Application of the Water-gas Shift Reaction. I. Hydrogenation and Hydroformylation Reactions of Olefins with Carbon Monoxide and Water Catalyzed by Rhodium Phosphine Complexes

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The hydrogenation of methyl crotonate with CO and H_2O is efficiently catalyzed by $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ or $[RhCl(C_7H_8)]_2/P(i\text{-}Pr)_3/n\text{-}BuLi$ (C_7H_8=norbornadiene). Both catalyst precursors are shown to form the same active species; *trans*-$Rh(OH)(CO)[P(i\text{-}Pr)_3]_2$. The catalytic activity of the system ($[RhCl(C_7H_8)]_2$/phosphine/*n*-BuLi) increases with increase of the basicity of the phosphine ligands (phosphine=$P(i\text{-}Pr)_3>P(n\text{-}Bu)_3>PPh(i\text{-}Pr)_2>PPh_2(i\text{-}Pr)>PPh_3$). This reaction is also applicable to the hydrogenation of the C=C bond of electron-withdrawing olefins and the C=O bond of ketones and aldehydes. Interestingly, the catalysis for the C=C bond, to which less electron-withdrawing groups are attached, gives dominantly aldehydes due to hydroformylation. The mechanism is also discussed.

The water-gas shift reaction (Eq. 1) attracts our attention from a viewpoint of the use of coal as a hydrogen source. Recently, many studies have been reported on the shift reaction using homogeneous catalysts,[1-4] which are active even at such a low temperature as the boiling point of water. The catalysis generates such a reactive reducing species that hydrogenation[5] and hydroformylation[6,7] of olefins, reduction of nitrobenzenes,[8,9] and α-methylation of ketones[10] and *N*-methylation of amines[11] with formaldehyde have been carried out in homogeneous phase without using molecular hydrogen.

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (1)$$

To date, metal carbonyls combined with base[1,5,6,8-11] or acid[2] have habitually been used for the shift reaction as well as the organic reactions, while these catalyst systems are perturbed by side reactions such as aldol condensation, hydrolysis, isomerization of double bond, *etc.* One of our authors has reported that homogeneous rhodium phosphine complexes possess high catalytic activities for the shift reaction in an essentially neutral solution.[4] Though few reports have appeared on the catalysis of phosphine complexes for Eq. 1, phosphine complexes are, in general, more active than metal carbonyls in the homogeneous catalytic hydrogenations and hydroformylation reactions.

Aiming at application of the water-gas shift reaction to the organic reactions, we employed the homogeneous rhodium phosphine complexes as the catalyst. The present paper deals with the hydrogenation and the hydroformylation of olefins using carbon monoxide and water in place of molecular hydrogen.

Table 1. Hydrogenation of methylcrotonate with CO and H_2O catalyzed by triphenylphosphine complexes of group VIII[a]

Catalyst precursor	Yield/% of methyl butyrate[b]
$RhH(CO)(PPh_3)_3$	90
$RhCl(PPh_3)_3$	66
$RuH_2(PPh_3)_4$	53
$CoH(N_2)(PPh_3)_3$	28
$Pd(PPh_3)_4$	23

a) Conditions; catalyst precursor=0.2 mmol, methyl crotonate=20 mmol, H_2O=100 mmol, P_{CO}=50 atm, 150 °C, 20 h. b) Based on methyl crotonate added.

Results and Discussion

Catalytic Activity of Group VIII Metal Complexes. Because it is easily hydrogenated and hydroformylated, methyl crotonate was used as a typical substrate to survey the catalytic activities of different Group VIII metal complexes of triphenylphosphine. The results are shown in Table 1. The catalytic activity increased in the order; Rh>Ru>Co≫Pd. Among them the halide-free rhodium complex, $RhH(CO)(PPh_3)_3$ (**1**), was found to be most active. Methyl butyrate was

Table 2. Effect of phosphine ligands in the catalyst system of $[RhCl(C_7H_8)]_2$/Phosphine/*n*-BuLi[a]

Phosphine	$CH_3CH_2CH_2COOCH_3$[b] A	$CH_3CH(CHO)CH_2COOCH_3$[b] B	$CH_3CH_2CH(CHO)COOCH_3$[b] C	CO_2[b]	A/(A+B+C)	B/(B+C)
PPh_3	15	≈0	≈0	8	1	—
$PPh_2(i\text{-}Pr)$	46	0.9	0.1	47	0.98	0.9
$PPh(i\text{-}Pr)_2$	55	2.6	0.5	59	0.95	0.8
$P(n\text{-}Bu)_3$	60	0	≈0	63	1	—
$P(i\text{-}Pr)_3$	72	4.8	4.3	82	0.87	0.5

a) Conditions; catalyst ($[RhCl(C_7H_8)]_2$=0.05 mmol, phosphine=0.2 mmol, *n*-BuLi=0.25 mmol), methyl crotonate=20 mmol, H_2O=50 mmol, P_{CO}=15 atm, THF=6.5 ml, 115 °C, 20 h. b) The yields/% are based on methyl crotonate used.

