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A water-soluble rhodium complex as a catalyst precursor for the hydroformylation of olefins

Seung Uk Son, Jin Wook Han, Young Keun Chung *

Department of Chemistry and Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-742, South Korea

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Abstract

The first synthesis of a water-soluble cationic (sugar-substituted arene)rhodium complex has been described. The water-soluble cationic rhodium complex was synthesized by the reaction of an ethanol solution of $[Rh(COD)Cl]_2$ with $AgBF_4$ and then with phenyl-β-D-glucopyranoside. This water-soluble rhodium complex acts as a catalyst precursor for the hydroformylation of olefins in a two-phase (water and hexane) system and displays high regioselectivity and high conversion to branched-chain aldehydes.

Keywords: Olefin; Hydroformylation catalyst; Water-soluble organometallics; Rhodium complex

1. Introduction

Homogeneous catalysis provides mild and selective synthetic routes to valuable chemicals from basic organic precursors [1]. However, separation of the organic products from the active catalyst is troublesome. Numerous attempts to anchor the complex on a support have been made to overcome this problem [2–4]. However, due to losses of activity and selectivity, it was found that the introduction of the active species in water with the appropriate ligand is a good means of retaining a high level of activity with a simple way of recycling. Thus, many water-soluble rhodium catalyst systems have been developed [5–7]. In most cases, water-soluble phosphines were prepared and their rhodium complexes, formed in situ, were used in a two-phase system [8–13]. Although numerous neutral and cationic rhodium complexes have been investigated, there have been no reports, to our knowledge, on the use of a water-soluble cationic rhodium complex without a water-soluble phosphine as a catalyst for the hydroformylation of olefins. Recently, Chen and Alper [14] reported a water soluble rhodium catalyst system bearing water-soluble polymers. We now report the synthesis of **1** and its use in the hydroformylation of a wide range of olefins under mild conditions and that the process is highly regioselective for certain classes of alkenes.

* Corresponding author.

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2. Experimental

2.1. Preparation of compound *1*

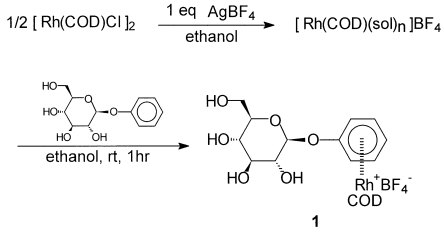
$[Rh(COD)Cl]_2$ (0.1 g, 0.20 mmol) and $AgBF_4$ (0.079 g, 0.40 mmol) were dissolved in 5 ml of EtOH. The solution was stirred for 30 min. After filtration of any precipitates under N_2, the precipitates were washed with EtOH (5 ml × 2). The washed ethanol solution and filtrate was combined. To the ethanol solution was added phenyl-β-D-glucopyranoside (0.15 g, 0.58 mmol). The resulting solution was stirred for 1 h. After evaporation of EtOH, the residue was recrystallized by acetone/ diethyl ether. Yield: 0.20 g (89%). ^{1}H NMR (d_6-acetone): δ 7.29 (t, 7.7 Hz, 2 H, Ph), 7.06 (d, 8.1 Hz, 2 H, Ph), 7.00 (t, 7.2 Hz, 1 H, Ph), 4.97 (d, 7.6 Hz, 1 H, sugar), 4.18 (s, 4H, COD), 3.88 (d, 9.7 Hz, 1 H, sugar), 3.65–3.43 (br., 5 H, sugar), 2.58 (m, 4 H, COD), 1.82 (8.5 Hz, 4 H, COD) ppm; ^{13}C NMR (d_6-acetone) δ 158.78, 130.26, 130.14, 122.90, 117.41, 101.77, 78.65, 78.53, 78.08, 77.57, 74.73, 71.45, 62.62, 30.85 ppm; $IR_{\nu_{B-F}}$ 1062, 1021 cm^{-1}; FAB MS (M^+) 467. Due to the easy loss of COD, we failed to obtain the combustion data.

