

Mechanistic Studies on Direct Ethylene Glycol Synthesis from Carbon Monoxide and Hydrogen

2. Homogeneous Ruthenium Catalyst

M. ISHINO, M. TAMURA, T. DEGUCHI, AND S. NAKAMURA

Organic Synthesis Research Laboratory, Sumitomo Chemical Company, Ltd., 2-10-1, Tsukahara, Takatsuki City, Osaka 569, Japan

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Mechanistic studies on direct syngas conversion to ethylene glycol by a homogeneous Ru catalyst combined with *N*-methylbenzimidazole (NMBI) were performed. High-pressure IR studies showed that $\text{Ru}(\text{CO})_5$ (A), $\text{Ru}(\text{CO})_4\text{L}$ (B), and $(\text{LH})^+[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ (C) (L = NMBI) coexist at equilibrium in the catalyst solution as major species. It was found that the activity of CO hydrogenation was proportional to the concentration of the complex (B). A neutral hydride complex, $\text{H}_2\text{Ru}(\text{CO})_3\text{L}$, derived from the complex (B) was considered to be the active form. Kinetic studies by means of complete-mixing flow-reaction experiments indicated that NMBI added to the Ru catalyst enhanced both the formation and the hydroformylation of formaldehyde (FAL), the key intermediate, and the subsequent reactions of FAL were rate-determining. It was suggested that NMBI enriches the Ru hydride species and accelerates the CO insertion to the hydride and the hydroxymethyl species by acting as a ligand and a base. The Ru anionic hydride species has a much lower activity for the CO hydrogenation to form FAL and a higher activity for the MeOH formation that proceeds via the methoxy species. The studies on catalyst concentration dependencies by means of batchwise reaction revealed the involvement of dinuclear mechanisms, which probably worked in the reductive elimination of the acyl complexes. © 1992 Academic Press, Inc.

INTRODUCTION

The direct conversion of synthesis gas to ethylene glycol (EG) is known to be catalyzed by various carbonyl complexes of transition metals such as Co, Rh, Ru, Ir, and Re (1–7). Kiso *et al.* already reported that *N*-methylbenzimidazole (NMBI) prominently improves the activity and the EG selectivity of the Ru carbonyl catalyst (4). We reported that formaldehyde (FAL) and glycolaldehyde (GAL) act as the intermediates for this reaction by using a halide-promoted Ru catalyst (8). In this paper, we performed high-pressure IR studies as well as kinetic studies to clarify the mechanism for the Ru/NMBI catalysts more specifically (9).

EXPERIMENTAL

$\text{Ru}_3(\text{CO})_{12}$ was used as the catalyst precursor, which was dissolved in the solvents. NMBI was synthesized through

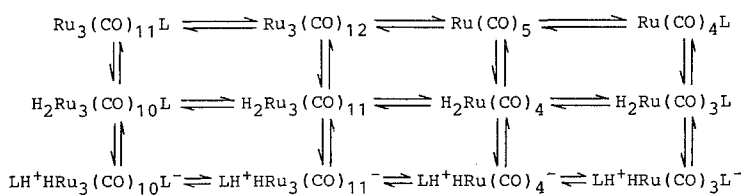
methylation of benzimidazole with dimethyl sulfate.

The methods of high-pressure IR experiments, complete-mixing flow-reaction (CMFR) experiments, batchwise reactions, and analyses for the liquid products were reported in Part 1.

RESULTS AND DISCUSSION

High-Pressure IR Studies

Imidazoles including NMBI may act both as a base and as a ligand to Ru carbonyls. Scheme 1 shows possible equilibrium relationships among Ru complexes in a $\text{Ru}_3(\text{CO})_{12}$ /imidazole catalyst system under reaction conditions. Many species such as Ru neutral carbonyls, Ru carbonyls coordinated by an imidazole, Ru hydride carbonyls, and Ru anionic carbonyls, which are trinuclear and mononuclear species, can be formed at equilibria. High-pressure IR studies were conducted in the following order:



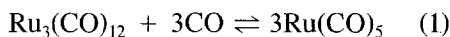
(L=an imidazole)

SCHEME 1. Possible ruthenium complexes.