Table 3. Activities of various catalyst precursors and effect of CO pressure in the hydrogenation of methyl crotonate with CO and H_2O[a)]

Catalyst precursor[b)]	CO (atm)[c)]	Products (%)[d)]				B/(A+B+C)	B/(B+C)
		CO_2	$CH_3CH_2CH_2$-$COOCH_3$ A	$CH_3CH(CHO)$-CH_2COOCH_3 B	CH_3CH_2CH-$(CHO)COOCH_3$ C		
$[RhCl(C_7H_8)]_2$/L/*n*-BuLi	15	82	72	4.8	4.3	0.88	0.53
$RhH_2(O_2COH)L_2$	15	102	91	4.2	3.9	0.91	0.52
$[Rh(CO)L_2]_2(CO_3)$[e)]	15		86	7.3	6.6	0.86	0.53
$RhH_2(O_2COH)L_2$[f)]	7.5	40	49	4.5	3.0	0.87	0.40
$RhH_2(O_2COH)L_2$[f)]	15	65	58	8.5	3.0	0.83	0.74
$RhH_2(O_2COH)L_2$[f)]	30	83	53	29	1.5	0.63	0.95
$RhH_2(O_2COH)L_2$[f)]	60	30	25	14	0.5	0.63	0.97

a) Conditions; catalyst precursor=0.1 mmol, methyl crotonate=20 mmol, H_2O=50 mmol, THF=6.5 ml, 115 °C, 20 h. b) L=P(*i*-Pr)$_3$. c) Initial pressure. d) Based on methyl crotonate used. e) Catalyst precursor=0.05 mmol. f) At 95 °C.

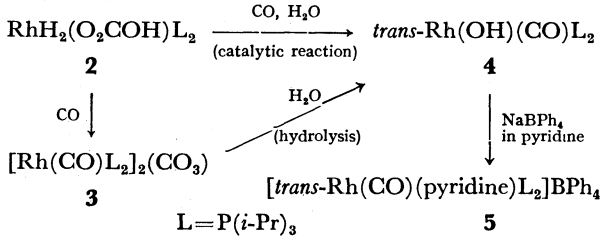
formed in a 90% yield. Thus, the halide-free rhodium complexes were used hereafter in the present study to widen the scope of the application of the water-gas shift reaction to the organic reactions.

Little is known about the synthetic method for the hydrido rhodium(I) complexes of various phosphines, which are expected as the effective catalyst precursor. Therefore, the effects of the phosphine ligands were examined using a catalyst precursor prepared *in situ* by the reaction of $[RhCl(C_7H_8)]_2$ with *n*-BuLi in the presence of phosphine, which affords the hydrido complex (*vide infra*). The results are summarized in Table 2. By successive replacement of the phenyl groups on the phosphorus of triphenylphosphine by alkyl groups, the catalytic activity for the hydrogenation increased in the order; P(*i*-Pr)$_3$>PPh(*i*-Pr)$_2$>PPh$_2$(*i*-Pr)>PPh$_3$. The replacement by the isopropyl group makes the phosphine more electron-donating and bulky.[12)] The activity of the system using P(*n*-Bu)$_3$, which is less bulky than any other ligands examined, was close to that using PPh(*i*-Pr)$_2$. In general, ligand effects may be separated into electronic and steric factors. According to Tolman,[13)] the infrared CO stretching frequencies of Ni(CO)$_3$L (L=P(*n*-Bu)$_3$ and PPh(*i*-Pr)$_2$), which reflect the electronic donor-acceptor property of L, are 2060.3 and 2062.4 cm^{-1}, respectively. Both are estimated to be similar in electronic nature. Consequently, the above results suggest that the electronic factor of the auxiliary ligand is more dominant than the steric factor over the greater part of the catalytic activity for the hydrogenation.

In some cases, small amounts of aldehydes were formed by hydroformylation. Their yields increased in the order similar to that of the hydrogenation product, but no appreciable amounts of aldehydes were formed in the case of P(*n*-Bu)$_3$. A plausible interpretation of the fact is described later. From these results, P(*i*-Pr)$_3$ was one of the most effective auxiliary ligands.

Catalyst Precursor. When a THF solution containing $[RhCl(C_7H_8)]_2$, P(*i*-Pr)$_3$, and *n*-BuLi was treated with H_2O and CO_2 (1 atm), a dihydrido hydrogencarbonato complex, $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (**2**), was obtained. This complex is known to be formed also *via* the oxidative addition of H_2O and CO_2 to $RhH[P(i\text{-}Pr)_3]_3$ or *trans*-$RhH(N_2)[P(i\text{-}Pr)_3]_2$.[14)] It has also been reported that *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ is isolated from the reaction mixture of $[RhCl(CH_2{=}CH_2)_2]_2$ with *n*-BuLi in the presence of the phosphine under an atmosphere of nitrogen.[15)] These facts indicate that the reaction of $[RhCl(C_7H_8)]_2$ with *n*-BuLi in the presence of phosphine presents a general method to provide the halide-free hydrido phosphine complexes. The dihydrido hydrogencarbonato complex (**2**) is known to react readily with CO to give a carbonyl carbonato complex, $\{Rh(CO)[P(i\text{-}Pr)_3]_2\}_2(CO_3)$ (**3**).[14)] Since large amounts of CO, H_2O, and CO_2 are present in the catalytic system, the three catalyst precursors, $[RhCl(C_7H_8)]_2$/P(*i*-Pr)$_3$/*n*-BuLi, **2**, and **3**, shown in Table 3 must form the same active species. The reaction mixture catalyzed by **2** was treated with $NaBPh_4$ in the presence of pyridine to give a cationic complex, {*trans*-Rh(CO)(pyridine)$[P(i\text{-}Pr)_3]_2$}BPh_4 (**5**), which is known to be formed by a similar treatment of **3**.[4)] This fact suggests that the hydroxo complex, *trans*-Rh(OH)(CO)-$[P(i\text{-}Pr)_3]_2$ (**4**), plays an important role in the catalysis, because **4** in pyridine is known to be in equilibrium with a solvated ion pair complex which produces **5** by an anion exchange with BPh_4^-.[4)]

