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Effective hydrogenation of carbon monoxide to ethylene glycol using rhodium-trialkylphosphine-nitrogen base catalyst: critical role of nitrogen base promoter in controlling selectivity

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Abstract

In the rhodium/alkylphosphine complex catalyzed hydrogenation of carbon monoxide, the reaction rate and the selectivity to ethylene glycol have been found to be much improved by the addition of nitrogen bases. Examination of the effects of a variety of nitrogen bases for $Rh/P\text{-}i\text{-}Pr_3$ and $Rh/P\text{-}n\text{-}Bu_3$ catalyst systems revealed the linear relationships between rate (to ethylene glycol and methanol) and pK_a value of the nitrogen base. Use of these catalysts, allowed a space time yield of 280 g/l · h and a selectivity to ethylene glycol of 76% to be achieved.

Introduction

In the preceding series of papers [1], it was demonstrated that trialkylphosphines (PR_3) such as tri-n-propylphosphine ($P\text{-}n\text{-}Pr_3$) and triisopropylphosphine ($P\text{-}i\text{-}Pr_3$) serve as effective promoters in the rhodium catalyzed hydrogenation reaction of carbon monoxide in which the main products are ethylene glycol and methanol. The reaction rate and selectivity to ethylene glycol depend on the steric and on the electronic properties of the phosphine ligand, and on the phosphine/rhodium ratio. Phosphines appear to stabilize the mono- or di-nuclear state of the present rhodium catalyst [1], in contrast to the rhodium cluster catalyst reported by chemists at Union Carbide [2]. Furthermore, it was found that the addition of an amount of nitrogen base promoter to the Rh/PR_3 catalyst system does result in a marked increase in the selectivity to ethylene glycol [3]. Herein, we report the critical role of the nitrogen base, especially of the amine promoter, in the production of ethylene glycol by the Rh/PR_3 catalyst.

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Result and discussion

Ethylene glycol formation by Rh/PR$_3$/nitrogen base catalyst

The Rh/PR$_3$ catalyzed hydrogenation of carbon monoxide was carried out in the presence of a nitrogen base under 47.0 MPa syngas (H_2/CO 1/1) pressure at 200–240 °C for 2 h. The representative results are given in Table 1. In absence of the nitrogen base, methanol is the only product in tetraethylene glycol dimethyl ether (TGM) solvent. However, moderate catalytic activities were observed in 1,3-dimethyl-2-imidazolidinone (DMI) and 1-methyl-2-pyrrolidinone (NMP) as solvents. Thus, DMI and NMP themselves are thought to act as promoters. Surprisingly, the addition of the tertiary amine to these solutions resulted in an almost two-fold increase in turnover frequency (TOF) for ethylene glycol formation, with concomitant retardation of the methanol formation.

We examined the effect of a variety of nitrogen bases on the Rh/P-i-Pr$_3$ and Rh/P-n-Bu$_3$ catalyst systems, at the same concentration of the base, in DMI solvent. Figure 1a shows the relationship between rate, turnover frequency for ethylene glycol and methanol, and pKa value of the base in the Rh/P-i-Pr$_3$/nitrogen base catalyst system. As the pK_a value increases, the rate of ethylene glycol formation increases linearly, whereas the rate of methanol formation decreases. Almost the same trend was observed in the Rh/P-n-Bu$_3$/nitrogen base catalyst system, as shown in Fig. 1b. Since the total production of the oxygenates, TOF (2EG) + TOF (MeOH), remained nearly constant, the selectivity to ethylene glycol was greatly enhanced. The observed selectivity, as high as 80%, is unprecedented [6]. The effects of bidentate nitrogen ligands such as 2-hydroxypyridine or 2,2′-bipyridyl were almost comparable with those observed for pyridine itself. An additional feature of the Rh/PR$_3$/nitrogen base catalyst is that the yield of ethylene glycol increases as the rhodium concentration increases, in the range 0.001 to 0.4 g-atom Rh · l^{-1}. Neither rhodium metal nor rhodium cluster complex was observed even at

Table 1

Hydrogenation of carbon monoxide by Rh/PR$_3$/amine catalysts [a]