- Cluster equilibrium between Ru₃(CO)₁₂ and Ru(CO)₅
- Ligand exchange of Ru(CO)₅ with imidazoles
- Analysis of Ru₃(CO)₁₂/NMBI catalyst.

a. Cluster equilibrium between Ru₃(CO)₁₂ and Ru(CO)₅. When Ru₃(CO)₁₂ in THF solution was pressurized with CO gas at 150°C, Ru(CO)₅ (A) (2040 and 1995 cm⁻¹) was formed as shown in Fig. 1. Only the two

carbonyl complexes were observed and they attained equilibrium within a few hours.



$$K_0 = [\text{Ru}(\text{CO})_5]^3 / [\text{Ru}_3(\text{CO})_{12}] P_{\text{CO}}^3$$

Table 1 shows the ratio of all species that are calculated by using the bands at 2060 and 1995 cm⁻¹ for the trinuclear and the mononuclear complexes, respectively. The ratio of Ru(CO)₅ increases with CO pressure. The estimated K₀ value at 150°C is about 3.5 × 10⁻⁹ (g-atom Ru/liter)² atm⁻³. This value (log K₀ = -8.5) agrees closely with the value (log K_p = -8.1 at 150°C in *n*-hexane solution) reported by G. Bor (10). Addition of H₂ gas (92 atm) did not lead to observation of any hydride complexes and had no effect on the K₀ value. Reaction tem-

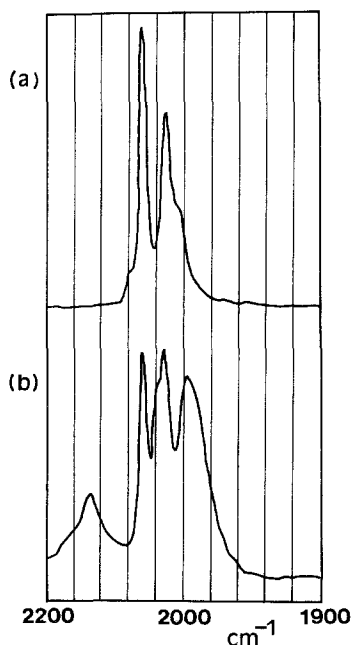


FIG. 1. IR spectra of the cluster equilibrium between Ru₃(CO)₁₂ and Ru(CO)₅ in THF. (a) Ru₃(CO)₁₂, 0.014 g-atom/liter; N₂, 1 atm, 20°C. (b) Ru₃(CO)₁₂, 0.014 g-atom/liter; CO, 30 atm, 150°C. The broad absorption at 2135 cm⁻¹ is based on dissolved CO gas.

TABLE 1

Measured Equilibrium Constants of the Ru Cluster Fragmentation Reactions (Eq. (1)) in THF under CO Pressures^a

P(CO) ^b (atm)	P(H ₂) ^b (atm)	Temp. (°C)	Ru(CO) ₅ ^c (%)	Ru ₃ (CO) ₁₂ ^c (%)	10 ⁹ K ₀ (g-atom/liter) ² atm ⁻³
16.5	—	150	36.8	63.2	3.44
39.3	—	150	69.6	30.4	3.57
70.4	—	150	>90	<10	—
35.2	—	180	65.0	35.0	3.53
34.2	—	200	63.1	36.9	3.33
25.3	92.1	150	51.7	48.3	3.47

^a Charged Ru₃(CO)₁₂ is 0.014 g-atom/liter.

^b The partial pressures of CO and H₂ were calculated by subtraction of vapor pressures of THF from total pressures.

^c The estimated absorption coefficients are Ru(CO)₅ (1995 cm⁻¹)/Ru₃(CO)₁₂ (2060 cm⁻¹) = 1/1.12.

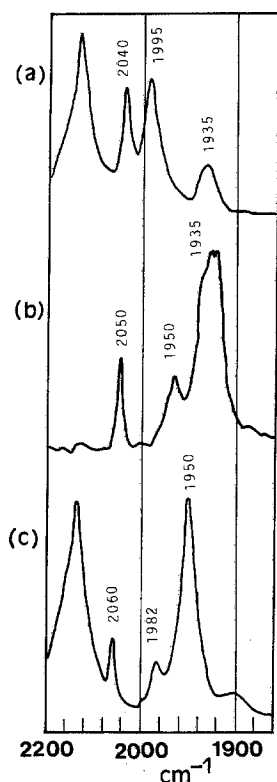
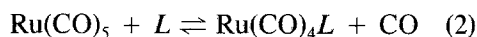


FIG. 2. IR spectra of the ligand exchange reactions of $\text{Ru}(\text{CO})_5$ in THF at 150°C . (a) $\text{Ru}_3(\text{CO})_{12}$, 0.007 g-atom/liter; NMBI, 0.25 mol/liter; CO, 62 atm. (b) $\text{Ru}_3(\text{CO})_{12}$, 0.3 mg-atom; NMBI, 250 mmol; THF, 20 ml; CO, 60 atm. (c) $\text{Ru}_3(\text{CO})_{12}$ 0.007 g-atom/liter; PPh_3 , 0.0125 mol/liter; CO, 90 atm.

perature scarcely affected the K_0 value in the range from 150 to 200°C in agreement with Bor's results. These results show that the cluster equilibrium shown by Eq. (1) substantially inclines to the mononuclear carbonyl under the reaction conditions of direct EG synthesis such as around 200°C and above 300 atm of CO/H_2 .