$$[RhCl(C_7H_8)]_2 + P(i\text{-}Pr)_3 + n\text{-BuLi} \longrightarrow [\text{rhodium(I) hydride}] \xrightarrow{H_2O,\ CO_2} RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2 \quad \mathbf{2}$$



Scheme 1.

Hydrogenation and Hydroformylation of Various Olefins. The reactions of electron-withdrawing and -donating olefins are summarized in Table 4. The hydrogenation of the electron-withdrawing olefins occurred exclusively, except for methyl crotonate. On the contrary, the hydroformylation of styrene occurred in preference to

Table 4. Hydrogenation and hydroformylation with CO and H_2O catalyzed by $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$[a)]

Substrate	Product	Yield/%[b)]
CH_2=CHCN	CH_3CH_2CN	≈100
CH_2=$CHCONH_2$	$CH_3CH_2CONH_2$	86
CH_3CH=$CHCOOCH_3$	$CH_3CH_2CH_2COOCH_3$	91
	$CH_3CH(CHO)CH_2COOCH_3$	4
	$CH_3CH_2CH(CHO)COOCH_3$	4
PhCH=$CHCOOCH_3$	$PhCH_2CH_2COOCH_3$	93
$(CH_3)_2C$=$CHCOCH_3$	$(CH_3)_2CHCH_2COCH_3$	92
	$(CH_3)_2CHCH_2CH(OH)CH_3$	2
PhCH=CHCHO	$PhCH_2CH_2CHO$	99
Cyclohexanone[c)]	Cyclohexanol	95
$PhCOCH_3$[c)]	$PhCH(OH)CH_3$	68
PhCHO[c)]	$PhCH_2OH$	92
$PhNO_2$[d)]	$PhNH_2$	95
PhCN[d)]	$PhCH_2NH_2$	2
PhCH=CH_2	$PhCH_2CH_2CHO$	57
	$PhCH(CHO)CH_3$	23
	$PhCH_2CH_3$	16
p-$CH_3OC_6H_4CH$=CH_2	*p*-$CH_3OC_6H_4CH_2CH_2CHO$	44
	p-$CH_3OC_6H_4CH(CHO)CH_3$	30
	p-$CH_3OC_6H_4CH_2CH_3$	18
$Ph(CH_3)C$=CH_2	$PhCH(CH_3)CH_2CHO$	80
	$PhC(CH_3)_2CHO$	5
$CH_3(CH_2)_3CH$=CH_2	$CH_3(CH_2)_3CH_2CH_2CHO$	42
	$CH_3(CH_2)_3CH(CHO)CH_3$	35
cyclo-C_8H_{14}	*cyclo*-$C_8H_{15}CHO$	54

a) Conditions; $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$=0.1 mmol, substrate=20 mmol, H_2O=50 mmol, P_{CO}=15 atm, THF=6.5 ml, 115 °C, 20 h. b) Based on the substrate used. c) At 150 °C. d) At 165 °C.

hydrogenation. α-Methylstyrene and alkenes gave only the corresponding aldehydes. It is well known that hydrogenation incidental to the hydroformylation with CO and H_2 becomes dominant in the reaction of electron-withdrawing olefins such as α,β-unsaturated aldehydes and ketones,[16] or under conditions of higher H_2/CO ratio.[17] The hydrogen pressure during the reaction of electron-withdrawing olefins is, however, estimated to be very low, because the amount of molecular hydrogen is, at the highest, equal to that of CO_2 produced by the water-gas shift reaction. For example, the yield of CO_2 shown in Table 3 is almost equal to the total yield of organic products. Actually, in the course of the reaction of methyl crotonate (at a 71% conversion), the partial pressure of hydrogen observed was *ca.* 0.09 atm, meaning the H_2/CO ratio to be 0.01. These facts suggest that the hydrogenation of electron-withdrawing olefins occurred at least to a great extent with CO and H_2O as the reducing agent, without intermediate generation of molecular hydrogen. The fitting mechanism is discussed below.

Hydrogenation of carbonyl groups was somewhat difficult. Ketones and aldehydes were reduced only above 150 °C. Namely, α,β-unsaturated carbonyl compounds afforded selectively the corresponding saturated ketones and aldehydes at 115 °C, and at 150 °C the corresponding alcohols were obtained. Nitrobenzene could also be reduced to aniline quantitatively at 165 °C, but the phenyl ring remained unchanged.

