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Homogeneous Hydroformylation of Methyl Acrylate Catalyzed by $Co_2(CO)_8$–Di(tertiary phosphine) Complexes

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Some complexes prepared *in situ* from $Co_2(CO)_8$ and various di(tertiary phosphine)s as ligands have been found to be more active than $Co_2(CO)_8$ for the hydroformylation of methyl acrylate. The activity decreased in the order; $Ph_2P(CH_2)_2PPh_2 > Ph_2PC{\equiv}CPPh_2 >$ *cis*-$Ph_2PCH{=}CHPPh_2 > Ph_2P(CH_2)_3PPh_2 >$ none $> Ph_2PCH_2PPh_2 > Ph_2P(CH_2)_4PPh$. The most active catalyst (I) was obtained when a molar ratio of $Ph_2P(CH_2)_2PPh_2$ to $Co_2(CO)_8$ was *ca.* 0.5. The catalyst (I) is also active even at low pressure, where the decomposition of $Co_2(CO)_8$ occurs.

Many efforts have been made to enhance the catalytic activity in the hydroformylation of olefin using $Co_2(CO)_8$ catalyst.[1] It is well known that the presence of small amounts of organic amines such as pyridine increases the rate of cobalt-catalyzed hydroformylation. From the reaction of cyclohexene in methylcyclohexane as solvent, for example, Wender *et al.* found a small rate increase for pyridine/$Co_2(CO)_8$ ratios between 0.15 and 1.2, the maximum being around 0.15.[2] For the hydroformylation of methyl acrylate in benzene, Iwanaga reported that the relative rate increased up to 3.14 times at 100 °C using pyridine/Co ratios of 10.[3]

On the other hand, recently, it has been reported by Sanger that the rate of hydroformylation of 1-hexene with $RhH(CO)(PPh_3)_3$ was enhanced by the addition of a small amount of a di- or tri(tertiary phosphine) to this system.[4] In the case of cobalt catalyst, however, the presence of phosphines such as PPh_3, PBu_3, $Ph_2P(CH_2)_nPPh_2$ (n=2,4,5) drastically decreased the rate, although a slight increase in product linearity was observed.[5]

We have found for the first time that complexes prepared *in situ* from $Co_2(CO)_8$ and some di(tertiary phosphine)s are more active catalysts for the homogeneous hydroformylation of methyl acrylate than $Co_2(CO)_8$. Now we would like to report on some of the interesting findings that have been obtained.

Experimental

Materials. Methyl acrylate, phosphines and toluene were obtained commercially and used with no further purifications. Cobalt carbonyl cluster ($CH_3CCo_3(CO)_9$) was prepared from $Co_2(CO)_8$, according to a procedure based on that given by Pályi.[6]

Reaction Procedure. The hydroformylation reactions were carried out in the 100 ml stainless-steel autoclave, in which methyl acrylate, $Co_2(CO)_8$, toluene, and phosphine were placed. After the vessel was sealed, a mixture of hydrogen and carbon monoxide (*ca.* 1/1 ratio) was introduced. The system was then brought to the desired reaction temperature and pressure by the additional charging of the same gas under heating. Stirring was begun and the reaction took place. The total pressure was kept constant during the reaction by supplying the gas from a 100 ml pressure storage vessel through a pressure regulator, and the reaction temperature was controlled within a range of ±1 °C. The amount of syn-gas supplied at constant pressure during the reaction was calculated from pressure drop in the storage.

Analysis of the Products. Liquid products were analyzed by gas chromatography. A gas chromatograph, equipped with a 6 m column of squalane was used at 100 °C. The IR spectra of catalyst solutions were recorded on a Hitachi-215 type spectrometer.

Determination of Molar Ratios of CO to Co, CO/Co, in Complexes Formed in the Catalytic System. Aliquat samples of catalyst solutions were withdrawn at definite times through a stainless-steel tube into a glass reciever in ice. After nitrogen of a high purity had been bubbled through these samples to purge the dissolved CO, the sample was heated with 3.6 M-H_2SO_4. The gas thus liberated was measured in volume and analyzed for CO by gas chromatography, while the resulting cobalt ions was determined by an EDTA-titration method.