b. Ligand exchange of $\text{Ru}(\text{CO})_5$ with imidazoles. Next, we studied the effect of amines including imidazoles under CO pressure in THF solvent. Figure 2a shows an IR spectrum of the $\text{Ru}_3(\text{CO})_{12}$ /NMBI system at 150°C under a CO pressure of 62 atm. This system gave a new band at 1935 cm^{-1} in addition to the bands of $\text{Ru}(\text{CO})_5$. When $\text{Ru}_3(\text{CO})_{12}$ was heated in the presence of a

large excess amount of NMBI under the same conditions for 2 h and then cooled and depressurized, the three bands (2050 , 1965 , and 1935 cm^{-1}) appeared as shown in Fig. 2b. These bands were assigned to a Ru mononuclear carbonyl coordinated by NMBI, $\text{Ru}(\text{CO})_4(\text{NMBI})$ (B), by comparison with the known $\text{Ru}(\text{CO})_4\text{PPh}_3$ complex (Fig. 2c) (11). This shows that the ligand exchange



took place ($K_1 = [\text{Ru}(\text{CO})_4L]P_{\text{CO}}/[\text{Ru}(\text{CO})_5][L]$, $K'_1 = [\text{Ru}(\text{CO})_4L][\text{CO}]/[\text{Ru}(\text{CO})_5][L]$). The band at around 1935 cm^{-1} also appeared in the case of other amines such as pyridine and *N*-methylmorpholine. We measured the equilibrium constants K_1 for various amines. The results are shown in Table 2, in which K'_1 represents the equilibrium constant, where the term of CO is represented by concentration. Imidazoles were found to have larger K_1 values, that is, stronger coordination abilities, than ordinary amines such as pyridine and *N*-methylmorpholine. The table also shows that the coordination ability of NMBI is on a level with that of CO, because the K'_1 value for NMBI is about 1. The activities of CO hydrogenation catalyzed by these Ru/amine catalysts at 230°C and under 300 atm of CO/H_2 (1/1) are also listed in Table 2. Imidazoles activate the Ru catalyst more effectively than ordinary amines. A good correlation between the K_1 values and the activities for CO hydrogenation was observed as shown in Fig. 3, suggesting that the promoting effects of imidazoles are attributable to their high coordination abilities to Ru carbonyl. However, there were no correlations between the K_1 values and the EG selectivities. On the other hand, PPh_3 does not promote the Ru catalyst, although it has a large K_1 value.

c. Analyses of $\text{Ru}_3(\text{CO})_{12}$ /NMBI catalyst. Figures 4a and 4b are the IR spectra for the Ru/NMBI and the Ru/*N*-ethylimidazole catalysts at 150°C under pressures of CO/H_2 in THF solvent. By comparison of these

TABLE 2

Measured Equilibrium Constants of the Ligand Exchange Reactions (Eq. (2)) in THF at 150°C under CO Pressures^a

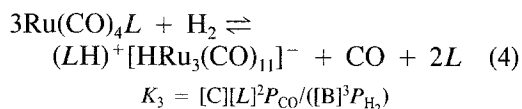
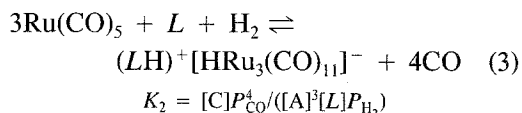
No.	Ligands	(mol/liter)	P_{CO} (atm)	[CO] ^b (mol/liter)	K_1^c	$K_1'^c$	Turnover ^d	
							EG	MeOH
1	<i>N</i> -methylmorpholine	3.0	44	0.65	5.6	0.082	0.0	1.2
2	Pyridine	1.0	49	0.72	13	0.18	0.0	1.5
3	1,2-Dimethylbenzimidazole	0.25	54	0.78	37	0.53	0.0	4.5
4	<i>N</i> -methylbenzimidazole	0.25	89	1.16	74	0.96	3.2	5.4
5	4-Dimethylaminopyridine	0.25	87	1.15	63	0.83	0.1	11.3
6	<i>N</i> -ethylimidazole	0.25	91	1.18	150	2.0	0.0	19.8
7	Benzimidazole	0.25	74	1.00	200	2.7	0.0	19.7
8	Triphenylphosphine	0.005	86	1.12	>10 ⁵	>10 ³	0.0	0.0

