July, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 2029—2037 (1985)*

Kinetics and Mechanistic Study of the Methanol Homologation with Cobalt–Ruthenium Mixed Catalyst

Kazuhiro WATANABE,* Kiyoshi KUDO, and Nobuyuki SUGITA
Institute for Chemical Research, Kyoto University, Gokanosho Uji, Kyoto 611

(Received January 26, 1985)

The role of each catalyst was examined in detail in the methanol homologation with cobalt–ruthenium mixed catalyst. Cobalt catalyst showed much higher activity for the hydrocarbonylation of methanol than ruthenium. On the other hand, the hydrogenation of acetaldehyde proceeded much more rapidly by ruthenium catalyst. The rate of methanol homologation in 1,4-dioxane with cobalt–ruthenium mixed catalyst system was found to be of the first order with respect to the partial pressure of CO. The *in situ* IR spectra indicated that $[Co(CO)_4]^-$ was an active species for the hydrocarbonylation of methanol and that $[RuI_x(CO)_y]$ existed under the reaction conditions. On the basis of both the kinetic studies and *in situ* IR spectral observations, the reaction mechanism of methanol homologation was fully discussed.

The conversion of synthetic gas to organic chemicals has become an important problem to be solved in both fundamental and applied fields.

Methanol homologation (Eq. 1) with cobalt catalyst, which is one of the most important reactions in the so-called C_1 chemistry, was first reported by Wender and his co-workers in 1949.[1)]

$$CH_3OH + CO + 2H_2 \rightarrow CH_3CH_2OH + H_2O \qquad (1)$$

Berty's[2)] and Mizoroki's[3)] groups found independently that the addition of an iodide increased the yield of ethanol. A recent study[4)] showed that the covalent CH_3I was more active than the ionic LiI, KI, and $MePBu_3I$. In order to improve the selectivity many studies have been carried out on the effect of solvents[5)] and ligands,[6)] and that of the addition of ruthenium[7,8)] or iron[9)] to cobalt catalytic system. From these results, it was revealed that the use of oxygen-containing solvent such as cyclic ether improved the selectivity of ethanol formation and that the optimum mole ratio of ruthenium to cobalt existed.

We found previously that the optimum mole ratio of ruthenium to cobalt depended on the reaction conditions such as the reaction temperature, pressure and H_2/CO.[10)]

Up to now, the role of ruthenium as well as the reaction mechanism was not fully elucidated yet. Thus we investigated the mechanism of the methanol homologation with $Co_2(CO)_8$–$RuCl_3$ mixed catalyst from a kinetic study and *in situ* IR observation.

This homologation reaction was accompanied by the side reactions of methanol, as shown in Eqs. 2—4. Therefore, the kinetic experiments

$$CH_3OH + ROH \rightarrow CH_3OR + H_2O$$
$$(R = CH_3 \text{ or } CH_3CH_2) \qquad (2)$$

$$CH_3CHO + 2\,CH_3OH \rightleftarrows CH_3CH(OCH_3)_2 + H_2O \qquad (3)$$

$$CH_3OH + CO \xrightarrow{ROH} CH_3COOR$$
$$(R = H,\ CH_3,\ CH_3CH_2) \qquad (4)$$

were carried out in 1,4-dioxane under such reaction conditions that the amounts of by-products could be minimized.

Experimental

Materials. The compounds, $Co_2(CO)_8$, $RuCl_3 \cdot nH_2O$ (Ru content: *ca.* 45 wt%), and methyl iodide were commercially obtained and used without further purification. Methanol and 1,4-dioxane were distilled over a Na–Pb alloy under nitrogen atmosphere. Hydrogen was a commercial material and its purity was above 99.9%. Carbon monoxide was prepared by decomposing formic acid in hot sulfuric acid, and its purity was above 98%.

Procedure. In all kinetic experiments, the reactions were carried out in a glass tube placed in a stainless-steel autoclave (*ca.* 200 ml) equipped with a Teflon stirrer and a Teflon sampling line.

Adequate amounts of the precatalysts ($Co_2(CO)_8$ and $RuCl_3 \cdot nH_2O$) and metyl iodide were dissolved in 1,4-dioxane and this mixture was charged in the autoclave. The air in the autoclave was purged three or four times with CO, and then the solution was pressured with CO and H_2 (total pressure: 150 kg cm^{-2} at room temperature). The vessel was heated to the reaction temperature (160 °C) for 40 min in an oil bath. After the temperature had been kept constant for 30 min, the substrate (methanol or acetaldehyde dimethyl acetal) was pumped into the autoclave with a high pressure injection pump. The mixture of CO and H_2 was introduced to the desired pressure, and stirring of the solution was started with an electromagnetic stirrer (1400 min^{-1}), this time being marked as zero time.

Stirring was stopped from time to time and an aliquot (*ca.* 0.2 ml) was withdrawn through the sampling line into a trap chilled in a dry-ice bath at interval of 10 to 30 min. To keep the pressure constant during the reaction, the consumed gas was supplied from a reservoir in which CO and H_2 had been mixed beforehand in the fixed ratio.

The IR spectra were recorded with Hitachi Model EPI-G3 spectrophotometer under a working pressure of the appropriately mixed gas of CO and H_2 and at the desired temperature (160 °C—180 °C) by using a high pressure IR cell (for *in situ* observation) designed in our laboratory. This high pressure cell consists of 60×70×80 mm block of stainless-steel through which a 30 mm diameter hole bored to form a central capacity for accommodating the window and the spacer (0.1 mm thick). The cell has optically flat surfaces. The temperature of the cell was monitored with a thermocouple which was inserted into the cell block. Repeated registration of spectrum allowed the reaction to be followed.

Analysis. Products were indentified by comparison of their retention times in the gas-liquid chromatography (GLC) with those of authentic samples (N_2 as carrier gas). A polyethylene glycol 1000 (PEG-1000) column (1.5 m, 3 mm ϕ) was used at 90 °C for the determination of the amounts of products with *m*-xylene as an internal standard.

