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Ruthenium-catalyzed one-pot hydroformylation of alkenes using carbon dioxide as a reactant

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Abstract

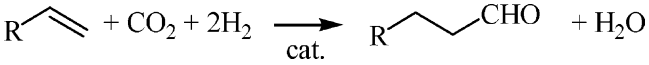
A new hydroformylation of alkenes using carbon dioxide as a reactant is shown to take place in the presence of ruthenium cluster complexes and halide salts. Similar or even better yields of alcohols were formed as compared to the conventional hydroformylation with CO under the same reaction conditions. The reaction proceeded in three steps: CO_2 is first converted to CO; then it is used as a reagent for hydroformylation to give aldehyde; subsequently, it is hydrogenated to alcohol. ESI-mass spectrometric analyses of the reaction solutions indicated formation of four kinds of ruthenium anionic complexes including tetra-, tri-, and mononuclear species. On the basis of experimental findings, possible roles of these complexes are discussed.

Keywords: Carbon dioxide; Hydroformylation; Ruthenium; Homogeneous catalysis

1. Introduction

Carbon monoxide (CO) is used widely as a raw material in the synthesis of alcohols, aldehydes, hydrocarbons, organic acids, and so on. It is extremely reactive in the presence of many kinds of catalysts, but it is so toxic that its reactions require facilities that address safety and environmental issues. For that reason, replacement of CO by carbon dioxide (CO_2), a non-toxic and abundant C1 resource, is attractive. In this regard, we have found that tetranuclear ruthenium cluster complexes show high catalytic activity toward hydrogenation of CO_2 to CO [1]. In addition, they can be used as catalysts for synthesis of methanol, methane, and ethanol, from CO_2 [2–6].

Hydroformylation is an important industrial process for synthesizing aldehydes and alcohols. Many reports describe the use of CO_2 as a *solvent* for hydroformylation, but none describe its use as a *reactant* in this process. An essential requirement for applying hydrogenation of CO_2 to the hydroformylation reaction is the depression of undesired hydrogenation of substrates. Our preliminary experiments have shown that the reaction is possible; although many complexes based on ruthenium clusters are known to have high catalytic activity toward the hydrogenation of alkenes [7,8], the tetranuclear ruthenium complexes can be employed as selective catalysts for hydroformylation using CO_2 as a reactant (Eq. (1)) [9]. This discovery is the first example of the use of CO_2 as a reactant in hydroformylation. This paper describes details of this novel reaction including some insights into its reaction mechanism.



(1)

2. Results and discussion

As we have reported previously, catalytic activity of the tetranuclear ruthenium complexes towards hydrogenation of CO_2 to CO is strongly dependent on the anionic species of the additive salts. The reaction rate increases in the order $I^- < Br^- < Cl^-$, which is also the order of their proton affinities. No other anionic species were found to be effective [1,6]. Table 1 summarizes the effects of salts on the

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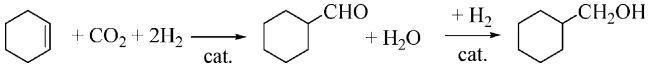
Table 1
Effects of salts on hydroformylation of cyclohexene using carbon dioxide[a]

Run	Salt	Conv. (%)	Yield (%)		
			Alcohol	Aldehyde	Alkane
1	None[b]	100	0	0	92
2	LiCl	100	88	2	6
3	LiCl[c]	100	82	3	4
4	LiBr	100	76	1	13
5	LiI	100	29	0	61
6	[PPN]Cl	100	82	0	15
7	NaCl	99	72	8	18
8	KCl	97	66	11	13
9	Li_2CO_3	18	0	0	14
10	LiOAc	73	0	0	68

[a] Conditions: $H_4Ru_4(CO)_{12}$ (0.1 mmol), salts (0.4 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO_2 (4.0 MPa), H_2 (4.0 MPa), 140 °C, 30 h.
[b] Reaction time was 5 h.
[c] This reaction used CO (4.0 MPa) in place of CO_2.

hydroformylation of cyclohexene using CO_2 (Eq. (2)).