2.2. Typical procedure for the hydroformylation reaction

A teflon liner containing an aqueous solution of **1** (7.0 mg, 0.013 mmol, in 5 ml of water) and a hexane solution of styrene (0.263 g, 2.53 mmol in 5 ml of hexane) was placed in a 100 ml of autoclave equipped with a magnetic stirring bar. The autoclave was flushed with CO and then pressurized to the desired pressure. The hydrogen line attached to the autoclave and then the pressure was gradually increased to the desired level. The autoclave was placed in an oil bath and heated. After the appropriate reaction time, the autoclave was cooled to room temperature, the excess H_2/CO gas was released, and the resulting solution was separated and immediately analyzed by ^{1}H NMR spectroscopy.

3. Results and discussion

Compound **1** was prepared according to Eq. (1). Treatment of an ethanol solution of $[Rh(COD)Cl]_2$ [15] with $AgBF_4$ and with phenyl-β-D-glucopyranoside gave compound **1**.



(1)

1

The overall yield was 89%. The ligand, phenyl-β-D-glucopyranoside, is slightly soluble in acetone. However, **1** is quite soluble in acetone, ROH (R = Me, Et), and water, moderately soluble in CH_3NO_2, and slightly soluble in CH_2Cl_2. Compound **1** is quite stable in water and in the solid state in air. However, the COD ligand is easily released under vacuum. Due to the presence of a formal positive charge on the metal and ease of displacement of the COD ligand, we anticipated that compound **1** could be used as a water-soluble hydroformylation catalyst. The formal positive charge on the metal could direct the regiochemistry of the process and make an intermediate more susceptible to olefin coordination and carbonyl insertion. In addition, the sugar substituent attached to the coordinated arene ring may exert steric and/or electronic effects, subject to the stereochemistry of the reaction.

Treatment of styrene in hexane and an aqueous solution of **1** in water with CO/H_2 gave the expected hydroformylation product. We tried to optimize the hydroformylation reaction condition by studying the reaction of styrene with CO/H_2 under various conditions (Table 1). Table 1 shows that the branched/linear (b/l)

Table 1
Hydroformylation of styrene by complex **1**

Entry	Temperature(°C)	Pressure (psi)	P_{H_2}/P_{CO}	Time (h)	b/l	Yield (convers.%)	Turnover no.
1	50	300	2/1	22	92.4/7.6	100[a]	200
2	50	300	2/1	22	89.6/10.4	94	188
3	60	300	2/1	22	68.5/31.5	100	200
4	40	300	2/1	48	93.8/6.2	100	200
5	50	500	2/1	22	92.3/7.7	100	200
6	50	200	2/1	48	80.6/19.4	100	200
7	50	300	1/2	22	84.2/15.8	100	200
8	25	500	2/1	22	97.1/2.9	9	18
9	40	500	2/1	22	94.6/5.4	100	200

[a] Five equivalent of PPh_3 was added as an additive.

ratio is dependent upon the reaction temperature, pressure, and the ratio of P_{H_2}:P_{CO}. As the reaction temperature decreases, the regioselectivity increases (entries 2–4 or 5, 8–9 in Table 1). When the reaction was carried out at 25°C, the b/l ratio was 97.1:2.9 with a poor yield (entry 8 in Table 1). As the total pressure increases, the regioselectivity increases (entries 2, 5, and 6 in Table 1). When the 2:1 ratio of P_{H_2}:P_{CO} was changed to 1:2, the regioselectivity decreased slightly (entry 7 in Table 1). After much experimentation, the optimum reaction condition was established as follows: at 40°C, under 500 psi with a 2:1 ratio of P_{H_2}:P_{CO}, and for 22 h. We have screened the hydroformylation reaction of various olefins under our optimized reaction conditions (Table 2). The efficiency of **1** was checked in the reaction of styrene with H_2/CO. The maximum turnover number was ca. 1000. However, for convenience, we used 0.5 mol% of catalyst for studying other reactions. This water-soluble rhodium catalyst was quite effective for aryl olefins and alkyl olefins. However, α-methylstyrene and diphenylethylene were not good substrates for this catalytic system (entries 8 and 9 in Table 2). The hydroformylation reaction is not sensitive to electronic effects, as demonstrated by the results obtained for the reaction of a series of para-substituted styrenes (H, CH_3, F, Cl, Br, and OCH_3), 2,4-dimethylstyrene, and 3,4-dimethoxystyrene (entries 1–7 in Table 2). There were some variations in the proportion of branched to linear aldehydes formed (89.5–