Results and Discussion

Preliminary Investigation. In 1,4-dioxane solvent, we have explored the optimum reaction conditions for the methanol homologation. Under the optimum reaction conditions, we obtained the high selective formation of ethanol (75 mol%) and high conversion of methanol (67 mol%) as shown in Table 1 (Run 2). The mole ratio of ruthenium to cobalt giving high selectivity of ethanol formation was revealed to be about 0.2 from Table 2. Under the optimum reaction conditions, acetaldehyde dimethyl acetal was the major by-product, and esters (methyl and ethyl acetates) and ethers (dimethyl, ethyl methyl and diethyl ethers) were merely minor by-products. Therefore, the reaction system consisting of $Co_2(CO)_8$-$RuCl_3$ mixed catalyst, methyl iodide and 1,4-dioxane as solvent was chosen for our kinetic studies.

Figure 1 shows that the total amount of acetaldehyde reaches maximum at the early stage of reaction (about 10 min), and then decreases to nearly zero. Here, the total amount of acetaldehyde is the sum of acetaldehyde and its dimethyl acetal formed by dehydration (Eq. 3), and the latter is major. This result indicates that acetaldehyde should be an intermediate for the formation of ethanol. Therefore, the methanol homologation proceeds *via* consecutive steps, that is, the hydrocarbonylation of methanol to acetaldehyde (Eq. 5) followed by the hydro-

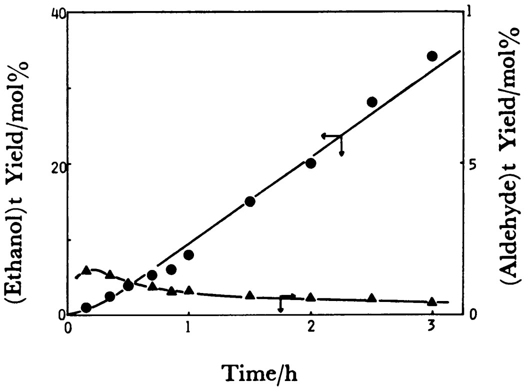

Fig. 1. Methanol homologation catalyzed by cobalt–ruthenium mixed catalyst.
[Ru]/[Co] = 0.2. Reaction conditions: see footnote of Table 2.
●: ethanol, ▲: acetaldehyde.

TABLE 1. EFFECT OF TEMPERATURE[a)]

Run	T/°C	CH_3OH Conv./%	Yield[b)]/%		Select.[c)]/%	
			(Ethanol)$_t$[d)]	(Aldehyde)$_t$[e)]	(Ethanol)$_t$	(Aldehyde)$_t$
1	160	56	34	0.39	60	0.70
2	180	67	50	0.25	75	0.37
3	200	83	38	0.20	46	0.24

a) Total pressure: 240 kg cm^{-2} at room temp ($H_2/CO = 2/1$), CH_3OH: 7 M, CH_3I: 0.14 M, 1,4-dioxane: 5 ml $Co_2(CO)_8 = (2.0—2.5) \times 10^{-2}$ M, $RuCl_3 = (0.9—1.0) \times 10^{-2}$, Time: 3 h. 1 M = 1 mol dm^{-3}. b) Yield = [product] (mol)/charged [CH_3OH] (mol) × 100. c) Select. = [Product] (mol)/converted [CH_3OH] (mol) × 100. d) (Ethanol)$_t$ = EtOH + EtOMe + 2 EtOEt. e) (Aldehyde)$_t$ = $CH_3CHO + CH_3CH(OCH_3)_2$.

TABLE 2. EFFECT OF RUTHENIUM MOLE RATIO[a)]

Run	Added Ru [M] × 10^2	Ru/Co	CH_3OH Conv./%	(Ethanol)$_t$		(Aldehyde)$_t$
				Yield/%	Select./%	Yield/%
1	0	—	50	10	21	26
2	0.58	0.1	55	33	59	1.1[c)]
3	1.2	0.2	51	43	78	1.1[c)]
4	1.7	0.3	56	42	74	0.8[c)]
5	2.3	0.4	54	32	64	0.8[c)]
6	1.0[b)]	—	38	2.8	10	0.9

a) Reaction temperature: 160 °C, Total pressure: 240 kg cm^{-2} at 160 °C ($H_2/CO = 2/1$), CH_3OH: 7 M, CH_3I: 0.14 M, 1,4-dioxane: 50 ml, $Co_2(CO)_8 = 2.8 \times 10^{-2}$, Time: 3 h. b) $Co_2(CO)_8 = 0$. c) Maximum amount during the reaction.

genation to ethanol (Eq. 6).

$$CH_3OH + CO + H_2 \rightarrow CH_3CHO + H_2O \quad (5)$$

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH \quad (6)$$

Figure 2 indicates that the ruthenium catalyst has much lower reactivity for the hydrocarbonylation than the cobalt catalyst. The hydrocarbonylation of methanol seems to be principally catalyzed by the cobalt catalyst.

In order to evaluate the relative activity of the mixed catalytic system, we made three seperate studies on the hydrogenation of acetaldehyde with the cobalt catalyst, the ruthenium catalyst and the mixed catalyst. We chose acetaldehyde dimethyl acetal as the starting substrate, charged it at low concentration and added the equivalent amount of H_2O to the reaction system in order to prevent side reactions such as polymerization of acetaldehyde. Other reaction conditions such as total pressure, partial pressure of CO and H_2, reaction temperature and charged amount of CH_3I were the same as those in the present methanol homologation.

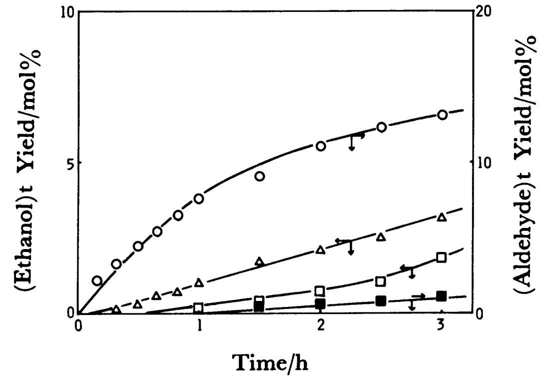

Fig. 2. Methanol homologation by cobalt catalyst and ruthenium catalyst.
Reaction conditions: see footnote of Table 2. ○, △: cobalt catalyst $[Co_2(CO)_8]_0=2.8\times10^{-2}$ M, □, ■: ruthenium catalyst $[RuCl_3]_0=5.6\times10^{-2}$ M. 1 M=1 mol dm^{-3}

