A novel Rh–PCy$_3$–CO–HCOOH catalytic system for the regioselective conversion of alkenes to aldehydes

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Abstract

Rhodium carbonyl and tricyclohexylphosphine, in the presence of CO and HCOOH, is an efficient catalytic system for the regioselective conversion of alkenes into branched and linear aldehydes. This process shows excellent functional group tolerance.

Keywords: Rhodium; Carbon monoxide; Formic acid; Regioselectivity; Alkene conversion; Aldehydes

1. Introduction

The metal catalyzed hydroformylation reaction which uses carbon monoxide and hydrogen is one of the most extensively investigated methods for the conversion of olefins to aldehydes [1–4]. Of the transition metal complexes, those containing rhodium or cobalt show the highest activity for the hydroformylation reaction [3], with rhodium being 10^3–10^4 times more active than cobalt [2,3]. Rhodium phosphine complexes exhibit the highest activity and the best regioselectivity at low pressure of CO and H$_2$, and at low temperature [3]. One of us recently reported that the heterogeneous catalyst Rh/C and 1,3-bis(diphenylphosphino)propane (dppp) catalyzes the regioselective hydroformylation of olefins with carbon monoxide and formic acid as the source of hydrogen [5]. The use of formic acid as an important component for the transformation of olefins into carboxylic acids, in excellent selectivity, has been previously reported using Pd(OAc)$_2$ [6] and Pd/C [7] and 1,4-bis(diphenylphosphino)butane (dppb). The present work is concerned with the conversion of olefins to aldehydes catalyzed by a soluble rhodium complex, phosphine ligand, and formic acid as the source of hydrogen and under CO pressure. The influence of phosphine ligand, temperature, solvent, concentration of formic acid, and CO pressure has been assessed concerning this reaction.

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2. Results and discussion

2.1. Hydroformylation of styrene catalyzed by $Rh_6(CO)_{16}$ and phosphine ligand in the presence of HCOOH or H_2 and CO. Effect of phosphine ligand, concentration of HCOOH, H_2 and CO pressure on the selectivity of the reaction
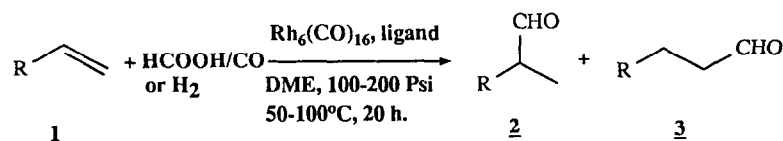
The hydroformylation of styrene (1, R = Ph) was attained using $Rh_6(CO)_{16}$ as a catalyst, phosphine ligand, formic acid or H_2 (as source of hydrogen) and CO at 50°C in 1,2-dimethoxyethane (DME) to give branched (2) and linear (3) aldehydes (Scheme 1).

We first examined the effect of concentration of HCOOH and the ratio of H_2/CO, using tricyclohexylphosphine, PCy_3, as a ligand of choice at 50°C [1000:1:25 ratio of styrene:$Rh_6(CO)_{16}$:PCy_3]. The results are summarized in Table 1 (entries 1–12). The hydroformylation reaction did not occur in the absence of either the phosphine ligand or CO (under CO_2 or N_2 atm). The use of 2 equivalents of HCOOH to styrene, and 100 psi of CO, gives the branched chain aldehydes, 2, in high yield (96%) and selectivity (83%). A low yield (44%) of aldehydes was obtained using less than one equivalent of formic acid (3.0 mmol) (Table 1, entry 4). The highest yield and selectivity was achieved using 6.0 mmol of HCOOH and 100 psi of CO (Table 1, entry 2). The use of high pressure of CO (500 psi) with 6.0 mmol of HCOOH considerably retarded the rate of the reaction (Table 1, entry 6). The addition of PCy_3 in a 5 fold excess over $Rh_6(CO)_{16}$, in the presence of 6.0 mmol of HCOOH, gave only

traces of aldehydes (Table 1, entry 8), while the use of H_2 (100 psi) instead of HCOOH increased the yield of aldehydes to 98% (Table 1, entry 9). Branched chain aldehydes (2) were formed in good selectivity and high yield using a 25/1 ratio of PCy_3/$Rh_6(CO)_{16}$ at 100 psi each of H_2 and CO. At higher pressure of CO or H_2 the yields of aldehydes decreased (54–76%) (Table 1, entries 11, 12). Different phosphine ligands have been examined for the reaction at 100 psi CO and 6.0 mmol of HCOOH (Table 1, entries 13–18). Low yields of aldehydes resulted (Table 1, entries 13, 14) with HCOOH or H_2 and 1,4-bis(diphenylphosphino)butane (dppb) as the phosphine ligand. The highest combined yield (99% of 2 + 3) and selectivity for 2 (92%) were achieved using PPh_3 and H_2 (almost no reaction occurred with HCOOH as the source of hydrogen) (Table 1, entries 15, 16).

