The Direct Conversion of Synthesis Gas into Ethylene Glycol catalysed by $RhX(CO)L_2$ [X = Anionic Ligand, L = $P(cyclo\text{-}C_6H_{11})_3$ or PPr^i_3]

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Higher catalytic activities have been found for $RhX(CO)L_2$ complexes compared to the $Rh_4(CO)_{12}$–L system (molar ratio L : Rh 2:1) for the formation of ethylene glycol from synthesis gas.

The direct conversion of synthesis gas into ethylene glycol is known to be catalysed by rhodium.[1—3] High catalytic activities have been found using trialkylphosphine species, such as tri-isopropylphosphine in 1-methylpyrrolidin-2-one or 1,3-dimethylimidazolidin-2-one (DMI) solvents,[4,5] the complex recovered from the reaction solution being $[Rh(CO)_3L]_2$ [L = PPr^i_3 or $P(cyclo\text{-}C_5H_9)_3$].[6] These compounds are stable only under a CO atmosphere and decompose even under N_2 or in the solid state.[7] The catalyst must be recoverable in a stable form for re-use, however $RhX(CO)L_2$ complexes are very stable in air even at elevated temperatures,[8] but it has not yet been determined whether or not $RhX(CO)L_2$ is recovered after treatment with high pressures of synthesis gas at high temperatures.

We examined the direct conversion of synthesis gas into ethylene glycol catalysed by $RhX(CO)L_2$ [L = $P(cyclo\text{-}C_6H_{11})_3$ or PPr^i_3].† The reaction was carried out under synthesis gas pressures of 54—51 MPa (CO : H_2 1 : 1) at 220 °C for 1 h using 0.1 mmol of the rhodium complex in 5 cm^3 of DMI or tetraglyme (TGM) solvent. Rates of formation of ethylene glycol and methanol are shown in Table 1, together with comparative data for $Rh_4(CO)_{12}$–L (Rh–L). Unexpectedly, the arylcarboxylato (**1**)—(**6**) and pentafluorophenolato (**7**) complexes are more active precursors compared to the

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† All $RhX(CO)L_2$ were prepared from $Rh_4(CO)_{12}$, L, and HX, and gave satisfactory analyses.

Table 1. Catalytic activities of $RhX(CO)L_2$[a] and initial reduction rate of the complexes under synthesis gas.[b]

		Solvent				Reduction
		DMI		TGM		rate/
Complex	X[c]	N(EG)[d]	N(MeOH)[d]	N(EG)[d]	N(MeOH)[d]	$10^3 \times min^{-1}$
(1)	$PhCO_2$	24.60	20.80	8.32	23.21	17.16
(2)	$4\text{-}HO_2CC_6H_4CO_2$	20.93	28.36	3.61	28.40	11.73
(3)	$4\text{-}HO_2CC_6H_4CO_2$	19.23	28.61	5.47	23.22	12.40
(4)	$3\text{-}FC_6H_4CO_2$	18.30	30.65	6.14	24.38	12.73
(5)	$4\text{-}O_2NC_6H_4CO_2$	17.16	30.01	6.79	23.31	9.87
(6)	$3\text{-}FC_6H_4CO_2$	14.12	42.40	3.85	35.67	8.00
(7)	C_6F_5O	11.49	37.53	2.68	30.78	6.80
(8)	$p\text{-}MeC_6H_4SO_3$	0.24	0.45	1.30	26.34	0
(9)	—[e]	7.09	43.41	0.90	17.36	—
(10)	—[e]	8.81	30.42	0	1.33	—

[a] [Rh] = 0.02 M, 5 cm^3 solvent, CO/H_2 (1 : 1) 54—51 MPa, 220 °C, 1 h. [b] [Rh] = 0.02 M, solvent (HMPT) 5 cm^3, CO/H_2 (1 : 1) 1 atmosphere, 20 °C. [c] L = $P(cyclo\text{-}C_6H_{11})_3$ for all complexes except **(6)** and **(10)** (L = PPr^i_3). [d] Turnover number (h^{-1}) for ethylene glycol (EG) or methanol (MeOH). [e] $Rh_4(CO)_{12}$ and L were employed (L : Rh = 2 : 1) instead of $RhX(CO)L_2$.

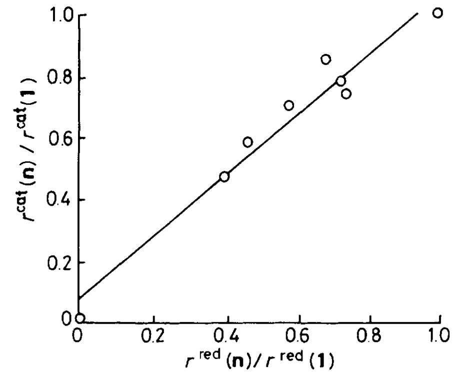

Figure 1. Relationship between the relative rate of ethylene glycol formation and the relative initial rate of reduction of $RhX(CO)L_2$, r^{cat}(**n**)/r^{cat} (**1**) and r^{red}(**n**)/r^{red} (**1**) respectively. For reaction conditions, see footnote b in Table 1.

