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Selective Dimerization of Aldehydes to Esters Catalyzed by Hydridoruthenium Complexes

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$RuH_2(PPh_3)_4$ and other hydridoruthenium complexes catalyze selective conversion of aldehydes into esters in high yields. The method is applicable to most aliphatic aldehydes as well as to aromatic aldehydes. The purity of aldehydes is critical for achieving high conversions, since the presence of carboxylic acid completely inhibits the reaction and alcohol and triphenylphosphine reduce the yields of esters. $RuH_2(PPh_3)_4$ is converted into $Ru(CO)_3(PPh_3)_2$ through the reaction indicating the occurrence of decarbonylation of aldehyde. A mechanism involving the acyl-H cleavage of aldehyde is proposed to account for the catalysis and formation of compounds accompanying the reaction. The mechanism is compared with an alternative one which comprises of consecutive insertions of two aldehyde molecules into Ru–H bond followed by β-hydrogen abstraction from an alkoxo intermediate formed. Addition of water changes the reaction course to give carboxylato carbonyl complexes $Ru(OCOR)_2(CO)_m(PPh_3)_2$ ($m=1$ and 2). Cross esterification studies showed the reactivity order of RCHO as $R=Et > Me > n\text{-}Pr > i\text{-}Pr \gg Ph$.

In contrast to the much utilized aldol reaction of aldehydes another type of aldehyde dimerization converting aldehydes into esters, known as Tishchenko reaction,[1)] has been much less explored. The reaction is usually catalyzed by aluminium alkoxides and somewhat detailed studies have been made concerning the structural effects of aldehydes and catalysts.[2–6)] Studies have been also made concerning the catalyst systems with boric acid[7)] and a system without catalyst.[8)] Only a limited study,[9)] however, has been made to utilize a transition metal complex for the Tishchenko reaction.

Some transition metal complexes coordinated with tertiary phosphines have been found to decarbonylate aldehydes to hydrocarbons,[10–17)] *e.g.*,

$$\mathrm{RCHO} + \mathrm{RhCl(PPh_3)_3} \longrightarrow \mathrm{RH} + \mathrm{RhCl(CO)(PPh_3)_2} + \mathrm{PPh_3}. \qquad (1)$$

The reaction is considered to proceed by coordination of the aldehyde to rhodium, followed by oxidative addition of the aldehyde group to give an acyl intermediate which is decarbonylated.[18)] Such an assumption seems reasonable in view of the known examples of aldehyde coordination to transition metal complexes[19,20)] and of acyl-H bond cleavage.[21–25)]

Hydrido-ruthenium complexes, particularly $RuH_2(PPh_3)_4$ (**1**) exhibit quite a variety of stoichiometric as well as catalytic reactions,[26–35)] and are considered to possess yet unexploited potentiality to catalyze various reactions. Catalytic hydrogenation of aldehydes to give alcohols with molecular hydrogen[36,37)] or with organic hydrogen donors[38,39)] using Ru, Rh, or Ir complexes have been reported. From a system containing **1** and propionaldehyde a reportedly "intermediate" complex formulated as $Ru(EtCHO)(PPh_3)_3$ has been isolated[38)] but this was later refuted as a mixture of $RuH_2(CO)(PPh_3)_3$ (**2**) and $RuH(OCOEt)(PPh_3)_3$ (**3a**).[29)]

We report here the catalytic conversion of aldehydes into carboxylic esters catalyzed by **1** and related ruthenium hydride complexes. Characterization of the ruthenium complexes recovered from the reaction systems is also included with a hope to shed light on the reaction mechanism. A preliminary account of this system was made previously.[40)]

Results

Reactions of Butyraldehyde with $RuH_2(PPh_3)_4$ (1). When carefully purified butyraldehyde is brought into contact with a catalytic amount of **1** *in vacuo* at room temperature, a violent, exothermic reaction starts in 2—3 min. The reaction is completed in several minutes to give a dark brown solution, the GLC analysis of which shows conversion of most butyraldehyde into butyl butyrate.

$$2\,\mathrm{Pr^nCHO} \xrightarrow{\text{cat.}} \mathrm{Pr^nCOOBu^n} \qquad \text{cat.} = \mathbf{1} \qquad (2)$$

Although the reaction is accompanied by the formation of a stoichiometric amount of 1-butanol, the reaction product is free of either aldol-condensation products or trimeric glycol ester, indicating the high selectivity of the reaction. On working up the system after completion of the reaction, the known tricarbonyl complex, $Ru(CO)_3(PPh_3)_2$[41–43)] (**4**) is isolated as a sole characterizable ruthenium complex. A careful purification of aldehyde, especially rigorous exclusion of carboxylic acid and water was found essential for initiating the catalytic reaction.

The results of typical experiments are listed in Table 1. The ester forming reaction took place at −20 to +100 °C, with the highest conversion around 0 °C (compare runs 3, 10, 20, and 21). The system kept at −20 °C afforded a lower yield of ester and a dihydrido carbonyl complex, tentatively assigned to $RuH_2(CO)(PPh_3)_3$(**2**),[44)] was isolated from the reaction mixture. The system is essentially inactive at −30 °C and the carboxylato complex, $RuH(OCOPr^n)(PPh_3)_3$(**3b**), was obtained on working up the system kept at −30 °C for 2 h. One

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TABLE 1. REACTION OF BUTYRALDEHYDE WITH $RuH_2(PPh_3)_4$ a)