2.2. Hydroformylation of styrene catalyzed by $Rh_6(CO)_{16}$–PCy_3–HCOOH–CO–DME. Effect of temperature on the regioselectivity of hydroformylation

The hydroformylation of styrene was carried out using the catalytic system $Rh_6(CO)_{16}$–PCy_3–CO–HCOOH and DME as the solvent. The effect of temperature on the yield and selectivity has been studied in order to determine the best experimental conditions for this transformation. The temperature was varied between 25°C and 150°C. The results are presented in Fig. 1. At 25°C no reaction occurred and at 40°C 2 and 3 were obtained in a combined yield of 30%. A high total yield (94% of

R⌐═⟍ + HCOOH/CO → $Rh_6(CO)_{16}$, ligand   →   CHO
                    or H_2 DME, 100-200 Psi   R⌐⟍ﬞ⟍ + R⌐⟍⟍⟍CHO
                              50-100°C, 20 h.

1   **2**   **3**

Scheme 1.

2 + 3), and good selectivity for **2** (85%), was observed at 50°C. The ratio of **2/3** decreased to 1.5 (i.e. more linear product (**3**) was formed) at 150°C, and no change was observed at temperatures greater than 150°C. It seems that 50°C is the temperature of choice for the hydroformylation of styrene.

2.3. Hydroformylation of styrene in the presence of PCy₃, HCOOH, CO in DME at 50°C. Effect of the rhodium catalyst and of the solvent

The effectiveness of different rhodium complexes was determined under standard experimental conditions (see above) using PCy₃ as

Table 1

Effect of phosphine ligand, HCOOH concentration, or H_2 and CO pressure, on the hydroformylation of styrene catalyzed by $Rh_6(CO)_{16}$ and phosphine [a]

Entry	HCOOH (mmol)	H_2 (psi)	CO (psi)	Ligand (mmol)	Yield [b] %	Product distribution [c], %	
						2	**3**
1	10.0	—	100	PCy₃ (0.125)	96	83	17
2	6.0	—	100	PCy₃ (0.125)	94	85	15
3	5.0	—	100	PCy₃ (0.125)	86	84	16
4	3.0	—	100	PCy₃ (0.125)	44	84	16
5	6.0	—	300	PCy₃ (0.125)	90	83	17
6	6.0	—	500	PCy₃ (0.125)	34	82	18
7	6.0	—	100	PCy₃ (0.125)	86	85	15
8	6.0	—	100	PCy₃ (0.025)	traces	—	—
9	—	100	100	PCy₃ (0.125)	98	84	16
10	—	100	100	PCy₃ (0.05)	65	83	17
11	—	500	100	PCy₃ (0.125)	76	88	12
12	—	100	500	PCy₃ (0.125)	54	86	14
13	6.0	—	100	dppb (0.125)	25	75	25
14	—	100	100	dppb (0.125)	30	75	25
15	6.0	—	100	PPh₃ (0.125)	traces	—	—
16	—	100	100	PPh₃ (0.125)	99	92	8
17	6.0	—	100	P(t-Bu)₃ (0.125)	traces	—	—
18	—	100	100	P(t-Bu)₃ (0.125)	14	81	19

[a] Reaction conditions: $Rh_6(CO)_{16}$ = 0.005 mmol; Substrate = 5.0 mmol; DME = 5.0 ml; 50°C; 20 h.
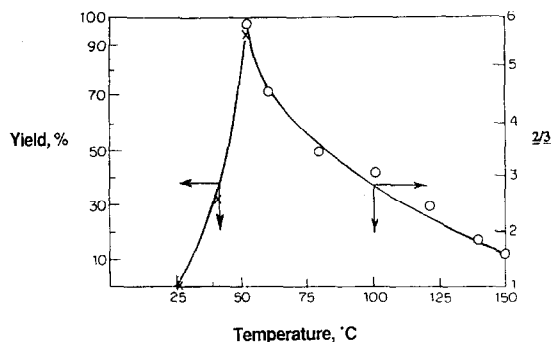[b] Isolated yield.
[c] Determined by GC and ^1H NMR.

