

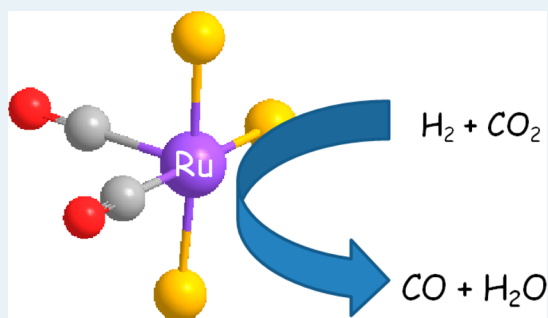
Reverse Water-Gas Shift Reaction Catalyzed by Mononuclear Ru Complexes

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S Supporting Information

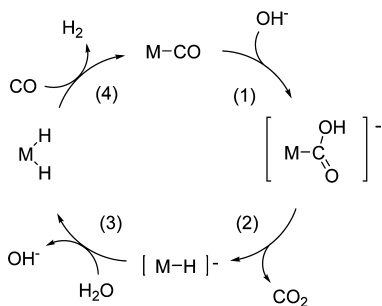
ABSTRACT: A series of mononuclear Ru halogen carbonyl complexes, $[\text{PPN}][\text{Ru X}_3(\text{CO})_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$), were found to catalyze the reverse water-gas shift reaction (RWGSR: $\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$). The Ru species in the reaction solution were investigated in situ using a high-pressure IR spectroscopy apparatus, which showed that $[\text{RuCl}_3(\text{CO})_3]^-$ was the exclusive Ru species when $[\text{PPN}][\text{RuCl}_3(\text{CO})_3]$ was used as a catalyst. On the basis of the IR spectra of stepwise reaction experiments, a plausible reaction mechanism for the mononuclear species is proposed.



KEYWORDS: carbon dioxide, hydrogenation, reverse water-gas shift reaction, ruthenium, in situ IR spectroscopy

The water-gas shift reaction (WGSR: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) is one of the well-known reactions catalyzed by metal complexes of Fe, Ni, Ru, Rh, and Os.¹ The mechanism of these catalytic reactions has also been well investigated.² Several reaction mechanisms, the outlines of which are shown in Scheme 1, have been proposed thus far. The starting carbonyl

Scheme 1. A Typical Reaction Mechanism of WGSR



complex is attacked by water to give a carboxylato complex (1), which in turn is decarboxylated to give a hydrido complex (2). The subsequent reaction of this complex with water gives a dihydrogen complex (3), which then undergoes ligand exchange with CO to release hydrogen gas (4).

In contrast, little is known about its reverse reaction, the reverse water-gas shift reaction (RWGSR). One of the difficult steps of the RWGSR is the formation of metal carboxylato complexes from metal hydrido complexes and CO_2 ; in most cases, the reaction of metal hydrido complexes and CO_2 gives formato complexes instead.³

We previously showed a successful example of the RWGSR by using tetranuclear Ru complexes as catalysts.^{4b} On the basis

of this catalytic reaction, we could further develop procedures for methanol synthesis, ethanol synthesis, homologation of methanol, and hydroformylation using CO_2 as a reactant.⁴ Because these tetranuclear Ru complexes have protonic hydrogens, CO_2 is assumed to coordinate its C atom on one of the Ru atoms.

In contrast, there has been little insight into the RWGSR catalyzed by mononuclear Ru complexes. Here, we report an example of RWGSR catalyzed by mononuclear Ru halogen carbonyl complexes, along with some insights into the catalytic mechanism of these complexes.

Representative results are summarized in Table 1. All of these reactions were carried out in a 20 mL stainless-steel autoclave. The Ru complexes were prepared according to the literature.⁵ $[\text{PPN}]\text{Cl}$ was purchased from Aldrich, and other salts were prepared by an anion-exchange reaction.⁶

When $[\text{PPN}][\text{RuCl}_3(\text{CO})_3]$ was used as a catalyst in the presence of $[\text{PPN}]\text{Cl}$ in NMP, the reaction of H_2 (6 MPa) and CO_2 (2 MPa) at 160 °C for 5 h formed CO in a yield of 87 TON based on a Ru atom (entry 1). This result indicates that the catalytic activity of the mononuclear Ru complex is almost 4 times as high as that of the conventional catalyst using a tetranuclear Ru complex (entry 10).