(2)

In the absence of salts, the ruthenium carbonyl complex released carbonyl ligands to precipitate metal, which caused marked hydrogenation of cyclohexene (run 1). Addition of salts stabilized the ruthenium complex and prevented such metal precipitation. In the presence of halide salts, hydroformylation proceeded (runs 2, 4–8), while only hydrogenation occurred with other kinds of salts (runs 9 and 10). The order of the effect of halide anion on the hydroformylation was identical to that observed in the hydrogenation of CO_2 to CO (runs 2, 4, 5) [1]. The most effective salt was LiCl, which gave the corresponding alcohol in almost the same yield as when CO was used as a reactant (runs 2 and 3). These results suggest that this reaction proceeds via CO formation; first, CO_2 is hydrogenated to CO, which is then used for the subsequent hydroformylation. Regarding the effects of cations, Li^+ cation was the most effective, but its Lewis acidity does not appear to be important because a large and delocalized PPN^+ [PPN = $N(PPh_3)_2$] cation behaved similarly to the alkali metal cations (run 6). Decreased catalytic activity when Na or K salts were used may be caused by their hard solubility in *N*-methyl-2-pyrrolidone (NMP).

Although a variety of ruthenium complexes including mononuclear and cluster ones have been known to catalyze the conventional hydroformylation with CO [10], only the carbonyl complexes could be used as catalyst precursors for hydroformylation using CO_2 (Table 2, runs 1–6). The most effective ones were $H_4Ru_4(CO)_{12}$, $Ru_3(CO)_{12}$, and [PPN][$RuCl_3(CO)_3$], all of which generate the same active species including tetra- and mononuclear ones during the reaction as addressed later. In contrast to conventional hydroformylation [11,12], introducing N or P ligands reduced

Table 2
Catalytic activities of various kinds of ruthenium complexes for the hydroformylation of cyclohexene using CO_2[a]

Run	Complex	Conv. (%)	Yield (%)		
			Alcohol	Aldehyde	Alkane
1	$H_4Ru_4(CO)_{12}$	100	88	2	6
2	$Ru_3(CO)_{12}$	100	86	0	12
3	[PPN][$Ru(CO)_3Cl_3$]	100	82	7	7
4	$Ru_3(CO)_{10}$(bpy)	94	31	2	56
5	$Ru_3(CO)_{10}$(dppm)	92	66	0	23
6	$Ru_2(CO)_8Cp^*_2$	32	2	0	28
7	$RuCl_3{\cdot}3H_2O$	100	0	0	100
8	$RuCl_2(PPh_3)_3$	100	0	0	92

[a] Conditions: complex (0.1 mmol), LiCl (0.4 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO_2 (4.0 MPa), H_2 (4.0 MPa), 140 °C, 30 h.

the catalytic activity probably because they inhibited CO formation (runs 4 and 5). For convenience, a combination of $Ru_3(CO)_{12}$ and [PPN]Cl was used as a typical catalyst system in this paper.

Influences of the reaction temperature were investigated using the $Ru_3(CO)_{12}$/[PPN]Cl system. As shown in Fig. 1, the optimum temperature for the alcohol formation was 140 °C, which was about 30 °C lower than that for the hydrogenation of CO_2 to CO [6]. The conversion of cyclohexene was decreased as the reaction temperature was lowered. It was clearly caused by the decrease in the catalytic activity for the CO formation, since almost no CO was recovered below 100 °C. In contrast to the conventional hydroformylation with CO using $[HRu_3(CO)_{11}]^-$ as a catalyst [13], it was difficult to prevent hydrogenation of aldehyde to alcohol even at lower temperatures. At higher temperatures,