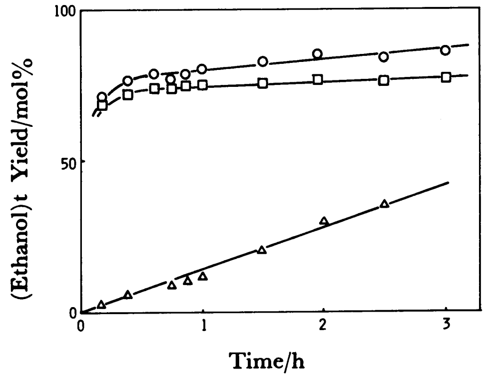

Fig. 3. The hydrogenation of acetaldehyde.
Reaction temperature: 160 °C, total pressure: 240 kg cm^{-2} at 160 °C (H_2/CO=2/1), solvent: 1,4-dioxane, substrate: acetaldehyde dimethyl acetal 0.7 M adding H_2O 0.8 M, total volume 70 ml, methyl iodide 0.14 M. ○: $[Co_2(CO)_8]_0=2.8\times10^{-2}$ M and $[RuCl_3]_0=1.1\times10^{-2}$ M, △: $[Co_2(CO)_8]_0=2.8\times10^{-2}$ M, □: $[RuCl_3]_0=1.1\times10^{-2}$ M.

Figure 3 shows that the ruthenium-catalyzed hydrogenation almost completed in 20 min. This rate was much faster than the rate of the cobalt-catalyzed hydrogenation. The hydrogenation rate of acetaldehyde by cobalt-ruthenium mixed catalyst was similar to that by a simple ruthenium catalyst. Hence ruthenium is considered to be the principal catalyst for the hydrogenation of acetaldehyde under the reaction conditions of methanol homologation. This fast hydrogenation should lead to the high selectivity of ethanol.

It has been reported that methyl iodide plays a part as the promoter in the formation of methylcobalt complex from methanol and the cobalt.[3,11,12] We examined the effect of methyl iodide on the hydrogenation of acetaldehyde. Figure 4 reveals that addition of methyl iodide suppresses the rate of the cobalt-catalyzed hydrogenation. We suppose that the result is due to the coordination of iodide to the vacant site

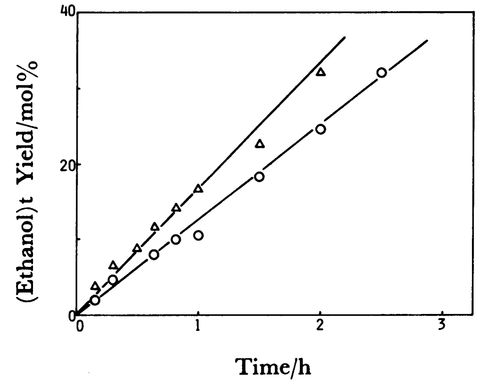

Fig. 4. The effect of methyl iodide on the hydrogenation of acetaldehyde by cobalt catalyst. ○: $[CH_3I]_0=0.14$ M, △: $[CH_3I]_0=0$.

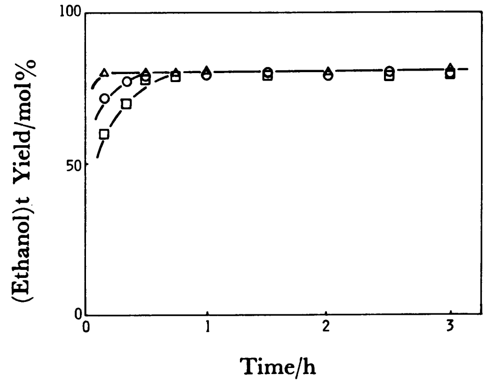

Fig. 5. The effect of methyl iodide on the hydrogenation of acetaldehyde by ruthenium catalyst. △: $[CH_3I]_0/[RuCl_3]_0=3$, ○: $[CH_3I]_0/[RuCl_3]_0=2$, □: $[CH_3I]_0=0$.

of coordinatively unsaturated [$HCo(CO)_3$], which is generally regarded as the active species for the hydrogenation of acetaldehyde. With ruthenium catalyst, the yield of ethanol at 10 min increases with the mole ratio of methyl iodide to ruthenium ([CH_3I]/[Ru]) up to [CH_3I]/[Ru]=2 (Fig. 5). The yield of ethanol becomes independent of the mole ratio when the ratio is higher than 2 (Figs. 3 and 5). This fact suggests that an iodocarbonylruthenium, [$RuI_x(CO)_y$], is an active catalyst for the hydrogenation, where x is supposed to be 2 or 3 from *in situ* IR observation. Therefore, it was found that methyl iodide gave no significant effect on the hydrogenation under the working conditions ([CH_3I]/[Ru]$\geqq$5).

Kinetic Study. As shown in Fig. 1, with the cobalt-ruthenium mixed catalyst, the time-yield plot of ethanol production is linear at the low yield of ethanol (less than 30%), and the induction period is less than 10 min. We could thus obtain the initial rate of ethanol production from the slope of the time-yield curve of ethanol. As both ethyl methyl and diethyl ethers were formed rapidly by thermal and/or acid-catalyzed dehydration of alcohols, the amounts of these ethers were included in the amount of ethanol. We investigated the effect of initial concentration of methanol, methyl iodide and ruthenium salt, and that of the partial pressure of CO and H_2 on the rate of formation of ethanol. From Figs. 6 and 7, the rate was found to be apparently of the order between the 0th and 1st in regard to the initial concentration of methyl iodide and ruthenium, and to the partial pressure of H_2. The effect of CO indicates that the insertion of CO to form acyl complex should be an important step, since the rate is of the 1st order in regard to its partial pressure. Figure 8 reveals that the rate with respect to the initial concentration of methanol is higher than the 1st order. With cobalt catalyst, the yield of ethanol at 50 min was less than 1% (Fig. 2), and that the yield of acetaldehyde (including its dimethyl acetal) was approximately proportional to the square of the initial concentration of methanol (Fig. 8). Hence, more than one molecule of methanol should take part in the hydrocarbonylation of methanol.

Determination of in situ *IR Spectra.* In order to obtain detailed information about active species involved in the catalytic cycle, IR spectra of octacarbonyldicobalt and ruthenium trichloride solution were observed under typical conditions (P_{CO}= 60 kg cm^{-2}, P_{H_2}=120 kg cm^{-2} at room temperature, and 160 °C). Since 1,4-dioxane absorbs light at 2000 cm^{-1} region, we chose methanol and hexane as the solvents for these measurements.