Effects of CO and H_2 Pressure. The rate and the product distribution of this reaction strongly depended upon the pressure of CO (Table 3). The maximum conversion of methyl crotonate was attained at 30 atm of the initial CO pressure, and the selectivity to the hydrogenation was decreased with increasing the CO pressure up to 30 atm because of the enhanced rate of the hydroformylation. The insertion of CO into the alkyl-rhodium bond, which is involved in an intermediate, seems to be favored at a moderate pressure. Under higher pressure of CO, however, both the hydrogenation and the hydroformylation were inhibited. The reduced activities are probably ascribed to the decrease in coordinative unsaturated species by the coordination of CO.[18]

To inquire how the addition of molecular hydrogen exerts action on this hydrogenation, methyl crotonate (40 mmol) was reduced in a THF solution containing D_2O (100 mmol) under H_2 (40.6 mmol) and CO (40.6 mmol). After the reaction, the gas phase in the autoclave was a mixture of CO_2 (8.5 mmol), H_2, HD, and D_2 (total 9.3 mmol), and CO (30.2 mmol). Methyl butyrate (38 mmol) was formed. The sum of the amounts of CO_2 formed and H_2 consumed is in good agreement with the yield of methyl butyrate. The result is a consequence of the fact that side reactions are negligible. Therefore, at the highest 21% (CO_2 formed (8.5 mmol)/[H_2 consumed (31.3 mmol)+CO_2 formed]) of the hydrogenation would occur with CO and D_2O rather than H_2 as the reducing agent. However, the

Table 5. Deuterium content of the products of the hydrogenation and the hydroformylation with CO, D_2O, and H_2[a]

Source of methyl butyrate[c]	Deuterium content (atm-%)[b]	
	α-CH	β-CH
Methyl crotonate CO (15 atm)/D_2O/H_2 (15 atm)	78	41
Methyl crotonate CO(1 atm)/D_2O/H_2 (15 atm)	70	15
Methyl butyrate CO(15 atm)/D_2O/H_2 (15 atm)	<5	<5
Source of β-phenylpropanal[d]	-CHO α-CH	β-CH
α-Methylstyrene CO(15 atm)/D_2O/H_2 (15 atm)	22 6	19

a) Conditions ; $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ = 0.2 mmol, D_2O=100 mmol, THF=6.5 ml, 115 °C. b) The values show deuterium contents out of the hydrogen and deuterium incorporated. c) For 7.5 h. d) For 1 h.

^{1}H-NMR analysis of the formed methyl butyrate showed 59% incorporation of deuterium. Its contents at the 2- and 3-positions were 78 and 41 atom-%,

$$CH_3CH{=}CHCOOCH_3 \xrightarrow{CO,\ D_2O,\ H_2} CH_3{-}CH_{1.59}D_{0.41}{-}CH_{1.22}D_{0.78}{-}COOCH_3$$

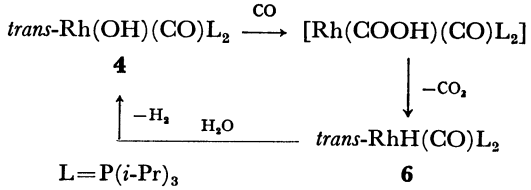
respectively. In a separated experiment, it was confirmed that theH-D exchange reaction of methyl butyrate with D_2O does not occur under these conditions. Another possibility of H-D exchange proceeding through alkylrhodium intermediates (**8a** and **8b**), *i.e.*, a half hydrogenated state, *via* metal hydride addition and elimination[19] (see Scheme 3, **4**⇌**6**⇌**7**⇌**8**) is excluded for the following reason. If this exchange were sufficiently fast, the deuterium contents at the 2- and 3-positions would be closely similar, and would not be effected by the amount of CO (*vide infra*). Therefore, the facts that the amount of deuterium incorporated into methyl butyrate is larger than that of CO_2 formed and that the deuterium content at the 2-position is higher than that at the 3-position rationalize the following assumption; D_2O itself participates in the hydrogenation to a considerable extent without generating D_2 and CO_2, and the hydrogen (deuterium) added to the 2-carbon atom comes dominantly from the water even under a pressure of H_2 (see Cycle B in Scheme 3). The nature of this hydrogenation process is discussed below in more detail.

A similar reaction of methyl crotonate with D_2O and H_2 under a low pressure of CO (1 atm, 2.7 mmol) also gave deuterated methyl butyrate (80% yield), of which deuterium content at the 2- and 3-positions was 70 and 15 atom-%, respectively. Interestingly, lowering CO pressure decreased the deuterium content at the 3-position more markedly than that at the 2-position. The result indicates that the reaction of methyl crotonate with CO–D_2O–H_2 includes the hydrogenations with CO–D_2O (Cycle A) and with D_2O–H_2 (Cycle B), which give methyl butyrate-2,3-d_2 and -2-d, respectively.