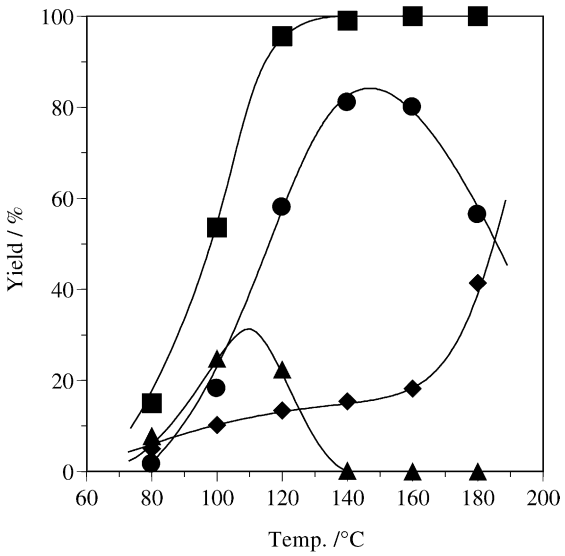


Fig. 1. Temperature dependency of the product distribution. Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), [PPN]Cl (0.4 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO_2 (4.0 MPa), H_2 (4.0 MPa), 30 h. (●), yield of cyclohexanemethanol; (▲), yield of cyclohexanecarboxaldehyde; (◆), yield of cyclohexane; (■), conversion of cyclohexene.

hydrogenation of cyclohexene was enhanced, thereby decreasing the yield of alcohol.

The solvent type also influences this catalysis. Two major constraints on the choice of the solvents exist: they must be resistant to hydrolysis because water is formed in this reaction; in addition, they should be materials that do not donate protons that inhibit CO formation [1]. The experiments were carried out using [PPN]Cl as an additive salt, which has good solubility in various organic solvents. Table 3 shows typical results. Alcohol formation was induced in many kinds of solvents, such as NMP, 1,3-dimethyl-imidazolidinone (DMI), dimethoxyethane (DME), toluene, and benzene (runs 1–5). Nevertheless, little relation was observed between catalytic activity and solvent properties. An exception was THF, in which a considerable amount of aldehyde remained unhydrogenated (run 6).

As stated above, this catalysis comprises three elementary reactions: hydrogenation of CO_2 to CO, hydroformylation with CO, and hydrogenation of aldehyde to alcohol. In addition, the hydrogenation of substrates occurred simultaneously as a side reaction. The time course of these reactions at 140 °C is shown in Fig. 2. The formation rate of CO was almost twice as rapid as that of hydroformylation. The hydroformylation is completed within ca. 8 h, whereas the hydrogenation of the aldehyde to the alcohol required more time to complete. On the other hand, hydrogenation of cyclohexene occurred only at the initial stage, so that the yield of cyclohexane was almost unchanged throughout the reaction.

In our previous study on hydrogenation of CO_2 to CO with $Ru_3(CO)_{12}$/[PPN]Cl system [1,6], it was shown that the presence of chloride salt was essential for the catalysis to proceed. Accordingly, we investigated the effects of the concentration of chloride anion on hydroformylation using CO_2 at 140 °C (Fig. 3). Data for [PPN]Cl/$Ru_3(CO)_{12}$ ratios <1 were excluded because ruthenium metal was precipitated, causing marked hydrogenation of substrates. Considering that CO formation is much faster than hydroformylation with CO at this temperature, this result reflects the effects of concentration of chloride anion on the second step of this reaction, the hydroformylation with CO. A considerable amount of aldehyde remained unhydrogenated at lower concentrations of chloride anion, whereas it was hydrogenated to alcohol as the concentration increased. At the [PPN]Cl/$Ru_3(CO)_{12}$ ratios over 4, the alcohol yield remained unchanged even under very high concentrations of chloride anion.

Hydroformylation of other substrates than cyclohexene is also facile using CO_2 as a reactant with this catalyst

Table 3
Hydroformylation of cyclohexene using CO_2 in different solvents[a]

Run	Solvent	Conv. (%)	Yield (%)		
			Alcohol	Aldehyde	Alkane
1	NMP	100	86	0	12
2	DMI	97	80	5	11
3	DME	99	91	1	4
4	Toluene	98	88	3	4
5	Benzene	99	88	0	5
6	THF	98	70	14	4

[a] Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), [PPN]Cl (0.4 mmol), cyclohexene (5.0 mmol), solvent (8.0 mL), CO_2 (4.0 MPa), H_2 (4.0 MPa), 140 °C, 30 h.