In the methanol solution of [$Co_2(CO)_8$], the infrared absorption at 1900 cm^{-1}, which can be ascribed to [$Co(CO)_4$]$^-$ species, was observed under high pressure of the mixture gas at 180—200 kg cm^{-2} in the range of temperature from 20 °C to 160 °C. GLC analysis revealed that the hydrocarbonylation

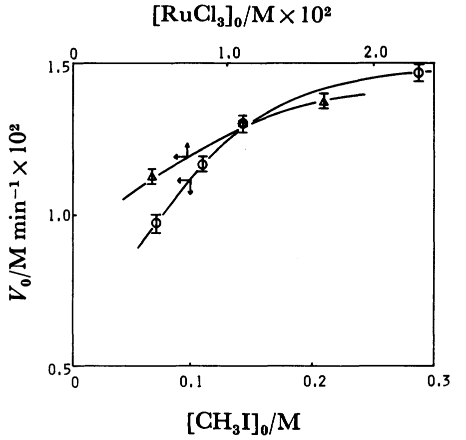

Fig. 6. Plots of v_0 vs. [CH_3I]$_0$ and [$RuCl_3$]$_0$.

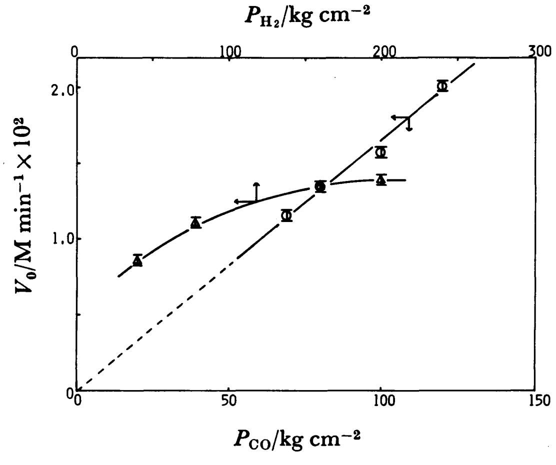

Fig. 7. Plots of v_0 vs. P_{CO} and P_{H_2}.

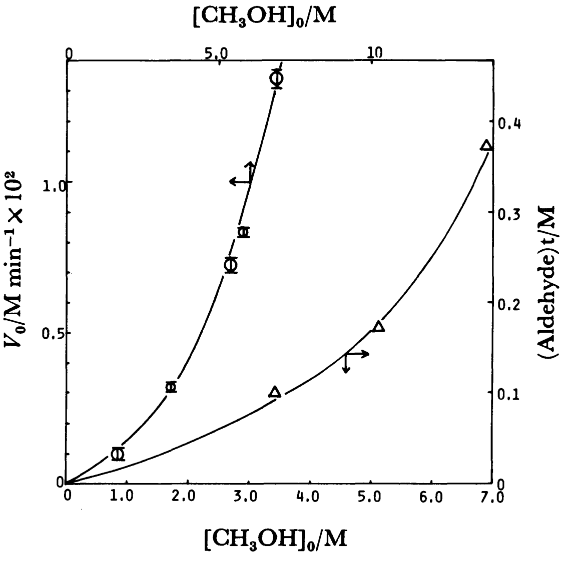

Fig. 8. The effect of the initial concentration of methanol.

Φ: the rate of ethanol formation, △: the yield of acetaldehyde at 50 min.

of methanol hardly proceeded under these conditions. When CH3I was added to this solution, a characteristic absorption at 1900 cm^{-1} was diminished as temperature raised, and ultimately disappeared at the working temperature (160 °C). GLC analysis revealed that the hydrocarbonylation proceeded. These results suggest that the steady-state concentration of $[Co(CO)_4]^-$ species becomes low with the progress of hydrocarbonylation, and that $[Co(CO)_4]^-$ is an active species in the hydrocarbonylation of methanol.

In the hexane solution of RuCl3, the observation of *in situ* IR showed that two kinds of iodocarbonylruthenium species existed under the same conditions as those in the homologation and that chlorocarbonylruthenium complex did not exist. One of the two iodo species is $[RuI_2(CO)_4]$ (2126, 2107, 2096, and 2066 cm^{-1})[13] and the other $[RuI_3(CO)_3]^-$ (2120 and 2050 cm^{-1})[14]. As G. Andlich and his co-workers reported[16] the existence of these iodo species in the carbonylation of dimethyl ether to ethyl acetate, we suppose that one of these iodocarbonylruthenium species is active for the homologation of methanol.

We also prepared a cobalt–ruthenium heterometallic cluster complex ($[RuCo_3(CO)_{12}]^-$) by the reported method[7b] in order to examine the formation of this cluster in the reaction system by *in situ* IR. The results are given in Table 3. It has been known that cobalt-iron heterometallic cluster ($[FeCo_3(CO)_{12}]^-$)[9] and triruthenium cluster ($[Ru_3(CO)_{12}]$)[17] are decomposed into the respective monometallic complexes under high pressure and high temperature. From Table 3, we can conclude that under the reaction conditions a cobalt–ruthenium heterometallic cluster does not remain intact as in the original form, but is decomposed.

Mechanism and Rate Equation. Based on the above results, we propose a reaction mechanism of the homologation of methanol (Scheme 1: the hydrocarbonylation of methanol, Scheme 2: the hydrogenation of acetaldehyde).