In contrast with the tetranuclear Ru cluster complexes, this mononuclear Ru complex exhibited little dependency on halogen salts (entries 1–3), which suggested a different mechanism in this catalysis. Even in the absence of salts, the yield of CO remained unchanged (entry 4). The yield of CO increased with an elevation of the reaction temperature from

Received: September 13, 2013

Revised: November 1, 2013

Published: November 1, 2013

Table 1. RWGSR Catalyzed by Ru Complexes^a

entry	complex	mmol	salt	TON ^b
1	[PPN][RuCl ₃ (CO) ₃]	0.02	[PPN]Cl	87
2	[PPN][RuCl ₃ (CO) ₃]	0.02	[PPN]Br	82
3	[PPN][RuCl ₃ (CO) ₃]	0.02	[PPN]I	92
4	[PPN][RuCl ₃ (CO) ₃]	0.02	[PPN]Cl	87
5 ^c	[PPN][RuCl ₃ (CO) ₃]	0.02	[PPN]Cl	43
6 ^d	[PPN][RuCl ₃ (CO) ₃]	0.02	[PPN]Cl	96
7	[RuCl ₂ (CO) ₃] ₂	0.01	[PPN]Cl	90
8	[RuBr ₂ (CO) ₃] ₂	0.01	[PPN]Br	64
9	[RuI ₂ (CO) ₃] ₂	0.01	[PPN]I	20
10	H ₄ Ru ₄ (CO) ₁₂	0.02	[PPN]Cl	23

^aReaction conditions: Ru complex, salts (0.1 mmol), NMP (2.0 mL), H₂ (6 MPa), CO₂ (2 MPa), 160 °C, 5 h. ^bBased on a Ru atom. ^cAt 140 °C. ^dAt 180 °C.

140 to 180 °C (entries 5 and 6). Even at 180 °C, only a trace of methanol was detected in the reaction solution.

Because the mononuclear Ru species, [RuCl₃(CO)₃]⁻, forms readily from a dinuclear Ru complex ([RuCl₂(CO)₃]₂)^{5b} and chloride salts, the reaction using [RuCl₂(CO)₃]₂ and [PPN]Cl gave almost the same result as that of entry 1 (entry 7). Although the type of halogen species of the additive salts has little effect on the catalytic activity as described above, the kind of halogen ligand markedly affects the catalytic activity, which decreased in the order of Cl⁻ > Br⁻ > I⁻ (entries 7–9).

Another important factor that affects the catalytic activity is the electron donatability of the solvents. As shown in Table 2, there is a positive correlation between the TON and DN (donation number) of the solvents, except for the case of γ -BL which showed a slightly lower TON against its DN.

Table 2. Effects of the Solvents^a

entry	solvent	DN	TON	ref
1	NMP	27.3	87	7
11	1,2-dichloroethane	0	0	7
12	dioxane	14.8	55	7
13	γ -BL	18.0	51	8
14	THF	20.0	58	7
15	DMA	27.8	91	7

^aReaction conditions are described in Table 1.

To investigate the Ru species under the reaction conditions, we used a 100 mL high-pressure autoclave reactor equipped with an in situ attenuated total reflectance (ATR) IR probe (Mettler Toledo). Before the [PPN][RuCl₃(CO)₃] and [PPN]Cl were reacted, two peaks were observed at 2034 and 2119 cm⁻¹, both of which were assigned to [RuCl₃(CO)₃]⁻ (Figure 1a).⁵ After they were reacted at 140 °C for 2 h, both peaks shifted 4 cm⁻¹ to lower wavenumbers, presumably because of the difference in analysis temperatures (Figure 1b), although [RuCl₃(CO)₃]⁻ was the only Ru species.

