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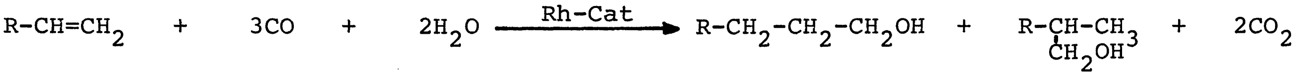
HIGHLY ACTIVE $Rh_6(CO)_{16}$-Diamine CATALYST SYSTEMS FOR ALCOHOL SYNTHESIS FROM OLEFINS USING CARBON MONOXIDE AND WATER

Kiyotomi KANEDA, Morito YASUMURA, Masahiko HIRAKI, Toshinobu IMANAKA, and Shiichiro TERANISHI
Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

α-Olefins are carbonylated to give corresponding alcohols under mild water gas shift reaction (WGSR) conditions using $Rh_6(CO)_{16}$-N,N,N',N'-tetramethyl-1,3-propanediamine and 4-dimethylaminopyridine catalyst systems. α,β-Unsaturated carbonyl compounds give selectively C=C reduction products.

We have recently found that addition of some kind of amines and pyridines to rhodium carbonyl clusters gave high catalytic activities for WGSR[1] and nitrobenzene reduction[2] using CO + H_2O. It is interesting that the amine effectiveness in the WGSR is quite different from that in the reduction. In the application of the WGSR to organic synthseis, we now wish to report that the systems of $Rh_6(CO)_{16}$-N,N,N',N'-tetramethyl-1,3-propanediamine and 4-dimethylaminopyridine are excellent catalysts for hydrohydroxymethylation reaction of olefins using CO + H_2O under mild conditions. Compared with the conventional oxo reaction, the present reaction using CO + H_2O must be potentially important because similar products can be obtained without the direct use of molecular hydrogen.[3]



$$R\text{-}CH{=}CH_2 \quad + \quad 3CO \quad + \quad 2H_2O \xrightarrow{\text{Rh-Cat}} R\text{-}CH_2\text{-}CH_2\text{-}CH_2OH \quad + \quad R\text{-}\underset{CH_2OH}{CH}\text{-}CH_3 \quad + \quad 2CO_2$$

A general reaction procedure is as follows. Rhodium compound, olefin, H_2O, amine, and ethoxyethanol were successively weighed into a stainless autoclave. The reaction system (120 ml) was flushed three times with CO and then charged at room temperature to an initial CO pressure of 5 atm. The vessel was heated with stirring at 80°C. After an appropriate time, gas and liquid phases were analyzed by gas chromatography.

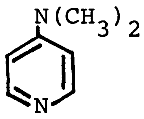
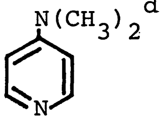
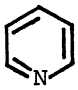
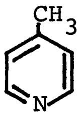
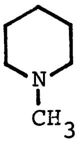
Representative examples of 1-octene using $Rh_6(CO)_{16}$ are shown in Table. The effectiveness of additives is similar to that in the nitrobenzene reduction.[2] N,N,N',N'-Tetramethyl-1,3-propanediamine and 4-dimethylaminopyridine are the best additives for the hydrohydroxymethylation among the amines and pyridines examined. Under mild conditions, e.g., initial CO pressure of 5 atm and 80°C, isomeric C-9 alcohols were obtained from 1-octene in high yield.[4] In a separated experiment, nonanal was completely converted to nonanol under the same conditions as above olefin reactions. In the case of 4-dimethylaminopyridine, the choice of its suitable concentrations attained the selective formation of the C_9-aldehydes or alcohols;[5] using 1.5 mmol of the pyridine (run 4), the aldehydes were exclusively obtained at slow reaction rate, while under higher concentrations, the formation of alcohols was observed during an initial stage of the reaction and the yield reached 80% after 10 h (run 3). Et_3N is not a good additive. Pettit and Laine have used KOH as an additive in hydroformylation of lower olefins with metal carbonyl catalysts.[3b,3c] Under the present reaction conditions, however, addition of KOH facilitated the double bond isomerization and led to low yield of carbonylation products (run 9). Similarly, in the conventional oxo reaction using rhodium catalysts, various amines as additives strongly influence yields of aldehydes and alcohols.[6] But the catalyst system of $Rh_6(CO)_{16}$-diamine gave a low yield of aldehydes under 5 atm of CO and H_2 (1:1) at 80°C.

$$n\text{-}C_8H_{17}\text{-}CHO \quad + \quad CO \quad + \quad H_2O \xrightarrow{\text{Rh-Cat}} n\text{-}C_8H_{17}\text{-}CH_2OH \quad + \quad CO_2$$

In this reaction, a $Rh_6(CO)_{16}$ cluster compound shows the highest catalytic activity among the rhodium compounds examined; $Rh_6(CO)_{16}$ (80% of carbonylation products) > $Rh_4(CO)_{12}$ (65%) > $Rh_2(CO)_4Cl_2$ (46%) > $RhCl(PPh_3)_3$ (29%) > $RhCl_3 \cdot 3H_2O$ (28%)

