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$Ru_3(CO)_{12}$/1,10-phenanthroline-catalyzed hydroformylation of α-olefins

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Abstract

$Ru_3(CO)_{12}$/1,10-phenanthroline shows excellent catalytic activity for hydroformylation of α-olefins. For example, propylene was hydroformylated under 80 atm of syngas ($CO:H_2 = 1:1$) at 120–130°C in an amide solvent to give C_4-aldehydes in high yield (65–93%) with high linearity (n-selectivity = 95%). In the case of 1-octene, corresponding C_9-aldehydes were obtained in moderate yields (49–55%) with high linearity (n-selectivity > 95%). In the reaction of ethylene, propionaldehyde was obtained in high yield.

Keywords: Ethylene; Hydroformylation; 1-Octene; 1,10-Phenanthroline; Propylene; Ruthenium

1. Introduction

Ruthenium complex-catalyzed carbonylation reactions have attracted much attention this past decade. For example, $Ru_3(CO)_{12}$-catalyzed carbonylation of pyridine in the presence of olefin, by activation of the ortho C–H bond of pyridine [1], $Ru_3(CO)_{12}$-catalyzed hydroamidation of olefins [2], $Ru_3(CO)_{12}$-catalyzed double carbonylation of 1,6-diynes [3] and $RuCl_2(PPh_3)_3/K_2CO_3$-catalyzed oxidative cyclocarbonylation of allylic alcohols [4] have been reported. Recently we reported the efficient $Ru_3(CO)_{12}$/1,10-phenanthroline-catalyzed carbonylation of allylic compounds [5].

The oxo process is one of the most important processes in chemical industry. Hydroformylation of olefin has been industrially performed since the 1940's and homogeneous cobalt and rhodium catalysts were employed in these processes. Cobalt precursors require severe reaction conditions, and n-selectivity (n-aldehyde/total aldehydes) is low (< 70%); rhodium ones are very expensive and a large excess (about 100 equiv.) of phosphine is required to achieve high linearity. Thus, studies on novel catalyst systems with higher catalytic efficiency are of interest.

On the other hand, ruthenium complex-catalyzed hydroformylation has been studied [6–43]. Süss-Fink et al. reported that the hydroformylation of propylene catalyzed by a cluster anion $Et_4N^+[HRu_3(CO)_{11}]^-$ gave n-butyraldehyde and isobutyraldehyde in 60 and 3% yields, respectively [21]. Knifton achieved high n-selec-

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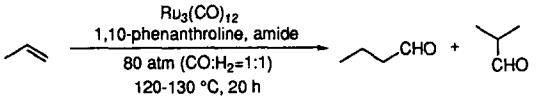
tivity using ruthenium catalysts in fused Bu_4PBr [29]. Tanaka et al. reported that $PPN^+[HRu(CO)_4]^-$ or $PPN^+[HRu_3(CO)_{11}]^-$ gave high n-selectivity on hydroformylation of 1-pentene under high pressure of syngas (300 atm) [34]. We now report a novel, versatile and highly efficient catalytic system, $Ru_3(CO)_{12}$/1,10-phenanthroline in amide solvent, for hydroformylation of α-olefins.

2. Results and discussion

2.1. Hydroformylation of propylene

Propylene was hydroformylated under 80 atm of syngas ($CO:H_2 = 1:1$) at 120°C in the presence of a catalytic amount of 1,10-phenanthroline and $Ru_3(CO)_{12}$ in amide solvent to give C_4-aldehydes in high yield with high n-selectivity (eq. 1).



(1)

The effects of solvents were examined and results are summarized in Table 1.

In toluene without 1,10-phenanthroline (run 2), the total yields of C_4-aldehydes were fairly good (69%) but the linearity was moderate (75%). In the gas phase, propane was formed in 13% yield, and unreacted propylene was not detected. In 1,4-dioxane without 1,10-phenanthroline (run 3), hydrogenation of propylene proceeded, and total yields of C_4-aldehydes were low. *N,N*-Dimethylacetamide in the absence of 1,10-phenanthroline (run 1) was not efficient. When 1,10-phenanthroline was added as a ligand in amide solvents (runs 4, 7–10), hydroformylation of propylene proceeded effectively with high n-selectivity, and propane was obtained in ca. 1% yield. The effects of ligands were examined and the results are summarized in Table 2.