^a Charged Ru₃(CO)₁₂ is 0.007 g-atom/liter.^b [CO] show the measured concentrations of CO dissolved into THF at 20°C.^c K_1 , in (atm) (mol/liter)⁻¹. The estimated absorption coefficients are (A) (1995 cm⁻¹)/(B) (1935 cm⁻¹) = 1/1.21.^d The activities in mol/g-atom Ru/h for CO/H₂ reaction. Conditions: Ru₃(CO)₁₂, 0.007 g-atom/liter; ligand, 0.5 mol/liter; THF solvent, CO/H₂ (1/1), 300 atm, 230°C, 2 h.

spectra with Fig. 2a, some new bands at 2014, 1985, and ca. 1950 cm⁻¹ are observed in addition to the bands of complexes (A) and (B). These bands were assigned to the well-known anionic hydride carbonyl complex, HRu₃(CO)₁₁⁻ (C) (II). Imidazoles probably afford the gegeneration (imidazole · H⁺) for the anionic species. Thus it was concluded that complexes (A), (B), and (C) are dominant in the Ru catalyst solutions under

the reaction conditions. The IR spectra shown in Fig. 4 remained unchanged after a few hours at 150°C, indicating that the equilibrium shown by Scheme 2 has been attained.

Table 3 shows the equilibrium concentrations of these species under various conditions. Although these data may have considerably large experiment errors because of the complexity of the spectra, we can know the equilibrium relationship more quantitatively. Based on Scheme 2, the equilibrium constants K_2 and K_3 are defined as



K_1 , K_2 , and K_3 values calculated by Eqs. (2), (3), and (4) are almost constant when the concentrations of Ru, NMBI, CO, and H₂ are varied. This confirms that complexes (A), (B), and (C) coexist at equilibrium. K_1 and K_2 values in tetraglyme solvent are larger than those in THF solvent, presu-

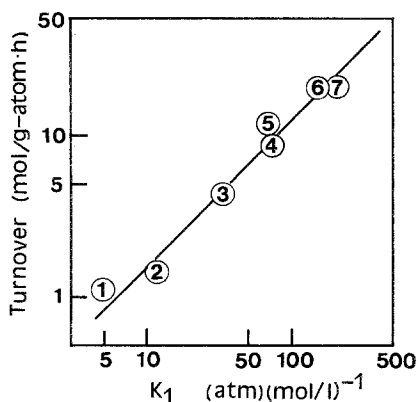


FIG. 3. Relationship between the K_1 values of amines and the activities of the Ru/amine catalysts. Data for these plots are found in Table 2.

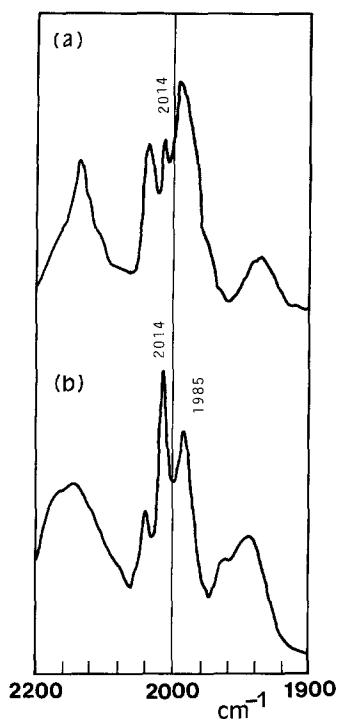
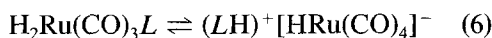
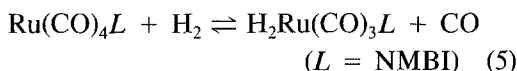


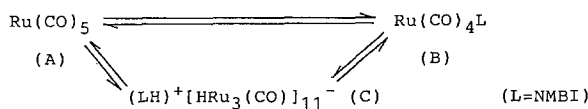
FIG. 4. IR spectra of the Ru/imidazoles catalysts in THF at 150°C under CO/H₂ pressures. (a) Ru₃(CO)₁₂, 0.007 g-atom/liter; NMBI, 0.25 mol/liter, CO 37 atm, H₂ 75 atm. (b) Ru₃(CO)₁₂, 0.014 g-atom/liter; *N*-ethylimidazole, 0.5 mol/liter; CO, 75 atm; H₂, 91 atm.

ably because the polarity is preferable for the formation of the ionic and polar complexes such as (C) and (B). Consequently, imidazoles act not only as a base but also as a ligand for Ru catalysts as shown in Scheme 2. Whyman reported that Ru(CO)₅ and Ru(CO)₄PPh₃ convert to the hydrides, H₂Ru(CO)₄ and H₂Ru(CO)₃PPh₃, respectively, under a pressure of H₂ (12). Therefore, we investigated the reaction of complex (B) with H₂. When complex (B) synthesized *in situ* was reacted with H₂ at