The addition of molecular hydrogen extremely accelerated the hydroformylation of α-methylstyrene with CO and D_2O, and a conversion of 68% was reached within 1 h at 115 °C. At the time, the yield of CO_2 was 4.5% based on α-methylstyrene converted. 3-Phenylbutanol, which was formed in a 67% yield, contained 22, 6, and 19 atom-% of deuterium at the 1, 2, and 3-positions, respectively. From the fact that the deuterium contents at the 1- and 3-positions are equal within experimental errors, the incorporated deuterium seems to come from D_2 and HD generated by H-D exchange reactions.[20]

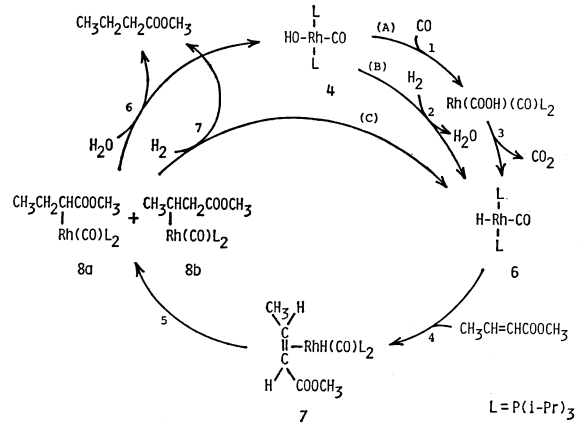
Reaction Mechanism. The hydrogenation with CO and H_2O occurs in two stages; (*i*) formation of a reducing species by a reaction of the catalyst with CO and H_2O, and (*ii*) hydrogenation of olefin with the reducing species. The catalysis in the former stage (*i*) is explained by the same mechanism as the water-gas shift reaction catalyzed by **2**,[4] because both the hydrogenation and the shift reaction were ascertained to contain the hydroxo complex (**4**) as one of the active key intermediates. The precise reaction pathway for the formation of a hydrido complex, *trans*-$RhH(CO)[P(i\text{-}Pr)_3]_2$ (**6**), and molecular hydrogen, in which **4** plays an important role, has been reported elsewhere.[4]

The hydrido complex (**6**) thus formed is a homologue of the active species of $RhH(CO)(PPh_3)_3$ (**1**) which is widely used as catalyst, not only for hydrogenation but also for hydroformylation. Therefore, complex **6** is most



Scheme 2.

suitable for the key intermediate in the latter stage (*ii*). The possible routes for the hydrogenation of methyl crotonate are shown in Scheme 3. In the hydrogenation and the hydroformylation using CO and H_2O, an σ-alkylrhodium intermediate formed by the insertion of olefin into the rhodium hydrido bond of the 16 valence-electron complex (**6**) is most probable. The hydrogenation following Cycles A and B involves the oxidative addition of H_2O followed by the reductive elimination of methyl butyrate to give **4**. The resultant complex is converted into **6** with CO in a similar manner to the water-gas shift reaction (Cycle A, Steps 1 and 3). Cycle C represents the same mechanism as the usual hydrogenation with molecular hydrogen. The mechanism for this hydrogenation with CO and H_2O is well represented by Cycle A from the following reasons. Methyl butyrate and CO_2 are formed in similar yields in the hydrogenation of methyl crotonate (see Table 3); the partial pressure of H_2 is very low during this reaction, therefore there is no appreciable amount of H_2 involved in Steps 2 and 7. Cycle B is not important unless a large amount of H_2 is present, but it is appropriate to illustrate the fact that the amount of deuterium in methyl butyrate formed by the hydrogenation with CO, D_2O, and H_2 is larger than that of CO_2 formed. Undoutedly, all the results indicate that Cycle C is not important.



Scheme 3. Possible mechanisms for the hydrogenation of methyl crotonate with CO and H_2O.

Between the two possible types of σ-alkylrhodium intermediate, the 2-metalated one is predominant in the reaction of electron-withdrawing olefins. This conclusion is based on the following evidence; (*i*) the reaction of methyl crotonate with CO, D_2O, and H_2 gives mainly methyl butyrate-2-*d*, and (*ii*) electron-withdrawing olefins are hydrogenated, whereas electron-donating olefins are hydroformylated. The above view is in accord with the previous reports based on the isomer distribution of the conventional hydroformylation products catalyzed by **1**.[21] The stability of the 2-metalated species is ascribed to the electronic effect of the substituent on the rhodium-bearing carbon atom, because the substituent is able to accept the excess charge on the rhodium induced by the electron-donating trialkylphosphine ligands. Consequently, using more electron-donating phosphines as the ligand, the 2-metalated species is expected to be more dominant. In fact, this expectation is consistent with the observation that the formylation at the 2-position prevails in the reaction of methyl crotonate, using $P(i\text{-}Pr)_3$ as the auxiliary ligand (Table 2).

The more strongly the phosphine is electron-donating, the more the catalytic activities are increased for hydrogenation as well as hydroformylation (Table 2). The enhancement of both rates is explicable in terms of the facilitated oxidative addition reactions of H_2O and H_2 toward the σ-alkyl and acyl intermediates, respectively. Similar ligand effects have been known in various oxidative addition reactions, and are ascribed to the elevated electron density on the metal caused by the donating ligands. For example, the oxidative additions of H_2[22] and H_2O[23] toward rhodium(I) and platinum(0) complexes are accelerated by the coordination of donating phosphines.

