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EFFECT OF PHOSPHINE LIGANDS ON HOMOGENEOUS HYDROGENATION OF CARBON MONOXIDE BY IRIDIUM CATALYSTS

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Summary

During the hydrogenation of carbon monoxide by carbonyl iridium catalyst under high pressure, triarylphosphines such as triphenylphosphine were found to enhance the activity and selectivity for ethylene glycol formation, whereas trialkylphosphines mostly promoted methanol formation. The moderate σ-donating ability of the ligand appears to be important for ethylene glycol formation. Crystalline $Ir_2(CO)_6(PPh_3)_2$ was isolated from the reaction mixture. This complex by itself showed a high catalytic activity for ethylene glycol.

Introduction

Many studies have been carried out on the reaction of CO and H_2 catalysed by homogeneous metal complexes to form oxygen-containing organic compounds, especially ethylene glycol (EG) and ethanol. Most of the studies have concentrated on complexes of cobalt, rhodium and ruthenium [1]. Since iridium is located under cobalt and rhodium in the Periodic Table and like them is active as a hydroformylation catalyst, it is also expected to be an effective catalyst for the synthesis of oxygen-containing C_2 compounds from CO and H_2. Keim et al. reported that a small amount of EG is formed together with methanol, the main product, by an carbonyl iridium catalyst in toluene and *N*-methylpyrrolidinone (NMP) solvents under a high pressure such as 200 MPa [2]. They also found that amines work as effective co-catalysts to increase the activity for methanol formation in n-pentane under a similar pressure, while EG selectivity remains slight and unimproved [3]. On the other hand, they showed, that phosphine ligands such as trialkylphosphines do

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not act as promotors of the reaction and EG formation is depressed by them. During our investigation under a lower pressure, however, we found that some phosphine ligands do have a positive effect on the reaction and increase the catalytic activity for EG as well as that for methanol [4].

Experimental

The reactions were carried out in a 30 cm^3 autoclave made of Hastelloy C-276 stainless steel. The reactor was charged with the iridium catalyst together with additives and solvent, pressurized with CO/H_2 (1/1) gas, and then heated under shaking. After rapid cooling of the reactor by immersion in running water, the gas was cautiously purged and analysed by GLC with a 6 m active carbon column at 160°C. The liquid products were analysed by programmed temperature (80 to 240°C at 8°C/min) GLC with a 1 m column packed with 10% PEG-20M-TPA on Chromosorb-102, and were identified by GLC/mass spectral analysis.

Results and discussion

The effect of the solvents on the reaction was tested using $Ir_4(CO)_{12}$ as catalyst at 230°C under a pressure of about 70-MPa. The results showed that the reaction rates were in the order of toluene < γ-butyrolactone < NMP. The main product was methanol, and a small amount of EG was detected when NMP was the solvent.

The reaction rate in NMP increased as the temperature was raised up to 290°C, as shown in Fig. 1. The ratio of EG to methanol was hardly affected by temperature, in contrast to the results obtained by Keim and co-workers, who used n-pentane solvent in which the ratio decreased with temperature [3]. It is notable that the Ir-NMP system was so stable that no precipitate due to the formation of higher clusters of metal was observed at such a high temperature as 290°C whereas the Rh-NMP system tends to form a precipitate even at lower temperatures *.

The effects of several kinds of additive were examined at 270°C under a pressure of about 70 MPa. The results are shown in Table 1 together with the catalytic performance of some of the carbonyliridium cluster anion complex. The most remarkable increase in catalytic activity for EG and methanol was achieved when phosphine ligands were used. Figure 2 illustrates the effects of various phosphines and phosphites, which are arranged according to their electronic nature [5]. The main features of the result are as follows:

(1) Triarylphosphines, which have a moderate σ-donating ability, give the highest activity and selectivity for EG formation, although their activity and selectivity are not as high as in the case of Rh and Ru systems [1].

(2) Trialkylphosphines, which have a higher σ-donating ability, act mostly as promotors for methanol formation and give a lower selectivity for EG. The only exception is tri-t-butylphosphine, which seems almost ineffective presumably because of its high bulkiness.