80°C and 200 atm, new bands appeared at 2065 and 2000 cm⁻¹ as shown in Fig. 5. These bands were assigned to the neutral hydride species, H₂Ru(CO)₃(NMBI) (D), by comparison with H₂Ru(CO)₃PPh₃ (2080s, 2021 vs, and 2010sh cm⁻¹) (11). Figure 5 also shows broadbands at lower wave number range, 1880 and 1850 cm⁻¹, which suggests the formation of a Ru anionic complex, such as HRu(CO)₄⁻ (E). These conversions are shown by



The bands based on complex (D) are stable up to about 100°C, although H₂Ru(CO)₄ is reported to decompose at about 20°C. This suggests that an imidazole ligand stabilizes the neutral hydride complex. Although no substantial amount of the hydride complexes (D) and (E) was observed spectroscopically under the reaction conditions, the formation of the hydride species, such as complexes (C), (D), and (E), by addition of NMBI may be closely connected with the activity for CO hydrogenation. Next, we investigated the relationship between the activity of the Ru/NMBI catalyst and the estimated ratio of the Ru complexes calculated by using the equilibrium constants in Table 3. The results of varying the concentration of Ru and NMBI are shown in Table 4. It was found that total activity (EG + MeOH) is proportional to the concentration of complex (B) and EG selectivity does not change as much as shown in Fig. 6. No simple relationships were observed between the activity and the concentrations of (A) and (C). The Ru(CO)₅ formed in Ru/THF catalyst showed almost no activity. Consequently,



SCHEME 2

TABLE 3

Measured Equilibrium Constants for the Ru₃(CO)₁₂/NMBI Systems (Scheme 2) in THF under CO/H₂ Pressures^a

No.	Ru (g-atom/liter)	NMBI (mol/liter)	P(CO) (atm)	P(H ₂) (atm)	Ratio (%) ^b			Equil. const. ^c		
					A	B	C	log K ₁	log K ₂	log K ₃
1	0.007	0.75	34	84	33	18	49	1.40	9.77	5.59
2	0.007	0.75	57	86	37	19	44	1.59	10.47	5.70
3	0.007	0.25	30	20	62	14	25	1.43	9.54	5.24
4	0.007	0.25	35	72	48	11	41	1.51	9.80	5.28
5	0.007	0.25	36	88	45	10	45	1.52	9.89	5.33
6	0.014	0.50	71	88	34	11	55	1.66	10.62	5.64
7	0.014	0.50	67	82	38	13	49	1.66	10.35	5.36
8 ^d	0.0089	0.89	93	93	13	17	71	2.14	12.60	6.18
9 ^e	0.014	0.50	75	91	17	15	68	2.12	11.70	5.34

^a Reaction temperatures: 150°C (1–6, 8, 9), 180°C (7). Temperatures at IR cell: 20°C (1–4), 150°C (5, 6, 8, 9), 180°C (7).

^b The estimated absorption coefficients are (A) (2040 cm⁻¹): (B) (1935 cm⁻¹): (C) (2014 cm⁻¹) = 1 : 1.61 : 0.68.

^c K₁, in (atm) (mol/liter)⁻¹; K₂, in (atm)³ (g-atom/liter)⁻² (mol/liter)⁻¹; K₃, in (g-atom/liter)⁻² (mol/liter)².

^d Tetraglyme solvent was used instead of THF.

^e N-Ethylimidazole was added instead of NMBI.

we concluded that the Ru carbonyl complex coordinated by imidazole or complexes (D) and (E), whose concentrations are proportional to that of complex (B), are the most closely related to both EG and MeOH formation, and complexes (A) and (C) take a minor part in the reaction.

Kinetic Studies by CMFR Experiments

The overall reaction can be shown by Scheme 1 in Part 1. Figure 7 shows the relationship between the overall production rate (P_O) and the FAL feed rate (F) in the case of Ru/NMBI/TGM catalyst system. Although P_O/V increased linearly with the increase in F/V , satisfying Eq. (1) in Part 1, only a small portion of FAL added converted to the products, indicating that a large portion of FAL decomposed to CO/H₂. We already reported that FAL was detected in the reaction solution of a Ru/halide catalyst at a near equilibrium concentration with CO/H₂ (8). The Ru/NMBI/TGM catalyst system also produced a small amount of FAL, suggesting that FAL exists in near equilibrium

with CO/H₂. These facts suggest that the subsequent reactions of FAL were more rate-determining than the FAL formation. Table 5 shows the kinetic data for several Ru catalysts and a Rh catalyst in Part 1. The unmodified Ru, which exists mainly as species (A), catalyzed neither the CO hydrogenation to form FAL nor the conversion of FAL. On the other hand, the Ru catalyst combined with *N*-octylpyrrolidine, which mainly affords species (C), exhibited the activity only for the MeOH formation, with a much smaller value of k_1 and a larger value of Kk'_2 than in the case of the Ru/NMBI/TGM system. This suggests that species (C) or, more plausibly, a mononuclear anion species (E) that is considered to exist in a small amount, has a relatively high FAL hydrogenation ability and a lower CO hydrogenation ability. Addition of NMBI enhanced the CO hydrogenation to form FAL and also the hydroformylation of FAL to form GAL. Considering the results of IR studies, it is suggested that NMBI stabilizes and enriches the neutral and anionic hydride