When pyridine was used in place of 1,10-phenanthroline, the C_4-aldehydes were obtained in high yields with lower n-selectivity. 2,2′-Bipyridyl was less effective. In the case of $Me_2N(CH_2)_nNMe_2$ ($n = 2$–4, 6), the longer the methylene chain, the greater was the total yield and the higher the linearity, however, C_4-alcohols formed as by-products. Triphenylphosphine completely suppressed the reaction. Thus the combination of 1,10-phenanthroline with amide solvents was essential to proceed hydro-

Table 1
Effects of solvents on ruthenium-catalyzed hydroformylation of propylene [a]

Run	Solvent	Ligand	Total yield [b] (%)	n-Selectivity [c] (%)
1	CH_3CONMe_2	–	25	84
2	toluene	–	69	75
3	1,4-dioxane	–	35	75
4	CH_3CONMe_2	1,10-phen. [d]	73	95
5	toluene	1,10-phen.	0	–
6	1,4-dioxane	1,10-phen.	15	76
7	$HCONMe_2$	1,10-phen.	65	95
8	cyclo-$(CH_2CH_2CH_2CON)Me$	1,10-phen.	84	95
9	cyclo-$(CH_2CH_2NMeCON)Me$	1,10-phen.	80	95
10 [e]	CH_3CONMe_2	1,10-phen.	93	95

[a] $Ru_3(CO)_{12}$ 0.11 mmol, propylene 40 mmol, solvent 10 ml, (1,10-phenanthroline 1.33 mmol) CO 40 atm, H_2 40 atm, 120°C, 20 h.
[b] GLC yields.
[c] n-Selectivity = n-butyraldehyde/C_4-aldehydes.
[d] 1,10-phen. is 1,10-phenanthroline.
[e] At 130°C.

Table 2
Effects of ligands on ruthenium-catalyzed hydroformylation of propylene [a]

Run	Ligand	Total yield [b] (%)	n-Selectivity [c] (%)
1	–	25	84
4	1,10-phenanthroline	73	95
11	2,9-dimethyl-1,10-phenanthroline	76	92
12	$Me_2N(CH_2)_2NMe_2$	31	95
13	$Me_2N(CH_2)_3NMe_2$	33	96
14	$Me_2N(CH_2)_4NMe_2$	57	96
15	$Me_2N(CH_2)_6NMe_2$	62	96
16	2,2′-bipyridyl	24	93
17	PPh_3	0	–
18	pyridine	79	91
10 [d]	1,10-phenanthroline	93	95

[a] $Ru_3(CO)_{12}$ 0.11 mmol, propylene 40 mmol, *N,N*-dimethylacetamide 10 ml, bidentate ligand 1.33 mmol or monodendate ligand 2.66 mmol, CO 40 atm, H_2 40 atm, 120°C, 20 h.
[b] GLC yields.
[c] n-Selectivity = n-butyraldehyde/C_4-aldehydes.
[d] At 130°C.

formylation of propylene effectively and to suppress the hydrogenation of propylene to propane.

Effects of the molar ratio of 1,10-phenanthroline to $Ru_3(CO)_{12}$ on the hydroformylation of propylene is shown in Fig. 1. In the reaction under 80 atm ($CO:H_2 = 1:1$) at 120°C, addition of a 4-fold amount of 1,10-phenanthroline to that of Ru atom gave the best result. The n-selectivity was almost constant (95%) in the range of 1,10-phenanthroline/Ru = 2 to 8.