Table 2
Hydroformylation reactions catalyzed by complex **1**

Entry	Olefin	Temperature (°C)	Pressure (psi)	P_{H_2}/P_{CO}	Time (h)	b/n	Yield (%)
1	4-Fluorostyrene	40	500	2/1	22	91.18.9	100
2	4-Chlorostyrene	40	500	2/1	22	92.5/7.5	100
3	4-Bromostyrene	40	500	2/1	22	92.5/7.5	100
4	4-Methylstyrene	40	500	2/1	22	91.9/81	100
5	4-Methoxystyrene	40	500	2/1	22	89.9/10.5	90
6	2,4-Dimethylstyrene	40	500	2/1	22	90.9/9.1	100
7	3,4-Dimethylstyrene	40	500	2/1	22	90.4/9.6	91
8	α-Methylstyrene	80	500	2/1	48	0/100	56
9	Diphenylethylene	80	500	2/1	48	0/100	11
10	1-Heptene	40	500	2/1	22	44/56	100
11	1-Octene	40	500	2/1	22	44/56	100
12	Allylbenzene	60	500	2/1	22	47/53	100
13	Allylphenyl ether	40	500	2/1	22	72/28	100

92.5% branched). Aromatic 1,1-disubstituted olefins (α-methylstyrene and diphenylethylene) underwent hydroformylation yielding the linear aldehyde as the only product in poor yields (entries 8 and 9 in Table 2). Hydroformylation of terminal olefins (1-heptene and 1-octene) resulted in 100% conversion to a 44:56 ratio of branched/linear aldehyde (entries 10 and 11 in Table 2). Thus, the water-soluble rhodium complex is not a useful catalyst for the hydroformylation of simple olefins since the branched/linear aldehyde ratio is close to unity. Hydroformylation of allylic compounds (allylbenzene and allyl phenyl ether) were cleanly converted to the corresponding aldehydes with 100% conversion with low regioselectivities (entries 12 and 13 in Table 2). Our result seems to be better than that of the water-soluble rhodium catalyst [14] containing water-soluble polymers and comparable with the homogeneous system of a zwitter rhodium complex [16].

One of the advantages of the use of **1** as a hydroformylation catalyst precursor is that this catalyst system does not use valuable phosphine ligands. There are not many hydroformylation catalyst systems with simple rhodium complexes that do not use phosphine ligands [16,17]. Most rhodium catalyst systems use phosphines which are slowly degraded under reaction conditions by oxidative addition of the phosphorus–carbon bond [18,19], resulting in some loss of valuable phosphines. When we took the IR spectrum of the organic layer after reaction, we could not see any bands related to the rhodium complex. There was no leaching of rhodium complex to the organic phase. We do not have any idea about the fate of **1** after reaction. However, from the study of Abatjoglou et al. [18] and Garrou [19], we expect that the complex retains the sugar-substituted arene ring during the reaction. Thus, when we reused the aqueous solution as a catalyst and reaction medium, we could isolate the corresponding aldehyde.

At first, we expected some asymmetric induction by the sugar substituent. However, the sugar moiety did not affect the asymmetry. When we used a rhodium complex of methylated form of (+)-(4,6-*O*-benzylidene)methyl-α-D-glucopyranoside as a catalyst, we could see only a slight enantiomeric excess (ca. 6%) (S.W. Son, J.W. Han, Y.K. Chung, unpublished results). The sugar moiety may be too far from the reaction site to give any effects on the reaction path. Now the sugar moiety serves in increasing the solubility of **1** in water.

In conclusion, we have demonstrated the first synthesis of a water-soluble cationic (arene)rhodium complex and that the cationic rhodium complex displays exceptionally high regioselectivity and high conversion in the hydroformylation of styrene derivatives to branched-chain aldehydes. From a practical standpoint, it is of particular note that instead of the use of water-soluble phosphine the new cationic rhodium complex has a cheap, commercially available sugar moiety to increase solubility in water. Further studies of asymmetric hydroformylation by the water-soluble rhodium complex are currently in progress.

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