TABLE 3. IR SPECTRAL DATA[a)]

No.	Complexes	ν(CO) / cm^{-1}
1	$HRuCo_3(CO)_{12}$[b)]	2070 vs, 2062 vs, 2050 vs, 2030 s, 2020 vs, 1884 s
2	$Co_2(CO)_8$-$RuCl_3$[c)]	2101 s, 2048 s, 2033 s
3	$Co_2(CO)_8$-$RuCl_3$[c,d)]	2101 s, 2045 s, 2033 sh, 2022 s, 2001 s
4	$HRuCo_3(CO)_{12}$	2102 s, 2050 s, 2032 s
5	$HRuCo_3(CO)_{12}$[d)]	2105 s, 2045 s, 2030 s, 2022 sh, 2001 s

Abbreviations: vs = very strong, s = strong, sh = shoulder. a) CH_3OH: 0.4 ml, hexane: 5 ml, Total pressure: 180 kg cm^{-2} at room temp ($H_2/CO = 2/1$), Temperature: 160 °C, $[CH_3I]/[CO] = 3$. b) From Ref. 7b. c) [Co]/[Ru] = 3. d) After cooling down the solution to room temperature (total pressure 180 kg cm^{-2}).

$$\underset{\mathbf{1}}{Co_2(CO)_8} + H_2 \overset{K_1}{\rightleftharpoons} 2\,\underset{\mathbf{2}}{HCo(CO)_4} \qquad \text{(I)}$$

$$\mathbf{2} \overset{K_2}{\rightleftharpoons} \underset{\mathbf{3}}{HCo(CO)_3} + CO \qquad \text{(II)}$$

$$CH_3OH + \mathbf{2} \overset{K_3}{\rightleftharpoons} \underset{\mathbf{4}}{[CH_3OH_2]^+[Co(CO)_4]^-} \qquad \text{(III)}$$

$$CH_3OH + HI \overset{K_4}{\rightleftharpoons} CH_3I + H_2O \qquad \text{(IV)}$$

$$CH_3I + \mathbf{4} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \underset{\mathbf{5}}{CH_3Co(CO)_4} + HI + CH_3OH \qquad \text{(V)}$$

$$\mathbf{5} + CO \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \underset{\mathbf{6}}{(CH_3CO)Co(CO)_4} \qquad \text{(VI)}$$

$$\mathbf{6} + H_2 \xrightarrow{k_7} CH_3CHO + \mathbf{2} \qquad \text{(VII)}$$

Scheme 1.

$$RuI_x(CO)_y + H_2 + CH_3OH \overset{K_8}{\rightleftharpoons} \underset{\mathbf{7}}{[HRuI_x(CO)_y]^-[CH_3OH_2]^+} \qquad \text{(VIII)}$$

$$CH_3CHO + \mathbf{7} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \underset{\mathbf{8}}{[(CH_3CH_2O)RuI_x(CO)_y]^-[CH_3OH_2]^+} \qquad \text{(IX)}$$

$$\mathbf{8} + H_2 \xrightarrow{k_{10}} CH_3CH_2OH + \mathbf{7} \qquad \text{(X)}$$

Scheme 2.

During the heating of the reaction system to the reaction temperature, the charged methyl iodide should have reacted with $[HCo(CO)_4]$ (or $[Co(CO)_4]^-$ which is formed from the dissociation of $[HCo(CO)_4]$) to produce hydroiodic acid. The *in situ* IR spectra suggest that ruthenium chloride (precatalyst) reacts with HI and CO to form iodocarbonylruthenium species.

The disproportionation of $[Co_2(CO)_8]$ was reported[19] to produce the species $[Co(CO)_4]^-$ (Eq. 7). But this disproportionation did not

$$6\,CH_3OH + 3\,Co_2(CO)_8 \rightarrow [Co(CH_3OH)_6]^{2+}([Co(CO)_4]^-)_2 + 4\,CO \qquad (7)$$

occur under the present conditions, since no libration of CO was observed in a stoichiometric reaction of methanol with $[Co_2(CO)_8]$.

The equilibrium constant K_4 was found to be 0.464 at 160 °C (calculated from a measured value at 30 °C and ΔH=1.25 kcal† mol^{-1}; ΔH was calculated from

---

† 1 cal$_{th}$=4.184 J.

the value of ΔH_f° of each substance cited in the literature).

Since the hydrocarbonylation hardly proceeded in the absence of iodide, the direct conversion of **4** to methylcobalt complex, **5**, (Eq. 8)[12] should be ruled out.

$$\mathbf{4} \longrightarrow \mathbf{5} + H_2O \tag{8}$$

As the hydrogenation of acetaldehyde with the ruthenium catalyst proceeded much more rapidly than with the cobalt catalyst, ruthenium plays a major catalytic role in the hydrogenation, and ruthenium hydride anion, **7**, in Eq. VIII is assumed to be the active species. We do not yet have any obvious evidence for the formation of this complex, but this is analogous to that suggested in a ruthenium-iodine system.[16] Although the number of iodides coordinated to ruthenium is still obscure, Dombek and his coworkers reported[15] that triiodotricarbonylruthenium was inactive for a hydrogenation of CO. Hence, diiodotetracarbonylruthenium is supposed to be the catalyst for the hydrogenation of acetaldehyde.

The initial rate of the production of ethanol, v_o, is derived as follows. Assuming the steady-state concentration for the intermediate **8**, v_o is obtained as Eq. 9. From Eqs. VIII and IX, the steady-state concentration of acetaldehyde is given as Eq. 10.

$$v_o = \frac{k_9k_{10}[CH_3CHO][\mathbf{7}][H_2]}{k_{-9}+k_{10}[H_2]} \tag{9}$$

$$[CH_3CHO] = \frac{k_7(k_{-9}+k_{10}[H_2])[\mathbf{6}]}{k_9k_{10}[\mathbf{7}]} \tag{10}$$

By substituting Eq. 10 into Eq. 9, v_o is represented as Eq. 11.

$$v_o = k_7[\mathbf{6}][H_2] \tag{11}$$

Assuming the steady-state conditions for acylcobalt (**6**) and alkylcobalt (**5**) intermediates, the rate equation is derived as Eq. 12, since the concentration of methanol is nearly equal to its initial concentration at the early stage of the reaction, *i.e.*, $[CH_3OH]_o \gg [CH_3I]_o$, $[\text{catalyst}]_o$ where the subscript $^\circ$ denotes the initial concentration.

$$v_o = \frac{k_5k_6k_7[CH_3I][\mathbf{4}][CO][H_2]}{k_{-5}(k_{-6}+k_7[H_2])[CH_3OH]_o[HI]+k_6k_7[CO][H_2]} \tag{12}$$

From the equilibrium IV, the concentration of methyl iodide is given as:

$$[CH_3I] = K_4[CH_3OH]_oA/2, \tag{13}$$

where A is given as:

$$A = -1 + \sqrt{1+4[HI]_o/(K_4[CH_3OH]_o)}, \tag{14}$$

and $[HI]_o=[CH_3I]_o-x[RuCl_3]_o$.

