleanly converted to signals of 3 with intact signals of 1. Also, a MeCN solution of the isolated complex 2 was exposed to air or bubbling CO_2 to give 3 in 85% or 80% yield, respectively. Facile decarboxylation of the alkylcarbonato ligand on transition-metal complexes has often been observed. Although partial elimination of CO_2 of 3 was observed under Ar bubbling for 2 h or in refluxing MeOH for 2 h, complex 3 was inert to the deinsertion when 3 was heated in a CD_3CN solution (70°C) for 3 h.

The feasible elimination of dimethylcarbonate was stoichiometrically confirmed by the treatment of 3 with methylating reagents. From the reaction of 3 with excess MeI in CD_3CN for 15 days, the desired dimethylcarbonate was detected in 15% yield, along with a CD_3CN coordinated complex $[(\text{CNC})\text{Ru}(\text{bpy})(\text{NCCD}_3)]^{2+}$ and a trace amount of the iodide analogue $[(\text{CNC})\text{Ru}(\text{bpy})\text{I}]^+$ (Scheme 2). Use of 5 eq. MeOTf completed the reaction immediately, affording dimethylcarbonate (80% yield) concomitant with $[(\text{CNC})\text{Ru}(\text{bpy})(\text{NCCD}_3)]^{2+}$. Finally, the reaction of the isolated CH_3CN complex $[(\text{CNC})\text{Ru}(\text{bpy})(\text{NCCD}_3)](\text{PF}_6)_2$ (4) with KOH–MeOH in air gave rise to 3 in 83% yield, closing the reaction cycle.

In conclusion, we report herein the capture of CO_2 from air by ruthenium complexes bearing an NHC-based pincer and a bipyridine ligand in KOH–MeOH, yielding the methylcarbonato complex 3. Intermediacy of the methoxido complex 2 was confirmed by facile CO_2 uptake of 2.

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