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High catalytic activity of $[HRu(CO)_4]^-$ for hydroformylation of olefins

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Abstract

Comparison of the catalytic activity of $[HRu(CO)_4]^-$ with those of the known catalyst systems ($[HRu_3(CO)_{11}]^-$ and $Ru_3(CO)_{12}$) has revealed that $[HRu(CO)_4]^-$ is an active catalyst for hydroformylation of 1-pentene, styrene, and ethyl acrylate. $[HRu(CO)_4]^-$ partly reduces the aldehydes initially formed into their corresponding alcohols. In the reaction of ethyl acrylate catalyzed by $[HRu(CO)_4]^-$ or $[HRu_3(CO)_{11}]^-$, significant amounts of carbonylative dimers (diethyl 2-formyl-2-methylglutarate and 4-ethoxycarbonyl-4-methyl-δ-valerolactone) were also formed.

Introduction

The hydroformylation of olefins is one of several important industrial processes that is carried out in the presence of homogeneous complex catalysts [1]. Since cobalt and rhodium complexes with or without phosphine ligands have been used as the industrial catalysts, their catalytic performance has been the subject of extensive investigation [2,3]. On the other hand, ruthenium complexes have attracted relatively little attention though they have been known to catalyze the reaction. Earlier papers reported on the reactions in the presence of neutral ruthenium carbonyl or phosphine complexes [4]. Recent trends in the use of ruthenium catalysts, however, feature the use of anionic ruthenium complexes such as $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_3(CO)_{11}]^-$ [5].

In our previous paper on the homogeneous hydrogenation of carbon monoxide, we reported the successful in situ generation of $[HRu(CO)_4]^-$ and its superiority over $[HRu_3(CO)_{11}]^-$ as a reductant at several elementary steps involved in the hydrogenation of carbon monoxide [6]. Our continued investigation has confirmed that $[HRu(CO)_4]^-$ is an active catalyst for the hydroformylation of olefins. Basic characteristics of $[HRu(CO)_4]^-$ as a hydroformylation catalyst and a comparison of its catalytic activity with those of $Ru_3(CO)_{12}$ and $[HRu_3(CO)_{11}]^-$ are described herein.

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Results and discussion

As shown previously [6], $[HRu(CO)_4]^-$ is stable in amide solvents. Accordingly, we examined the reaction of 1-pentene, styrene, and ethyl acrylate in DMF. The results of the comparison of the catalysis by $[HRu(CO)_4]^-$ with those of the known catalyst systems ($[HRu_3(CO)_{11}]^-$ and $Ru_3(CO)_{12}$) are listed in Tables 1–3.

Hydroformylation of 1-pentene

At 150 °C, $[HRu(CO)_4]^-$ actively promoted hydroformylation of 1-pentene. Its catalytic activity was nearly the same as that of $[HRu_3(CO)_{11}]^-$, and the selectivity to carbonylation was slightly higher. As was anticipated from its strong reduction ability [6], a small amount of hexanol was also formed. In addition, undesirable isomerization to less-reactive *cis*- and *trans*-2-pentene was not extensive. Although $Ru_3(CO)_{12}$ appeared to be the most active of the three catalysts, the selectivity to carbonylation was very low owing to extensive isomerization to 2-pentenes, thus proving it to be not a productive catalyst for hydroformylation of 1-olefins.

When the reactions were carried out at 100 °C, the isomerization to 2-pentenes was found to be the main reaction, irrespective of the structure of the catalysts. Nevertheless, the superior selectivity of $[HRu(CO)_4]^-$ towards carbonylation was clear. Both $[HRu_3(CO)_{11}]^-$ and $Ru_3(CO)_{12}$ were more active than $[HRu(CO)_4]^-$, but 2-pentenes comprised more than 75% of the product.

