



Highly regioselective hydroformylation of 1-dodecene catalyzed by Rh-BISBIS in aqueous two-phase system

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Abstract

The hydroformylation of 1-dodecene catalyzed by $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ -BISBIS [TPPTS: $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$, BISBIS: sulfonated 1,1'-bis(diphenylphosphino methyl)-2,2'-biphenyl] in aqueous/organic two-phase system was studied. The addition of cationic surfactant cetyltrimethylammonium bromide (CTAB) greatly accelerated the reaction rate and the high regioselectivity for linear aldehyde using diphosphine as ligand was attained under two-phase conditions. Both high activity (TOF: 740 h^{-1}) and excellent regioselectivity (96.5% of 1-tridecanal) were obtained at 120°C , 2.0 MPa and [BISBIS]/[Rh] ratio of 3 in the presence of CTAB.

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Keywords: Aqueous two-phase system; 1-Dodecene hydroformylation; Diphosphine; Surfactant

1. Introduction

Rhodium catalyzed hydroformylation is one of the most important applications of homogeneous catalysis in industry [1]. Since the discovery of the rhodium catalysts by Wilkinson and co-workers [2], much effort has been made to enhance the regioselectivity of the reaction toward the formation of the more desirable linear aldehyde. High selectivities in the hydroformylation of terminal olefin have been obtained for both diphosphine- and phosphite-modified catalysts [3–14]. The chelating diphosphines with natural bite angle near 120° , such as 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BISBI) [3–5] and xantphos (diphosphines based on a xan-

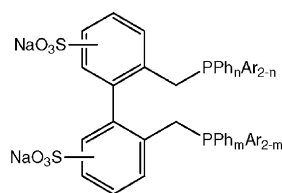
thene-type backbone) [8,12], can be used with rhodium to give the highly selective catalysts for the hydroformylation of terminal olefin. However, the separation of catalyst from product is still one of the major problems of these catalysts for practical applications. For simplifying the separation of catalysts from products and facilitating catalyst recycling, the sulfonated version of BISBI (BISBIS) [15], sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene (BINAS) [16] and 2,7-bis(SO_3Na)xantphos [17] have been prepared for use in aqueous/organic two-phase reaction system, exhibiting high regioselectivity for the formation of *n*-butyraldehyde in the rhodium-catalyzed hydroformylation of propene. The regioselectivity is also good for the hydroformylation of 1-hexene in aqueous solution; however, the rates are very low because of the very poor solubility of the substrate in water. The amphiphilic diphosphines modified by incorporating surface-active groups into

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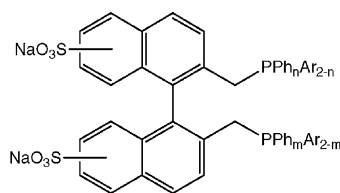
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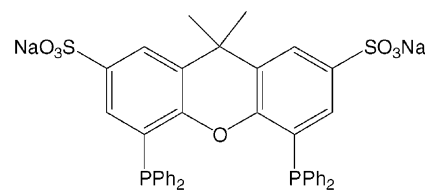
phosphines can aggregate to form the micelle and improve the solubility of substrates in water [18–21]. The accelerated reaction rates were correlated to the ability of aggregation of these ligands when these amphiphiles are used as ligands for rhodium catalyzed hydroformylation of higher olefin in water. However, the preparation of diphosphines with long-chain alkyl [19–21] is not convenient and is difficult to the practical application.



BISBIS, Ar = *m*-C₆H₄SO₃Na, m, n = 0, 1



BINAS, Ar = *m*-C₆H₄SO₃Na, m, n = 0, 1



2,7-bis(SO₃Na)Xantphos

We reported previously that water-soluble rhodium-TPPTS catalyst exhibited high activity and regioselectivity for the hydroformylation of higher olefin in the presence of surfactant, such as cetyltrimethylammonium bromide (CTAB), due to the increase of substrate solubility in micelle solution and the concentration of active species containing rhodium on the interface of micelle [22,23]. Here, we report the effect of surfactant on the hydroformylation of 1-dodecene catalyzed by BISBIS–rhodium complex in aqueous/organic biphasic solution. The high rate and high regioselectivity are obtained through the combination of BISBIS with the cationic surfactant.