Other α-olefins can be easily carbonylated by using the present catalysts; that is, the reaction of 1-hexene using the diamine gave a 85% yield of corresponding alcohols in 5 h. But in the case of α,β,-unsaturated carbonyl compounds, cinnamaldehyde and mesityl oxide, their olefinic double bonds were selectively reduced giving no carbonylation products. Even at pressure below 1 atm of CO, the reduction occurred.[7]

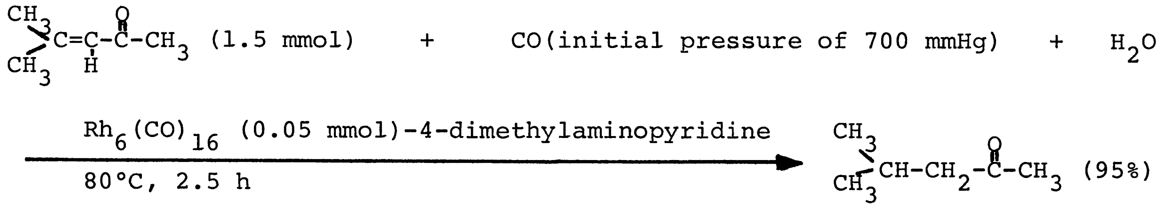
Table. Oxo Reaction of 1-Octene with CO and H_2O Catalyzed by $Rh_6(CO)_{16}$ in the Presence of Various Additives[a]

Run	Additive (pKa)	Product selectivity (%)[b]		2-Octene	Total conversion (%)
		$C_8H_{17}CH_2OH$ (normal/iso)	$C_8H_{17}CHO$ (normal/iso)		
1	$(CH_3)_2N(CH_2)_3N(CH_3)_2$ (10.2)	84(2.8)	0	16	95
2	$(CH_3)_2N(CH_2)_2N(CH_3)_2$ (8.97)	58(4.8)	26(1.9)	16	88
3[c]	 (9.70)	83(1.6)	1	16	97
4	 [d]	0	89(3.9)	11	62
5	 (5.17)	0	39(2.6)	60	53
6	 (6.02)	0	50(2.9)	50	54
7	 (10.1)	43(4.4)	18(2)	39	66
8	Et_3N (10.65)	9(3.5)	4(2)	86	42
9	KOH[d]	24(3.8)	10(2.3)	63	59

[a] Reaction conditions: 1-octene, 3 mmol; $Rh_6(CO)_{16}$, 0.05 mmol; additive, 15 mmol; H_2O, 40 mmol; ethoxyethanol [3-(volume of amine)] ml; initial P_{CO}, 5 atm; temperature, 80°C; reaction time, 5 h.

[b] Trace amounts of octane ($<$ 1%) were observed. In the case of KOH (run 9), a 2% yield of octane was formed.

[c] Reaction time, 10 h. [d] Additive, 1.5 mmol.



$$\overset{CH_3}{\underset{CH_3}{>}}C=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-CH_3\ (1.5\ \text{mmol})\ +\ CO(\text{initial pressure of 700 mmHg})\ +\ H_2O\ \xrightarrow[80°C,\ 2.5\ h]{Rh_6(CO)_{16}\ (0.05\ \text{mmol})\text{-4-dimethylaminopyridine}}\ \overset{CH_3}{\underset{CH_3}{>}}CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\ (95\%)$$

The catalyst systems have high activities not only for carbonylation of olefins, but also for reduction of aldehydes. So, this hydrohydoxymethylation reaction provides a convenient alcohol synthesis from olefins. We are currently investigating the scope of this reaction with various olefins.

References

1) K. Kaneda, M. Hiraki, K. Sano, T. Imanaka, and S.Teranishi, J. Mol. Catal., 1980, 9, 227.

2) K. Kaneda, M. Hiraki, T. Imanaka, and S. Teranishi, J. Mol. Catal., 1981, 12, 385.

3) Concerning the oxo reaction using CO + H_2O, cf. a) W. Reppe and H. Vetter, Justus Liebigs Ann. Chem., 1953, 582, 133; b) H. C. Kang, C. H. Mauldin, T. Cole, W. Slegeir, K. Kann, and R. Pettit, J. Am. Chem. Soc., 1977, 99, 8323; c) R. W. Laine, J. Am. Chem. Soc., 1978, 100, 6451; d) K. Murata, A. Matsuda, K. Bando, and Y. Sugi, J. Chem. Soc., Chem. Commun., 1979, 785; d) K. Murata, A. Matsuda, Bull. Chem. Soc. Jpn., 1981, 54, 245, 249; e) T. Okano, T. Kobayashi, H. Konishi, and J. Kiji, Shokubai, 1981, 23(No.1),54.

4) In the course of the reaction, trace amounts of H_2 could be detected.

5) It seems that strong basicity of a reaction medium is favorable to the reduction of carbonyl compounds to alcohols.

6) A. T. Jurewicz, L. D. Rollmann, and D. D. Whitehurst, Advan. Chem. Ser., 1974, 132, 240.

7) Joh reported that the reaction of α,β-unsaturated carbonyl compounds using $Rh_6(CO)_{16}$-Et_3N gave reduction products of olefinic double bonds under 100 atm of CO. T. Kitamura, N. Sakamoto, and T. Joh, Chem. Lett., 1973, 379.

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