(3) Phosphites show an inhibiting effect on both EG and methanol formation.

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* A black precipitate was observed when $Rh_4(CO)_{12}$ was heated in NMP at 270°C under the same CO/H_2 pressure for 1 h.

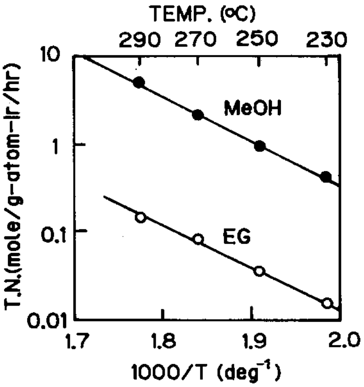

Fig. 1. Temperature dependence of the catalytic activity of the Ir/NMP system. $Ir_4(CO)_{12}$ 0.5 mg-atom, NMP 7.5 ml, CO/H_2 (1/1) 75–67 MPa, 4 h.

TABLE 1

CATALYTIC ACTIVITY OF IRIDIUM CARBONYL COMPLEXES AND EFFECT OF ADDITIVES [a]

Ir compound	Additive (mmol)		Yield (mmol)				
			EG	MeOH	EtOH	CH_4	CO_2
$Ir_4(CO)_{12}$	–		0.17	4.27	0.00	0.12	1.33
$[PPN][HIr_4(CO)_{11}]$ [b,c]	–		0.09	2.67	0.01	0.02	0.41
$[PPN]_2[Ir_8(CO)_{20}]$ [b,c]	–		0.07	2.46	0.00	0.02	0.28
$[PPN]_2[Ir_6(CO)_{15}]$ [b,c]	–		0.09	3.34	0.00	0.03	0.38
$Ir_4(CO)_{12}$	Ph_3P	(0.5)	1.24	9.10	0.12	0.47	1.08
$Ir_4(CO)_{12}$	$n\text{-}Bu_3P$	(0.5)	0.57	14.5	0.01	0.24	0.64
$Ir_4(CO)_{12}$ [d]	Ph_3As	(0.5)	0.10	2.10	0.01	0.11	0.49
$Ir_4(CO)_{12}$ [c]	PPNCl	(1.0)	0.19	1.59	0.26	7.83	5.41
$Ir_4(CO)_{12}$ [c]	PPNI	(1.0)	0.32	1.52	0.21	6.84	5.16

[a] Reaction conditions: Ir complex 0.5 mg-atom, NMP 7.5 ml, CO/H_2 (1/1) ca. 75–70 MPa, 270°C, 4 h. [b] Amount of Ir complex was 0.3 mg-atom. [c] Reaction time was 3 h. [d] Reaction temperature was 250°C.

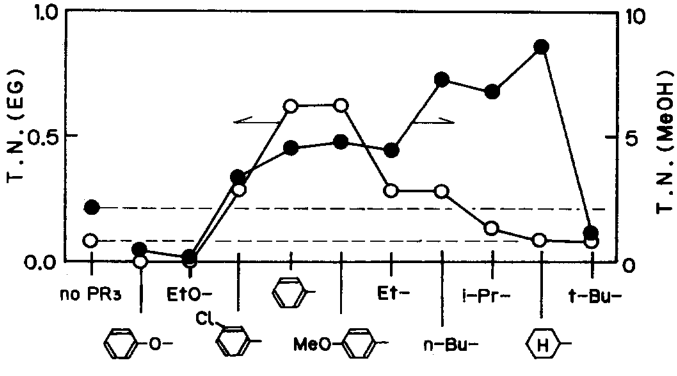

Fig. 2. Effect of phosphines and phosphites. $Ir_4(CO)_{12}$ 0.5 mg-atom, PR_3 0.5 mmol, NMP 7.5 ml, CO/H_2 (1/1) 75–65 MPa, 270°C, 4 h. (The substituents along the abscissa represent R in PR_3.)