Run	Pr^nCHO (mmol)	$RuH_2(PPh_3)_4$ (mmol)	Pr^nCHO/Cat. (molar ratio)	Temp °C	Pr^nCOOBu^n (mmol)	Conv. b) %
1	68.6	0.547	125	100	31.0	90
2	15.1	0.132	114	20	7.4	98
3	49.7	0.132	377	20	19.4	78
4	49.7	(0.039) c)	291	20	20.7	83
5	49.7	(0.057) c)	218	20	21.2	85
6	49.7	(0.043) c)	183	20	21.7	87
7	49.7	(0.050) c)	155	20	22.9	92
8 d)	43.6	0.145	301	20	6.0	28
9 e)	35.8	0.119	301	20	0.0	0
10	52.4	0.129	406	0	26.0	99
11 f)	56.4	0.115	490	0	25.4	90
12 g)	99.9	0 256	390	0	35.4	71
13 h)	41.5	0.060	692	0	20.4	98
14	70.1	0.088	797	0	30.7	88
15	67.8	0.034	1994	0	30.2	89
16 i)	56.1	0.138	407	0	25.4	91
17 j)	45.8	0.142	323	0	20.6	90
18 k)	55.6	0.156	356	0	27.8	100
19 l)	63.0	0.145	434	0	4.3	14
20	53.8	0.175	307	−10	25.0	93
21	61.1	0.150	407	−20	18.7	61
22	63.9	0.156	410	−30	0.2	1

a) Reactions were carried out for 2 h *in vacuo* without solvent unless otherwise stated. b) On the basis of the amount of Pr^nCHO initially used. c) $RuH_2(PPh_3)_4$ was added successively to the reaction system of run 3 after completion of each run. d) 1-Butanol (0.291 mmol) was added to the system. e) Butyric acid (0.239 mmol) was added to the system. f) Reaction was carried out under nitrogen atmosphere. g) Reaction was carried out under H_2 pressure (*ca.* 2 atm). h) Reaction was carried out for 30 min. i) Hexane (20 ml) was used as solvent. j) Toluene (20 ml) was used as solvent. k) Reaction was carried out in the presence of 6 ml of tetrahydrofuran. l) Pyridine (15 ml) was used as solvent.

TABLE 2. REACTION OF ALDEHYDES (RCHO) OTHER THAN BUTYRALDEHYDE WITH $RuH_2(PPh_3)_4$ a)

Run	RCHO (mmol)	$RuH_2(PPh_3)_4$ (mmol)	RCHO/Cat. (molar ratio)	Temp °C	Time h	$RCOOCH_2R$ (mmol)	Conv. b) %
23	CH_3CHO	90.0 0.147	612	20	2/3	31.7	70
24	CH_3CHO	81.0 0.153	529	0	2/3	38.0	94
25	CH_3CHO	67.3 0.120	561	−20	2	0.0	0
26	CH_3CH_2CHO	68.5 0.250	274	20	2	17.4	51
27 c)	CH_3CH_2CHO	27.8 0.100	280	20	2	1.2	9
28	$(CH_3)_2CHCHO$	59.8 0.226	264	20	4.5	21.1	71
29	$CH_3(CH_2)_3CHO$	23.5 0.142	165	85	2	5.1	43
30	$(CH_3)_2CHCH_2CHO$	18.2 0.131	140	85	3	6.2	68
31	$CH_3(CH_2)_4CHO$	16.0 0.200	80	85	3	3.5	44
32	C_6H_5CHO	14.8 0.120	120	20	2	1.7	23

a) Reactions were carried out *in vacuo* in a glass autoclave. b) On the basis of the amount of RCHO initially used. c) PPh_3 (1.00 mmol) was added to the system.

possible reaction for the catalyst deactivation at the low temperature is the conversion of catalyst **1** into the carboxylato complex **3b** prior to the initiation of the esterification reaction. Complex **3b** was found to be inactive for the esterication reaction (*vide infra*).

For pure aldehydes, complex **1** proved to be quite active achieving *ca.* 2000 turnovers at 0 °C with the concentration of as low as 0.05 mol% (run 15). Although the catalyst is deactivated at the completion of the reaction, addition of the new crop of the catalyst to the reaction system containing remaining unreacted aldehyde initiated the catalysis (runs 3—7).

Addition of butyric acid completely inhibits the reaction (run 9) whereas the presence of two equivalents of 1-butanol per catalyst did not completely block the reaction but considerably reduced the conversion of aldehyde to ester (run 8). The reaction can be performed under nitrogen as well as in vacuum (run 11) whereas hydrogen somewhat reduced the conversion (run 12). Solvents such as hexane, toluene and tetrahydrofuran may be used provided they are appropriately purified (runs 16—18) but employment of the more coordinating solvent such as pyridine notably reduced the catalytic activity (run 19).

Complex **1** can be used for conversion of other aldehydes such as acetaldehyde, propionaldehyde,

TABLE 3. CROSS-ESTERIFICATION OF ALDEHYDES CATALYZED BY $RuH_2(PPh_3)_4$a)

$$R^1CHO + R^2CHO \xrightarrow{RuH_2(PPh_3)_4} \begin{cases} R^1COOCH_2R^1 \text{ (A)} \\ R^1COOCH_2R^2 \text{ (B)} \\ R^2COOCH_2R^1 \text{ (C)} \\ R^2COOCH_2R^2 \text{ (D)} \end{cases}$$

Run	R^1CHO (mmol)	R^2CHO (mmol)	$\frac{R^1CHO}{R^2CHO}$	Cat. (mmol)	Total conv. %b)	Products (mmol) A	B	C	D	$\frac{A}{D}$
33	CH_3CHO (17.8)	CH_3CH_2CHO (18.1)	0.98	0.161	74	2.76	1.47	5.37	3.73	0.74
34	CH_3CHO (19.5)	$CH_3(CH_2)_2CHO$ (22.7)	0.86	0.088	71	7.31	3.09	1.20	3.35	2.18
35	CH_3CHO (17.8)	$(CH_3)_2CHCHO$ (22.1)	0.81	0.167	31	1.49	3.03	0.67	1.03	1.45
36	$CH_3(CH_2)_2CHO$ (11.3)	$(CH_3)_2CHCHO$ (11.0)	1.03	0.167	90	2.74	(5.06)c)		2.22	1.23
37	C_6H_5CHO (14.8)	$CH_3(CH_2)_2CHO$ (13.6)	1.09	0.101	48	0.10	0.17	1.47	5.04	0.02
38	C_6H_5CHO (14.8)	$(CH_3)_2CHCHO$ (15.6)	0.95	0.102	44	0.13	0.43	2.42	3.72	0.04

a) Reactions were carried out *in vacuo* at room temperature. b) Total conversion (mol%) = 200 [A (mmol) + B (mmol) + C (mmol) + D (mmol)]/[R^1CHO (mmol) + R^2CHO (mmol)]. c) Total amount of isobutyl butyrate and butyl isobutyrate was recorded as they were not distinguishable each other by means of GLC analysis.