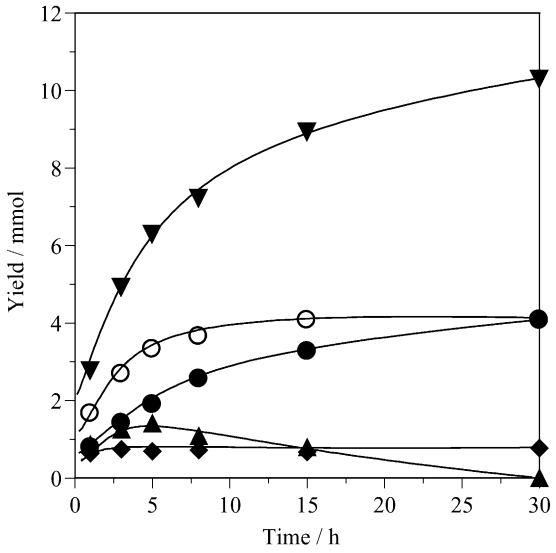


Fig. 2. Time course of the hydroformylation of cyclohexene using CO_2 as a reactant. Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), [PPN]Cl (0.4 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO_2 (4.0 MPa), H_2 (4.0 MPa), 140 °C. (●), yield of cyclohexanemethanol; (▲), yield of cyclohexanecarboxaldehyde; (◆), yield of cyclohexane; (○), total yield of hydroformylated products (cyclohexanecarboxaldehyde + cyclohexanemethanol); (▼), total yield of CO (CO + cyclohexanecarboxaldehyde + cyclohexanemethanol).

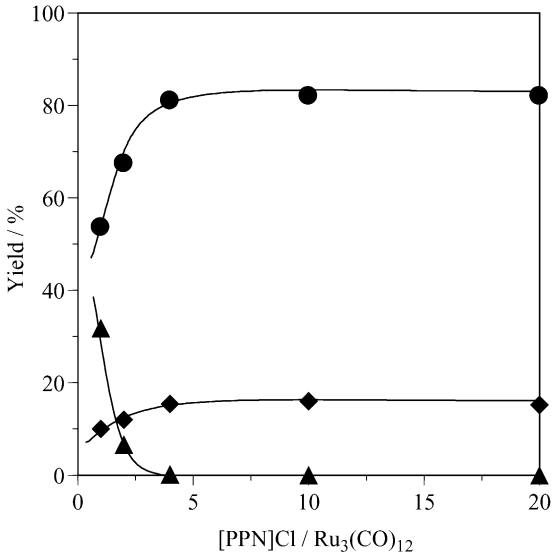


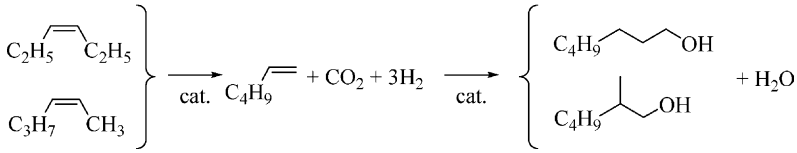
Fig. 3. Effects of the concentration of additive salts. Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO_2 (4.0 MPa), H_2 (4.0 MPa), 140 °C, 30 h. (●), yield of cyclohexanemethanol; (▲), yield of cyclohexanecarboxaldehyde; (◆), yield of cyclohexane.