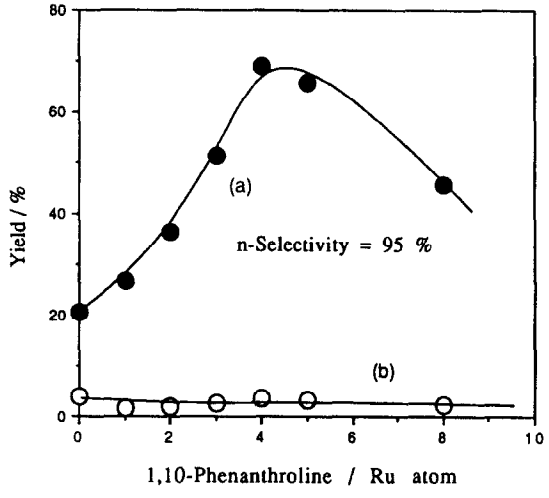


Fig. 1. Effect of molar ratio of 1,10-phenanthroline/$Ru_3(CO)_{12}$ on hydroformylation of propylene. Yield of (a) n-butyraldehyde and (b) isobutyraldehyde. Reaction conditions; propylene (40 mmol), $Ru_3(CO)_{12}$ (0.11 mmol), *N,N*-dimethylacetamide (10 ml), under CO 40 atm, H_2 40 atm at 120°C for 20 h.

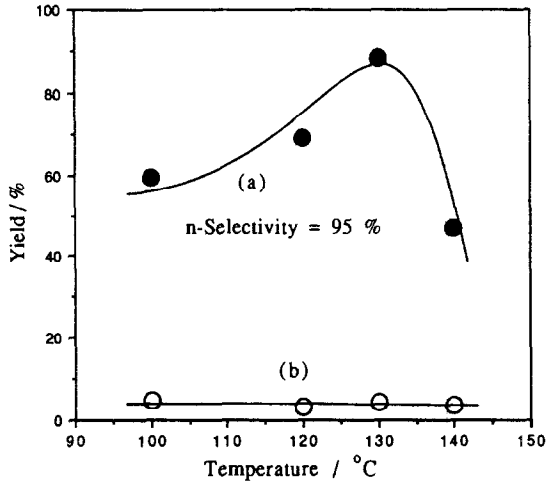


Fig. 2. Effect of temperature on hydroformylation of propylene. Yield of (a) n-butyraldehyde and (b) isobutyraldehyde. Reaction conditions; propylene (40 mmol), $Ru_3(CO)_{12}$ (0.11 mmol), 1,10-phenanthroline (1.33 mmol), *N,N*-dimethylacetamide (10 ml), under CO 40 atm, H_2 40 atm for 20 h.

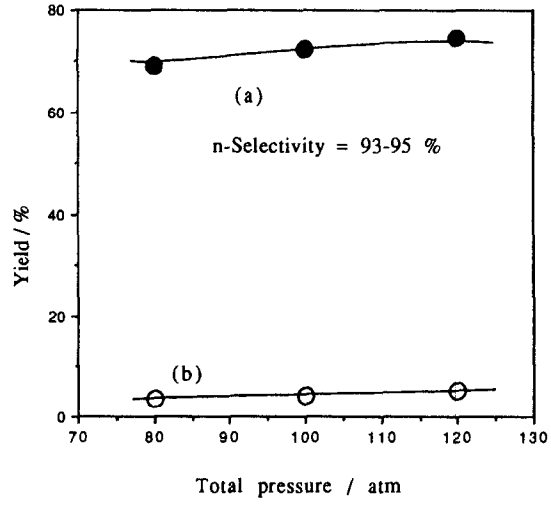


Fig. 3. Effect of total pressure on hydroformylation of propylene. Yield of (a) n-butyraldehyde and (b) isobutyraldehyde. Reaction conditions; propylene (40 mmol), $Ru_3(CO)_{12}$ (0.11 mmol), 1,10-phenanthroline (1.33 mmol), *N,N*-dimethylacetamide (10 ml), $CO:H_2 = 1:1$ at 120°C for 20 h.