TABLE 4. COMPLEXES FORMED BY THE REACTION OF BUTYRALDEHYDE WITH $RuH_2(PPh_3)_4$ AND $RuH(OCOPr^n)(PPh_3)_3$ UNDER VARIOUS CONDITIONSa)

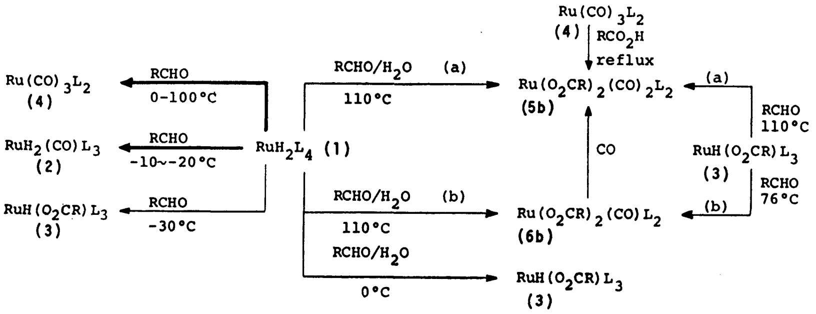
Run	$RuH_2(PPh_3)_4$ (mmol)	Pr^nCHO (mmol)	H_2O (mmol)	$\frac{\text{Temp}}{°C}$	Pr^nCOOBu^n (mmol)(Conv/%)	Bu^nOH (mmol)	Resulting complex (mmol)b)
1	0.547	68.6	0	100	31.0(90)	0.10	**4** (0.31)
39	0.198	51.6	0	0	23.2(90)	tracec)	**4** (0.16)
20	0.175	53.8	0	−10	25.0(93)	0	**2**d)
21	0.150	61.1	0	−20	18.7(61)	trace	**2**d)
22	0.156	63.9	0	−30	0.2(1)	trace	**3b**d)
40e)	0.552	66.5	5.55	0	0	trace	**3b** (0.500)
41f)	0.83	187	2.87	110	8.4(9)	1.07g)	**5b** (0.51)
42f)	1.10	167	11.1	110	d)	d)	**5b** (0.59)
43f)	2.22	340	16.0	110	d)	d)	**6b** (1.5)
44f)	0.171h)	59.9	0	110	0.03	trace	**5b** (0.094)
45i)	1.84h)	330	0	75	d)	d)	**6b** (1.4)

a) Reactions were carried out *in vacuo* for 2 h in a Schlenk type flask unless otherwise stated. b) **2**: $RuH_2(CO)(PPh_3)_3$; **3b**: $RuH(OCOPr^n)(PPh_3)_3$; **4**: $Ru(CO)_3(PPh_3)_2$; **5b**: $Ru(OCOPr^n)_2(CO)_2(PPh_3)$; **6b**: $Ru(OCOPr^n)_2(CO)(PPh_3)_2$. c) Other products (yield in mmol): H_2 (0.04), C_3H_6 (0.018), C_3H_8 (0.059), and CO (trace). d) The yield was not measured. e) Reactions were carried out in a Pyrex glass-autoclave. f) Reactions were carried out in a stainless steel-autoclave. g) Other products: H_2 (0.21), C_3H_6 (0.04), C_3H_8 (0.05), and CO(0.272). h) Amount of $RuH(OCOPr^n)(PPh_3)_3$ **3b**. i) Heated under reflux under N_2 atmosphere for 2 h in a Schlenk type flask.

isobutyraldehyde, valeraldehyde, isovaleraldehyde, hexanal, and benzaldehyde (Table 2). The yields are somewhat low for some aldehydes, but optimization of the reaction conditions may well enhance the yields. Considerable hindrance of the catalysis by addition of triphenylphosphine was noted (run 27). The reaction of acrylaldehyde with **1** either at 0° or at −20 °C afforded a massive brown polymeric material, which is insoluble in most organic solvents.45)

Cross-esterification Reaction. For examining relative reactivities of aldehydes cross esterifications using about 1 : 1 binary mixtures of aldehydes have been carried out. Cross esterification of the 1 : 1 mixture of acetaldehyde and propionaldehyde, for example, catalyzed by **1** at room temperature afforded ethyl acetate (A), propyl acetate (B), ethyl propionate (C), and propyl propionate (D) in a ratio of 1.00 : 0.53 : 1.95 : 1.35. The result, indicating the higher yield of D than A as well as the higher yield of C than B, suggests that the reactivity of propionaldehyde to the esterification reaction is slightly higher than that of acetaldehyde. Similar comparison of the product distributions, using especially the ratios of A/D as the reactivity index in Table 3 in the mixed esterification reactions of various aldehydes, allows one to estimate their relative reactivities toward esterification reaction as $CH_3CH_2CHO > CH_3CHO > CH_3(CH_2)_2CHO > (CH_3)_2CHCHO \gg PhCHO$. The same order was obtained for the relative proton donor ability of each aldehyde which was estimated from the comparison of values B and C in Table 3. The similar values of the product distribution have been reported for the systems containing acetaldehyde and butyraldehyde, and benzaldehyde and butyraldehyde catalyzed by aluminium alkoxides.2,3)

Absence of the ester exchange reaction between the product esters under the reaction conditions was confirmed by the additional experiments in which propionaldehyde and butyraldehyde, respectively, were allowed to react with **1** at 85 °C in the presence of ethyl acetate. In both cases, the resulting systems contained only propyl propionate and butyl butyrate, respectively, in addition to the added ethyl acetate and no mixed esters were detected showing the absence of the ester exchange reaction.