It is not clear why the electron-donating and -withdrawing olefins give the respective products selectively, because a number of factors are involved. One plausible explanation is as follows. The modification of the catalyst with donating phosphines causes the activity for the hydroformylation to increase more markedly than that for the hydrogenation (Table 2). The coordination of the donating phosphines increases the electronic density on the rhodium. The equilibrium between alkyl and acyl complexes under the pressure of CO, which has well been established,[18] is displaced to the acyl species by the coordination, because the acyl ligand is capable of accepting the excess charge from the rhodium. This displacement tends to facilitate the hydroformylation. This explanation is supported by the facts that an acyl complex from oxidative addition to $RhCl(CO)(PPh_3)_2$ have not yet been successful and that the addition of acyl bromide to more nucleophilic $RhBr(CO)(PPhEt_2)_2$ was reported to give stable $RhBr_2(CH_3CO)(CO)(PPhEt_2)_2$.[24] Similarly, it is explainable that the electronic property of the substituent of olefins has a large effect on the selectivity. When the substituent is electron-donating, the equilibrium is displaced more markedly to the acyl species than in the case of electron-withdrawing olefins. The α-metalated alkyl complexes formed from electron-withdrawing olefins are considered to be stabilized by its electron-withdrawing group at the α-position, but those from electron-donating olefins are never. This view is also consistent with the observations that the reaction of **1** with $CF_2=CF_2$ gives a stable insertion product, $CHF_2CF_2Rh(CO)(PPh_3)_2$, in which the insertion of CO no longer takes place, and that $CH_2=CH_2$ does not give the corresponding stable alkyl complex but the acyl one.[25]

Exceptional is the function of $P(n\text{-}Bu)_3$, which is strongly electron-donating but less bulky than $P(i\text{-}Pr)_3$. The alkyl ligand of the key intermediate has a larger cone angle than the corresponding acyl ligand.[12] Therefore, the steric repulsion between the alkyl moiety and the bulky triisopropylphosphine, which has displaces the equilibrium, is more evident. When using less bulky $P(n\text{-}Bu)_3$ as the ligand, however, the steric repulsion appears not to be important. Thus, the alkyl intermediate is relatively stable and subjected to hydrolysis to give the hydrogenation product.

Experimental

All reactions and manipulations were carried out under a nitrogen atmosphere. All organic compounds were purified by distillation or recrystallization under a nitrogen atmosphere before use. Literature methods were employed for preparations of $RhH(CO)(PPh_3)_3$,[26] $RhCl(PPh_3)_3$,[27] $RuH_2(PPh_3)_4$,[28] $CoH(N_2)(PPh_3)_3$,[29] $Pd(PPh_3)_4$,[30] $PPh_2(i\text{-}Pr)$,[31] $PPh(i\text{-}Pr)_2$,[32] $P(i\text{-}Pr)_3$,[33] $[RhCl(C_7H_8)]_2$,[34] $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$,[14] and $\{Rh(CO)[P(i\text{-}Pr)_3]_2\}_2(CO_3)$.[14] The ^{1}H-NMR and IR spectra were recorded on a Varian T-60-A spectrometer and a JASCO IRA-1 spectrometer, respectively.

Catalytic Hydrogenation and Hydroformylation. The following procedure is illustrative. To a 65 ml stainless steel autoclave containing a THF solution (6.5 ml) of $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (**2**) (48.7 mg, 0.1 mmol) were added H_2O (0.9 g, 50 mmol), methyl crotonate (2.0 g, 20 mmol), and CO (15 atm, 40.6 mmol) in that order. After heating at 115 °C for 20 h, the autoclave was cooled to room temperature. The GLC analysis of the gaseous products (on a column, active carbon, 3 m; at 50 °C; carrier gas, H_2) using nitrogen as an internal calibrant showed the presence of CO_2 (19.5 mmol, 98% based on methyl crotonate) and CO (19 mmol). The GLC analysis of the solution (on a column, PEG 20M, 2 m; at 110 °C; carrier gas, H_2) employing naphthalene as an internal standard showed the formation of $CH_3CH_2CH_2COOCH_3$ (1.87 g, 91%), $CH_3CH(CHO)CH_2COOCH_3$ (0.11

g, 4.2%), and $CH_3CH_2CH(CHO)COOCH_3$ (0.1 g, 3.9%).

The other catalytic reaction experiments were carried out according to similar procedures. The amount of H_2 formed was determined by GLC (on a column, molecular sieve 5A, 3 m; at 80 °C; carrier gas, Ar). The catalyst solution from $[RhCl(C_7H_8)]_2$ was prepared in the following manner. A hexane solution of *n*-BuLi (0.15 ml, 0.25 mmol) was slowly added to a mixture of $[RhCl(C_7H_8)]_2$ (23.1 mg, 0.05 mmol) and phosphine (0.2 mmol) in THF (6.5 ml), and the stirring was continued for 30 min. This freshly prepared pale brown solution was used immediately.