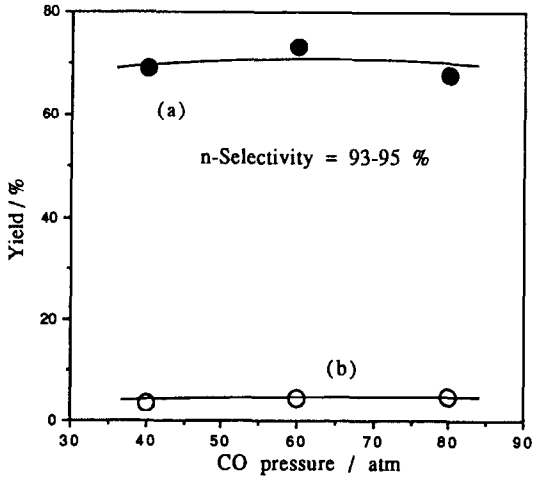


Fig. 4. Effect of CO pressure on hydroformylation of propylene. Yield of (a) n-butyraldehyde and (b) isobutyraldehyde. Reaction conditions; propylene (40 mmol), $Ru_3(CO)_{12}$ (0.11 mmol), 1,10-phenanthroline (1.33 mmol), *N,N*-dimethylacetamide (10 ml), under H_2 40 atm at 120°C for 20 h.

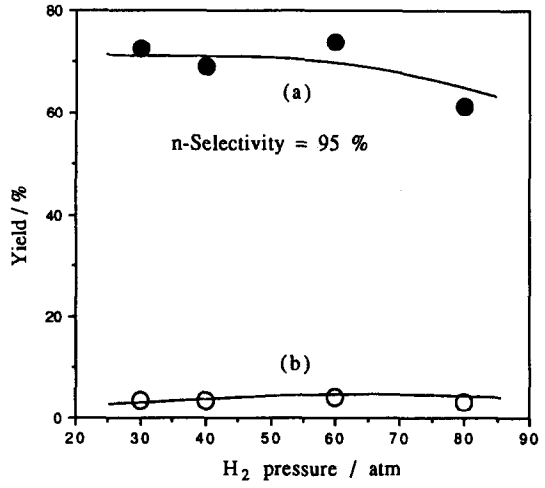


Fig. 5. Effect of H_2 pressure on hydroformylation of propylene. Yield of (a) n-butyraldehyde and (b) isobutyraldehyde. Reaction conditions; propylene (40 mmol), $Ru_3(CO)_{12}$ (0.11 mmol), 1,10-phenanthroline (1.33 mmol), *N,N*-dimethylacetamide (10 ml), under CO 40 atm at 120°C for 20 h.

Effects of the reaction temperature on the hydroformylation of propylene is shown in Fig. 2. With the increase of the temperature, the total yields of C_4-aldehydes increased; the maximum yield was 93% (n-selectivity = 95%) at 130°C. Further increase of the reaction temperature caused a decrease of the total yield of the aldehydes because of the progress of aldol condensation.

Effects of the total pressure ($CO:H_2 = 1:1$) on the hydroformylation of propylene is shown in Fig. 3. The total yields of C_4-aldehydes slightly increased (from 72 to 80%) in the range of 80–120 atm ($CO:H_2 = 1:1$).

Effects of CO pressure on the hydroformylation of propylene is shown in Fig. 4. When P_{H_2} was kept at 40 atm, the total yields and n-selectivity of C_4-aldehydes were almost constant in the range of P_{CO} = 40–80 atm. The tendency of these effects of CO pressures is somewhat different from that reported; usually the yield of aldehyde decreased with the increase of P_{CO} [24]. The total yield of aldehydes and n-selectivity in our system, however, were higher than those reported [9,17,24,29].

Effects of the H_2 pressure on the hydroformylation of propylene is shown in Fig. 5. When P_{CO} was kept at 40 atm, the total yields and n-selectivity of the aldehydes were almost constant in the range of P_{H_2} = 30–60 atm. At P_{H_2} = 80 atm, the yield of aldehydes decreased.