Table 4
Hydroformylation of various alkenes using CO_2[a]

Run	Substrate	Carbonyl source	Conv. (%)	Yield (%) (liner/branch ratio)		
				Alcohol	Aldehyde	Alkane
1	Cyclooctene	CO_2	100	81 (–)	8 (–)	7
2		CO	100	33 (–)	8 (–)	3
3	3-Hexene	CO_2	100	74 (57/43)	10 (45/55)	8
4		CO	100	65 (50/50)	15 (18/82)	7
5	2-Hexene	CO_2	100	73 (60/40)	9 (34/66)	7
6		CO	100	71 (53/47)	12 (17/83)	5
7	1-Hexene	CO_2	100	70 (59/41)	7 (23/73)	14
8		CO	100	48 (76/24)	20 (43/57)	8
9	α-Methylstyrene	CO_2	100	48 (100/0)	1 (100/0)	40
10		CO	100	15 (100/0)	3 (100/0)	44
11	1,1-Diphenylethylene	CO_2	100	9 (100/0)	0 (–)	86
12		CO	100	4 (100/0)	0 (–)	90
13	Styrene	CO_2	100	4 (60/40)	6 (60/40)	90
14		CO	100	43 (56/44)	5 (81/19)	24
15	*Trans*-stilben	CO_2	78	58 (–)	4 (–)	22
16		CO	76	49 (–)	9 (–)	15
17	*Cis*-stilben	CO_2	66	26 (–)	5 (–)	34
18		CO	68	37 (–)	15 (–)	10

[a] Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), LiCl (0.4 mmol), alkene (5.0 mmol), NMP (8.0 mL), CO_2 or CO (4.0 MPa), H_2 (4.0 MPa), 140 °C, 30 h.

system (Table 4). Compared to the reactions using CO under similar condition, the reactions using CO_2 gave the corresponding alcohols almost comparable to much better yields except for 1,1-diphenylethylene and styrene, which were susceptible to hydrogenation. Such inefficiency of the alcohol formation using CO was caused not only by the decrease in hydrogenation of aldehydes but also by the aldol condensation of aldehydes. On the other hand, the undesirable aldol condensation could be avoided in hydroformylation using CO_2, since hydrogenation of aldehyde proceeded prior to it. Another interesting finding is that the hydroformylation of 3- and 2-hexene did not give a simple hydroformylated product, 2-ethyl-1-pentanol, but a mixture of 2-methyl-1-hexanol and 1-heptanol, which was identical to those formed by the hydroformylation of 1-hexene. This result suggests that double bond migration from 3- and 2-hexene to 1-hexene occurred prior to hydroformylation (Eq. (3)). Knifton also reported analogous linear alcohol formation by hydroformylation of internal alkenes with CO [14]. Unfortunately, the regioselectivity of this catalyst system in hydroformylation of 1-hexene was exhibited to be low (runs 7 and 8), although Laine reported high regioselectivity of ruthenium cluster complexes toward linear products in hydroformylation of 1-alkene [15]. Exceptionally, only linear alcohols were formed from α-methylstyrene and 1,1-diphenylethylene probably because of their steric effects (runs 9–12).



(3)

To elucidate active species in hydroformylation of cyclohexene, the reaction solutions were analyzed with electrospray-ionization (ESI) mass spectrometry. Four kinds of ruthenium species were detected in the solution obtained after reaction using CO_2 with the $Ru_3(CO)_{12}$/[PPN]Cl system for 3 h at 140 °C (Fig. 4a): a tetranuclear complex, $[H_3Ru_4(CO)_{12}]^-$ (**1**); a trinuclear complex, $[HRu_3(CO)_{10}]^-$, which is derived from $[HRu_3(CO)_{11}]^-$ (**2**); a mononuclear complex, $[RuCl_3(CO)_3]^-$ (**3**); its cyclohexene complex, $[RuCl_2(CO)_3(C_6H_{10})]^-$ (**4**). Each isotope profile closely matches that predicted by theory. An almost identical spectrum was observed in the solution with the $H_4Ru_4(CO)_{12}$/[PPN]Cl system (Table 2, run 1), whereas no formation of the complex **2** was observed with the [PPN][$Ru(CO)_3Cl_3$]/[PPN]Cl system (Table 2, run 3). The latter result suggests that condensation of mononuclear to

tetranuclear species took place in the presence of CO_2/H_2. Although its clusterization mechanism is not clear, this may have relevance to the cluster syntheses from complex **3** reported by Lavigne, in which reductive elimination of HCl was a key step [16]. On the other hand, no formation of complex **1** but complexes **2**, **3**, and **4** were observed in the reaction solution of hydroformylation using CO (Fig. 4b). Such a difference in the catalytic species appears to be responsible for the difference between hydroformylations using CO_2 and CO.