(a): Reactions were carried out *in vacuo* in a stainless steel autoclave.
(b): Reactions were carried out *in vacuo* or under N_2 in a Pyrex glass flask.
L=PPh$_3$, R=*n*-C$_3$H$_7$, broad arrows stand for the reactions accompanied with catalytic ester-formation reactions.

Scheme 1. Reactions of $RuH_2(PPh_3)_4$ with butyraldehyde and related reactions.

TABLE 5. SPECTRAL DATA OF SOME RELEVANT CARBOXYLATO–RUTHENIUM COMPLEXES

Complex		IR bands[a)]			^{1}H-NMR signals[b)]			^{31}P-NMR signals[b)]
		ν(C=O) / cm^{-1}	ν_a(CO$_2$) / cm^{-1}	ν_s(CO$_2$) / cm^{-1}	δ(CH$_3$)	δ(γ-CH$_2$)	δ(β-CH$_2$)	
RuH(OCOPr^n)-(PPh$_3$)$_3$	**3b**	2000w[c)]	1520m[e)]	1420m[e)]	0.57 (t, 3H) δ(RuH)	1.07(hex, 2H) −17.6 (q, 1H)	1.43 (q, 2H)	43.60 (d, 2P) 77.46 (t, 1P) ^2J(PP)=27.3 Hz
Ru(OCOPr^n)$_2$-(CO)$_2$(PPh$_3$)$_2$	**5b**	2010vs 1960vs	1610s[d)] 1590s[d)]	1325s[d)]	0.51 (t, 6H)	1.01 (hex, 4H)	1.33 (t, 4H)	31.56 (s)
Ru(OCOPr^n)$_2$-(CO)(PPh$_3$)$_2$	**6b**	1965vs	1640s[d)] 1505m[e)]	1315m[d)] 1460m[e)]	0.67 (t, 6H)	1.17 (hex, 4H)	1.49 (m, 4H)	48.15 (s)
Ru(OCOEt)$_2$ (CO)(PPh$_3$)$_2$	**6a**	1960vs	1620s[d)] 1510m[e)]	1325m[d)] 1445m[e)]	0.66 (t, 6H) {0.55 (t, 3H)[f)] {0.65 (t, 3H)[f)]	—	1.62 (q, 4H) {1.40 (q, 2H)[f)] {1.68 (q, 2H)[f)]	48.22 (s)

a) KBr disc. b) In CD$_2$Cl$_2$ at room temperature unless otherwise stated. ^3J(HH)=7 Hz. ^{31}P-NMR chemical shifts are based on external H$_3$PO$_4$ reference, with downfield positive values. c) ν(Ru–H). d) CO$_2$ stretching bands due to a unidentate carboxylato ligand. e) CO$_2$ stretching bands due to a bidentate carboxylato ligand. f) The spectrum taken at −20°C.

Examination of Ruthenium Complexes Recovered from the Reaction Mixture of Aldehyde and $RuH_2(PPh_3)_4$ in the Presence or Absence of Added Water. In order to obtain insight into the mechanism of the present reaction, the ruthenium complexes recovered after completion of the reactions under various conditions were examined. The results are summarized in Table 4 and Scheme 1. As mentioned previously, tricarbonyl complex **4** was isolated from the reaction system carried out at temperatures above 0 °C where high conversions to ester was achieved (run numbers 1 and 39 in Table 4). Hydridocarbonyl complex **2** was also formed when the reaction was carried out at −10 —−20 °C (runs 20 and 21). On the other hand, wherever no esterification reaction proceeded, as in the reaction at −30 °C (run 22) or at 0 °C in the presence of water (run 40), hydridocarboxylato complex **3b** was isolated a as sole ruthenium complex. Heating the reaction mixture at 110 °C in the presence of water resulted in the formation of carboxylato-carbonyl-complexes, Ru(OCOPr^n)$_2$(CO)$_2$(PPh$_3$)$_2$ (**5b**) or Ru-(OCOPr^n)$_2$(CO)(PPh$_3$)$_2$ (**6b**) depending on the experimental conditions (runs 41—43).

In some reaction systems listed in Table 4, examination of gaseous product revealed the formation of H$_2$, methane, propane and propene (runs 39 and 41).

Properties of Dicarboxylato-mono- and -dicarbonyl Complexes and Some Related Reactions. Spectroscopic data for the new carboxylato–carbonyl complexes **5b** and **6b** thus obtained are listed in Table 5. Their reactions with an excess of methyl iodide afforded methyl propionate, although their yields were less than stoichiometric amount. Complex **6b** absorbed about one mole of carbon monoxide per mole of **6b** in toluene at room temperature to give complex **5b** quantitatively. Complexes **5b** and **6b** were also obtained by the reaction between hydridocarboxylato complex **3b** and butyraldehyde in the absence of water (runs 44 and 45 in Table 4). The reaction of **4** with Pr^{n}CHO at 100 °C either with or without added water only resulted in the recovery of the unreacted complex. These results suggest that the ability of the ruthenium complexes to decarbonylate aldehydes decreases with increase in the number of CO ligand attached to ruthenium.