Time dependence of the hydroformylation of propylene is shown in Fig. 6. Laine reported that in the early stage of the hydroformylation

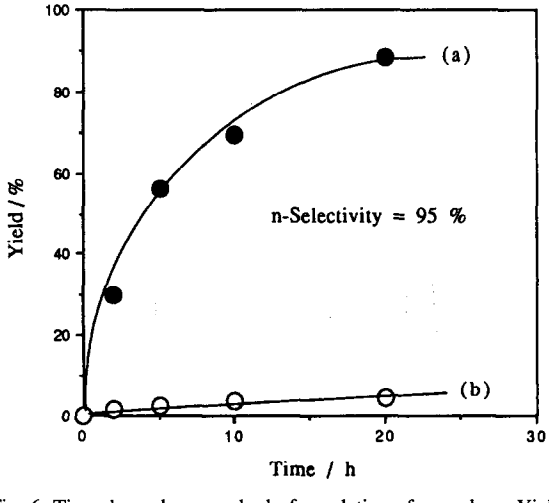
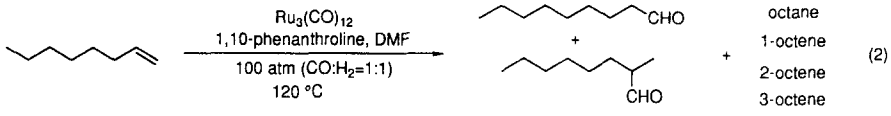


Fig. 6. Time dependence on hydroformylation of propylene. Yield of (a) n-butyraldehyde and (b) isobutyraldehyde. Reaction conditions; propylene (40 mmol), $Ru_3(CO)_{12}$ (0.11 mmol), 1,10-phenanthroline (1.33 mmol), *N,N*-dimethylacetamide (10 ml), under CO 40 atm, H_2 40 atm at 130°C.

catalyzed by $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ under water–gas shift reaction conditions, n-selectivity was very high (> 97%), then the n-selectivity decreased rapidly with increase of olefin conversion [19]. In our system, this decrease of the n-selectivity was not observed.

2.2. Hydroformylation of 1-octene

1-Octene was hydroformylated to C_9-aldehydes in moderate yields with high n-selectivity in the presence of a catalytic amount of $Ru_3(CO)_{12}$/1,10-phenanthroline (eq. 2).



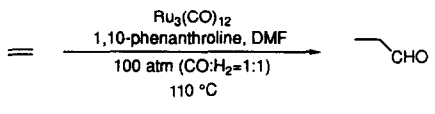
(2)

After the reaction was completed, 2-octene and 3-octene were obtained in 26% and 7% yields, respectively. Results are shown in Table 3.

When 2-octene was employed under the same reaction conditions, C_9-aldehydes were obtained in 20% yield. In case of 3-octene, no C_9-aldehyde was formed. When the 1-octene was treated for 50 h under the same reaction conditions, the yields of C_9-aldehydes increased slightly, and most of the octenes recovered were 3-octene. Thus, the rate of hydroformylation of 1-octene and that of isomerization of the olefins, determine the distribution of the products.

2.3. Hydroformylation of ethylene

Ethylene was hydroformylated under 100 atm of syngas ($CO:H_2 = 1:1$) at 120°C in the presence of a catalytic amount of 1,10-phenanthroline and $Ru_3(CO)_{12}$ in *N,N*-dimethylformamide to give propionaldehyde (eq. 3). Results are shown in Table 4.



(3)

The yield of propionaldehyde obtained was shown by TON [propionaldehyde (mmol)/molar amount of $Ru_3(CO)_{12}$] and TOF [TON/time (h)], because the amount of ethylene introduced to the 50 ml autoclave (10 atm) could not be determined exactly. After 3 h, propionaldehyde was obtained in TON = 227 with TOF of 76. The reaction was completed in 20 h (TON = 461).

2.4. IR spectrum of the reaction solution

After the reaction of run 4 was completed, the IR spectrum of the solution at room temperature under 1 atm of Ar, showed four absorptions at 2074(vw), 2016(vs), 1989(s), 1952(m) cm^{-1}. These absorptions are similar to those of $Et_4N^+[HRu_3(CO)_{11}]^-$ [44]. The IR spectrum of the solution taken under 80 atm of syngas ($CO:H_2 = 1:1$) at 120°C, showed in addition to these four absorptions, another absorption of 1988(vs) cm^{-1}. Taking the effect of molar ratio of 1,10-phenanthroline/$Ru_3(CO)_{12}$ into consideration, this absorption at 1988 cm^{-1} would be due to a catalytically active species in which 1,10-phenanthroline coordinates to the Ru atom.