Fig. 1. Hydroformylation of styrene catalyzed by $Rh_6(CO)_{16}$–PCy_3–HCOOH–CO–DME. Effect of temperature on the regioselectivity of the reaction. (a) Reaction conditions: $Rh_6(CO)_{16}$ = 0.005 mmol; PCy_3 = 0.125 mmol; substrate = 5.0 mmol; HCOOH = 6.0 mmol; CO = 100 psi; DME = 5.0 ml; 20 h. (b) Isolated yield. (c) The ratio 2/3 was determined by GC and ^1H NMR.

rhodium complex, $Rh^+(COD)(\eta^6\text{-}C_6H_5BPh_3^-)$, previously shown [8] to be an excellent catalyst for hydroformylation reactions with H_2, did not react when HCOOH was used as the source of hydrogen in the absence of PCy_3 (Table 2, entry 7). The addition of PCy_3 to the system did result in the formation of aldehydes in 57% yield (Table 2, entry 8). No hydroformylation occurred using ruthenium carbonyl, $Ru_3(CO)_{12}$, with or without PCy_3. In THF or acetone the yield of aldehydes were lower (60–70%) than in DME, and no reaction was observed in benzene, toluene, dichloromethane, chloroform, hexane and triethylamine. Based on these studies the best catalytic system for the hydroformylation of olefins using HCOOH as the source of hydrogen is the combination of $Rh_6(CO)_{16}$ and PCy_3 in DME at 100 psi of CO.

ligand, CO, HCOOH as the source of hydrogen, in DME as solvent at 50°C. The results of these experiments are present in Table 2. The use of Rh/C at 50°C gave aldehydes in low yields (10%), but at 80°C the product yield was 82% (Table 2, entries 3, 4). The catalyst, $RhH(CO)(PPh_3)_3$, in the presence of PCy_3 (Table 2, entry 6), afforded the branched aldehyde (80%) in good selectivity, while PPh_3 as added ligand was much less selective. The zwitterionic

2.4. Hydroformylation of different olefinic substrates catalyzed by $Rh_6(CO)_{16}$–PCy_3–CO–HCOOH–DME

Various olefinic substrates were utilized for the hydroformylation reaction catalyzed by

Table 2

Effect of the rhodium catalyst on the hydroformylation of styrene in the presence of HCOOH

Entry	Catalyst	Yield [b]	Product distribution [c], %	
	(mmol)	%	2	3
1	$Rh_6(CO)_{16}$ (0.002)	traces	–	–
2	$Rh_6(CO)_{16}$ (0.005)	94	85	15
3	Rh/C (0.02)	10	80	20
4 [d]	Rh/C (0.02)	82	79	21
5 [e]	$RhH(CO)(PPh_3)_3$ (0.02)	traces	–	–
6	$RhH(CO)(PPh_3)_3$ (0.02)	92	80	20
7 [e]	$Rh^+(COD)(\eta^6\text{-}C_6H_5BPh_3^-)$ (0.02)	traces	–	–
8	$Rh^+(COD)(\eta^6\text{-}C_6H_5BPh_3^-)$ (0.02)	57	84	16

[a] Reaction conditions: Substrate = 5.0 mmol; PCy_3 = 0.125 mmol; DME = 5.0 ml; HCOOH = 6.0 mmol; CO = 100 Psi; 50°C; 20 h.
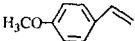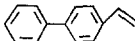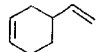[b] Isolated yield.
[c] Determined by GC and ^1H NMR.
[d] T = 80°C.
[e] No PCy_3 was added.
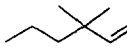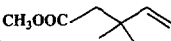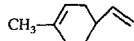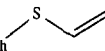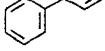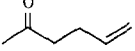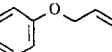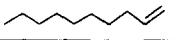
$Rh_6(CO)_{16}$–PCy_3–CO–HCOOH–DME (Table 3). At 50°C, the substituted styrenes (Table 3, entries 1–6) and 2-vinylnaphthalene (Table 3, entry 7) gave excellent yields of aldehydes (88–97%) and high selectivities for the branched chain isomer, **2**, (82–89%). The control of the regioselectivity of the reaction depends in part on the electronic effect and the effective bulk of substituent R in the olefin; for example, the linear aldehydes, **3**, were formed as major products in the hydroformylation of 4-vinyl-1-cyclohexene and vinylcyclohexane at 50°C (Table 3, entries 8, 9). 3,3-Dimethyl-1-butene, 3,3-dimethyl-1-hexene and methyl 3,3-dimethyl-5-hexanoate ester undergo the hydroformylation reaction to form the linear aldehyde, **3**, as a principal product of the reaction in very high selectivities (80–90%) with **2** and **3** obtained in excellent combined yield (80–92%) (Table 3, entries 10–12). 1,1-Disubstituted olefins behave

Table 3

Hydroformylation of olefins by $Rh_6(CO)_{16}$–PCy_3–CO–HCOOH–DME [a]