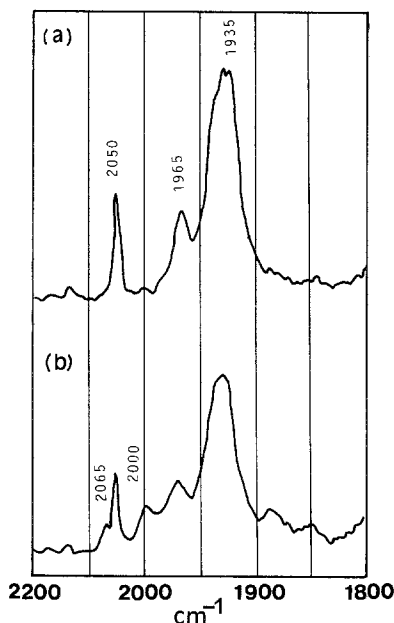


FIG. 5. IR spectra of the reaction of the $\text{Ru}(\text{CO})_4$ (NMBI) with H_2 in THF. (a) The same spectrum as that in Fig. 2b. (b) After the reaction at 80°C under a H_2 pressure of 195 atm.

species such as (C), (D), and (E), which are connected with the CO hydrogenation to form FAL, and also NMBI ligand enhances the CO insertion ability of Ru which is connected with the hydroformylation of FAL to form GAL. Table 5 clarifies the mechanistic differences between Rh and Ru catalysts. The Ru/NMBI catalyst has a higher activity for the CO hydrogenation to form FAL than the Rh/phosphine catalyst. However, the Ru catalyst has a poorer activity for the hydroformylation of FAL to form GAL because of the fast decomposition of FAL to CO/H_2 .

Dependence on the Catalyst Concentration

We studied the catalyst concentration dependencies to clarify the involvement of dinuclear mechanisms in the elementary reactions. Collman *et al.* (13) and Dombek and Harrison (14) suggested the participation of dinuclear mechanisms in the reaction of ole-

TABLE 4

Activities for CO/H_2 Reaction and the Estimated Ratio of the Ru Complexes by Ru/NMBI Catalyst System

Ru (g-atom/liter)	NMBI (mol/liter)	Turnover ^a		Sel. ^b (%)	Estimated ratio (%) ^c		
		EG	MeOH		(A)	(B)	(C)
0.014	0	0	0.03	—	100	0	0
0.014	0.1	0	0.42	—	88.4	2.7	8.9
0.014	0.2	0.37	0.61	38	81.2	5.0	13.8
0.014	0.5	0.82	1.38	37	68.7	10.5	20.8
0.014	1.0	1.65	2.09	44	57.7	17.7	24.6
0.005	1.0	2.09	3.02	41	71.9	22.0	6.1
0.010	1.0	1.99	2.64	43	63.6	19.5	16.9
0.020	1.0	1.64	1.92	46	50.6	15.5	33.9
0.040	1.0	1.09	1.23	47	36.7	11.3	52.0
0.060	1.0	0.92	1.03	47	29.6	9.1	61.3

^a The activities in mol/g-atom Ru/h for the CO/H_2 reactions. Conditions: NMBI + THF = 10 ml; CO/H_2 (1/1), 300 atm, 180°C , 3 h.

^b Sel. (%) = $100 \times \text{EG}/(\text{EG} + \text{MeOH})$.

^c The equilibrium constants used are the values of entry 7 in Table 3.

fin hydroformylation and CO hydrogenation, respectively. Figure 8 shows the dependencies of the catalyst activity on the Ru concentration in the case of the Ru/NMBI/TGM catalyst system. When the Ru concentration was low, the formation of EG and GLY was of second order with respect to Ru while the formation of MeOH was almost

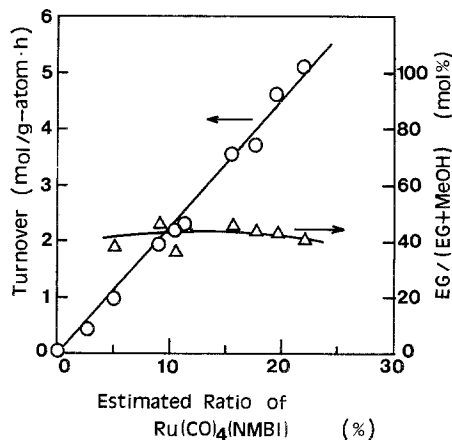


FIG. 6. Relationship between the activities for the CO/H_2 reaction and the estimated ratio of the $\text{Ru}(\text{CO})_4$ (NMBI) complex in the Ru/NMBI catalyst solution. Data for these plots are found in Table 4.