Regarding formation of complexes **2** and **3**, the reaction of Eq. (4), an analogous reaction reported by Dombek, may be involved [17]. Complex **2** is known to be interchangeable with complex **1** according to Eq. (5) [18]. Combination of Eqs. (4) and (5) leads to Eq. (6), which represents equilibrium among these three complexes. Fig. 4 indicates that the equilibrium lies mostly to the left in the reaction solution. Considering the facts that higher concentration of Cl^- did not affect the alcohol formation (Fig. 3) and that a tetranuclear species could be generated from a mononuclear precursor, it appears that the contribution of Cl^- to the shift of the equilibrium of Eq. (6) to the right is rather small.

$$\tfrac{7}{3}Ru_3(CO)_{12} + 3Cl^- + H_2 \rightleftarrows 2[HRu_3(CO)_{11}]^- + [RuCl_3(CO)_3]^- \quad (4)$$

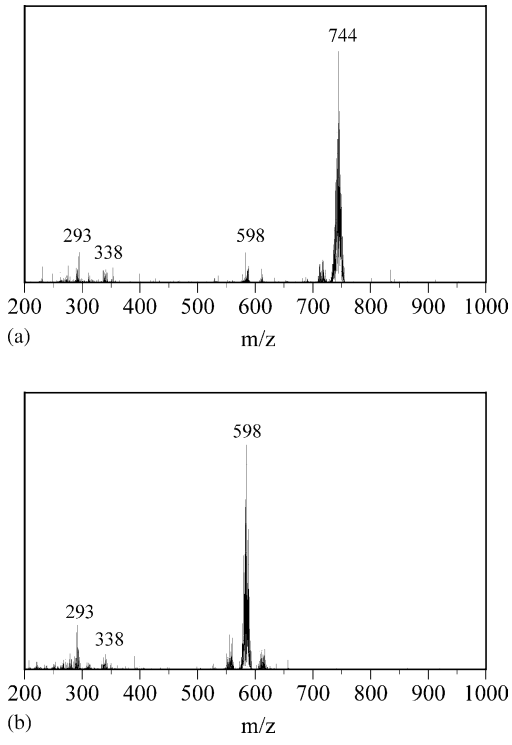


Fig. 4. Negative ion ESI-MS spectra of the solutions after (a) hydroformylation using CO_2 and (b) hydroformylation using CO. Each peak is assigned to following ruthenium species: $[H_3Ru_4(CO)_{12}]^-$ (**1**, $m/z = 744$), $[HRu_3(CO)_{10}]^-$ (**2**, CO, $m/z = 598$), $[RuCl_3(CO)_3]^-$ (**3**, $m/z = 293$), and $[RuCl_2(CO)_3(C_6H_{10})]^-$ (**4**, $m/z = 338$). Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), [PPN]Cl (0.4 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO_2 or CO (4.0 MPa), H_2 (4.0 MPa), 140 °C, 3 h.

$$3[H_3Ru_4(CO)_{12}]^- + 9CO \rightleftarrows 3[HRu_3(CO)_{11}]^- + Ru_3(CO)_{12} + 3H_2 \quad (5)$$

$$\tfrac{7}{3}[H_3Ru_4(CO)_{12}]^- + 9CO + Cl^- \rightleftarrows 3[HRu_3(CO)_{11}]^- + 2H_2 + \tfrac{1}{3}[RuCl_3(CO)_3]^- \quad (6)$$