The concentration of the intermediate **4**, **5**, and **6** are represented in function of [**2**] as Eq. 15 to Eq. 17 ($K_4'=K_4/2$).

$$[\mathbf{4}] = K_3[\mathbf{2}][CH_3OH]_o \tag{15}$$

$$[\mathbf{5}] = \frac{K_3K_4'k_5(k_{-6}+k_7[H_2])[CH_3OH]_o{}^2A[\mathbf{2}]}{k_{-5}(k_{-6}+k_7[H_2])([HI]_o-K_4'[CH_3OH]_oA)[CH_3OH]_o+k_6k_7[CO][H_2]} \tag{16}$$

$$[\mathbf{6}] = \frac{K_3K_4'k_5k_6[CH_3OH]_o{}^2A[\mathbf{2}][CO]}{k_{-5}(k_{-6}+k_7[H_2])([HI)_o-K_4'[CH_3OH]_oA)[CH_3OH]_o+k_6k_7[CO][H_2]} \tag{17}$$

The total concentration of cobalt complexes is as follows:

$$2[\mathbf{1}]_o = 2\,[\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] + [\mathbf{4}] + [\mathbf{5}] + [\mathbf{6}] \tag{18}$$

Since the equilibrium II lies to the left under high pressure of CO, the concentration of **3** can be neglected. By substituting Eqs. 15, 16, and 17 in Eq. 18, the concentration of **2** is represented as the function of $[\mathbf{1}]_o$ as Eq. 19 using the equilibrium relation derived from I. In Eq. 19, α_1, α_2, and α_3 are denoted as Eqs. 20 to 23.

$$[\mathbf{2}] = (1+\alpha_1+\alpha_2+\alpha_3)K_1[H_2]\{\sqrt{1+16[\mathbf{1}]_o/\{K_1[H_2](1+\alpha_1+\alpha_2+\alpha_3)^2\}}-1\}/4 \tag{19}$$

$$\alpha_1 = K_3[CH_3OH]_o \tag{20}$$

$$\alpha_2 = \frac{K_3K_4'k_5(k_{-6}+k_7[H_2])[CH_3OH]_o^2A}{k_{-5}(k_{-6}+k_7[H_2])([HI]_o-K_4'[CH_3OH]_oA)[CH_3OH]_o+k_6k_7[CO][H_2]} \tag{21}$$

$$\alpha_3 = \frac{k_6[CO]\alpha_2}{k_{-6}+k_7[H_2]} \tag{22}$$

Markó and his coworkers reported[21] that K_1 was small. So, Eq. 19 can be approximately expressed as Eq. 23.

$$[\mathbf{2}] = \sqrt{K_1[H_2][\mathbf{1}]_o}-(1+\alpha_1+\alpha_2+\alpha_3)K_1[H_2]/4 \tag{23}$$

Finally, the rate equation is obtained as Eq. 24 by substituting Eqs. 15 and 23 in Eq. 12.

$$v_o = \frac{K_3K'_4k_5k_6k_7[\mathrm{CH_3OH}]_o{}^2A[\mathrm{CO}][\mathrm{H_2}]}{k_{-5}(k_{-6}+k_7[\mathrm{H_2}])([\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA)[\mathrm{CH_3OH}]_o+k_6k_7[\mathrm{CO}][\mathrm{H_2}]}\{\sqrt{K_1[\mathrm{H_2}][\mathbf{1}]_o}-(1+\alpha_1+\alpha_2+\alpha_3)K_1[\mathrm{H_2}]/4\} \tag{24}$$

Equation 24 is rearranged as Eq. 25 by substituting Eqs. 20, 21, 22, and 23 into Eq. 24.

$$\begin{aligned} v_o = {} & \frac{K_3K'_4K_5K_6k_7[\mathrm{CH_3OH}]_o{}^2A\{\sqrt{K_1[\mathrm{H_2}][\mathbf{1}]_o}-K_1(1+K_3[\mathrm{CH_3OH}]_o)[\mathrm{H_2}]/4\}[\mathrm{CO}]}{(1+k_7[\mathrm{H_2}]/k_{-6})([\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA)[\mathrm{CH_3OH}]_o+k_6k_7[\mathrm{CO}][\mathrm{H_2}]/(k_{-5}k_{-6})} \\ & -\frac{K_1K_3^2K_4'^2K_5^2K_6k_7(1+k_7[\mathrm{H_2}]/k_{-6})[\mathrm{CH_3OH}]_o{}^4A^2[\mathrm{H_2}]^2[\mathrm{CO}]}{4\{(1+k_7[\mathrm{H_2}]/k_{-6})([\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA)[\mathrm{CH_3OH}]_o+k_6k_7[\mathrm{CO}][\mathrm{H_2}]/(k_{-5}k_{-6})\}^2} \\ & -\frac{K_1K_3^2K_4'^2K_5^2K_6^2k_7[\mathrm{CH_3OH}]_o{}^4A^2[\mathrm{H_2}]^2[\mathrm{CO}]^2}{4\{(1+k_7[\mathrm{H_2}]/k_{-6})([\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA)[\mathrm{CH_3OH}]_o+k_6k_7[\mathrm{CO}][\mathrm{H_2}]/(k_{-5}k_{-6})\}^2} \end{aligned} \tag{25}$$

From Fig. 7, we conclude that the last term of the right side of Eq. 25 related to the acylcobalt intermediate, **6**, can be neglected and that the rate equation is approximately expressed as Eq. 26.

$$v_o = \left\{\frac{\beta_1\beta_2[\mathrm{CH_3OH}]_oA\sqrt{[\mathbf{1}]_o}}{[\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA}-\frac{\beta_2\beta_3(1+K_3[\mathrm{CH_3OH}]_o)[\mathrm{CH_3OH}]_oA[\mathrm{H_2}]^{0.5}}{4([\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA)}-\frac{\beta_1^2\beta_2[\mathrm{CH_3OH}]_o{}^2A^2[\mathrm{H_2}]^{0.5}}{4([\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA)^2}\right\}[\mathrm{CO}][\mathrm{H_2}]^{1.5} \tag{26}$$

where $\beta_1=\sqrt{K_1}K_3K'_4K_5$, $\beta_2=K_6k_7$, $\beta_3=K_1K_3K'_4K_5$ and $[\mathrm{HI}]_o=[\mathrm{CH_3I}]_o-x[\mathrm{RuCl_3}]_o$. From the slope in Fig. 7, we obtained the following value.