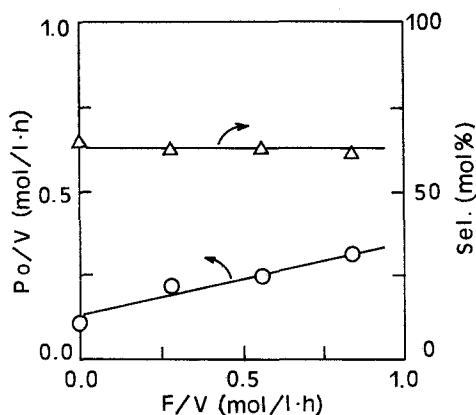


FIG. 7. P_0/V vs F/V for Ru/NMBI/TGM catalyst; $\text{Ru}_3(\text{CO})_{12}$, 0.01 g-atom/liter; NMBI, 0.5 mol/liter; CO/H_2 (1/1), 500 atm, 220°C, catalyst solution feed rate 90 g/h. Sel. = $100 \times (\text{GAL} + \text{EG} + \text{GLY})/(\text{MeOH} + \text{GAL} + \text{EG} + \text{GLY})$.

of first order. In this region of Ru concentration, the monomeric species such as (A), (B), (D), and (E) prevail according to the calculation using the equilibrium constants. Taking into account that the anionic species can catalyze the hydrogenation of FAL to form MeOH as described previously, the monomeric anionic species (E) is considered to take part in the MeOH formation. The anionic complex, which is considered to exist at equilibrium with species (B), may react with FAL to form the methoxy species

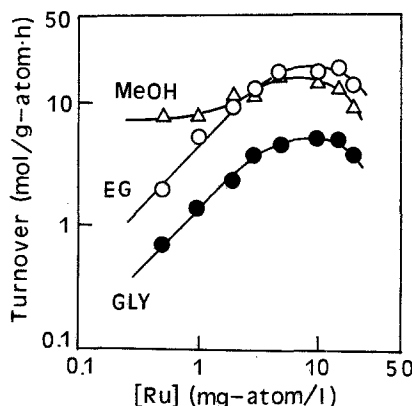
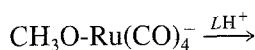


FIG. 8. Influence of Ru concentration; NMBI, 20 mmol; TGM, 10 ml; CO/H_2 (1/1), 500 atm, 220°C.

because of the hydride nature of a hydrogen ligand. The anionic methoxy complex may easily react with the counteranion to liberate MeOH. This is in accordance with the first-order kinetics of the MeOH formation.



On the other hand, GAL is considered to be formed via the hydroxymethyl complex bearing NMBI ligand, which accelerates the CO insertion. The second-order kinetics for

TABLE 5

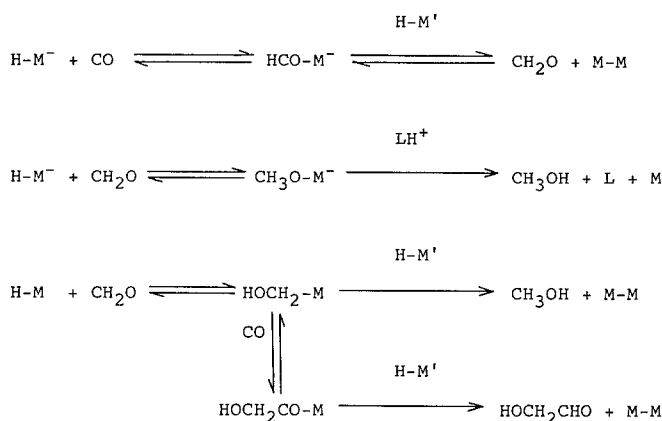
Kinetic Data for Ru and Rh Catalysts^a

No.	Catalyst ^b (g-atom/liter)	Additives ^b (mol/liter)	Solv.	Rate constants ^c				Formation ratio	
				k_1	k_{-1}/k_2	Kk_2'	Kk_2''	EG/MeOH	GLY/EG
1	Ru(0.01)	None	THF	0.0	—	0.0	0.0	—	—
2	Ru(0.01)	NMBI(0.5)	TGM	48	4.6	3.9	3.9	1.1	0.24
3	Ru(0.01)	NOPD(0.5)	TGM	2.5	0.23	11	0.0	0.0	—
4	Rh(0.04)	P ^t Pr ₃ (0.04) NMPD(0.14)	NMP	30	0.30	24	76	2.6	0.17

^a Conditions: CO/H_2 (1/1), 500 atm, 220°C.