A propionato homolog of **6b**, Ru(OCOEt)$_2$(CO)-(PPh$_3$)$_2$ (**6a**), was obtained by the reaction of RuH$_2$-(PPh$_3$)$_4$ **1** with a slightly impure propionaldehyde at 80 °C *in vacuo*.[46)] Spectral data of **6a** are included in Table 5. In the ^{1}H-NMR spectrum of **6a**, triplet and multiplet signals at room temperature assignable to the

TABLE 6. CATALYTIC ACTIVITIES OF VARIOUS TRANSITION METAL COMPLEXES FOR CONVERSION OF ALDEHYDES TO ESTERS[a)]

Run	Catalyst		RCHO[b)]	Temp	Time	$RCOOCH_2R$[c)]	Conv.	Gases evolved
	Complex	mmol	(mmol)	°C	h	(mmol)	%	(mol/mol complex)
46	$RuH_2(PPh_3)_3$	0.30	21.5	85	3	10.5	96	
47	$RuH_2(CO)(PPh_3)_3$	0.35	20.6	90	3	8.42	77	
48	$RuHCl(PPh_3)_3$	0.11	5.8	85	1.5	1.31	45	
49	$RuHCl(CO)(PPh_3)_3$	0.19	25.1	85	2	3.72	29	
50	$RuH(-CH{=}CMeCOOEt)-(PPh_3)_3$	0.45	36.2	85	4	18.1	98	
51	$Ru(C_2H_4)(PPh_3)_3$	0.16	16.6	90	2	7.66	91	
52	$RuCl_2(PPh_3)_3$	0.19	17.7	85	3	0	0	
53	$Ru(CO)_3(PPh_3)_2$	0.54	41.7	90	3	0	0[d)]	
54	$[RuH(PPh_3)_4]^+[PF_6]^-$	0.13	55.5	20	5	11.9	43	
55	$RhH(PPh_3)_4$	0.18	27.6	100	1.5	0.74	5.3	
56	$FeH_2(N_2)(PEtPh_2)_3$	0.18	27.7	85	1	0.066	0.48	N_2(main)$+H_2$ (total 1.49)
57	$CoH(N_2)(PPh_3)_3$	0.22	55.9	20	6	0.012	0.04	N_2(1.00)
58	$MoH_4(Ph_2PCH_2CH_2PPh_2)_2$	0.26	62.3	100	2	0	0[d)]	
59	$MoH_4(PMePh_2)_4$	0.31	55.3	85	1	0	0	H_2(0.96)
60	$Mo(C_2H_4)(Ph_2PCH_2CH_2PPh_2)_2$	0.23	56.7	85	1	0	0	C_2H_4(1.00)
61	$Pd(C_2H_5)_2(PMePh_2)_2$	0.50	56.9	0	4	trace	≈0	C_2H_4(0.20)$+C_2H_6$ (1.06)
62	$Pt(C_2H_5)(C_5H_7O_2)(PPh_3)_2$	0.17	55.6	20	6	trace	≈0	C_2H_6(0.76)

a) Reactions were carried out *in vacuo* in a Schlenk type glass flask. b) Propionaldehyde ($R=C_2H_5$) for runs 46—52 and butyraldehyde ($R=n\text{-}C_3H_7$) for runs 54—62. c) Propyl propionate for runs 46—52 and butyl butyrate for runs 53—62. d) Starting complex was recovered quantitatively.

ethyl groups of the propionato ligands split into a set of pairs of triplets and quartets at −20 °C indicating the existence of two unequivalent carboxylato groups in **6a**. Similarly to **6b**, complex **6a** released about a half mole of methyl propionate per mole of complex on reaction with excess methyl iodide.

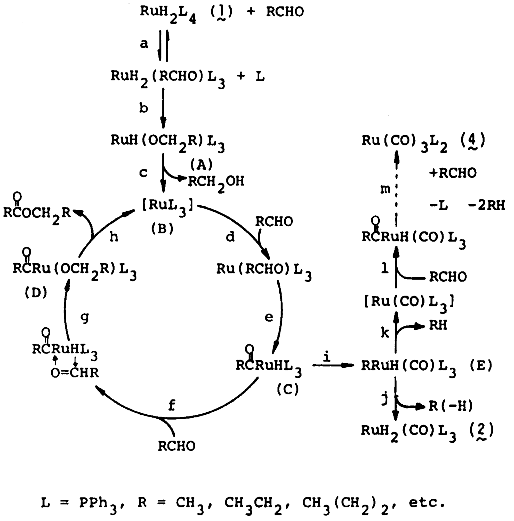
Examination of the Catalytic Activities of Various Transition Metal Complexes for Conversion of Aldehydes into Esters. As shown in Table 6, most hydrido ruthenium complexes possess catalytic ability of esterification reaction among various transition metal complexes examined. That the "ethylene" complex of a composition $Ru(C_2H_4)(PPh_3)_3$ also shows the catalytic activity may be due to the presence of the hydrido species such as $RuH(o\text{-}C_6H_4PPh_2)(PPh_3)_2(C_2H_4)$ or $RuH_2(o\text{-}C_6H_4PPh_2)(CH{=}CH_2)(PPh_3)_n$ in solution.[28,29] The introduction of a chloride anion to the hydrido complex considerably reduced its efficiency (runs 48 and 49). Dichloro derivative and tricarbonylruthenium(0) complex were inactive, although a stoichiometric amount of 1-propanol was formed in the reaction with the former complex.

Among hydrido and alkyl transition metal complexes other than ruthenium ones examined, only hydrido rhodium complex showed a feeble activity yielding ester in more than a stoichiometric amount (run 55).

Discussion

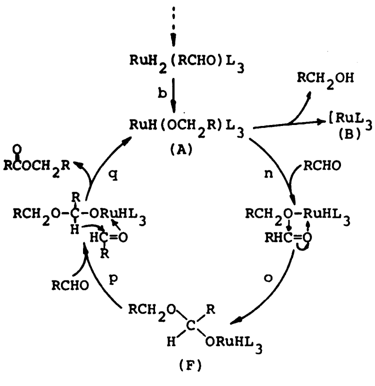
The Mechanism of the Catalytic Reaction. Two alternative routes, shown in Schemes 2 and 3 are conceivable for the present catalytic conversion of aldehyde to ester.