Results

Effect of Some Diphosphorus Ligands. A hydroformylation catalyst was prepared *in situ* from $Co_2(CO)_8$ and a complementary diphosphine. As shown in Table 1, where the initial rate of gas consumption was taken, remarkable ligand effects on the activity were observed; 1,2-bis(diphenylphosphino)ethane (hereafter, abbreviated as diphos) was found to be the most effective ligand, and in this case the activity was *ca.* 3 times that in $Co_2(CO)_8$ (Run 1, 3).

For comparison, the use of bis(2-diphenylphosphinoethyl) phenylphosphine results in the slight increase in the activity (Run 9), but triphenylphosphine is an unfavorable ligand (Run 10). A cobaltcarbonyl cluster ($CH_3CCo_3(CO)_9$) instead of $Co_2(CO)_8$ appears to be undesirable as a catalyst precursor (Run 4).

The results of analysis of the products are also listed in Table 1. The competitive hydrogenation to give methyl propionate occurred very little (Run 3), and little difference between Run 1 ($Co_2(CO)_8$) and Run 3 ($Co_2(CO)_8$–diphos) was observed in the α/β ratio.

Effect of Diphos to $Co_2(CO)_8$ Ratio on the Activity. The results tested under standard conditions are illustrated in Fig. 1, where the amount of $Co_2(CO)_8$ was kept constant at 0.25 mmol. The maximum activity was achieved when the molar ratio was *ca.* 0.5 and subsequent addition of diphos drastically decreased the activity. (Thereafter, the complex showing the maximum activity will be called 'cobalt–diphos catalyst'.)

Another feature of the cobalt–diphos catalyst is that it is active even under lower pressure than $Co_2(CO)_8$; as shown in Table 2, for instance, at 110 °C under 30 kg/cm² of total pressure ($CO/H_2=1$) aldehyde($\alpha+\beta$) is produced in *ca.* 77% yield after 107 min-reaction

Table 1. Hydroformylation of methyl acrylate catalyzed by $Co_2(CO)_8$ with some diphosphines
$Co_2(CO)_8$ 0.25 mmol, phosphine 0.125 mmol, toluene (solvent) 50 ml
methyl acrylate 50 mmol, $H_2/CO=1$, 50 kg/cm² (const.), temp 120 °C.

Run No.	Added phosphine	Initial rate of gas consumption / mmol min⁻¹	Time / min	$\beta+\alpha$[a] yield/%[b]	Methyl Propionate yield/%	β/α[c]
1	None	1.3	132	77.0	0.6	19.4
2	$Ph_2PCH_2PPh_2$	1.2	—	—	—	—
3	$Ph_2P(CH_2)_2PPh_2$	3.8	35	84.1	1.4	18.3
4	$Ph_2P(CH_2)_2PPh_2$[d),e)]	1.5	—	—	—	—
5	$Ph_2P(CH_2)_3PPh_2$	1.8	—	—	—	—
6	$Ph_2P(CH_2)_4PPh_2$	0.4	—	—	—	—
7	*cis*-$Ph_2PCH{=}CHPPh_2$	2.7	—	—	—	—
8	$Ph_2PC{\equiv}CPPh_2$	2.8	—	—	—	—
9	$PhP(CH_2CH_2PPh_2)_2$	1.8	—	—	—	—
10	PPh_3	0.6	252	85.0	0.5	17.9

a) α, β denote methyl α-formylpropionate and methyl β-formylpropionate, respectively. b) Aldehydes produced/methyl acrylate initially added (50 mmol). c) The molar ratio of β-isomer to α. d) Cobalt carbonyl cluster ($CH_3CCo_3(CO)_9$, 0.25 mmol) in place of $Co_2(CO)_8$ was used as catalyst precursor. e) The value of this rate was 0.6 (mmol/min) when diphos was absent.