2. Experimental

2.1. Materials

The catalyst precursor, RhCl(CO)(TPPTS)₂ [24], and BISBI [25] were prepared according to the literature methods. CTAB and organic solvents and 1-dodecene (Fluka) were commercial and not treated prior to use. Water was doubly distilled. Hydrogen (99.99%) and carbon monoxide (99%) were purchased and mixed directly with the ratio of 1:1 and treated with a deoxidizer and a desulfurizer.

2.2. Sulfonation of BISBI

To a 50 ml three-neck flask charged with 2 ml sulfuric acid was added 0.5 g of BISBI under N₂ atmosphere. Oleum (50%, 6 ml) was dropped carefully into the mixture at 0–6 °C. The mixture was allowed to warm up to 22–24 °C and stirred for 48 h, and then it was poured into degassed ice–water (100 ml) at 0–5 °C. After the aqueous solution was neutralized with

1N NaOH to pH 8–9 and was concentrated to about 10 ml, 15 ml of ethanol was added to remove sodium sulphate. The filtrate was evaporated to dryness; a light yellow solid was obtained and dried at 60 °C in vacuum to give 1.2 g of BISBIS. ¹H NMR (D₂O, 500 MHz): δ 6.5–7.9 (m, 24H, Ar-H), 2.8–3.6 (m, 4H, –CH₂–) ppm. ³¹P{¹H}NMR (D₂O, 500 MHz): δ –6.3(s), –6.8(s), –7.1(s), –7.6(s), –9.2(s), –9.7(s) ppm. The average of sulfonation degree was 4 according to the ratio of phenyl hydrogen to methylene hydrogen in ¹H NMR data. The solid was used without further purification for the catalytic reaction.

2.3. Catalytic reaction

A typical procedure was conducted as follows: catalyst precursor RhCl(CO)(TPPTS)₂, BISBIS, surfactant, water, 1-dodecene were added to a stainless steel autoclave of 60 ml with a magnetic stirrer. The autoclave was evacuated and purged with synthesis gas for three times. When the solution was heated to the desired temperature, synthesis gas was introduced. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water until ambient temperature. The autoclave was vented slowly, and the organic and aqueous phases were transferred to a separatory funnel. The organic products were analyzed by a gas chromatograph HP 1890II equipped with an FID detector and a capillary column

(30 m × 0.25 mm) SE-30, H₂ was the carrier gas. In all cases the organic layer was colorless and readily separated from aqueous layer after the reaction. The rhodium concentration leaching in organic phase determined by ICP was lower than 1 ppm.

3. Results and discussion

3.1. Effect of surfactant concentration

We had proved that the cationic surfactants could greatly accelerate the aqueous hydroformylation of 1-dodecene catalyzed by Rh-TPPTS in aqueous/organic two-phase system [23]. In this way, CTAB was chosen to improve the reaction rate in water when BISBIS was used as ligand. The results are summarized in Table 1. The conversion of 1-dodecene was only 1.6% in the absence of CTAB, at 100 °C, 2.0 MPa. The reaction rate increased when the concentration of CTAB was increased in the range of (0–5.49) × 10⁻³ mol/l. The conversion of 1-dodecene to aldehydes reached 43.5% upon the addition of 5.49 × 10⁻³ mol/l of CTAB for 120 min. In contrast to the Rh-TPPTS catalyst system, however, the further increase in the CTAB concentration caused a drop of the reaction rate. According to the previous report [23], these could be attributed to the following two factors. First, the formation of micelle by the addition