Preparation of $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (2). To a catalyst solution, which was prepared from a mixture of $[RhCl(C_7H_8)]_2$ (46.1 mg, 0.1 mmol), $P(i\text{-}Pr)_3$ (96 mg, 0.6 mmol), and *n*-BuLi (0.6 mmol in 0.36 ml of hexane) in THF (2 ml) with stirring at room temperature for 30 min, was added H_2O (0.25 g, 14 mmol). The resultant brown mixture was stirred under an atmosphere of CO_2 at room temperature for 1 h. The IR spectrum of the concentrated residue showed the formation of a mixture of **2** (ν_{Rh-H} 2140, 2120; $\nu_{C=O}$ 1590 cm^{-1}) and $\{Rh(CO)[P(i\text{-}Pr)_3]_2\}_2(CO_3)$ (**3**) ($\nu_{C\equiv O}$ 1930; $\nu_{C=O}$ 1530 cm^{-1}). The residue was recrystallized from toluene to give colorless crystals of **2** (20 mg, 21%)

Isolation of $\{trans\text{-}Rh(CO)(pyridine)[P(i\text{-}Pr)_3]_2\}BPh_4$ (5) from the Reaction Mixture. A solution from the hydrogenation reaction of methyl crotonate catalyzed by **2** (48.7 mg, 0.1 mmol) was concentrated under reduced pressure, and the oily residue was redissolved in pyridine (5 ml). After addition of $NaBPh_4$ (34.7 mg, 0.1 mmol), the brown solution was stirred at room temperature for 10 min. The mixture was concentrated to dryness, and the solid residue was recrystallized from THF–toluene to give $\{trans\text{-}Rh(CO)(pyridine)[P(i\text{-}Pr)_3]_2\}BPh_4 \cdot 2toluene$ as pale yellow crystals (45 mg, 45%), mp 150 °C dec, $\nu_{C\equiv O}$ 1985 cm^{-1}.

Hydrogenation of Methyl Crotonate with CO, D_2O, and H_2. To a 65 ml autoclave containing a mixture of **2** (97.3 mg, 0.2 mmol, methyl crotonate (4.0 g, 40 mmol), and D_2O (2.0 g,100 mmol) in THF (6.5 ml) were charged CO (15 atm, 40.6 mmol) and H_2 (15 atm, 40.6 mmol), successively. After heating at 115 °C for 7.5 h, the autoclave was cooled to room temperature. The pressure inside the autoclave was 18 atm. The GLC analysis of the gas phase showed the presence of CO_2 (8.5 mmol, 3.1 atm), H_2, HD, and D_2 (total 9.3 mmol, 3.5 atm) and CO (30.1 mmol ,11.3 atm). The GLC analysis of the solution showed the formation of methyl butyrate 3.88 g, 95%). The methyl butyrate was collected into a cold trap under reduced pressure, and purified by distillation. The ^1H-NMR showed the 2-CH_2 (δ 2.2, m), 3-CH_2 (δ 1.62, m), CH_3C (δ 0.95, t), and CH_3O proton signals (δ 3.63, s) in a corrected relative intensity of 1.22 : 1.59 : 3 : 3. The incorporated deuterium contents calculated from these values were 78 and 41% at 2- and 3-positions, respectively.

Hydroformylation of α-Methylstyrene with CO, D_2O, and H_2. In a 65 ml autoclave pressured with CO (15 atm, 40.6 mmol) and H_2 (15 atm, 40.6 mmol), a mixture of **2** (97.3 mg, 0.2 mmol), α-methylstyrene (4.72 g, 40 mmol), and D_2O (2.0 g, 100 mmol) in THF (6.5 ml) was heated at 115 °C for 1 h. The gas phase (2.5 atm) was analyzed by GLC, and shown to contain CO_2 (1.4 mmol, 0.5 atm), H_2, HD, and D_2 (total 0.5 mmol, 0.2 atm), and CO (4.9 mmol, 1.8 atm). The ^1H-NMR spectrum of 3-phenylbutanal purified by preparative GLC showed to contain 22, 6, and 19% of deuterium at the 1-, 2-, and 3-positions, respectively.

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References

1) A. D. King, Jr., R. B. King, and D. B. Yang, *J. Am. Chem. Soc.*, **102**, 1028 (1980); A. D. King, R. B. King, and D. B. Yang, *J. Chem. Soc., Chem. Commun.*, **1980**, 529; C. Ungermann, V. Landis, S. A. Moya, H. Cohen, H. Walker, R. G. Peason, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **101**, 5922, (1979); R. B. King, C. C. Frazier, R. M. Hanes, and A. D. King, Jr., *ibid.*, **100**, 2925 (1978); R. M. Raine, R. G. Rinker, and P. C. Ford, *ibid.*, **99**, 252 (1977).

2) E. C. Baker, D. E. Hendriksen, and R. Eisenberg, *J. Am. Chem. Soc.*, **102**, 1020 (1980); P. C. Ford, R. G. Rinker, C. Ungermann, R. M. Laine, V. Landis, and S. A. Moya, *ibid.*, **100**, 4595 (1978); C.-H. Cheng and R. Eisenberg, *ibid.*, **100**, 5968 (1978); C.-H. Cheng, D. E. Hendriksen, and R. Eisenberg, *ibid.*, **99**, 2791 (1977).