The IR spectra of the reaction solutions showed that $[HRu(CO)_4]^-$ (2010, 1932, and 1888 cm^{-1}) and $[HRu_3(CO)_{11}]^-$ (2075, 2020, 1992, and 1954 cm^{-1}) had not been altered during reaction. In the $Ru_3(CO)_{12}$-catalyzed reaction at 100 °C, the ruthenium species present in the mixture after the reaction was $Ru_3(CO)_{12}$ (2050, 2010, and 1990 cm^{-1}), but at 150 °C, $Ru_3(CO)_{12}$ was transformed into $[HRu_3(CO)_{11}]^-$.

Hydroformylation of styrene

As shown in Table 2, $[HRu(CO)_4]^-$ was the most active species for the reaction of styrene at 150 °C. Because $[HRu(CO)_4]^-$ is strongly reducing, the aldehydes

Table 1

Effect of catalyst on the hydroformylation of 1-pentene [a]

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			
			C_6-aldehydes (Linearity [b])	C_6-alcohols (Linearity [c])	Pentane	2-Pentenes
$PPN[HRu(CO)_4]$	150	90.5	61.7 (90.1)	2.9 (93.9)	3.6	15.4
$PPN[HRu_3(CO)_{11}]$	150	90.8	60.6 (94.8)	0.1 (100)	2.2	22.8
$Ru_3(CO)_{12}$	150	94.3	42.7 (84.9)	0.8 (94.9)	5.9	32.1
$PPN[HRu(CO)_4]$ [d]	100	39.3	30.6 (92.0)	1.3 (100)	1.3	54.6
$PPN[HRu_3(CO)_{11}]$ [d]	100	96.4	3.2 (95.5)	0 (–)	0	93.8
$Ru_3(CO)_{12}$ [d]	100	71.0	20.4 (89.2)	0 (–)	1.6	77.8

[a] Catalyst 0.1 mg-atom Ru; 1-pentene 20 mmol; DMF 10 ml; reaction time 16.5 h; initial pressure of $CO+H_2$ (1/1) 300 atm. [b] 100 × hexanal/(all isomeric C_6-aldehydes). [c] 100 × hexanol/(all isomeric C_6-alcohols). [d] 1-Pentene 5 mmol; DMF 5 ml.

Table 2

Effect of catalyst on the hydroformylation of styrene [a]

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)		
			Phenylpropionaldehydes (Linearity [b])	Phenylpropanols (Linearity [c])	Ethylbenzene
$PPN[HRu(CO)_4]$	150	98.4	43.6 (4.1)	52.3 (6.8)	2.8
$PPN[HRu_3(CO)_{11}]$	150	90.1	75.7 (19.5)	0.4 (–)	3.9
$Ru_3(CO)_{12}$	150	76.3	65.8 (36.8)	0.6 (24.8)	31.0
$PPN[HRu(CO)_4]$	100	9.9	84.4 (6.8)	1.2 (–)	1.2
$PPN[HRu_3(CO)_{11}]$	100	7.1	61.0 (12.0)	0 (–)	1.2
$Ru_3(CO)_{12}$	100	10.2	73.3 (26.0)	0 (–)	7.5

[a] Styrene 20 mmol; DMF 10 ml; other conditions are the same as in Table 1. [b] 100×3-phenylpropionaldehyde/(2-phenylpropionaldehyde + 3-phenylpropionaldehyde). [c] 100 × 3-phenylpropanol/(2-phenylpropanol + 3-phenylpropanol).

initially formed were reduced to the alcohols under the conditions mentioned. The combined selectivity of the aldehydes and alcohols was higher than 95%. Thus, $[HRu(CO)_4]^-$ was the best catalyst also in terms of the carbonylation selectivity. In addition, $[HRu(CO)_4]^-$ was most regioselective for the formation of the branched isomers (2-phenylpropionaldehyde and 2-phenylpropanol). $[HRu_3(CO)_{11}]^-$ also exhibited rather good performance for 2-phenylpropionaldehyde synthesis though the regioselectivity was not very high. By contrast, $Ru_3(CO)_{12}$ was much less selective, and a large amount of ethylbenzene was also formed. The superior performance of $[HRu(CO)_4]^-$ compared with the other two catalysts was also observed at 100 °C.