Run	Rh	PR$_3$	P/Rh	Amine	Amine Rh	Solvent	TOF [b]		Selectivity [c]
							EG	MeOH	
1 [d]	0.1	P-i-Pr$_3$	1	–	–	TGM	0.0	22.1	0.0
2	0.1	P-i-Pr$_3$	1	Et$_3$N	100	TGM	15.1	18.3	62.3
3	0.5	P-i-PR$_3$	1	–	–	DMI	7.1	15.8	61.7
4	0.5	P-i-Pr$_3$	1	Et$_3$N	1	DMI	15.8	7.3	81.2
5	0.5	P-i-Pr$_3$	1	4-DMAP	1	DMI	15.2	7.4	80.5
6	0.5	P-i-Pr$_3$	1	py	1	DMI	12.4	10.6	70.1
7	0.5	P-i-Pr$_3$	1	2-pyOH	1	DMI	9.0	15.9	53.2
8	0.5	P-i-Pr$_3$	1	dipy	1	DMI	15.6	10.0	75.6
9 [e]	0.6	P-i-Pr$_3$	1.5	Im-1-Me	5	DMI	20.1	12.9	75.7
10	0.15	P-n-Bu$_3$	5	–	–	DMI	0.0	22.1	0.0
11	0.1	P-n-Bu$_3$	5	Et$_3$N	100	DMI	15.7	16.5	65.5

[a] Reaction conditions: solvent, 10 ml; 47 MPa, H_2/CO(1/1); 220 °C, 2h. [b] mol(g-atom Rh)$^{-1}$ h^{-1}. [c] 100 × 2EG/(2EG + MeOH)(%), an approximate carbon efficiency. [d] 240 °C. [e] DMI, 4 ml; 230 °C; 1 h. Abbreviations: 4-DMAP, 4-dimethylaminopyridine; py, pyridine; 2-pyOH, 2-hydroxypyridine; dipy, 2,2′-dipyridyl; Im-1-Me, 1-methylimidazole; EG, ethylene glycol.