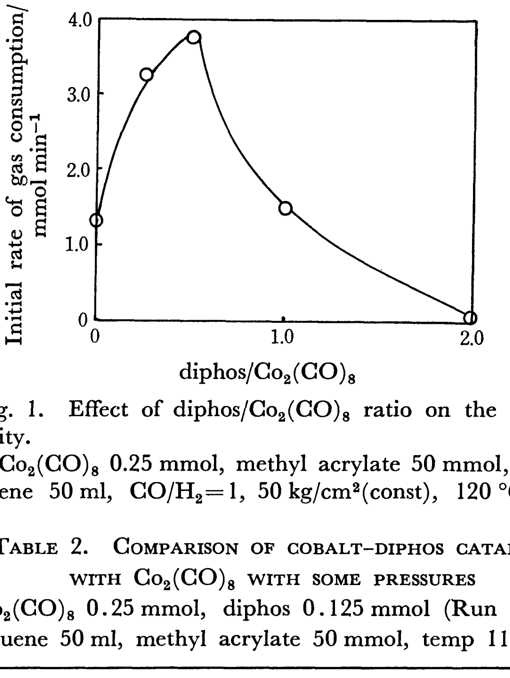


Fig. 1. Effect of diphos/$Co_2(CO)_8$ ratio on the activity.
$Co_2(CO)_8$ 0.25 mmol, methyl acrylate 50 mmol, toluene 50 ml, $CO/H_2=1$, 50 kg/cm²(const), 120 °C.

Table 2. Comparison of cobalt-diphos catalyst with $Co_2(CO)_8$ with some pressures
$Co_2(CO)_8$ 0.25 mmol, diphos 0.125 mmol (Run 1, 2), toluene 50 ml, methyl acrylate 50 mmol, temp 110 °C.

Run No.	Pressure kg/cm² CO	Pressure kg/cm² H_2	Time / min	$\alpha+\beta$[b] yield/%	Methyl propionate yield/%
1	25	10	168	86	0.6
2	15	15	107	77	0.2
3[a]	25	10	553	45	—
4[a]	15	15	372	34	—

a) Without diphos. b) See footnotes in Table 1.

with the resulting catalyst solution remaining homogeneous (Run 2), whereas confined yield in aldehyde is significantly low in $Co_2(CO)_8$ under the same conditions, because the catalyst decomposition occurs completely during the course of the reaction (Run 4).

Effect of Reaction Parameters. Using both cobalt-diphos and $Co_2(CO)_8$ catalysts kinetic properties were examined, the purpose of which is to shed light on the reasons for the promoting effect of diphos in this cobalt-catalyzed hydroformylation.

For the calculation of the reaction rate, the correlation between the amount of reacted methyl acrylate (MA) and that of the gas ($CO/H_2=1$), which was supplied during the reaction, must be known. In order to obtain information on change in the amount of aldehyde formation with time, the reactions at 100—110 °C under 50 kg/cm² (const., $CO/H_2=1$) were carried out and aliquot samples were withdrawn from autoclave at several reaction times and analyzed.

As can be seen from a comparison of Fig. 2A(○) with Fig. 2B(○), the amount of total aldehydes ([TA]) was approximately equal to one-half that of the corresponding gas uptake ([C]), indicating that the hydroformylation (but not hydrogenation) principally occurs under these conditions. Also, [TA] increases with time with a first order behavior with respect to the concentration of (MA), similar to [C], according to Eq. 1,

$$r = -\mathrm{d}[\mathrm{MA}]_t/\mathrm{d}t = k[\mathrm{MA}]_t, \qquad (1)$$

where r, k, and [MA] stand for the overall rate, apparent rate constant and the concentration of (MA) at time 't', respectively. These observations on cobalt-diphos catalyst allow us to assume that $[\mathrm{TA}]=[\mathrm{C}]/2$. Thus $[\mathrm{MA}]_t$ in Eq. 1 can be expressed as follows;

$$[\mathrm{MA}]_{\mathrm{Initial}} = 50(\mathrm{mmol}) = [\mathrm{MA}]_t + [\mathrm{C}]/2. \qquad (2)$$

Good linear plots of $\ln(50/[\mathrm{MA}]_t)$ *vs.* time are provided in Fig. 2B(●, ▲), apparent rate constant, k, being calculated from the slope.[7)]

In case of $Co_2(CO)_8$, on the other hand, Figs. 2A(△), C(○, △) show rather zero order behavior with respect to the concentration of (MA), though the hydroformylation predominantly occurs. Thus, apparent rate constant, k', was calculated from the slope, according to Eq. 3;

