

### Preliminary communication

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## A NEW CATALYST FOR THE DIRECT SYNTHESIS OF ETHYLENE GLYCOL FROM CARBON MONOXIDE AND HYDROGEN

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### Summary

Bulky alkylphosphines (with large cone angles around the P atom), such as P-*i*-Pr<sub>3</sub> (L), prominently enhance the activity and the stability of the rhodium carbonyl catalyst in the direct synthesis of ethylene glycol from carbon monoxide and hydrogen. Arylphosphines, alkyl- and aryl-phosphites and also alkylphosphines with small cone angles, such as P-*n*-Bu<sub>3</sub>, all decompose to form the phosphido-carbonyl cluster anion, [Rh<sub>9</sub>P(CO)<sub>21</sub>]<sup>2-</sup> and hence inhibit the catalysis.

High pressure IR analysis indicates that HRh(CO)<sub>3</sub>L, rather than anionic rhodium carbonyl clusters, plays an important role in the formation of ethylene glycol. Thus 0.3 mg-atom of Rh<sub>4</sub>(CO)<sub>12</sub> and 0.3 mmol of P-*i*-Pr<sub>3</sub> in 7.5 ml of 1-methyl-2-pyrrolidinone were allowed to react at 220°C in an autoclave and under 450 kg cm<sup>-2</sup> H<sub>2</sub>/CO pressure for 3 h. Turn-over frequencies for ethylene glycol and methanol were 6.2 and 4.3, respectively, and selectivity was 58.8%.

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We wish to report our finding [1] that the addition of alkylphosphines, with large cone angles, such as triisopropylphosphine, prominently enhance the activity and the stability of the rhodium carbonyl catalyst in the direct synthesis of ethylene glycol (EG) from synthesis gas [2]. Union Carbide Corp. pioneered work in this field [3]. Their discovery that the anionic rhodium carbonyl cluster are effective for this reaction attracted much attention.

One of the most attractive features of the homogeneous transition metal catalyst is the possibility that its activity and selectivity may be modified by the addition of coordinating ligands. Modification of the rhodium catalyst by phosphines has been successfully applied to a variety of catalytic synthesis including hydroformylation of olefins. The Rh/PPh<sub>3</sub> system was also reported to be effective for the hydroformylation of formaldehyde to give glycol aldehyde, which is considered to be a key step in forming EG directly from CO and H<sub>2</sub> [4]. Furthermore, we recently reported that some phosphine ligands, including PPh<sub>3</sub>, have positive effects on the iridium

TABLE 1  
EFFECT OF PHOSPHORUS COMPOUNDS ON RHODIUM CATALYST <sup>a</sup>

Phosphine	Minimum cone angle (°)	<i>N</i> <sup>b</sup>		Selectivity <sup>c</sup> (%)
		EG	MeOH	
None	—	1.52	4.16	26.7
P- <i>i</i> -Pr <sub>3</sub>	160	6.19	4.34	58.8
P- <i>s</i> -Bu <sub>3</sub>	160	3.78	8.31	31.3
P(cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	170	3.73	3.13	54.4
P- <i>t</i> -Bu <sub>3</sub>	182	3.43	0.93	78.7
P- <i>n</i> -Bu <sub>3</sub>	132	0.30	0.51	37.1
PPh <sub>3</sub>	145	0.0	0.0	—
P( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	194	0.0	0.0	—
P( <i>n</i> -BuO) <sub>3</sub>	109	0.0	0.0	—
P(PhO) <sub>3</sub>	128	0.0	0.0	—

<sup>a</sup> A 30-ml Hastelloy C-276 autoclave was charged with 0.3 mg-atom Rh<sub>4</sub>(CO)<sub>12</sub>, 0.3 mmol phosphorus compound and 7.5 ml 1-methyl-2-pyrrolidinone. Synthesis gas (H<sub>2</sub>/CO 1/1) was then introduced and the autoclave heated at 220 °C for 3 h with shaking. The maximum pressure reached during the reaction was about 450 kg cm<sup>-2</sup>. The products were analyzed by GLC. <sup>b</sup> *N* = turn-over frequency: mol/g-atom Rh/h. <sup>c</sup> EG/(EG + MeOH).

catalyst in the direct synthesis of EG [5]. It is believed, however that phosphines have an inhibitive effect on direct synthesis of EG by rhodium catalysts, since it was reported that, at the temperature, and under the pressure necessary for EG formation, rhodium carbonyl complexes react readily with PPh<sub>3</sub> to form a phosphido-carbonyl cluster anion, [Rh<sub>9</sub>(CO)<sub>21</sub>]<sup>2-</sup>, which is hardly active for the formation of EG [6].