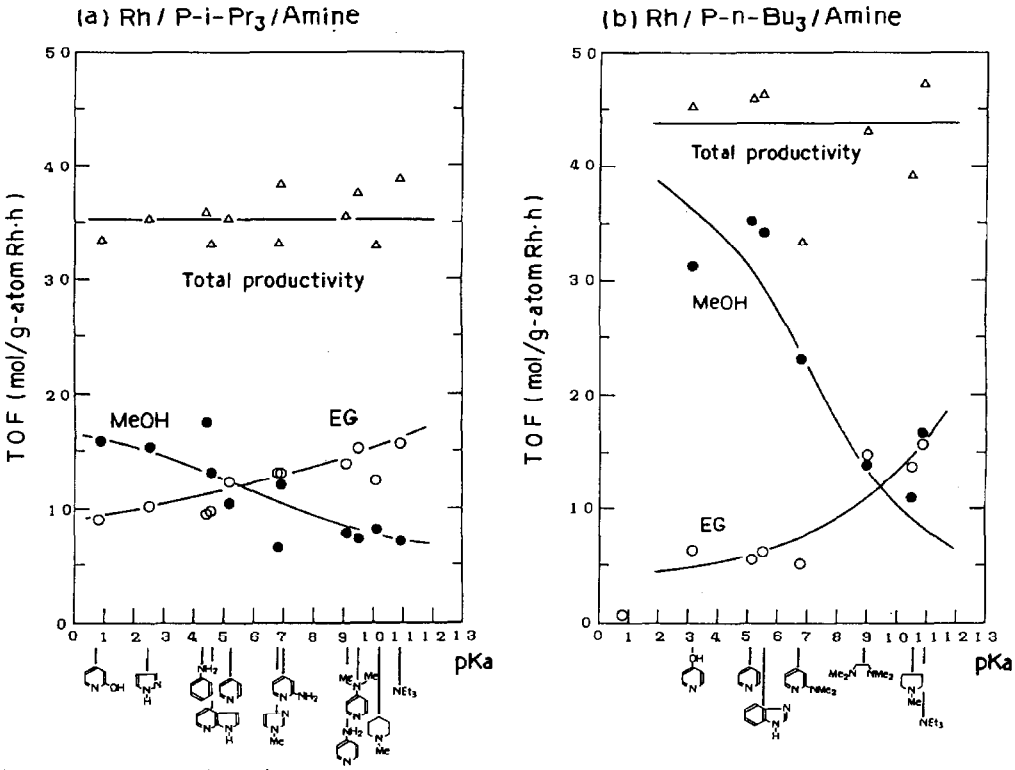


Fig. 1. Dependency of individual turnover frequency and total productivity on the pK_a values of nitrogen bases. Reaction conditions: (a) $Rh(CO)_2acac$, 0.5 mmol; P-i-Pr_3, 0.5 mmol; nitrogen base, 0.5 mmol, DMI, 10 ml; 47 MPa, H_2/CO 1/1; 220 °C, 2 h. (b) $Rh(CO)_2acac$, 0.1 mmol; P-n-Bu_3, 0.5 mmol; nitrogen base, 10 mmol; DMI, 8 ml, 47 MPa, H_2/CO 1/1; 220 °C. 2h.

0.4 g-atom $Rh \cdot l^{-1}$. Thus, surprisingly high catalyst performance was attained with the Rh/P-i-Pr_3/1-methylimidazole catalyst system which gave a space time yield of ethylene glycol as high as 280 $g \cdot l^{-1} \cdot h^{-1}$ with 76% selectivity (Run 9, Table 1).

Rhodium species in the reaction mixture

$^{31}P\{^1H\}$ NMR and IR spectroscopy revealed that in the absence of the nitrogen base, the cooled reaction mixture of the Rh/P-i-Pr_3 catalyst system contained only the non-bridged dimeric rhodium(0) complex, $(P\text{-i-}Pr_3)(CO)_3RhRh(CO)_3(P\text{-i-}Pr_3)$ (1) [1d]. For example, a reaction solution of Rh/P-i-Pr_3/TGM showed a strong IR band at 1960 cm^{-1} and a ^{31}P NMR multiplet at δ 69.0 (an AA'XX' spin pattern, typical for 1) under atmospheric pressure of syngas (H_2/CO 1/1) at room temperature. The solution showed a relatively low specific conductivity, κ 0.03×10^{-4} Scm^{-1} at 20 °C, consistent with the neutral complex 1. On the other hand, the reaction mixtures of Rh/P-i-Pr_3/nitrogen base/TGM, Rh/P-i-Pr_3/NMP, and Rh/P-i-Pr_3/DMI all contain significant amounts of the mononuclear rhodate, $Rh(CO)_4^-$, together with 1. The formation of $Rh(CO)_4^-$ was confirmed by the typical IR absorption at 1900 cm^{-1}, and by an increase in the specific conductivity of the reaction solution, κ 1.88×10^{-4} Scm^{-1} at 20 °C.