3. Experimental

3.1. General methods

The reagents employed in this study were commercial materials and were used without purification except for solvents and 1-octene which were distilled before use. The GLC analyses of the solutions were performed on a Shimadzu GC-14A gas chromatograph with columns (3.0 mm i.d. × 2.6 m) packed with

Table 3
Ruthenium-catalyzed hydroformylation of octenes [a]

Run	Octene	Total yield of aldehydes [b] (%)	n-Selectivity [c] (%)	1-octene/2-octene/3-octene/octane [b] (in %)
19	1-octene	49	97	trace/26/7/trace
20 [d]	1-octene	52	97	trace/1/23/1
21	2-octene	20	89	trace/58/24/trace
22	3-octene	trace	–	trace/trace/100/trace
23 [e]	1-octene	55	95	trace/21/4/3

[a] $Ru_3(CO)_{12}$ 0.11 mmol, octene 40 mmol, DMF 5.0 ml, 1,10-phenanthroline 1.33 mmol, CO 50 atm, H_2 50 atm, 120°C, 20 h.
[b] GLC yields.
[c] n-Selectivity = n-butyraldehyde/C_4-aldehydes.
[d] For 50 h.
[e] *N,N*-dimethylacetamide was used in place of DMF.

OV-17 (2% Chromosorb WAW DMCS, 60–80 mesh). The GLC analyses of the gas phase were performed on a Shimadzu GC-4A gas chromatograph with columns (2.6 mm i.d. × 3 m) packed with Porapak-Q (80–100 mesh). IR spectra were obtained on a Shimadzu FTIR-8100 spectrometer.

3.2. Ruthenium-catalyzed hydroformylation of propylene

In a 50 ml stainless autoclave were placed $Ru_3(CO)_{12}$ (0.068 g, 0.11 mmol), 1,10-phenanthroline (0.24 g, 1.33 mmol), and *N,N*-dimethylacetamide (10 ml). Then propylene (896 ml at 0°C, 40 mmol) was introduced into a 50 ml stainless autoclave in dry ice–methanol (−78°C). After CO (40 atm) and H_2 (40 atm) were introduced at 25°C, the mixture was magnetically stirred at 130°C for 20 h. Gas phase was stored in a polyethylene gas bag and analyzed by GLC. Liquid phase was analyzed by GLC. n-Butyraldehyde and isobutyraldehyde were obtained in 88% and 5% respectively.

Table 4
Ruthenium-catalyzed hydroformylation of ethylene [a]

Run	Time (h)	TON [b]	TOF (h^{-1}) [b]
24	3	227	76
25	10	404	40
36	20	461	23

[a] $Ru_3(CO)_{12}$ 0.05 mmol, ethylene 10 atm, DMF 10.0 ml, 1,10-phenanthroline 0.66 mmol, CO 50 atm, H_2 50 atm, 110°C.
[b] GLC yields. TON = propionaldehyde/$Ru_3(CO)_{12}$, TOF = TON/h.

3.3. Ruthenium-catalyzed hydroformylation of 1-octene

In a 50 ml stainless autoclave were placed $Ru_3(CO)_{12}$ (0.068 g, 0.11 mmol), 1,10-phenanthroline (0.24 g, 1.33 mmol), DMF (5.0 ml), and 1-octene (10 mmol). After CO (50 atm) and H_2 (50 atm) were introduced at 25°C, the mixture was magnetically stirred at 120°C for 50 h. Nonanal and 2-methyloctanal were obtained in 51% and 1% respectively.

3.4. Ruthenium-catalyzed hydroformylation of ethylene

In a 50 ml stainless autoclave were placed $Ru_3(CO)_{12}$ (0.034 g, 0.055 mmol), 1,10-phenanthroline (0.12 g, 0.66 mmol) and DMF (10.0 ml). After ethylene (10 atm), CO (50 atm) and H_2 (50 atm) were introduced at 25°C, the mixture was magnetically stirred at 110°C for 20 h. TON of propionaldehyde was 461.

Acknowledgements

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