We then carried out stepwise reaction experiments by changing the gas introduced. At first, when [PPN][RuCl₃(CO)₃] was treated at 140 °C for 2 h under 2 MPa of He gas, the in situ IR spectrum showed peaks at 1958 and 2038 cm⁻¹, both of which were assigned to [RuCl₃(CO)₂(solvent)]⁻ (Figure 2a, b).^{5b} This Ru species was also confirmed by the ESI-MS analysis of the reaction solution after cooling to room temperature (Figure 3a, b). These results indicate that a CO

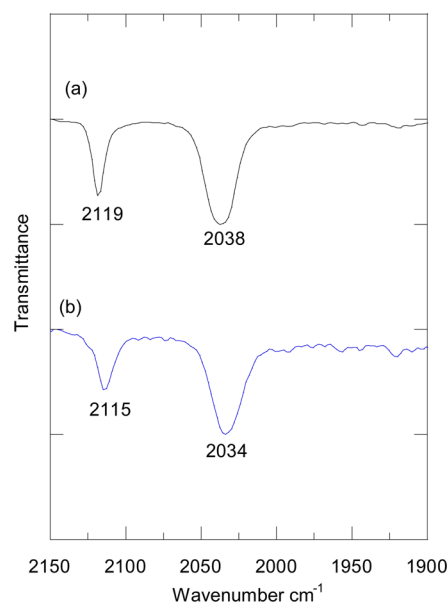


Figure 1. In situ IR spectra of RWGSR catalyzed by a mononuclear Ru complex: (a) before the reaction (room temperature) and (b) after the reaction at 140 °C for 1 h. Reaction conditions: [PPN][RuCl₃(CO)₃] (0.2 mmol), [PPN]Cl (1.0 mmol), NMP (20 mL), H₂ (6 MPa), CO₂ (2 MPa).

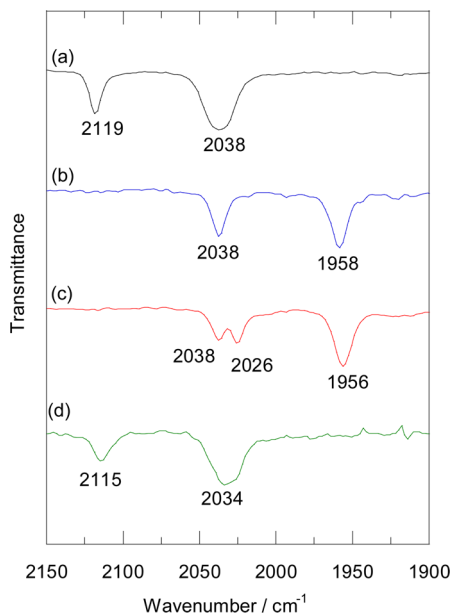


Figure 2. In situ IR spectra of a stepwise reaction experiment: (a) before the reaction (room temperature), (b) after treatment of (a) at 140 °C for 90 min under 1 MPa of He, (c) after treatment of (b) with 3 MPa of H₂ at 60 °C for 80 min, (d) after treatment of (c) with 3 MPa of H₂ and 1 MPa of CO₂ at 140 °C for 80 min. Other reaction conditions are described in Figure 1.

ligand of [RuCl₃(CO)₃]⁻ is released by ligand exchange with a solvent molecule.

Next, the above reaction solution in the autoclave was treated with 3 MPa of H₂ gas at 80 °C for 0.5 h. The in situ IR spectrum showed a new carbonyl peak at 2026 cm⁻¹ (Figure 2c). The ESI-MS analysis showed the formation of [RuCl₂(CO)₂H]⁻ (Figure 3c), which is in good agreement