Rhodium species originating from the complex 1

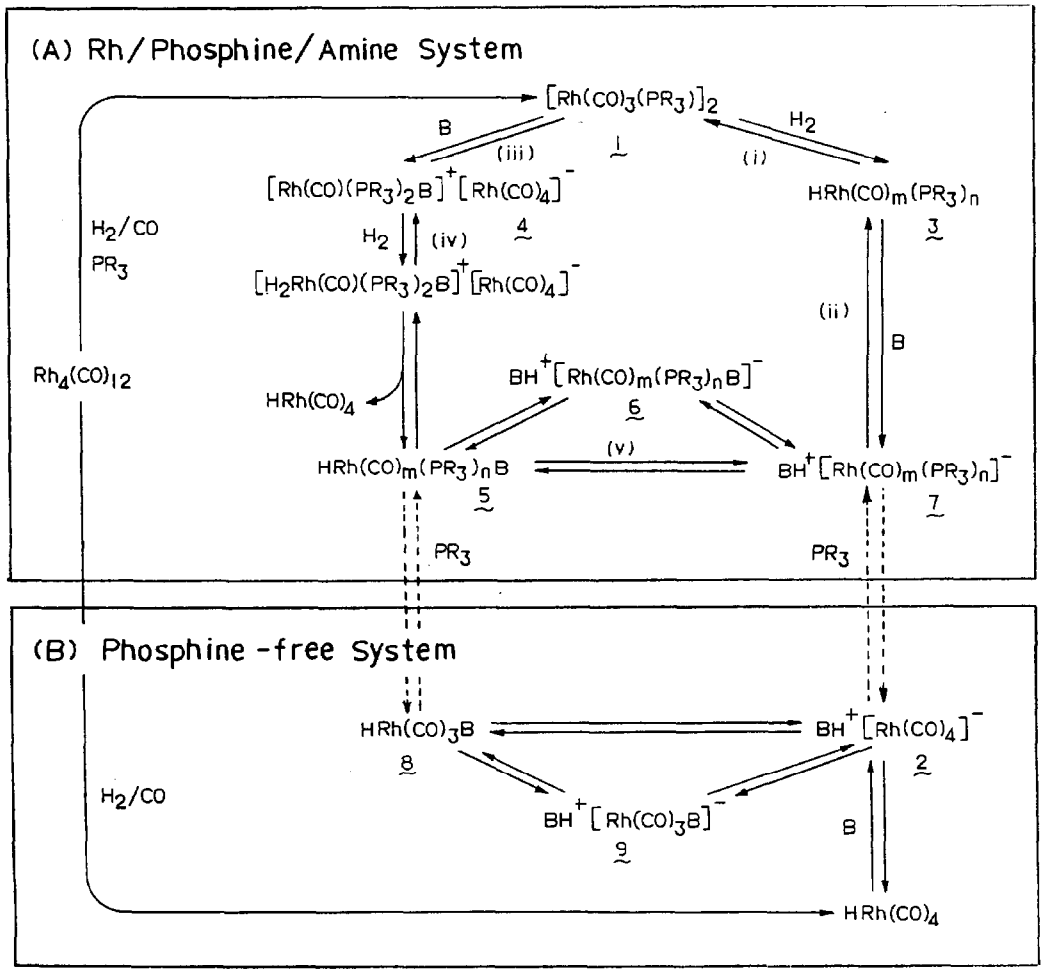
Separate experiments, carried out under syngas and ambient conditions, have confirmed that rhodium hydrides (3) [4] are formed in the reaction of dimer **1** with hydrogen:

$$\underset{(1)}{[Rh(CO)_3P\text{-}i\text{-}Pr_3]_2} + H_2 \rightarrow 2\ \underset{(3)}{HRh(CO)_m(P\text{-}i\text{-}Pr_3)_n} \quad (1)$$

The reaction of dimer **1** with the nitrogen base, on the other hand, gives a homonuclear disproportionation product **4** [5]:

$$\underset{1}{[Rh(CO)_3P\text{-}i\text{-}Pr_3]_2} + B \rightleftarrows \underset{(4)}{[Rh(CO)(P\text{-}i\text{-}PR_3)_2(B)]^+}[Rh(CO)_4]^- + CO \quad (2)$$

The rate of the disproportionation by the nitrogen bases is in the order: triazoles > imidazoles > 4-aminopyridines > triethylamine and 1-methylpiperidine, which may be an indication of the ease of nucleophilic attack at, or ligation to, the rhodium center [5].



Scheme 1

When **4** (B = 1-methylimidazole) was treated with hydrogen a decrease in intensity of the 1900 cm^{-1} absorption was observed. ^1H NMR measurement confirmed the presence of an unidentified hydride (δ −15.1 ppm) together with $HRh(CO)_2(P\text{-}i\text{-}Pr_3)_2$ (**3**) (δ −10.1 ppm) [4].

Treatment of the hydrides **3** with nitrogen bases such as 1-methylimidazole produces some unidentified rhodium hydrides, together with the species which exhibits an IR absorption at 1900 cm^{-1} due to $Rh(CO)_4^-$. Thus the species exhibiting 1900 cm^{-1}, generated in the reaction of **3** with nitrogen base, is most likely to be the species **4**, which is produced via **5**, **6**, or **7** in Scheme 1 (vide infra).