IR spectral characteristics were the same as those with 1-pentene used as the substrate.

Hydroformylation of ethyl acrylate

$[HRu(CO)_4]^-$ was very active for the hydroformylation of ethyl acrylate. However, the branched aldehyde (ethyl 2-formylpropionate) initially formed (eq. 1)

Table 3

Effect of catalyst on the hydroformylation of ethyl acrylate [a]

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)				
			Ethyl 2-formylpropionate	Ethyl 2-(hydroxymethyl)-propionate	Ethyl propionate	**1** [b]	**2** [c]
$PPN[HRu(CO)_4]$ [d]	100	100	15.0	15.1	23.4	4.5	27.9
$PPN[HRu_3(CO)_{11}]$ [d]	100	100	57.8	0.9	23.4	2.3	0
$Ru_3(CO)_{12}$ [d]	100	100	46.4	1.2	45.4	0.2	0
$PPN[HRu(CO)_4]$	70	90.7	30.9	2.9	15.2	38.2	18.2
$PPN[HRu_3(CO)_{11}]$	70	60.9	67.1	1.9	16.5	26.4	2.6
$Ru_3(CO)_{12}$	70	10.0	60.9	0.3	38.1	0.8	0

[a] Ethyl acrylate 20 mmol; DMF 10 ml; other conditions are the same as in Table 1. [b] Diethyl 2-formyl-2-methylglutarate. [c] 4-Ethoxycarbonyl-4-methyl-δ-valerolactone. [d] Ethyl acrylate 5 mmol; DMF 5 ml.

underwent extensive secondary reactions to give not only ethyl 2-(hydroxymethyl)-propionate arising from the strong reducing ability of $[HRu(CO)_4]^-$ but also diethyl 2-formyl-2-methylglutarate (**1**) and 4-ethoxycarbonyl-4-methyl-δ-valerolactone (**2**). In addition, hydrogenation, to yield ethyl propionate, was also a serious side reaction though not as extensive as the other reactions in the presence of $[HRu_3(CO)_{11}]^-$ or $Ru_3(CO)_{12}$. Ethyl 3-formylpropionate was not formed at all.

$$CH_2{=}CHCOOEt + CO + H_2 \rightarrow CH_3CH(CHO)COOEt + CH_3CH(CH_2OH)COOEt + CH_3CH_2COOEt + EtOOCCH_2CH_2C(COOEt)(CH_3)CHO + \underset{\textbf{(1)}}{} \overline{OCCH_2CH_2C(COOEt)(CH_3)CH_2O} \quad (1)$$
$$\textbf{(2)}$$

Taking account of the mechanism of the formation of **1** and **2** (vide infra), the carbonylation selectivity with $[HRu(CO)_4]^-$ at 100 °C was calculated to be 46.4% (= 15.0 + 15.1 + 4.5/2 + 27.9/2). In this respect, $[HRu(CO)_4]^-$ was on the same level with $Ru_3(CO)_{12}$ (47.7%), but was inferior to $[HRu_3(CO)_{11}]^-$ (59.9%). If we evaluate the catalyst performance from a synthetic viewpoint, $[HRu_3(CO)_{11}]^-$ is the best of the three since, at 100 °C, it afforded the highest selectivity for ethyl 2-formylpropionate without the secondary reactions taking place to a serious extent.

$[HRu(CO)_4]^-$ was the most active of the three at 70 °C. We could not suppress the secondary reactions at this temperature, either. By contrast, the extent of these secondary reactions was more significant at 70 °C than at 100 °C when $[HRu_3(CO)_{11}]^-$ was used as the catalyst. At 70 °C, $Ru_3(CO)_{12}$ was not as active.