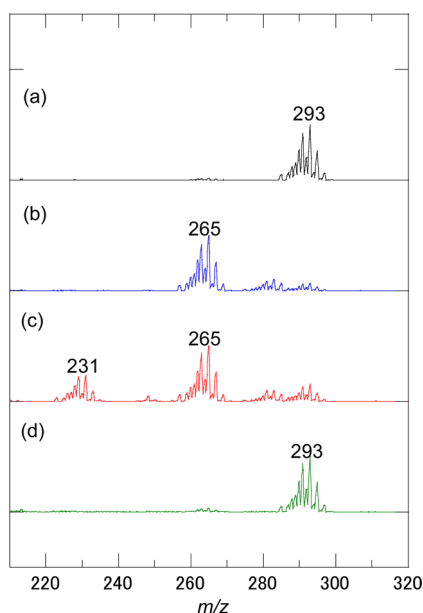


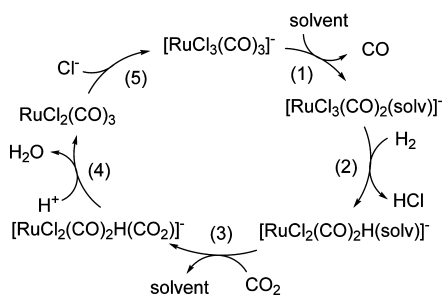
Figure 3. ESI-mass spectra of a stepwise reaction experiment: (a) before the reaction (room temperature), (b) after treatment of (a) at 140 °C for 90 min under 1 MPa of He, (c) after treatment of (b) with 3 MPa of H₂ at 60 °C for 80 min, (d) after treatment of (c) with 3 MPa of H₂ and 1 MPa of CO₂ at 140 °C for 80 min. Other reaction conditions are described in Figure 1.

with its calculated isotope distribution spectrum (see Supporting Information).

When 1 MPa of CO₂ was introduced into this reaction solution containing [RuCl₂(CO)₂H]⁻ at 80 °C, the IR peak at 2026 cm⁻¹ disappeared, and only the peaks corresponding to [RuCl₃(CO)₂(solvent)]⁻ remained. However, when 1 MPa of CO₂ and 3 MPa of H₂ were introduced into the reaction solution containing [RuCl₂(CO)₂H]⁻ at 140 °C for 2 h, the IR peak at 2026 cm⁻¹ disappeared, and the peaks corresponding to [RuCl₃(CO)₃]⁻ reappeared (Figure 2d). This Ru species was also confirmed by ESI-MS analysis (Figure 3d).

On the basis of these results, we propose the reaction mechanism shown in Scheme 2. The starting complex,

Scheme 2. A Plausible Reaction Mechanism of RWGSR



[RuCl₃(CO)₃]⁻, releases CO by ligand exchange with the solvent to form [RuCl₃(CO)₂(solvent)]⁻ (step 1). The reaction of [RuCl₃(CO)₂(solvent)]⁻ with hydrogen forms a hydrido complex, [RuCl₂(CO)₂H(solvent)]⁻, with the release of HCl (step 2). After coordination of CO₂ (step 3), the coordinated CO₂ reacts with a hydrogen ligand and a proton formed in step 2 to give a carbonyl ligand and water (step 4). A similar stoichiometric reduction of coordinated CO₂ to CO with protons has been reported with respect to a Ru complex.⁹

Finally, ligand exchange of RuCl₂(CO)₃ with Cl⁻ regenerates the starting complex.

In this reaction cycle, the rate-determining step appears to be step 1 because [RuCl₃(CO)₃]⁻ was the sole Ru species under the reaction conditions (Figure 1). This suggestion is also supported by the dependency on the reaction rates on the solvent; TON increases as the electron donatability of the solvent increases. Moreover, it is further supported by the effect of the halogen ligand. The CO stretching frequency of [RuX₃(CO)₃]⁻ decreases in the order of Cl⁻ > Br⁻ > I⁻, which indicates that the degree of backdonation from the metal center to the CO ligands increases in the order of Cl⁻ < Br⁻ < I⁻. This suggests that the coordination bond energy of the CO ligand increases in the same order so that TON decreases in the order of Cl⁻ > Br⁻ > I⁻.

In summary, a mononuclear Ru complex, [RuCl₃(CO)₃]⁻, exhibits higher catalytic activity per Ru atom toward RWGSR than the conventional catalyst using tetranuclear Ru cluster complexes. A portion of its reaction mechanism can be observed using an in situ IR spectroscopy apparatus. We are now attempting to detect the CO₂-coordinating intermediate and to apply this RWGSR to reactions that use CO₂ as a reactant.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, in situ IR spectroscopy apparatus, and ESI-MS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

PPN, bis(triphenylphosphine)iminium; TON, turnover number; DN, donation number; NMP, *N*-methyl-imidazolone; γ -BL, γ -butyrolactone; THF, tetrahydrofuran; DMA, dimethylacetamide

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