Both of the hydride mixtures, prepared by treating **3** and **4** with hydrogen, show the same catalytic activity as the original $Rh/P\text{-}i\text{-}Pr_3$/nitrogen base catalyst solution.

Role of the nitrogen base promoter in the catalyst

The most notable features of the Rh/PR_3/nitrogen base catalyst are: (1) In the absence of nitrogen base, no ethylene glycol is formed. Not only the amine but also amide or urea derivatives are effective promoters of ethylene glycol production. (2) The reactivity correlates well with the pK_a value of the nitrogen base. The rate of ethylene glycol formation increases, whereas the rate of methanol formation decreases, as the pK_a value of the base increases. Accordingly, the selectivity to ethylene glycol is much improved. (3) The degree of carbon monoxide hydrogenation remains apparently constant irrespective of the presence or absence of the nitrogen base.

These results indicate that the nitrogen base is a requisite for the ethylene glycol formation in the Rh/PR_3 catalyzed hydrogenation of carbon monoxide, suggesting its critical role in controlling the reaction paths to ethylene glycol and methanol. As to the key step which determines the selectivity to ethylene glycol, two reaction paths, (a) and (b), leading to the hydroxylmethylrhodium and the methoxyrhodium intermediates, respectively, have been considered [6].

$$\mathrm{Rh{-}H + CH_2{=}O} \begin{cases} \xrightarrow{(a)} \mathrm{HOCH_3Rh \rightarrow HOCH_2CH_2OH} \\ \xrightarrow{(b)} \mathrm{CH_3ORh \rightarrow CH_3OH} \end{cases} \tag{3}$$

The factors for the choice of reaction route (a) or (b), have been often discussed in terms of the acidity of the hydrogen atom in the rhodium hydrides [6]. In our catalytic system, this explanation appears inadequate since the highly basic amine, which is the effective promoter, may capture the acidic hydrogen, if any, during the reaction. For the Union Carbide catalyst system, Rh/Lewis base/aprotic polar solvent [2], the function of the base promoter has been described [6]. The presence of the rhodium clusters such as $[H_xRh_{13}(CO)_{24}]$ $(5-x)$, under syngas at about 1000 atm and at 200 °C, ($x = 2$, 3) was confirmed by infrared spectroscopy, which implies the participation of the anionic rhodium clusters in the hydrogenation of carbon monoxide. It was noted that the Lewis base does facilitate the generation of an anionic cluster complex on interaction with a neutral cluster complex. Furthermore it was postulated that the nature and the degree of ion-pairing between the rhodium carbonyl cluster anion and counter cation are crucial to the ethylene glycol formation. Thus the bases, being combined with a charge delocalized cation such as Cs^+ or bis(triphenylphosphine)iminium ($[(C_6H_5)_3P]_2N^+$), should be the effective

promoters. However, it seems unlikely that the cluster anion intermediate is involved in the present Rh/PR_3/nitrogen base catalyst system, on the basis of the following reasons. Firstly, the reaction of syngas, in the presence of the dimer complex **1** (0.15 mmol) and 1-methylimidazole (1.5 mmol) in DMI (10 ml) under 47.0 MPa at 220 °C, produces ethylene glycol and methanol, in turnovers of 16.8 and 8.72 mol · (g-atom Rh)$^{-1}$ · h^{-1}, respectively. The catalytic performance is comparable to that of the mixture consisting of $Rh(CO)_2(acac)$ (0.3 mmol), P-i-Pr_3 (0.3 mmol), 1-methylimidazole (1.5 mmol) and DMI (10 ml). Secondly, ethylene glycol is produced selectively under the conditions used, when a large excess of phosphine is present, in which the cluster complex would be decomposed into mono- or di-nuclear complexes [1b]. In fact, any visible absorption due to the anionic cluster could not be detected in the catalyst solution at 200 °C and under 20.0 MPa.