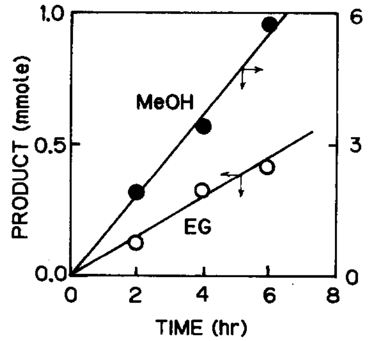

Fig. 3. Conversion vs. reaction time. $Ir_4(CO)_{12}$ 0.1 mg-atom, PPh_3 0.1 mmol, NMP 7.5 ml, CO/H_2 (1/1) 75–72 MPa, 270°C.

A small amount of benzene was detected in the case of triphenylphosphine, indicating that hydrogenolysis of the phosphine had occurred. However, the Ir–PPh_3 system is much more stable than the corresponding Rh system, which gives phosphido cluster anion complexes easily under much milder conditions * [6]. As shown in Fig. 3, no substantial change in reaction rate was observed in 6 h.

At this point, the dependence on the solvent was once again studied, using triphenylphosphine as ligand. As shown in Table 2, the amide solvent gave the highest activity and selectivity for EG while the less basic ether solvent gave almost only methanol.

The dependence on the amount of triphenylphosphine is shown in Fig. 4. The activity for EG reached a maximum at a P/Ir ratio of 1 to 2, while that for methanol was almost unchanged at a P/Ir ratio higher than 1. When reaction mixtures of these compositions were left to stand at about 10°C, a yellow, rhombohedral, crystalline solid was precipitated. It was identified as $Ir_2(CO)_6(PPh_3)_2$ by elemental analysis, IR spectra [7] and X-ray diffraction **. This complex, when used as catalyst, gave the same result *** as the Ir–PPh_3 system in which the P/Ir ratio was equal to 1. Drakesmith and Whyman showed that $Ir_2(CO)_6(PPh_3)_2$ is easily hydrogenolysed to form $HIr(CO)_3(PPh_3)$ under pressure of CO and H_2 at elevated temperatures [7]. They suggested that this hydride might be the active species for hydroformylation of olefins in the phosphineiridium system. Although our reaction

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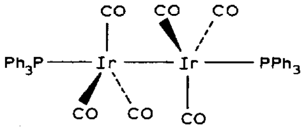
* When $Rh_4(CO)_{12}$ was heated with PPh_3 in NMP at 200°C for 1 h (otherwise under the same conditions as in Fig. 2), the IR data showed the formation of the phosphido cluster anion $[Rh_9P(CO)_{21}]^{2-}$ (2015 cm^{-1}) together with $[Rh(CO)_4]^-$ (1900 cm^{-1}). The counter cation was probably either protonated NMP or protonated *N*-methylpyrrolidine which was derived from NMP by hydrogenation. From the relative absorbances, the conversion to the phosphido complex was calculated to be about 60%.

** The data, a 10.10 Å, α 99.34°, V 984 $Å^3$, $\rho_{obs.}$ 1.81 g/cm^3 (measured in CCl_4/CH_3I medium), $\rho_{calc.}$ 1.818 g/cm^3 (for $Z=1$), and the space group $R\bar{3}$ suggest that the structure is as follows:



*** T.N. (EG) and T.N.(MeOH) were 0.59 and 4.15 h^{-1}, respectively, for this complex and 0.62 and 4.55 h^{-1} for the in situ prepared catalyst under the conditions given in Fig. 4.

TABLE 2

DEPENDENCE OF Ir–PPh$_3$ CATALYST ON SOLVENT [a]

Solvent	T.N. (mol/g-atom-Ir/h)	
	EG	MeOH
NMP	0.31	2.68
γ-Butyrolactone	0.23	2.29
Sulfolane	0.09	3.06
1,4-Dioxane	0.00	2.65

[a] Reaction conditions: $Ir_4(CO)_{12}$ 0.5 mg-atom, PPh_3 1 mmol, solvent 7.5 ml, CO/H_2 (1/1) ca. 75–70 MPa, 250°C, 4 h.

conditions are more severe than theirs and the solvent used is different, it is plausible that the same hydride complex plays an important role in our reaction system too. Anyhow this system represents one of the rare instances in which the complexes, which have the same composition as the optimum recipe, can be isolated from the catalyst solution.