$$4.25 \times 10^4\beta_1\beta_2 - 7.91 \times 10^5\beta_2\beta_3(1+K_3[\mathrm{CH_3OH}]_o) - 9.78 \times 10^7\beta_1\beta_2 = 1.66 \times 10^{-4} \tag{27}$$

With respect to [H2], the rate equation is rewritten as Eq. 28 which agrees with the experimental facts (Fig. 9).

$$v_o/[\mathrm{H_2}]^2 = B_1/[\mathrm{H_2}]^{0.5} - B_2 \quad (B_1,\ B_2\text{: constants}) \tag{28}$$

The slope and the intercept in Fig. 9 give:

$$\beta_1\beta_2 = 2.81 \times 10^{-8} \tag{29}$$

$$2.47 \times 10^3\beta_2\beta_3(1+K_3[\mathrm{CH_3OH}]_o) + 3.06 \times 10^5\beta_1\beta_2 = 3.21 \times 10^{-6} \tag{30}$$

From the effect of $[\mathrm{CH_3I}]_o$ and $[\mathrm{RuCl_3}]_o$ (Fig. 6), a value of x to satisfy Eq. 26 is found to be 2.5 from the trial and error method. This value is consistent with the result of the *in situ* IR observation which showed the presence of both diiodo- and triiodo-carbonyl complex of ruthenium (see above). Equation 26 is rearranged as Eq. 31.

$$v_o([\mathrm{HI}]_o - K'_4[\mathrm{CH_3OH}]_oA)^2/A^2 = B_3([\mathrm{HI}]_o-K'_4[\mathrm{CH_3OH}]_oA)/4A-B_4 \quad (B_3,\ B_4\text{: constant}) \tag{31}$$

Figure 10 indicates that Eq. 26 explains the experimental results of the initial concentration of methyl iodide and ruthenium. From the slope and the intercept, the following values are obtained.

$$1.90 \times 10^5\beta_1\beta_2 - 3.54 \times 10^6\beta_2\beta_3(1+K_3[\mathrm{CH_3OH}]_o) = (1.32 \pm 0.04) \times 10^{-3} \tag{32}$$

$$\beta_1^2\beta_2 = (1.23 \pm 0.02) \times 10^{-12} \tag{33}$$

By substituting the value of $\beta_1\beta_2$ and $\beta_1^2\beta_2$ in Eqs. 27, 30, and 32, the values of $\beta_2\beta_3$ $(1+K_3[\mathrm{CH_3OH}]_o)$ are found independently from each equation to be 1.15×10^{-9} within the experimental error. The above analysis, therefore, does not conflict with each other. Equation 26 is rewritten as Eq. 34. The plot of 1/

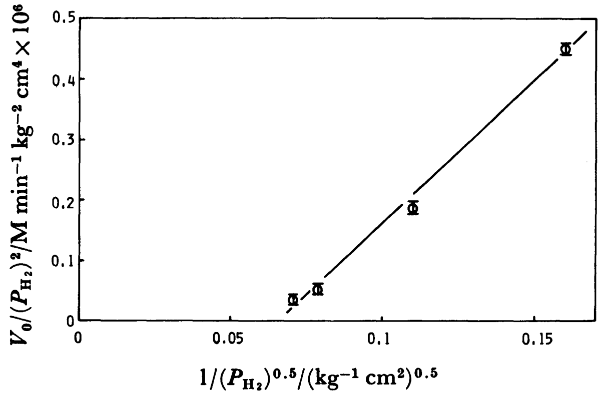

Fig. 9. Plots of $v_0/(P_{H_2})^2$ *vs.* $1/(P_{H_2})^{0.5}$.

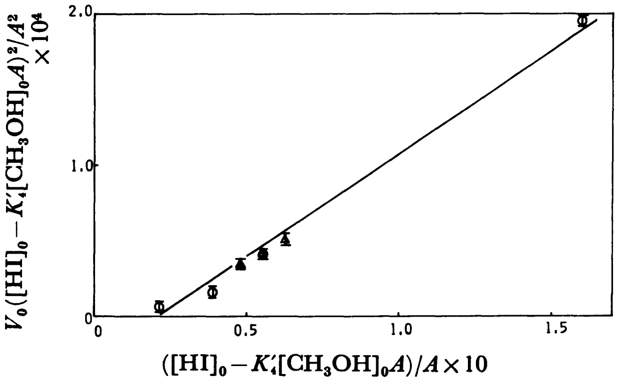

Fig. 10. Plots of v_0 $([\mathrm{HI}]_0-K'_4[\mathrm{CH_3OH}]_0A)^2/A^2$ *vs.* $([\mathrm{HI}]_0-K'_4[\mathrm{CH_3OH}]_0A)/A$.
△: $[\mathrm{CH_3I}]_0=0.14$ M, ⏀: $[\mathrm{RuCl_3}]_0=1.1\times10^{-2}$ M.

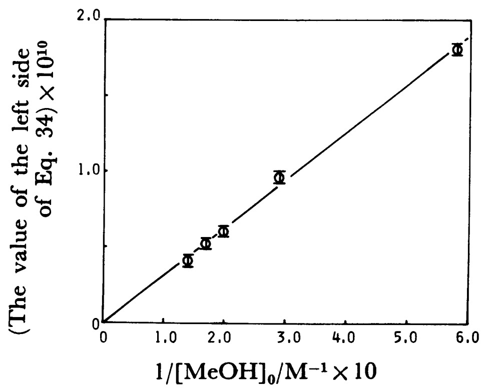

Fig. 11. Plots of the value of the left side of Eq. 34 against $1/[CH_3OH]_0$

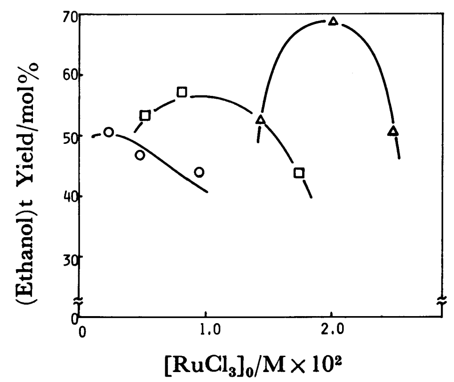

Fig. 12. The effect of the initial concentration of methyl iodide on the methanol homologation by cobalt–ruthenium mixed catalyst.
Reaction temperature: 180 °C, total pressure: 240 $kg\,cm^{-2}$ at room temperature ($H_2/CO=2/1$), solvent: 1,4-dioxane 5 ml, methanol 2 ml, $[Co_2(CO)_8]_0=(2.3$—$2.4)\times10^{-2}$ M, Time: 3 h.
○: $[CH_3I]_0=0.07$ M, □: $[CH_3I]_0=0.14$ M, △: $[CH_3I]_0=0.28$ M.