Complex **1** was found to be a catalyst precursor for the hydrogenation of CO_2 to CO, which is the first step of this catalysis [1,6]. For subsequent hydroformylation with CO, both complexes **1** and **2** have been known to be active catalysts [13,15]. To compare the catalytic activity, we synthesized the complexes **1**, **2** and **3** individually, then employed them as catalysts for hydroformylation of cyclohexene with CO. Since the partial pressure of CO was very low in hydroformylation using CO_2, these experiments were carried out under conditions of excess H_2 ($H_2/CO = 7/1$). Although a slight interconversion between complexes **1** and **2** was observed according to Eq. (6), the reaction rates reflected the complexes that were used (Fig. 5). Complexes **1** and **2** were shown to be slightly active for hydroformylation, but complex **3** was quite inert. However, it is noteworthy that when complex **1** or **2** was used in combination with complex **3**, the catalytic activity was greatly enhanced and that the former combination was more active than the latter; its catalytic activity was enhanced almost 40 times as fast as that of the complex **1** alone.

Although several reaction pathways are probably involved in the hydroformylation step, the above results suggest that it is mostly catalyzed through cooperation of complexes **1** and **3**. The latter mononuclear complex appears to provide a coordination site for substrates because cyclohexene coordinating complex **4** was observed in the reaction solution (Fig. 4). It is inactive for hydroformylation in the absence of other ruthenium species; however, tetranuclear complex **1** may induce hydrogen donation, which seems to be responsible for the procession of catalysis.

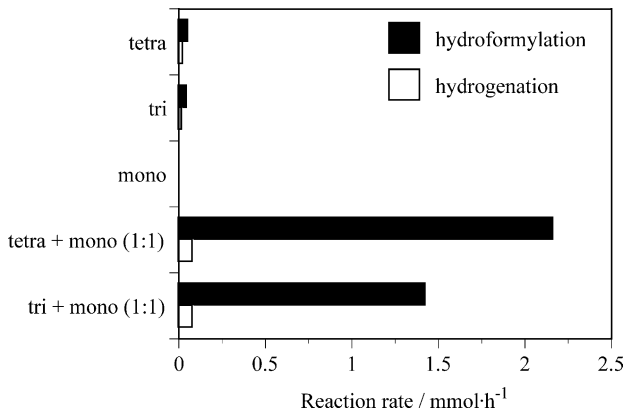
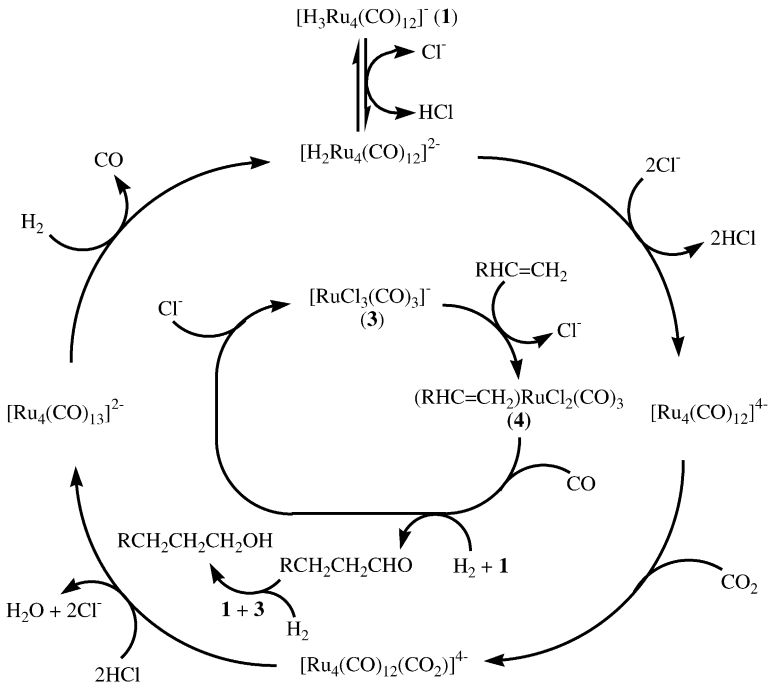


Fig. 5. Comparison of the rates of the hydroformylation with CO. Conditions: complex (0.1 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO (1.0 MPa), H_2 (7.0 MPa), 140 °C, 0.5 h.