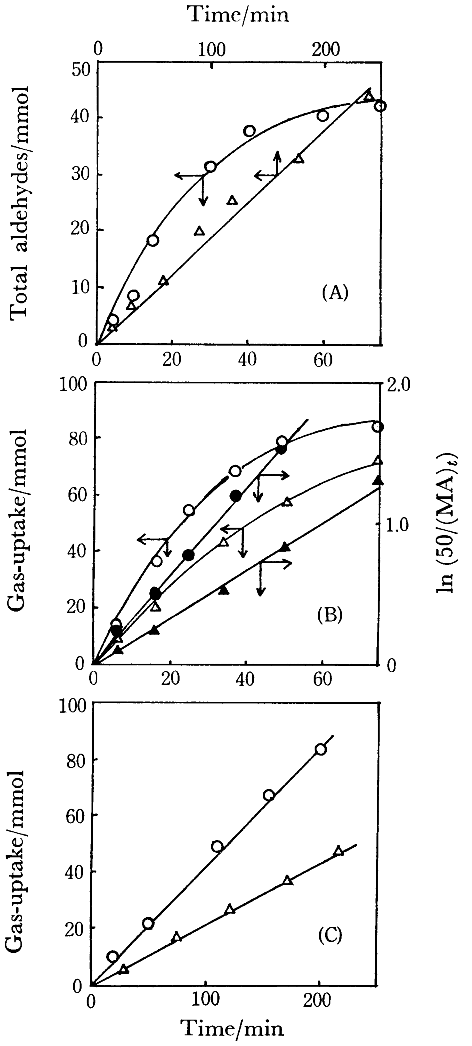


Fig. 2. Results plotted against time.
$Co_2(CO)_8$ 0.25 mmol, diphos 0.125 mmol (A,B), toluene 50 ml, $CO/H_2=1$, 50 kg/cm^2(const.), methyl acrylate 50 mmol.
(A) Total aldehydes (mmol), temp 110 °C.
—O—: Cobalt-diphos, —△—: $Co_2(CO)_8$.
(B) Cobalt-diphos
—O—, —●—: 110 °C; —△—, —▲—: 100 °C.
(C) $Co_2(CO)_8$
—O—: 110 °C, —△—: 100 °C.

$$k't = ([MA]_{initial}-[MA]_t) = [C]/2. \tag{3}$$

Good Arrhenius plots of the rate constants, k or k', provide the apparent activation energies, respectively; the values obtained when the reactions were carried out in the temperature range from 90 to 120 °C were 23.0 kcal/mol with respect to k, 26.7 kcal/mol to k'.

Effects of catalyst concentrations on k or k' were examined under total pressure of 50 kg/cm^2 ($CO/H_2=1$) with the diphos/$Co_2(CO)_8$ molar ratio kept constant at 0.5 in the case of cobalt-diphos catalyst. Figure 3 reveals first order dependence of k as well as k' on the catalyst concentration over this range.

Effects of partial pressure of hydrogen (carbon monoxide) on k or k' were examined, where carbon monoxide (hydrogen) partial pressure in each run was adjusted to 25±2 kg/cm^2 and syn-gas ($CO/H_2=1$) was supplied during the reaction. The rate constants, k or k', were calculated from the slopes as mentioned above. As shown in Fig. 4, these constants increase with the increase in hydrogen pressure. Also, Figure 5 shows that k value tends to decrease more greatly with the increased CO pressure than does k', in the range from 25 to 77 kg/cm^2.

Change in the CO/Co Molar Ratio with Time. The CO/Co molar ratio, which was determined by withdrawing samples from the vessel at definite time, may give some hints to discuss the promoting effect of diphos on the reaction. Interestingly, the ratio for the cobalt-diphos catalyst slightly increases from a value of *ca.* 1.5 to 2, as the reaction proceeds, and it is apparently lower than that for $Co_2(CO)_8$ (from 3 to 4).