In Scheme 2 aldehyde first coordinates to $RuH_2(PPh_3)_3$, formed by ligand dissociation, to give $RuH_2(RCHO)(PPh_3)_3$ followed by insertion of the carbonyl group of aldehyde into Ru–H bond (path b). The insertion of the organic carbonyl group into the metal to carbon or hydrogen bond, not unusual reaction for the main group elements such as Grignard reagent and alkyllithium, has been postulated in some reactions involving organo transition metal complexes.[47] Reductive elimination of alkoxo and hydrido ligands from intermediate A yielding RCH_2OH and the Ru(0) species, $[RuL_3]$, then follows (path c). The similar processes to paths a—c have been proposed by Imai



L = PPh_3, R = CH_3, CH_3CH_2, $CH_3(CH_2)_2$, etc.

Scheme 2.



L = PPh$_3$; R = CH$_3$, CH$_3$CH$_2$, etc.

Scheme 3.

et al. for the catalytic hydrogen transfer reaction from organic hydrogen donor molecule to aldehyde by complex **1**.[38]

The second molecule of aldehyde coordinates to [RuL$_3$] and oxidatively adds to Ru to give hydrido acyl intermediate (path e). The oxidative addition of aldehyde involving a cleavage of aldehydic hydrogen-carbon bond has been postulated in many examples accounting for the decarbonylation from aldehyde with transition metal complexes,[10–17] and the hydridoacyl type complex corresponding to the intermediate C has been isolated in some cases.[21–25]

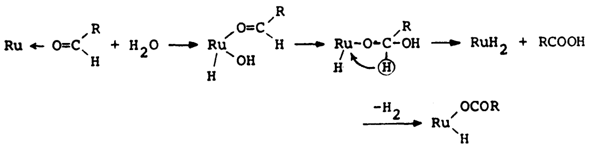
The third aldehyde molecule coordinates to the intermediate C and is inserted into the Ru–H bond to give an acyl-alkoxo type intermediate D, which on reductive elimination releases ester accompanied by regeneration of B. In this catalytic cycle, acyl intermediate C may isomerize *via* a decarbonylation reaction (path i) to alkyl carbonyl intermediate E, which may give hydrido carbonyl complex **2** and alkene by the β-elimination reaction (path j), or tricarbonyl complex **4** on repetition of the reductive elimination of alkane, the oxidative addition of aldehyde, and decarbonylation (paths k, l, and m). Both complexes **2** and **4** are the final products isolated in the ester formation reaction carried out at −20 °C and above 0 °C, respectively.

The mechanism of catalytic ester formation alternative to Scheme 2 is shown in Scheme 3 which is somewhat similar to those proposed for the so called Tishchenko reaction catalyzed by aluminium alkoxide.[5] In this mechanism, hydridoalkoxo intermediate A which is formed in a similar path as in Scheme 2 reacts with the second aldehyde molecule (path n) which is inserted into Ru–O bond to give another alkoxo intermediate F (path o). The following hydrogen transfer from alkoxo ligand to the third aldehyde, presumably by a β-hydrogen elimination mechanism, affords ester regenerating A. The hydrido and alkoxo ligands in A may be eventually removed as alcohol by a reductive elimination process.

It is difficult to decide which mechanism is operative in the catalytic conversion on the basis of limited information presently available. However, formation of the carbonyl complexes **2**, **4**, **5**, and **6** indicates that a decarbonylation reaction of aldehyde involving the acyl-H bond cleavage is taking place during or after the catalytic process. Assumption of the oxidative addition of aldehyde is consistent in Scheme 2, although the occurrence of the oxidative addition of aldehyde to RuL$_3$ (B) to give the carbonyl complexes *after* the completion of the catalytic process can not be excluded. Furthermore the high activity of hydrido ruthenium complexes is in favor of the mechanism involving aldehyde insertion into Ru–H.

The presence of a small amount of water drastically alters the reaction path (run 40 of Table 4).

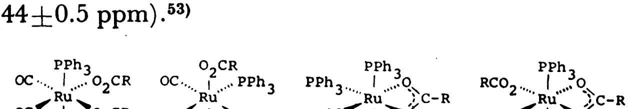
The formation of the hydrido(carboxylato) complex **3** may be caused by interaction of water with **1** by a possible mechanism as shown below. Disproportionation



of aldehydes into alcohols and carboxylic acids in the presence of water was recently found to be catalyzed by ruthenium and rhodium complexes under neutral conditions presumably by a different mechanism.[48] The reaction of **1** with carboxylic acid is known to give **3**.[49]

Recently, catalytic dimerization of terminal epoxides to carboxylic ester by RuCl$_2$(PPh$_3$)$_3$ has been reported.[50] Although epoxides can be regarded as one of the isomeric forms of aldehyde, the mechanism of the ester formation of this system differs from that of the present study described above, since the order of reactivity, *i.e.*, aromatic epoxides >aliphatic epoxides, is opposed to that found in our system.

The Configuration of Carboxylato Complexes of Ruthenium(II). Analogous complexes to di(butyrato)dicarbonylbis(triphenylphosphine)ruthenium **5b** was previously prepared by reaction of Ru(CO)$_3$(PPh$_3$)$_2$ with carboxylic acids RCOOH in benzene,[51] or in 2-methoxyethanol,[49,52] by treatment of RuH(OCOR)(PPh$_3$)$_3$ with CO,[42] for R=H, CH$_3$, C$_2$H$_5$, p-ClC$_6$H$_4$, p-NO$_2$C$_6$H$_4$, and CF$_3$. By analogy to discussion presented for Ru(OCOCF$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$,[53] complex **5b** probably has the configuration (I). However, the possibility of (II) is not completely ruled out since the ^{31}P{^{1}H} NMR chemical shift of **5b** (Table 5) deviates from that observed in this type of complexes where two phosphorus atoms are in mutually *trans* positions (44±0.5 ppm).[53]



(I) (II) (III) (IV)