$[CH_3OH]_o$ *vs.* the value of the left side of Eq. 34 is

$$\frac{\beta_1\beta_2B_5}{[CH_3OH]_o}-\frac{\beta_1^2\beta_2A}{4([HI]_o-K_4'[CH_3OH]_oA)}-\frac{v_o([HI]_o-K_4'[CH_3OH]_oA)B_6}{[CH_3OH]_o{}^2A}$$
$$=\frac{\beta_2\beta_3}{4[CH_3OH]_o}+\frac{\beta_2\beta_3K_3}{4}\quad(B_5,\ B_6\text{: constant})\qquad(34)$$

verified as shown in Fig. 11. From the intercept, the second term of the right side in Eq. 35 related to tetracarbonylcobalt anion, **4**, is neglected. In fact, **4** was not observed by *in situ* IR during the reaction (see above). Therefore, $\beta_2\beta_3\ (1+K_3[CH_3OH]_o)$ is nearly equal to $\beta_2\beta_3$. The slope in Fig. 11 gives the value of $\beta_2\beta_3$ as:

$$\beta_2\beta_3 = 1.25\times10^{-9}\qquad(35)$$

This value agrees with that obtained above (1.15×10^{-9}). From the above analysis, the values of constants are found as follows: $K_1=(1.83\pm0.1)\times10^{-3}$ [M/(kg cm^{-2})], $K_3K_5=(4.15\pm0.04)\times10^{-3}$ and $K_6k_7=(6.42\pm0.1)\times10^{-4}$ [(kg cm^{-2})·min^{-1}]. From the results reported by Alemdaroḡlu and his coworkers,[18] K_1 at 160 °C is calculated to be 2.0×10^{-3} M/kg cm^{-2}. This value is well consistent with the value obtained from the above kinetic analysis.

The rate equation 26 also explains the reason why an optimum concentration of ruthenium exists. When ruthenium is added in excess to this system, the concentration of iodide (HI or CH_3I) is significantly decreased by the coordination of iodide to ruthenium. Consequently, the rate of hydrocarbonylation promoted by iodide is retarded. Figure 12 reveals that the optimum concentration of ruthenium increases with the initial concentration of methyl iodide and that the presence of ruthenium in excess causes the retardation of the hydrocarbonyltion of methanol, resulting in the low yield of ethanol. Thus, the mole ratio of ruthenium to iodide is important for the high yield of ethanol.

All of the above results prove that cobalt principally catalyzes the hydrocarbonylation of methanol while ruthenium only takes part in the hydrogenation of acetaldehyde.

The authors wish to thank Messers. Y. Ichikawa and M. Yasumoto for the contribution of manufacturing the *in situ* high-pressure IR cell and assembling the high-pressure experimental equipment.

References

1) I. Wender, R. Levine, and M. Orchin, *J. Am. Chem. Soc.*, **71**, 4160 (1949).

2) J. Berty, L. Markó, and D. Kallo, *Chem. Tech.*, **3**, 260 (1956).

3) T. Mizoroki and N. Nakayama, *Bull. Chem. Soc. Jpn.*, **37**, 236 (1964).

4) J. G. Lafaya, R. Perron, and Y. Colleuille, *J. Mol. Cat.*, **17**, 339 (1982).

5) W. E. Slinkard, U. S. Patent 4168391 (1979).

6) a) L. H. Slaugh, Ger. Offen. Patent 2625727 (1976). b) L. H. Slaugh and R. D. Mullineaux, *J. Organomet. Chem.*, **13**, 469 (1968). c) Y. Sugi, K. Bando, and Y. Takami, *Chem. Lett.*, **1981**, 63.

7) a) M. Hidai, M. Orisaku, M. Ue, and Y. Uchida, *Chem. Lett.*, **1981**, 143. b) M. Hidai, M. Orisaku, M. Ue, Y. Koyasu, T. Kodama, and Y. Uchida, *Organomettalics*, **2**, 292 (1983).

8) H. F. Schultz and F. Bellstdt, *Ind. Eng. Chem. Prod. Res. Dev.*, **12**, 176 (1973).

9) G. Doyle, *J. Mol. Cat.*, **13**, 237 (1981).

10) K. Kudo and N. Sugita, *Nippon Kagaku Kaishi*, **1982**, 462.

11) H. Barhmann and B. Cornils, "New Syntheses with Carbon Monoxide," ed by J. Falbe, Springer-Verlag, New York (1980) pp. 226

12) I. Wender, *Catal. Rev. -Sci. Eng.*, **14**, 97 (1976).

13) B. F. Johnson, R. D. Johnston, and J. Lewis, *J. Chem.*

Soc. A, **1969**, 792.

14) R. Clton and R. H. Farthino, *Aust. J. Chem.*, **24** 903 (1971).

15) B. K. Warren and B. D. Dombek, *J. Cat.*, **79**, 334 (1983).

16) a) G. Braca, G. Andlich, L. Paladinl, G. Sbrana, and G. Valentil, *Ind. End. Chem. Prod. Res. Dev.*, **20** 115 (1981); b) G. Jenner, H. Kheradmand, A. Kiennenmann, and A. Deluzarche, *J. Mol. Cat.*, **18**, 61 (1983).

17) J. N. Nicolls, D. H. Farrar, P. F. Jackson, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. Dalton Trans.*, **1982**, 1395.

18) N. H. Alemdaroğlu, J. M. L. Penninger, and E. Oltay, *Monatsh. Chem.*, **107**, 1043 (1976).

19) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **74**, 1216 (1952).

20) A. Slsak, F. Ungváry, and L. Markó, *Organometallics*, **2**, 1244 (1983).