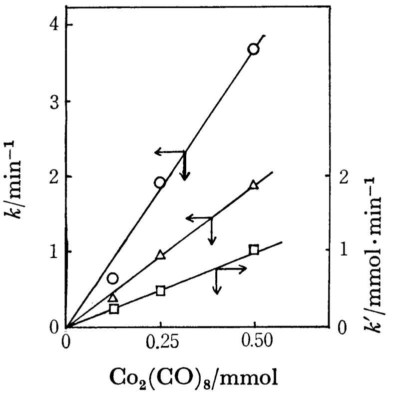


Fig. 3. Effect of catalyst concentration.
Methyl acrylate 50 mmol, toluene 50 ml, $CO/H_2=1$, 50 kg/cm^2(const.), —O—: 110 °C, cobalt-diphos (diphos/$Co_2(CO)_8$=0.5 (const.)). —△—: 100 °C, cobalt-diphos(diphos/$Co_2(CO)_8$=0.5(const.)).
—□—: 110 °C, $Co_2(CO)_8$.

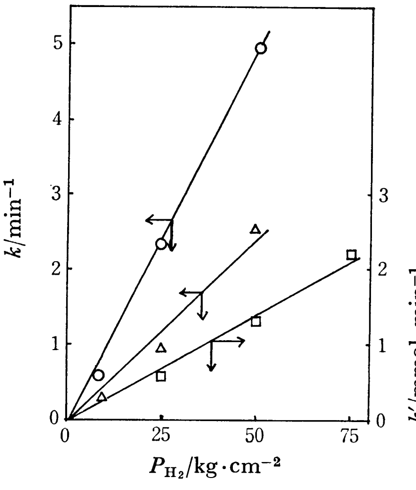


Fig. 4. Effect of partial pressure of hydrogen.
$Co_2(CO)_8$ 0.25 mmol, toluene 50 ml, P_{CO} 25 kg/cm^2 (const.), cobalt-diphos (diphos 0.125 mmol).
(const.), —O—: 110 °C, cobalt-diphos (diphos 0.125 mmol). —△—: 100 °C, cobalt-diphos (diphos 0.125 mmol). —□—: 110 °C, $Co_2(CO)_8$.

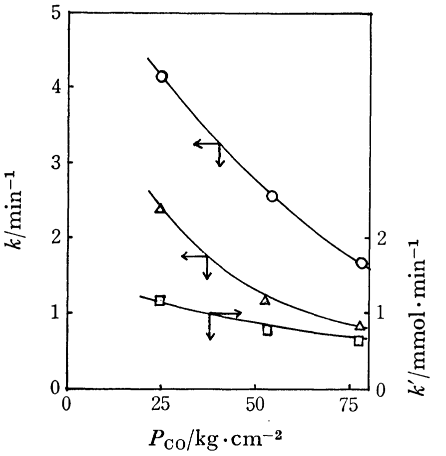


Fig. 5. Effect of partial pressure of CO.
$Co_2(CO)_8$ 0.25 mmol, toluene 50 ml, P_{H_2} 25 kg/cm^2 (const.), —○—: 120 °C, cobalt-diphos (diphos 0.25 mmol). —△—: 110 °C, cobalt-diphos (diphos 0.25 mmol). —□—: 120 °C, $Co_2(CO)_8$.

Discussion

By numerous workers effects of different phosphines on the rate of $Co_2(CO)_8$-catalyzed hydroformylation have been already investigated, and the general conclusion obtained was that the addition of phosphorus ligands always decreases the rate, though certain ligands such as PBu_3 are favorable for high product linearity.[1,5)] Of all these reports, that published by Slaugh and Mullineaux is interesting to us, since $Co_2(CO)_8$ complex with diphos ligand has been used as a catalyst for the hydroformylation of 1-pentene.[5a)] The catalytic features of both our system(A) and Slaugh(B) may be summarized as in Table 3.

Our catalyst system (cobalt–diphos) is relatively favorable for the measurement of the hydroformylation rate, because little hydrogenation of methyl acrylate occurs under the conditions employed. As shown in Figs. 2—5, cobalt–diphos catalyst gave similar kinetic behavior to $Co_2(CO)_8$, except for first order with respect to the concentration of (MA).