Rh–L system. The highest rate and selectivity for ethylene glycol are achieved by the use of complex **(1)**. The rate increases with decreasing basicity of the phosphines **(4)** and **(6)**. The order of the catalytic activities and selectivities are considered to depend on the electronic and the steric nature of X. From a reaction solution of 0.5 mmol of **(4)** in TGM, the starting complex is recovered (*ca.* 70%) as yellow crystals on standing overnight in air at 0 °C.

$[Rh(CO)_3P(cyclo\text{-}C_6H_{11})_3]_2$ **(11)**

$Rh(CO)_4^-$ **(12)**

$HRh(CO)_2[P(cyclo\text{-}C_6H_{11})_3]_2$ **(13)**

$Rh(CO)_3L^-$ **(14)**

The i.r. spectrum of a solution of **(1)** in DMI or TGM under a synthesis gas pressure of 28 MPa at room temperature was examined. Rhodium species are identified mainly as $[Rh(CO)_3P(cyclo\text{-}C_6H_{11})_3]_2$ **(11)** (1952s cm^{-1}) and $Rh(CO)_4^-$ **(12)** (1900s cm^{-1})[9] in DMI. Weak bands at 2041 and 1972 cm^{-1} assignable to $HRh(CO)_2[P(cyclo\text{-}C_6H_{11})_3]_2$ **(13)**[10] are also observed. Complexes **(11)** (1955s cm^{-1}) and **(13)** (2041w, 1972m, and 1944w, sh cm^{-1}) are also formed in TGM. No absorptions due to **(1)** are observed in either solution. Rhodium exists in the form of **(1)** under N_2 at 1 atmosphere (a single band at 1942 cm^{-1} in DMI or at 1944 cm^{-1} in TGM). Only species **(11)** and **(12)** (in DMI) or **(11)** (in TGM) are found in the reaction solutions with the Rh–$P(cyclo\text{-}C_6H_{11})_3$ system under either N_2 or synthesis gas.

The complexes $RhX(CO)L_2$, except for the toluene-*p*-sulphonato complex **(8)**, are reduced to **(12)** under synthesis gas at 1 atmosphere in hexamethylphosphoric triamide (HMPT) at room temperature. Initial reduction rates‡ are shown in Table 1. The reduction is suppressed and small amounts of $Rh(CO)_3L^-$ **(14)** (1841 cm^{-1}) are formed on addition of excess of L or in the presence of $[(PPh_3)_2N]OAc$. The anion **(14)** is one of the plausible intermediates. The other possible intermediate, $HRh(CO)_2L_2$, is known for L = PPh_3,[11] and can be generated by the reduction of $Rh(3\text{-}FC_6H_4CO_2)(CO)(PPh_3)_2$.§ On the other hand, no analogous rhodium hydride species are detected in the i.r. spectra of the reduction products of either $P(cyclo\text{-}C_6H_{11})_3$ or PPr^i_3 complexes. This intermediate is stable under high pressures as described above, but it is known to be unstable under atmospheric pressure.[7] Thus the intermediate is rapidly converted into **(12)** under the reduction conditions. The reduction is reversible, and by allowing reduced solutions to stand under N_2, the starting complexes $RhX(CO)L_2$ can be recovered.

In Figure 1, the ordinate represents the relative rate of ethylene glycol formation catalysed by $RhX(CO)L_2$ in DMI [r^{cat}(**n**)/r^{cat} (**1**)] and the abscissa is the relative initial rate of the reduction of $RhX(CO)L_2$ [r^{red}(**n**)/r^{red} (**1**)]. A linear relationship between the two relative rates is found, with a slope of 0.997 and a correlation coefficient of 0.979. As the i.r. spectra of the synthesis gas reaction solutions could not be measured at elevated temperatures, we cannot conclude that the observed rhodium compounds are the active species, but the relationship in Figure 1 suggests that the rhodium hydride species, which may be formed by the reduction of $RhX(CO)L_2$ under an atmospheric pressure of synthesis gas, play an important role in ethylene glycol formation.

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‡ Determined from the decrease in $\nu_{max.}$ (CO) intensities.

§ $\nu_{max.}$ (Rh–H) 2039w; $\nu_{max.}$ (CO), 1989s sh, 1942s cm^{-1}; δ (Rh–H) −9.5 p.p.m.

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