Dicarboxylato monocarbonyl complexes Ru(OCOR)$_2$(CO)(PPh$_3$)$_2$ **6** have been prepared by treating RuH$_2$(CO)(PPh$_3$)$_3$ with carboxylic acid in 2-methoxyethanol (R=p-ClC$_6$H$_4$, and p-NO$_2$C$_6$H$_4$)[49] or in toluene (R=CF$_3$).[52] Acetato analogue has been prepared by the action of NaOCOCH$_3$ with trifluoroacetato complex,[54] or by the action of CO with $Ru_2O(OCOMe)_4(PPh_3)_2$.[55] According to the configurational assignment made by Dobson and Robinson,[54] complexes **6a** and **6b** may have structure III where unidentate and bidentate carboxylato ligands are exchanging in an NMR time scale above room temperature. The alternative structure IV which has been assigned for the acetato complex prepared by Wilkinson's method[55] can be ruled out for the present product because of the significant resemblance of the spectra of complexes **6a** and **6b** to those reported by Dobson and Robinson.[54] Similarly to the trifluoroacetato complex,[54] complex **6** was converted into dicarbonyl analogue **5** on treatment with carbon monoxide.

Experimental

All reactions and manipulations were carried out under dry, oxygen-free nitrogen or *in vacuo* using Schlenk-type flasks unless otherwise stated. Solvents were dried and purified in the usual manner and stored under an inert atmosphere. Commercial aldehydes were purified by a careful distillation over calcium hydride or molecular sieve 5A through the Widmer type fractionating column of 30 cm length under nitrogen. Aldehydes thus purified was stirred with calcium hydride or, more preferably to avoid the formation of aldol condensates, molecular sieve 5A for about 1 h just before the reaction and distilled at room temperature directly into the flask containing the catalyst complex *in vacuo* (*ca.* 10^{-3} mmHg, 1 mmHg$\approx$133.3 Pa). Dihydridotetrakis(triphenylphosphine)ruthenium(II) **1** was prepared from $RuCl_3 \cdot 3H_2O$ (Nippon Engelhard) by the methods reported by Levison and Robinson[56] and Harris *et al.*[57] The other complexes used in the present study were prepared according to the reported method as follows: $RuH_2(PPh_3)_3$,[56] $RuH_2(CO)(PPh_3)_3$,[58] $RuHCl(PPh_3)_3$,[59] $RuHCl(CO)(PPh_3)_3$,[58] $\overline{RuH\{-CH{=}C(Me)-COOEt\}}(PPh_3)_3$,[31] $Ru(C_2H_4)(PPh_3)_3$,[28] $RuCl_2(PPh_3)_3$,[60] $Ru(CO)_3(PPh_3)_2$,[58] $[RuH(PPh_3)_4]^+[PF_6]^-$,[61] $RhH(PPh_3)_4$,[56] $FeH_2N_2(PEtPh_2)_3$,[62] $CoH(N_2)(PPh_3)_3$,[63] $MoH_4(Ph_2PCH_2CH_2PPh_2)_2$,[64] $Mo(C_2H_4)(Ph_2PCH_2CH_2PPh_2)_2$,[65] $Pd(C_2H_5)_2(PMePh_2)_2$,[66] and $Pt(C_2H_5)(C_5H_7O_2)(PPh_3)_2$.[67] Hydridopropionato complex $RuH(OCOPr^n)(PPh_3)_3$ **3b** was prepared according to the method reported for the preparation of the acetato analogue $RuH(OCOMe)(PPh_3)_3$[49] with some modification.

The reaction products in the ester formation reaction was quantitatively analyzed by GLC using internal standard. GLC was performed on Shimadzu GC-3BT, GC-5AP$_3$F, and GC-6APT models using Shimadzu ITG-2A and Chromatopac-ElA integrators. SDC-410 (4m) and -550 (4m), PEG-20M (3 and 4m), TCP (3 m), and DOP (3 m) were employed as columns for the analyses of esters. Gaseous products were analyzed quantitatively by a Toepler pump and characterized by GLC using Molecular sieve 5A (for H_2, N_2, and CH_4 analyses), activated charcoal (for C_2) and Porapak Q (for C_3–C_4) as columns. Infrared spectra were recorded on a Hitachi model 295 spectrometer using KBr disks prepared under inert atmosphere. ^1H- and ^{31}P-NMR spectra were measured on JEOL's JNM-PS-100 and FX-100 instruments at 100 MHz for ^1H and 40.5 MHz for ^{31}P operated by Mr. Y. Nakamura of our Laboratory. Microanalyses were carried out on a Yanagimoto's CHN autocorder type MT-2 by Mr. T. Saito of our Laboratory.

Catalytic Ester Formation Reaction. Reactions were carried out with various aldehydes under a variety of conditions. However, since the routine procedure does not differ so much with each other, the typical process is described below for the reaction of butyraldehyde at different temperatures. Schlenk type flasks were used for the most of runs, but the use of small autoclave made of Pyrex glass or stainless steel is indispensable for reactions of acetaldehyde in order to avoid the dangerous breakage of the vessel due to the violent exothermic reaction.

The reaction can also be carried out in the atmosphere of nitrogen instead of under vacuum (run 11). This method is more convenient in a practical sense than that using vacuum line technique, but a sufficient care is necessary to control the explosive exothermic reaction.

Although the reactions were usually brought to completion in the initial several minutes, most reactions were carried out for 2 h unless otherwise stated.

a) Reactions of Butyraldehyde at 0 °C: Into the Schlenk flask containing $RuH_2(PPh_3)_4$ **1** (0.149 g, 0.129 mmol), 4.71 cm^3 (52.4 mmol) of butyraldehyde was distilled over molecular sieve 5A *in vacuo* by a trap-to-trap method. In about 2 or 3 min at 0 °C *in vacuo*, the system evolved a lot of heat causing refluxing and the initial yellow suspension was converted into a dark brown turbid solution. The rapid heat evolution is ceased in a few min. After the system was stirred in an ice-bath for 2 h, gases evolved by the reaction were analyzed to reveal the formation of H_2, propane and propene. GLC analysis of the resulting solution indicated the presence of butyl butyrate (26.0 mmol) and a small amount of 1-butanol. The reactions at 20 °C and 100 °C proceeded similarly.