EG formation from CO and H_2 consists of several reaction steps, in which formaldehyde and glycol aldehyde are considered to be the intermediates [8]. Spencer studied the rhodium-catalysed hydroformylation of formaldehyde [9]. He showed that (a) triarylphosphines give the highest activity and selectivity for glycol aldehyde and its yield decreases with increasing basicity of the phosphine, (b) amide solvents are preferable for glycol aldehyde formation while methanol formation prevails in other solvents, and (c) the optimum PPh_3/Rh ratio is around 1 to 2, above which hydroformylation is suppressed with an increase in methanol formation. The common features between their results and ours imply that in principle both catalyses proceed by the same mechanism.

The reaction path is outlined in Scheme 1, where H–M represents the hydrogen–metal bond in the complex [1,10]. It is not clear at this point what roles the phospine ligands play in these steps. They may possibly affect the CO insertion step kinetically and thermodynamically [11]. They may also control the selectivity by affecting the nature of the hydrogen in the hydride complex. The less protonic (or more hydridic) nature of the H–M species coordinated by a phosphine may facilitate its reaction with the acyl complex, leading to the formation of EG. The

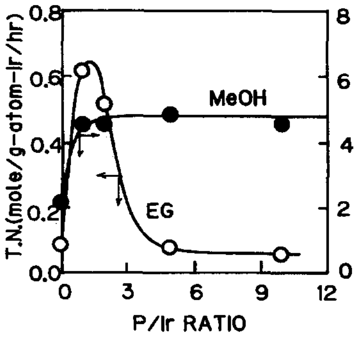
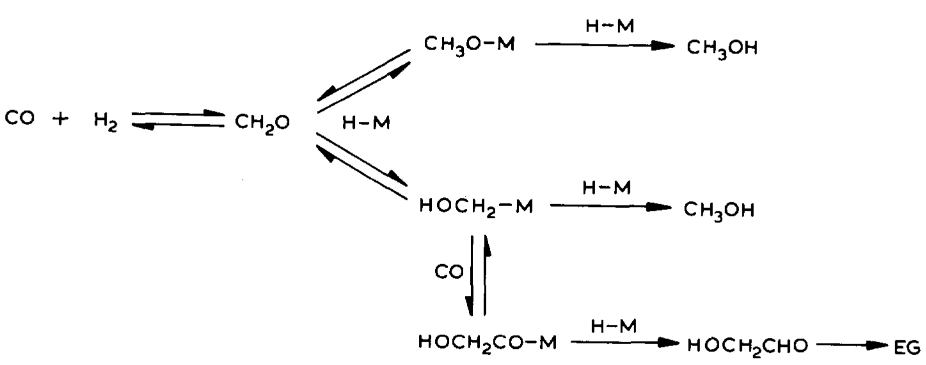


Fig. 4. Influence of the PPh_3/Ir ratio. $Ir_4(CO)_{12}$ 0.5 mg-atom, NMP 7.5 ml, CO/H_2 (1/1) 75–66 MPa, 270°C, 4 h.



SCHEME 1

acyl complex is considered to be more electrophilic than the methoxy or methylol complexes. However, the excessive hydridic property may in turn favour the formation of the methoxy complex, which would be transformed into methanol. This might explain the higher methanol selectivity exhibited by trialkylphosphines and by excesses of triphenylphosphine.

Although the phosphineiridium system has only a poor activity and selectivity for EG, this is the first case where phosphines play a positive role as ligands in EG synthesis with the transition-metal complex catalyst. We have recently found another case where phosphines with bulky alkyl substituents enhance the EG formation activity of a rhodium catalyst [12]. Furthermore, Watanabe et al. have reported that the addition of a large excess of a tri-n-alkylphosphine to the rhodium catalyst enhances the hydrogenation of CO [13]. Consideration of this behaviour of phosphines may help in understanding the nature of the reaction for EG synthesis from CO and H_2.

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