IR spectra of the $[HRu(CO)_4]^-$-catalyzed reactions revealed that the species was not stable in the reaction system and was converted into $[HRu_3(CO)_{11}]^-$. Ethyl

Mechanism of the formation of 1 and 2

Two pathways are conceivable for the formation of **1**. One involves the Michael addition of ethyl 2-formylpropionate to the starting material (eq. 2).

$$EtOOCCH{=}CH_2 + CH_3CH(CHO)COOEt \rightarrow \textbf{1} \quad (2)$$

2-Formylpropionate is an active hydrogen compound. At the same time, $[HRu(CO)_4]^-$ is considered to be a strong base as evidenced by its easy proton abstraction from water or methanol (eq. 3) [7]. On the other hand, when the ready protonation of $[HRu_3(CO)_{11}]^-$ with an acid (eq. 4) [8] is taken into account, $[HRu_3(CO)_{11}]^-$ is also considered to be a base though not as strong as $[HRu(CO)_4]^-$.

$$3\,[HRu(CO)_4]^- + 2H^+ \rightarrow [HRu_3(CO)_{11}]^- + 2H_2 + CO \quad (3)$$

$$[HRu_3(CO)_{11}]^- + H^+ + CO \rightarrow Ru_3(CO)_{12} + H_2 \quad (4)$$

In light of these considerations, the Michael addition is very likely to occur in the presence of $[HRu(CO)_4]^-$, or to a lesser extent when $[HRu_3(CO)_{11}]^-$ is present.

The alternative pathway is the sequential occurrence of dimerization of ethyl

acrylate [9] and hydroformylation of the resulting dimer **3** as outlined in eqs. 5 and 6. However, attempted hydroformylation of **3** in the presence of $[HRu(CO)_4]^-$ or

$$2\ CH_2{=}CHCOOEt \rightarrow \underset{\textbf{(3)}}{EtOOCCH_2CH_2C(COOEt){=}CH_2} \quad (5)$$

$$\mathbf{3} + CO + H_2 \rightarrow \mathbf{1} \quad (6)$$

$[HRu_3(CO)_{11}]^-$ resulted in extensive C=C double bond isomerization, and very little **1** was formed. Accordingly, this alternative pathway for **1** is less likely.

The formation of **2** can be ascribed to the reduction of the formyl group in **1** followed by the lactonization.

Experimental

Materials

DMF was distilled under nitrogen. All of the substrates were commercial products and were freshly distilled under nitrogen before use. PPN$[HRu(CO)_4]$ [7] and PPN$[HRu_3(CO)_{11}]$ [10] were prepared as reported. $Ru_3(CO)_{12}$ was used as purchased (Engelhard).

Reaction procedure

A ruthenium complex (0.1 mg-atom Ru) was placed in a 40-ml autoclave made of Hastelloy C. The autoclave was evacuated and filled with nitrogen. DMF (10 ml) and 20 mmol of substrate were introduced by syringe. The autoclave was then pressurized with $CO + H_2$ (1/1) up to 300 atm and was heated in a temperature-controlled oil bath for 16.5 h.

Analysis

Some of the reaction solution was subjected to IR spectroscopy under nitrogen, and the rest was used for GC. IR spectra were recorded on a Hitachi 215 IR spectrometer. NMR spectra were measured on a Hitachi R-40 spectrometer. GC-MS analyses were performed on Shimadzu QP-1000 (EI), JEOL JMC-D300 (CI), and JEOL JMC-DX302 (high resolution) spectrometers.

Diethyl 2-formyl-2-methylglutarate (1). B.p. 135–140 °C/2 torr (Kugelrohr); IR (neat): ν(C(O)H) 2750 and ν(C=O) 1735 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.24 (t, 3H, CH_3CH_2O, J 7 Hz), 1.28 (t, 3H, CH_3CH_2O, J 7 Hz), 1.31 (s, 3H, CH_3C), 2.1–2.35 (m, 4H, CH_2CH_2), 4.13 (q, 2H, CH_3CH_2O, J 7 Hz), 4.22 (q, 2H, CH_3CH_2O, J 7 Hz), and 9.72 ppm (s, 1H, CHO). MS (70 eV): m/z (relative intensity) 185 (28), 156 (28), 128 (79), 99 (84), 55 (90), 43 (44), 41 (38), 29 (100), and 27 (83). MS (CI, isobutane): m/z 231 ($M+1^+$). Found: C, 57.13; H, 7.91. $C_{11}H_{18}O_5$ calcd.: C, 57.38; H, 7.88%.