However, these do not always appear to mean the participation of active species such as $HCo(CO)_x$ (x= 3 or 4),[8)] since the CO/Co molar ratio obtained for this catalyst is apparently lower than that for $Co_2(CO)_8$, and since different IR spectral patterns during the reaction were observed for these catalyst solutions.[9)] This view may be also supported by the finding that cobalt-diphos catalyst is active even under lower pressure than $Co_2(CO)_8$. (Table 2).

Thus, $HCo(CO)_2(P\text{–}P)$, (**A**), which is responsible for the increase in the activity, may be postulated as one of principal active catalysts. Though attempts to isolate the species **A** and to identify it were not successful, following two facts would prompt us greatly;

1) The treatment of $Co_2(CO)_8$ with trialkylphosphine(PR_3) under the hydroformylation reaction conditions leads to the formation of $HCo(CO)_3(PR_3)$, which is an active catalyst for the reaction.[5b,c,10)]

2) Apparently, diphos acts as a bidentate ligand.[11,12)] In fact, Ikariya and Yamamoto have reported the preparation and properties of **A**, $HCo(CO)_2(P\text{–}P)$, which has been characterized by elemental analysis and IR spectrum.[13)]

A speculative reaction scheme and rate equation containing the species **A** is given in *Appendix*, where a rate law of the form in Eq. 7 is derived. According to Eq. 7, r is first order in [MA] and decreases as the CO pressure is increased (Fig. 5). Also, according to Eq. 7, the overall rate, r, is closely related to the concentration of both $HCo(CO)_2(P\text{–}P)$ and $HCo(CO)(P\text{–}P)$. Namely, the mean ratio of CO coordinated to cobalt atom, (CO/Co), should be of the value between 1 and 2 so long as a steady state is reached, and should approach to 2 at the end of the reaction, since steps [1], [7] are still present.; these are in accordance with the foregoing results.

Equation 7, however, does not necessarily justify the first order behavior in catalyst concentration (Fig. 3) and in hydrogen pressure (Fig. 4). Therefore, these facts reveal that cobalt–diphos system is very complex, and that more than one active species or other reaction schemes are probably involved.

The reason for the drastic decrease in the activity, which is shown in Fig. 1, cannot be explained by paths [1]—[7]. Therefore, another paths leading to, probably, the formation of inactive catalyst species consisting of $Co_2(CO)_8$ and diphos, would be also present.[11,14)]

Appendix

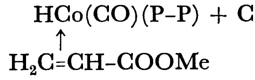
Overall possible reaction scheme may be postulated as follows;

$$Co_2(CO)_8 + H_2 + 2P\text{-}P \longrightarrow \underset{\mathbf{A}}{2HCo(CO)_2(P\text{-}P)} + 4CO \qquad [1]$$

Table 3. Comparison of our catalyst system(A) with Slaugh(B)

		(A)	(B)
1)	Olefin	Methyl acrylate	1-Pentene
2)	Diphos/$Co_2(CO)_8$ ratio	0—1.0 (0.5 for the most active catalyst, Fig. 1)	4.0
3)	Temperature	90—120 °C	150—200 °C
4)	Catalytic activity in comparison with $Co_2(CO)_8$	*ca.* 3 times active (Table 1, Fig. 1)	Less active by a factor of, at least, 100
5)	Main products	Aldehydes (Table 1, 2)	Alcohols
6)	Thermal stability	Active at 110 °C under 30 kg/cm^2 (CO/H_2=1) (Table 2)	Active at 150—200 °C under 7—20 kg/cm^2

$$\mathrm{HCo(CO)_2(P\text{-}P) + H_2C{=}CH\text{-}COOMe} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$

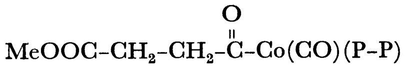


$$\begin{matrix}\mathrm{HCo(CO)(P\text{-}P) + CO} \\ \uparrow \\ \mathrm{H_2C{=}CH\text{-}COOMe}\end{matrix} \qquad [2]$$

1

$$\mathbf{1} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{MeOOC\text{-}CH_2\text{-}CH_2\text{-}Co(CO)(P\text{-}P)} \qquad [3]$$

2



$$\mathbf{2} + \mathrm{CO} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{MeOOC\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}Co(CO)(P\text{-}P)} \qquad [4]$$