Now, for the Rh/PR_3/nitrogen base catalyst system, we speculate that the nitrogen base, B, acts as an electron donor towards the neutral rhodium precursors, **1** and **2**, to form mononuclear species such as **5**, **6**, and **7**, as tentatively described in Scheme 1. The net result of the electron transfer from the nitrogen base to the neutral rhodium moiety is either the ligation of the nitrogen base to the rhodium or the concurrent formation of a tertiary ammonium cation and an anionic rhodium species [7]. The formation of the ions during the reaction was manifested by an increase in the specific conductivity of the catalyst solution. The species **1** and **3**, by themselves are apparently inert to ethylene glycol formation since the Rh/PR_3/TGM catalyst system, in which the species **1** and **3** exist predominantly, does not produce ethylene glycol at all. Although not properly identified as yet, the species, **5**, **6**, and **7**, are believed to be the key intermediates. The analogous complexes **2** and **8** have been suggested to be the possible active species for the phosphine-free catalyst system [7]. Thus, we suggest that one of the functions of the nitrogen base is to generate the active catalytic species from the neutral precursors. The second function of the nitrogen base may be connected with the enhanced nucleophilic character of the rhodium center leading to the formaldehyde intermediate (see eq. 3a). The nitrogen base affects the electronic nature of the rhodium either as the ligand, in **5** and **6**, or as the ammonium cation, in **6** and **7**.

The nitrogen base as the ligand to the rhodium atom and the intervention of the tertiary ammonium cation, in the phosphine-free catalyst system, have been suggested previously by us [8]. A recent report on a ruthenium catalyst system by Kiso et al. supports our view [9].

The ligation of the nitrogen base to low valent rhodium has been strongly suggested for the species **4** [5]. However, no direct evidence for ligation of the nitrogen base has been observed for the actual catalyst solution. In light of the observed relationship between selectivity to ethylene glycol and pK_a value of the nitrogen base, but not the ease of its ligation to the rhodium center (vide supra), further ligation of the nitrogen base is not essential in the phosphine-ligated rhodium catalyst. In other words, the species **7**, one of the possible rhodium hydrides in Scheme 1, seems to be most closely related to the active catalytic species.

The generation of the tertiary ammonium cation is accompanied by formation of the mononuclear anionic rhodium species. It is expected that the anionic rhodium species, like **7**, as compared with the neutral or cationic rhodium species, has the greater tendency to interact with the carbonyl carbon atom of the formaldehyde intermediate (eq. 3a). The observed relationship between selectivity to ethylene

Table 2

Syngas reaction with mononuclear rhodium complexes

Catalyst	(mmol)	PR_3	(mmol)	Additive	(mmol)	TOF [a]	
						EG	MeOH
$PPN^+Rh(CO)_4^-$	(0.5)	–	–	–	–	0.0	0.0 [b]
$PPN^+Rh(CO)_4^-$	(0.5)	P-i-Pr_3	(0.5)	–	–	0.0	0.0 [b]
$PPN^+Rh(CO)_4^-$	(0.5)	P-i-Pr_3	(0.5)	1-Me–ImH^+OTs^-	0.5	7.6	10.4 [b]
$PPN^+Rh(CO)_4^-$	(0.1)	–	–	–	–	0.0	0.0 [c]
$PPN^+Rh(CO)_4^-$	(0.1)	P-n-Bu_3	(1.0)	–	–	0.0	0.0 [c]
$PPN^+Rh(CO)_4^-$	(0.1)	P-n-Bu_3	(1.0)	1-Me–ImH^+OTs^-	0.1	1.1	43.3 [c]
$PPN^+Rh(CO)_4^-$	(0.1)	PPh_3	(0.1)	–	–	0.0	0.0 [c]
$PPN^+Rh(CO)_4^-$	(0.1)	PPh_3	(0.1)	1-Me–ImH^-OTs^-	0.1	0.0	0.0 [c]

[a] mol(g-atom·Rh)$^{-1}$ h^{-1}. [b] TGM, 10 ml; 47 MPa, H_2/CO (1/1); 220 °C, 2 h. [c] DMI, 10 ml; 47 MPa, H_2/CO (1/1); 240 °c, 2 h. Abbreviations: PPN, bis(triphenylphosphine)iminium; 1-Me–Im, 1-methylimidazole; OTs, toluene-*p*-sulphonate; EG, ethylene glycol.