For the purpose of isolating the complex formed by the reaction, the similar reaction as above was carried out in a larger scale. From the dark brown solution obtained as above from 0.630 g of **1** (0.547 mmol) and 69 mmol of Pr^nCHO, volatile matters were evaporated off *in vacuo* to leave brown solid which was washed with Et_2O and hexane to afford a brown powder. The powder was dissolved in 40 ml of toluene. The resulting brown solution was repeatedly filtered to remove traces of decomposed product such as ruthenium metal. On concentration of the filtrate *in vacuo*, a yellow precipitate came out which was filtered, washed with hexane and dried *in vacuo*. The yellow complex thus obtained was charaterized as the known $Ru(CO)_3(PPh_3)_2$ (0.217 g, yield 56%) on the basis of its IR spectrum (ν(CO) 1900 cm^{-1} vs; lit, 1900 cm^{-1} vs[58]).

b) Reactions of Butyraldehyde at −10—−20 °C: The reaction mixture prepared as *a*) from 0.173 g of $RuH_2(PPh_3)_4$ (0.150 mmol) and 61.1 mmol of Pr^nCHO, when kept at −20 °C, evolved heat in 10 min to give a dark grey, turbid solution. After stirring at −20 °C for 2 h, formation of 18.7 mmol of butyl butyrate was observed by GLC analysis together with a small amount of 1-butanol. On working up the system as *a*), about 50 mg of a white micro crystalline powder was obtained which was identified tentatively on the basis of IR spectrum as $RuH_2(CO)(PPh_3)_3$ (ν(Ru–H) 1960 sh, and ν(CO) 1935 cm^{-1} vs; lit, ν(Ru–H), 1960 m, 1898 m, and ν(CO), 1940 cm^{-1} vs[58]).

c) Reactions of Butyraldehyde at −30 °C: Stirring the yellow suspension of $RuH_2(PPh_3)_4$ (0.180 g, 0.156 mmol) in 63.9 mmol of Pr^nCHO prepared similarly to the method described in *a*) at −30 °C resulted in the color change of the system to a greenish yellow, heterogeneous mixture in 2 h without any heat evolution. No ester was detected in the system. Working up the system as *a*) yielded 0.12 g of a yellow microcrystalline powder which was identified as $RuH(OCOPr^n)(PPh_3)_2$ (yield 80%) on the basis of the comparison of the IR data with those reported for RuH-

(OCOR)$(PPh_3)_2$ where R=Me or Et[49] (ν(Ru–H) 1990 w and $\nu(CO_2)$ 1515 m and 1415 cm^{-1}).

*Preparation of Dibutyratodicarbonylbis(triphenylphosphine)ruthenium(II), $Ru(OCOPr^n)_2(CO)_2(PPh_3)_2$ **5b**.* Dihydrido-complex **1** $RuH_2(PPh_3)_4$ (0.96 g, 0.83 mmol) was put into a stainless steel autoclave flashed with nitrogen, then the autoclave was connected to a vacuum line and evacuated. Butyraldehyde (187 mmol) and 2.87 mmol of water were added successively *in vacuo* by means of a trap-to-trap method to the reaction vessel. The system was heated at 110 °C *in vacuo* by immersing the autoclave in an oil bath. After 2 h, the amounts of gases evolved by the reaction were measured and the resulting pale grey heterogeneous mixture was transferred to the Schlenk flask and worked up as already described. An off-white powder thus obtained was recrystallized from toluene to give pale yellow crystals of $Ru(OCOPr^n)_2(CO)_2(PPh_3)_2$ **5b** (0.22 g, yield 30%). IR and ^{1}H- and ^{31}P-NMR data are as listed in Table 5. Found: C, 63.9; H, 5.3%. Calcd for $C_{46}H_{44}O_6P_2Ru$: C, 64.6; H, 5.2%. The purified sample was still contaminated with a trace amount of $RuH_2(CO)(PPh_3)_2$ **2** as indicated by its IR spectrum.

Complex **5b** was also obtained by the similar reaction as above from $RuH(OCOPr^n)(PPh_3)_2$ **3b** and butyraldehyde in a stainless steel autoclave at 110 °C. The reaction was accompanied by the formation of a small amount of H_2, CO, Pr^nCOOBu^n, and Bu^nOH.

*Preparation of Dibutyratocarbonylbis(triphenylphosphine)ruthenium(II), $Ru(OCOPr^n)_2(CO)(PPh_3)_2$ **6b**.* The similar reaction as above between 2.95 g of $RuH_2(PPh_3)_4$ **1** (2.22 mmol) and 340 mmol of Pr^nCHO in the presence of 16.1 mmol of water in a glass autoclave yielded a clear, orange solution. On cooling the solution to room temperature, pale yellow crystals deposited, which were filtered, washed with diethyl ether and hexane and dried in vacuo and identified as $Ru(OCOPr^n)_2(CO)(PPh_3)_2$ **6b** (1.21 g, yield 55%) on the basis of IR and ^{1}H- and ^{31}P-NMR spectra (Table 5). Found: C, 64.4; H, 5.4%; Mw, 806. Calcd for $C_{45}H_{44}O_5P_2Ru$: C, 65.3; H, 5.3%; Mw, 828. The reaction accompanied the formation of the dicarbonyl complex **5b** which was sometimes difficult to remove.

Complex **6b** was also obtained by the reaction of hydridocarboxylato complex **3b** (1.84 g, 1.64 mmol) with butyraldehyde (222 mmol) in a Pyrex glass Schlenk flask heated under reflux under nitrogen for 2 h. On working up, 1.00 g of **6b** was obtained (yield 86%).

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