3

$$\mathbf{3} + \mathrm{H_2} \xrightarrow{k_5} \mathrm{MeOOC\text{-}CH_2\text{-}CH_2\text{-}CHO} + \mathrm{HCo(CO)(P\text{-}P)} \qquad [5]$$

$$\mathrm{HCo(CO)(P\text{-}P) + H_2C{=}CH\text{-}COOMe} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathbf{1} \qquad [6]$$

$$\mathrm{HCo(CO)(P\text{-}P) + CO} \xrightarrow{k_7} \mathrm{HCo(CO)_2(P\text{-}P)}, \qquad [7]$$

where P–P stands for diphos.

An active species **A** is formed by step [1], and the step is not probably rate determining, because no induction period was observed at the beginning of the reaction (Fig. 2A) and rate constant, *k*, is first order in [MA] (Fig. 2B).

Subsequent steps [2]—[7] are similar to that presented previously by Heck.[8] That the reversal of step [5] is negligible under the conditions employed has been already confirmed by an additional experiment.[9] Also, if the reversal of step [7] is present, the CO/Co molar ratio would be still of the value between 1 and 2 at the end of the reaction; our result is not consistent with this. Thus, steps [5], [7] are proposed as irreversible steps.

The overall rate, *r*, is expressed as in Eq. 4;

$$r = k_5[\mathbf{3}]P_{\mathrm{H_2}}, \qquad (4)$$

where [**3**] stands for the concentration of an intermediate ***3***. A rate law of the form in Eq. 5 would be obtained, provided that steady state concentrations for intermediates ***1***, ***2***, ***3*** are assumed, respectively;

$$r = \frac{k_3k_4P_{\mathrm{co}}(k_2[\mathrm{HCo(CO)_2(P\text{-}P)}]+k_6[\mathrm{HCo(CO)(P\text{-}P)}])\cdot[\mathrm{MA}]\cdot k_5P_{\mathrm{H_2}}}{(k_{-2}k_{-3}k_{-4}P_{\mathrm{co}}+k_{-3}k_{-4}k_{-6})+k_5P_{\mathrm{H_2}}[k_{-3}k_{-6}+(k_{-2}k_{-3}+k_3k_4+k_4k_{-6}+k_{-2}k_4P_{\mathrm{co}})P_{\mathrm{co}}} \qquad (5)$$

where $[\mathrm{HCo(CO)_2(P\text{-}P)}]$, $[\mathrm{HCo(CO)(P\text{-}P)}]$ stand for the concentrations of species $\mathrm{HCo(CO)_2(P\text{-}P)}$, $\mathrm{HCo(CO)(P\text{-}P)}$, respectively. Here, if the second term in the denominator is assumed to be much larger than the first one, Eq. 6 is obtained;

$$r = \frac{k_3k_4P_{\mathrm{co}}(k_2[\mathrm{HCo(CO)_2(P\text{-}P)}]+k_6[\mathrm{HCo(CO)(P\text{-}P)}])\cdot[\mathrm{MA}]}{k_{-3}k_{-6}+(k_{-2}k_{-3}+k_3k_4+k_4k_{-6}+k_{-2}k_4P_{\mathrm{co}})P_{\mathrm{co}}}. \qquad (6)$$

Furthermore, if $k_{-3}k_{-6} \ll (k_{-2}k_{-3}+k_3k_4+k_4k_{-6}+k_{-2}k_4P_{\mathrm{CO}})P_{\mathrm{CO}}$, the overall rate, *r*, is expressed as Eq. 7;

$$r = \frac{k_3k_4[\mathrm{MA}](k_2[\mathrm{HCo(CO)_2(P\text{-}P)}]+k_6[\mathrm{HCo(CO)(P\text{-}P)}])}{(k_{-2}k_{-3}+k_3k_4+k_{4-6})+k_{-2}k_4P_{\mathrm{co}}}. \qquad (7)$$

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7) The value of *k* obtained when 30 mmol of (MA) was initially introduced, was in good accordance with that of *k* in Fig. 2B(●).

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14) We also have failed in explaining the reason why a maximum activity was achieved when a ratio diphos/$\mathrm{Co_2(CO)_8}$ was 0.5.