Scheme 1.

The third step of this catalysis, hydrogenation of aldehyde to alcohol, was enhanced as the concentration of chloride anion increased (Fig. 3). For that reason, this step may be also catalyzed by a combination of complexes **1** and **3**, which may involve an analogous hydrogen transfer.

In summary, we propose a reaction mechanism illustrated in Scheme 1. The outside cycle represents the first step of this catalysis, hydrogenation of CO_2 to CO, which is catalyzed by the tetranuclear anionic species. As we have already reported [1,6], a key step is deprotonation of hydride complexes with Cl^- to give a hydrogen-free complex, $[Ru_4(CO)_{12}]^{4-}$, which can coordinate CO_2 [19]. Followed by the coordination of CO_2, electrophilic attack with proton of HCl converts CO_2 to CO ligand and releases water. The inside cycle represents the second step of this reaction, hydroformylation with CO, catalyzed by the combination of the tetranuclear and mononuclear anionic species. This step involves the coordination of substrates to the mononuclear species, followed by insertion of CO and the hydrogen donation from the tetranuclear species. The third step is hydrogenation of the aldehyde to the alcohol, which may be also catalyzed by the combination of these two complexes.

Compared to the conventional hydroformylation, this catalyst system proved effective in utilizing non-toxic and abundant CO_2 directly as a reactant. Besides, it exhibited almost comparable to better yields and chemoselectivity toward alcohol formation. However, it is still inferior with respect to controlling regioselectivity. Attempts to improve this catalysis are underway.

3. Experimental

Reagents used in this study were chemical grade. The solvents were dried and purified by common methods. We prepared $H_4Ru_4(CO)_{12}$ [20], $Ru_3(CO)_{10}$(bpy) (bpy = 2,2′-bipyridine) [21], $Ru_3(CO)_{10}$(dppm) (dppm = diphenylphosphinomethane) [22], [PPN][$H_3Ru_4(CO)_{12}$] [23], [PPN][$HRu_3(CO)_{11}$] [24], and [PPN][$RuCl_3(CO)_3$] [25] as described in the literature. Other reagents were commercial products that were used without further purification.

The GLC analyses for the liquid products were performed either on a GC-353 (GL Sciences Co., Ltd.) gas chromatograph with a TC-FFAP (0.25 mm × 25 m) capillary column (GL Sciences Co., Ltd.) or a GC-14A gas chromatograph (Shimadzu Corp.) with a ZB-1 capillary column (0.25 mm × 30 m; Phenomenex, Inc.). A GC-20B fuel gas chromatograph system (Shimadzu Corp.) was used for gaseous products. Products were identified with GC–MS analysis on a GCMS-QP5050A (Shimadzu Corp.). ESI mass spectra were obtained by the infusion method on a ZQ-2000 spectrometer (Waters Corp.). A DME solution of the reaction solution (50 ppm) was introduced into the ESI source (capillary voltage = 3.0 kV, cone voltage = 10 V) using a syringe pump at a flow rate of 5 μL/min.

In a typical experiment, an NMP (8.0 mL) solution of $H_4Ru_4(CO)_{12}$ (0.1 mmol), LiCl (0.4 mmol) and cyclohexene (5.0 mmol) were placed in a 50 mL stainless steel autoclave. CO_2 (4.0 MPa) and H_2 (4.0 MPa) were introduced at room temperature. Then the reactor was heated to 140 °C and held at that temperature for 30 h with stirring. GC analyses

showed that CO (10.1 mmol) was present in the gas phase and that cyclohexanemethanol (4.4 mmol), cyclohexanecarboxaldehyde (0.1 mmol), and cyclohexane (0.3 mmol) were present in the liquid phase.

Acknowledgements

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