4-Ethoxycarbonyl-4-methyl-δ-valerolactone (2). B.p. 165–175 °C/2 torr (Kugelrohr). IR (neat): ν(C=O) 1730 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.28 (t, 3H, CH_3CH_2O J 7 Hz), 1.29 (s, 3H, CH_3C), 1.55–2.05 (m, 2H, $OCCH_2CH_2C$), 2.2–2.8 (m, 2H, $OCCH_2CH_2C$), 4.06 and 4.61 (d, 1H each, OCH_2C, J 12 Hz), and 4.21 ppm (q, 2H, CH_3CH_2O, J 7 Hz). MS (70 eV): m/z (relative intensity) 186 (M^+; 2), 158 (10), 130 (12), 128 (13), 113 (14), 99 (32), 69 (31), 55 (38), 41 (50), 29 (100), and 27 (53). MS (CI, isobutane): 187 ($M+1^+$). Found: m/z 186.0913. $C_9H_{14}O_4$ calcd.: M 186.0934.

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References

1 G.W. Parshall, Homogeneous Catalysis, Wiley-Interscience, New York, 1980, Ch. 5.
2 J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, Berlin, 1980, Ch. 1.
3 P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. 2, Wiley-Interscience, New York, 1977, p. 43.
4 (a) D. Evans, J.A. Osborn, F.H. Jardine and G. Wilkinson, Nature, 208 (1965) 1203; (b) D. Evans, J.A. Osborn and G. Wilkinson, J. Chem. Soc., A, (1968) 3133; (c) G. Braca, G. Sbrana, F. Piacenti and P. Pino, Chim. Ind. (Milan), 52 (1970) 1091; (d) H.F. Schultz and F. Bellstedt, Ind. Eng. Chem., Prod. Res. Develop., 12 (1973) 176; (e) R.A. Sanchez-Delgado, J.S. Bradley and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1976) 399; (f) E. Cesarotti, A. Fusi, R. Ugo and G.M. Zanderighi, J. Mol. Catal., 4 (1978) 205; (g) F. Piacenti, G. Menchi, P. Frediani, U. Matteoli and C. Botteghi, Chim. Ind. (Milan), 60 (1978) 808; (h) K. Kurtev, D. Ribola, R.A. Jones, D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1980) 55; (i) C.U. Pittman, Jr. and G.M. Wilemon, J. Org. Chem., 46 (1981) 1901; (j) M. Bianchi, G. Menchi, P. Frediani, U. Matteoli and F. Piacenti, J. Organomet. Chem., 247 (1983) 89; (k) T. Suarez and B. Fontal, J. Mol. Catal., 32 (1985) 191.
5 (a) R.M. Laine, J. Am. Chem. Soc., 100 (1978) 6451; (b) G. Süss-Fink, J. Organomet. Chem., 193 (1980) C20; (c) G. Süss-Fink and J. Reiner, J. Mol. Catal., 16 (1982) 231; (d) G. Süss-Fink and G. Herrmann, J. Chem. Soc., Chem. Commun., (1985) 735; (e) B.H. Chang, U.S. Patent 4506101 (1985) to Ashland Oil, Inc.; Chem. Abstr., 103 (1985) 123000c; (f) R.M. Hanes, U.S. Patent 4633021 (1986) to National Distillers and Chemical Corp.; Chem. Abstr., 106 (1987) 155896c.
6 M. Tanaka, T. Sakakura, T. Hayashi and T. Kobayashi, Chem. Lett., (1986) 39.
7 H.W. Walker and P.C. Ford, J. Organomet. Chem., 214 (1981) C43.
8 J.B. Keister, J. Organomet. Chem., 190 (1980) C36.
9 F.R. Goss and C.K. Ingold, J. Chem. Soc., 127 (1925) 276.
10 B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Süss, J. Chem. Soc., Dalton Trans., (1979) 1356.