^b Ru, $\text{Ru}_3(\text{CO})_{12}$; Rh, $\text{Rh}(\text{CO})_2\text{acac}$; NMBI, *N*-methylbenzimidazole; NOPD, *N*-octylpyrrolidine; NMPD, *N*-methylpyrrolidine; NMP, *N*-methyl-2-pyrrolidone; TGM, tetraglyme.

^c k_1 , Kk_2' , and Kk_2'' , in mol/g-atom/h.



H-M : $\text{H}_2\text{Ru}(\text{CO})_3\text{L}$ (L=an imidazole)

H-M⁻: $\text{HRu}_3(\text{CO})_{11}^-$ or $\text{HRu}(\text{CO})_4^-$

H-M': H-M⁻ or H-M

SCHEME 3

the EG formation in the lower Ru concentration range suggests that a dinuclear mechanism takes part in the hydrogenolysis of the acyl complex. In the higher Ru concentration range, the rate-determining step may be shifted to the formation of the hydroxymethyl complex or the CO insertion to it, which compete with the formation of the methoxy complex. As for the subsequent reactions of GAL to produce EG and GLY, the formation of the hydroxymethyl-type complex is considered to remain rate-determining in the studied range of Ru concentration, resulting in the constant EG/GLY ratio.

CONCLUSION

Based on high-pressure IR studies and kinetic studies, we propose the mechanism represented by Scheme 3 for the direct conversion of CO/H₂ to produce EG and methanol by the Ru/NMBI catalyst. The three species, Ru(CO)₅, Ru(CO)₄L, and (LH)⁺[HRu₃(CO)₁₁]⁻ (L = NMBI), mainly coexist at equilibrium in the catalyst solution and the CO hydrogenation activity is most closely connected with the concentra-

tion of the complex Ru(CO)₄L, more plausibly H₂Ru(CO)₃L and (LH)⁺[HRu(CO)₄]⁻. Addition of NMBI enhances both the CO hydrogenation to form FAL and the hydroformylation of FAL. The role of NMBI is considered to enrich the Ru hydride species indispensable to CO hydrogenation both as a base and as a ligand and to enhance the CO insertion step to form the formyl and the hydroxyacetyl complexes as a ligand. The subsequent reactions of FAL are supported to be rate-determining. The anionic hydride complex has a much lower activity for the CO hydrogenation to form FAL and a higher activity for the MeOH formation, which proceeds via the methoxy complex.

Finally, we conclude that the neutral and anionic hydride species such as H₂Ru(CO)₃ (NMBI), [HRu(CO)₄]⁻ in the Ru catalyst and HRh(CO)₃(PR₃), HRh(CO)₄ in the Rh catalyst are considered active forms in the reaction.

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REFERENCES

1. Dombek, B. D., in "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 32, p. 325. Academic Press, San Diego, 1983.
2. Tamura, M., Ishino, M., Deguchi, T., and Nakamura, S., *J. Organomet. Chem.* **312**, C75 (1986).
3. Tanaka, H., Hara, Y., Watanabe, E., Wada, K., and Onoda, T., *J. Organomet. Chem.* **312**, C71 (1986).
4. Kiso, Y., Saeki, K., Hayashi, T., Tanaka, M., Matsunaga, Y., Ishino, M., Tamura, M., Deguchi, T., and Nakamura, S., *J. Organomet. Chem.* **335**, C27 (1987).
5. Takano, T., Deguchi, T., Ishino, M., and Nakamura, S., *J. Organomet. Chem.* **309**, 209 (1986).
6. Ishino, M., Deguchi, T., Takano, T., and Nakamura, S., *J. Mol. Catal.* **49**, 315 (1989).
7. The Research Association for C1 Chemistry, "Progress in C1 Chemistry in Japan." Kodansha, Tokyo, 1989.
8. Ishino, M., Tamura, M., Deguchi, T., and Nakamura, S., *J. Catal.* **105**, 478 (1987).
9. Deguchi, T., Tamura, M., Ishino, M., and Nakamura, S., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1035. Chem. Institute of Canada, Ottawa, 1988.
10. Bor, G., *Pure Appl. Chem.* **58**, 543 (1986).
11. Seddon, E. A., Seddon, K., "The Chemistry of Ruthenium." Elsevier, Amsterdam, 1984.
12. Whyman, R., *J. Organomet. Chem.* **56**, 339 (1973).
13. Collman, J. P., Belmont, J. A., and Brauman, J. I., *J. Am. Chem. Soc.* **105**, 7288 (1983).
14. Dombek, B. K., and Harrison, M., *J. Am. Chem. Soc.* **105**, 2485 (1983).