Entry	Substrate 1	T °C	Yield[b] %	Products[c], % 2	3
9		50	86	30	70
10		50	80[d]	20	80
11		50	92[d]	10	90
12	CH_3OOC	100	99	16	84
13		100	65	6	94
14	CH_3	100	75	0	100
15		100	84[d]	0	100
16		100	86	0	100
17		100	96	40	60

Entry	Substrate 1	T °C	Yield[b] %	Products[c], % 2	3
18	Ph–S	100	80	96	4
19	Ph_3Si	50	80	20	80
20	PhCOO	100	47	100	0
21		50	87	35	65
22	CN	100	80[d]	75	25
23		50	96[d]	55	45
24		100	66	82	18
25		50	91	46	54

Entry	Substrate 1	T °C	Yield[b] %	Products[c], % 2	3
1	CH_3	50	93	86	14
2	CH_3	50	95	86	14
3	H_3CO	50	97	82	18
4	Cl	50	88	89	11
5	Cl	50	97	87	13
6		50	96	84	16
7		50	93	85	15
8		50	66	40	60

[a] Reaction conditions: $Rh_6(CO)_{16}$ = 0.005 mmol; substrate = 5.0 mmol; HCOOH = 6.0 mmol; CO = 100 Psi; DME = 5.0 ml; 20 h.
[b] Isolated yield (see footnote d).
[c] The ratio of **2/3** was determined by GC and ^{1}H NMR.
[d] Determined by GC and ^{1}H NMR, using anisole as the internal standard.

Scheme 2.

	Yield, %	Product distribution, %	
trans	46	0	100
cis	70	54	46
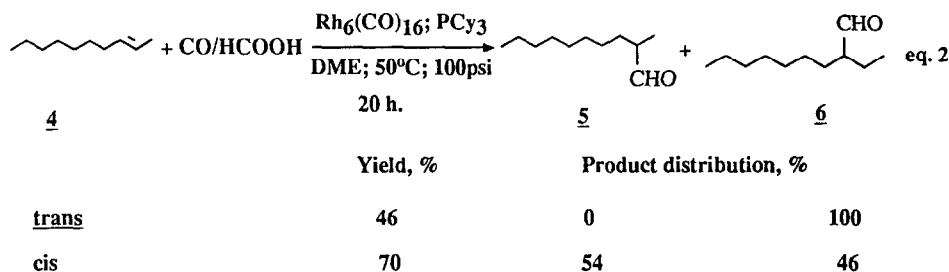
in an analogous fashion (Table 3, entries 13–16) with the linear aldehydes usually formed as the only reaction product in high yields (65–86%). The hydroformylation of N-vinylpyrrolidinone, phenylvinylsulfide, triphenylvinylsilane, vinylbenzoate, allyl cyanide, 5-hexen-2-one and phenyl allyl ether (Table 3, entries 17–20, 22–24) gave useful bifunctional products in high combined yields (66–96%). These results demonstrate the tolerance of the system for a wide variety of functional groups.

Internal olefins can also react under the described conditions, but the selectivity of the reaction depends on the stereochemistry of the substrate; for example, the hydroformylation of trans-2-decene gave only one product in moderate yield. However cis-2-decene behaved differently and almost an equimolar mixture of aldehydes 5 and 6 was formed (Scheme 2).

In conclusion, the catalytic system $Rh_6(CO)_{16}$–PCy_3–CO–HCOOH is a new, simple, and efficient approach to aldehydes, containing a variety of functional groups. The process is often regioselective and the product yields are very good.

3. Experimental

3.1. General

All reactants and solvents were purchased from commercial suppliers. The olefins and the solvents were purified prior to use. A 45 ml stainless-steel autoclave (Parr Instrument) was used for these reactions. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Gemini 200 spectrometer. Mass spectral determinations were made using a VG 7070E instrument. A Hewlett-Packard 5890 gas chromatograph, equipped with an OV-17 column, was used for GC determinations.

3.2. General procedure for the hydroformylation of olefins

A mixture of $Rh_6(CO)_{16}$ (0.005 mmol), PCy_3 (0.125 mmol) and olefin (5.0 mmol) was dissolved in 5 ml of DME, HCOOH (6.0 mmol) was then added, and the resulting solution was placed in a 45 ml autoclave. The autoclave was purged with carbon monoxide and then pressurized and heated (see Tables 1–3 for temperature and pressure in each case). The reaction was then cooled to room temperature, filtered through Celite or silica gel, and concentrated by rotary evaporation. The separation and purification of aldehydes was achieved by silica gel chromatography using a mixture of hexane-ethyl acetate (9:1) as the eluant. The products were identified by comparison of spectral data with those for authentic materials or literature data.

Acknowledgements

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