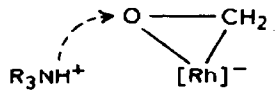
glycol and pK_a value of the nitrogen base must be a reflection of the electronic nature of the anionic rhodium species thus formed.

The tertiary ammonium cation also releases its own hydrogen to the carbonyl oxygen atom of the formaldehyde intermediate to form the hydroxylmethylrhodium species in eq. 3a. This situation can be illustrated by the following separate experiments. The simple mononuclear rhodate complexes with a quaternary ammonium cation, $PPN^+[Rh(CO)_4]^-$, were found to be totally inactive. Introduction of a tertiary ammonium salt, such as 1-methylimidazolium tosylate (1-Me–ImH^+OTs^-), to the inactive rhodate solution leads to significant catalytic activity to give ethylene glycol, probably due to the formation of **7a** (R; n-Bu, i-Pr, t-Bu, and cyclohexyl) via a cation exchange reaction (eq. 4) (Table 2).

$$PPN^+[Rh(CO)_3PR_3]^- + \text{1-Me–}ImH^+OTs^- \rightleftharpoons \underset{\textbf{(7a)}}{\text{1-Me–}ImH^+[Rh(CO)_3PR_3]^+} + PPN^+OTs^- \qquad (4)$$

At nearly the same time that our patent on this work [3] was disclosed, Chan et al. reported the isolation and characterization of the anionic rhodium complexes such as $[Rh(CO)_3L]^-$ and $[Rh(CO)_2L_2]^-$ ($L = PPh_3$) [10]. They proposed these complexes as key species for the hydroformylation of formaldehyde. However, in contrast to the trialkylphosphine complexes, neither $PPN^+[Rh(CO)_3PPh_3]^-$ itself nor a combination of $PPN^+[Rh(CO)_3PPh_3]^-$ and 1-Me–ImH^+OTs^- showed any catalytic activity in syngas conversion to ethylene glycol (Table 2). A similar lack of catalytic activity has been observed for the Rh/PPh_3/DMI system [1a]. This result is ascribed to the inadequate electronic and steric properties of the PPh_3 ligand [1b]. For the Rh/trialkylphosphine/amine system, we assume the complex **7**, bearing a tertiary ammonium cation, to be the species most closely related to the active species.

However, overestimation of the interaction between the tertiary ammonium cation and the carbonyl oxygen atom in the transition state has been avoided. As has been mentioned already, the more basic amine, which may produce the less-acidic



tertiary ammonium cation, BH^+, results in the higher selectivity to ethylene glycol. Therefore, we do not agree with the idea of simple proton transfer [11] or the proposal of "amine-promoted" proton transfer [12], from rhodium to formaldehyde in the intermediate.

Experimental

All operations were carried out under dry argon or carbon monoxide. 1,3-Dimethyl-2-imidazolidinone (DMI), tetraethylene glycol dimethylether (TGM), P-n-Bu_3 and nitrogen bases were purchased from the Tokyo Kasei Kogyo Co., and used as received. $Rh(CO)_2$acac and P-i-Pr_3 were purchased from the Strem Chemicals Inc. $PPN^+[Rh(CO)_4]^-$ was prepared according to the literature [11].

Infrared spectra were recorded on a Shimadzu infrared spectrophotometer IR-435 and calibrated against a polystyrene standard. NMR spectra were recorded on a JEOL-GX270 FT NMR spectrometer.

A general procedure of syngas reactions

Into a Hastelloy C autoclave (35 cm^3), containing acetylacetonatobis(carbonyl) rhodium, $Rh(CO)_2$acac, trialkylphosphine, PR_3, nitrogen base and solvent was introduced syngas ($H_2/CO = 1/1$) up to a pressure of 29.4 MPa at room temperature. The autoclave was heated to 220 °C, whereupon the reactor pressure reached 47.0 MPa. The pressure was maintained at 47.0 MPa and the reaction was continued for 2 h. After it had been cooled to room temperature, the autoclave was vented to atmospheric pressure and the liquids were analyzed by gas chromatography (10% PEG20M TPA, Chromosorb 102, 1 m, FID).

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