Based on the hypothesis that the phosphorus ligands might work effectively as far as they may remain intact under the reaction conditions, we thoroughly investigated different kinds of phosphorus compounds. This led to the discovery that bulky alkylphosphines (with large cone angles around P [7]) characteristically enhance activity and selectivity. Contrary to this, arylphosphines, alkyl- and aryl-phosphites, and also alkylphosphines with small cone angles, such as P-*n*-Bu<sub>3</sub>, are all found to inhibit the reaction. The results are summarized in Table 1. Arylphosphines, even when they are as bulky as P-*o*-tolyl<sub>3</sub> or P-*o*-anisyl<sub>3</sub> only inhibited the reaction. Among the bulky alkylphosphines P-*i*-Pr<sub>3</sub> showed the highest activity, while P-*t*-Bu<sub>3</sub> gave the best selectivity. The optimum P/Rh ratio for the bulky alkylphosphines were found to be between 0.5 and 2. Amides such as 1-methyl-2-pyrrolidinone and 1,3-dimethyl-2-imidazolidinone were found to be the best solvents for this reaction.

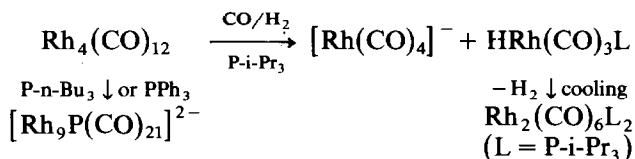
A high pressure IR study revealed the following \*. At 150–180 °C and 170–180 atm the Rh/P-*n*-Bu<sub>3</sub> catalyst gave a single carbonyl band at 2010 cm<sup>-1</sup>, which corresponds to the characteristic absorption [6] \*\* of [Rh<sub>9</sub>P(CO)<sub>21</sub>]<sup>2-</sup>. The Rh/P-*i*-Pr<sub>3</sub> gave bands at 1900 and 1980 cm<sup>-1</sup>. Of these two, 1900 cm<sup>-1</sup> was identified as the absorption by [Rh(CO)<sub>4</sub>]<sup>-</sup> [8] \*\*\*. When cooled, the band at 1980 cm<sup>-1</sup> shifted

\* The IR spectra were recorded by a Hitachi 270-30 IR spectrometer using a heated high-pressure liquid cell with a CaF<sub>2</sub> window directly connected to an autoclave.

\*\* The same spectrum was observed when the phosphine was PPh<sub>3</sub>.

\*\*\* A single absorption at 1900 cm<sup>-1</sup> was observed when phosphorus compound was absent.

to 1950  $\text{cm}^{-1}$  which coincides with the characteristic absorption of binuclear  $\text{Rh}_2(\text{CO})_6(\text{P-i-Pr}_3)_2$  [9]. As the behavior of the corresponding iridium complexes [10] is analogous to that of rhodium the species with absorption at 1980  $\text{cm}^{-1}$  was assigned to  $\text{HRh}(\text{CO})_3\text{P-i-Pr}_3$ . Above inferences are summarized in the following equations:



The degree of difficulty with which the inactive phosphidocarbonyl cluster anion is formed increases in the order  $\text{PPh}_3 < \text{P-n-Bu}_3 \ll \text{P-i-Pr}_3$ , coinciding with the increasing order of the catalytic activity.

Based on all these observations, it was concluded that the mononuclear rhodium complex coordinated by a bulky alkylphosphine plays an important role in the formation of EG, rather than the anion clusters\*.

At about the same time our discovery was made Watanabe et al. found that addition of a very large excess of  $\text{P-n-Bu}_3$  to the rhodium catalyst also enhances the hydrogenation of CO [12]. They also studied the dependence on their electronic nature [13] of trialkyl- and tricycloalkyl-phosphines. Details of the effect of these phosphines call for further studies.

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\* Participation of mononuclear rhodium complex was also noted in the case of  $\text{Rh}_4(\text{CO})_{12}/1\text{-methyl-2-pyrrolidinone}$  system [11].

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