3) T. Yoshida, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, **100**, 4941 (1978).

4) T. Yoshida, T. Okano, and S. Otsuka, *J. Am. Chem. Soc.*, **102**, 5966 (1980); T. Yoshida, T. Okano, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, **103**, 3411 (1981).

5) T. Kitamura, T. Joh, and N. Hagihara, *Chem. Lett.*, **1975**, 203; T. Kitamura, N. Sakamoto, and T. Joh, *ibid.*, **1973**, 379.

6) R. M. Laine, *J. Am. Chem. Soc.*, **100**, 6451 (1978); H. Kang, C. Mauldin, T. Cole, W. Slegeir, K. Cann, and R. Pettit, *ibid.*, **99**, 8323 (1977).

7) K. Murata, A. Matsuda, K. Bando, and Y. Sugi, *J. Chem. Soc., Chem. Commun.*, **1979**, 785.

8) R. C. Ryan, G. M. Wilemon, M. P. Dalsanto, and C. U. Pittman, Jr., *J. Mol. Cat.*, **5**, 319 (1979); K. Cann, T. Cole, W. Slegeir, and R. Pettit, *J. Am. Chem. Soc.*, **100**, 3969 (1978); A. F. M. Iqbal, *Tetrahedron Lett.*, **1971**. 3385.

9) Y. Watanabe, N. Suzuki, S. C. Shim, M. Yamamoto, T. Mitsuda, and Y. Takegami, *Chem. Lett.*, **1980**, 429.

10) Y. Watanabe, K. Takatsuki, and Y. Takegami, *Tetrahedron Lett.*, **1978**, 3369; Y. Watanabe, Y. Shimizu, K. Takatsuki, and Y. Takegami, *Chem. Lett.*, **1978**, 215.

11) Y. Sugi, A. Matsuda, K. Bando, and Murata, *Chem. Lett.*, **1979**, 363; Y. Watanabe, M. Yamamoto, T. Mitsudo, and Y. Takegami, *Tetrahedron Lett.*, **1978**, 1289.

12) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977); C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).

13) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).

14) T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers, and S. Otsuka, *J. Am. Chem. Soc.*, **101**, 4212 (1979).

15) T. Yoshida, T. Okano, D. L. Thorn, T. H. Tulip, S. Otsuka, and J. A. Ibers, *J. Organomet. Chem.*, **181**, 183 (1979).

16) For example, see B. Heil and L. Markó, *Magy. Kem. Lapja*, **23**, 669 (1968); *Chem. Abstr.*, **70**, 56861 (1968); B. Fell and W. Rupilius, *Tetrahedron Lett.*, **1969**, 2721; J. Falbe and N. Huppes, *Brennstoff-Chem.*, **48**, 248 (1971).

17) C. K. Brown and G. Wilkinson, *J. Chem. Soc., A*, **1970**, 2753.

18) P. Pino, F. Piacenti, and M. Bianchi, "Reactions of Carbon Monoxide and Hydrogen with Olefinic Substrates," in "Organic Syntheses *via* Metal Carbonyls," ed by I. Wender and P. Pino, J. Wiley and Sons, New York, N. Y. (1977).

19) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **88**, 3491 (1966).

20) A similar H-D exchange reaction catalyzed by rhodium

complexes is known. See T. Yoshida, T. Okano, K. Saito, and S. Otsuka, *Inorg. Chim. Acta*, **44**, L135 (1980).
21) C. U. Pittman, Jr., W. D. Honnick, and J.J. Yang, *J. Org. Chem.*, **45**, 684 (1980), and references therein.
22) J. Chatt and S. A. Butter, *J. Chem. Soc., Chem. Commun.*, **1967**, 501; C, A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974); T. Yohisda and S. Otsuka, *ibid.*, **99**, 2134 (1977).
23) T. Yoshida, T. Matsuda, T. Okano, T. Kitani, and S. Otsuka, *J. Am. Chem. Soc.*, **101**, 2027 (1979); T. Yoshida, T. Okano, K. Saito, and S. Otsuka, *Inorg. Chim. Acta*, **44**, L135 (1980).
24) J. Chatt and B. L. Shaw, *J. Chem. Soc., A*, **1966**, 1437.
25) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc., A*, **1970**, 1392.
26) D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc., A*, **1968**, 2660.
27) J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, **10**, 67 (1967).
28) R. O. Harris, N. K. Hota, L. Sandavoy, and J. M. C. Yuen, *J. Organomet. Chem.*, **54**, 259 (1973).
29) A. Sacco and M. Rossi, *Inorg. Synth.*, **12**, 18 (1970).
30) D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).
31) W. Kuchen and H. Buchwald, *Chem. Ber.*, **92**, 227 (1959).
32) E. Fluck and J. Lorenz, *Z. Naturforsch., Teil B*, **22**, 1095 (1967).
33) A. H. Cowly and M. W. Taylor, *J. Am. Chem. Soc.*, **91**, 2915 (1969).
34) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, **1959**, 3178.