of CTAB increased the solubility of 1-dodecene in the aqueous phase containing the catalyst. Secondly, the cationic micelle could attract the rhodium active species with anionic BISBIS-SO₃⁻ on the interface of micelle by static electronic interaction. The synergic interaction of these two factors was responsible for the improvement of reaction rate. Initially, the increase in the CTAB concentration would mainly induce the increase in the micelle number that was responsible for the increase in the reaction rate. When the micelle concentration in the system reached to some extent, the further increase in the CTAB concentration mainly contributed to the increase in the aggregation number of micelle, the micelle would become tighter and unfavorable for the penetration of water to the “Stern” layer of micelle [26], which would make the rhodium active species with the chelated ligand BISBIS difficult to reach the interface of micelle and to interact with 1-dodecene dissolved in the micelle core. Therefore, when the CTAB concentration was increased to over 5.49 × 10⁻³ mol/l, the reaction rate decreased, but the molar ratio of linear to branched aldehyde was not affected and the original high regioselectivity of BISBIS was still kept owing to the favorable steric effect. This hypothesis was supported by the opposite trend which was observed using the monophosphine TPPTS or TPPDS [PhP(*m*-C₆H₄SO₃Na)₂] as a ligand. In the two-phase catalytic system of Rh-TPPTS [23a] (or Rh-TPPDS/TPPTS [23b]), the microenvironment

Table 1
Influence of CTAB concentration on hydroformylation of 1-dodecene catalyzed by RhCl(CO)(TPPTS)₂-BISBIS

Entry	CTAB (10 ⁻³ mol/l)	Aldehydes (%) ^a	L/B ^b	Dodecane, (%) ^c	Isomerization (%) ^d	TOF (h ⁻¹) ^e
1	0	1.6	–	0.3	0.7	18.4
2	1.57	19.8	23.3	1.1	1.1	227
3	2.75	27.8	24.4	1.7	–	319
4	3.92	34.1	18.7	1.7	1.4	391
5	5.49	43.5	21.9	2.0	1.6	499
6	6.67	34.4	20.7	2.3	1.6	395
7	7.85	21.9	21.2	1.1	1.1	251
8 ^f	2.75	49.0	3.1	2.4	1.7	562

Reaction conditions: [Rh] = 8.4 × 10⁻⁴ mol/l, H₂O: 7 ml, [BISBIS]/[Rh] = 3, 1-dodecene: 13.5 mmol, 100 °C, initial pressure: 2.0 MPa (CO/H₂ = 1), 120 min.

^a Conversion of olefin to aldehyde.

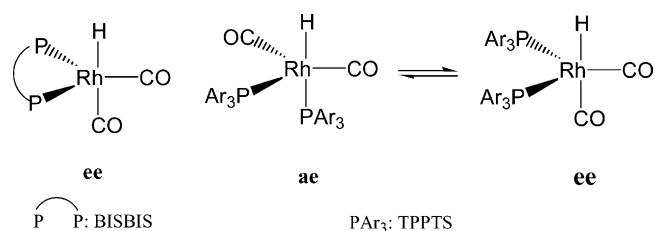
^b Molar ratio of linear to branched aldehydes.

^c Hydrogenation product of olefin.

^d Isomerization product of 1-dodecene, mainly 2-dodecene.

^e Mole of aldehydes per mole of Rh per hour.

^f TPPTS instead of BISBIS as ligand, [TPPTS]/[Rh] = 30.



Scheme 1.

of tighter micelle did not obviously influence the reaction rate due to the less crowded rhodium active species with TPPTS or TPPDS and could benefit the formation of linear aldehyde.

The high regioselectivity for linear aldehyde in the hydroformylation of 1-dodecene was obtained in the presence of the cationic surfactant when BISBIS was used as a ligand, as shown in Table 1. However, when TPPTS was used as a ligand instead of BISBIS even at higher molar ratio of phosphine to rhodium (Entry 8 in Table 1) the regioselectivity was low in the same conditions. According to the results reported by Casey et al. [4,5] and van Leeuwen and co-workers [8,10], it was possible that the rhodium active species still kept the highly selective structure with **ee** configuration in the case of BISBIS, and in contrast, the less selective structure with **ea** configuration could be the main active species in the case of TPPTS (as shown in Scheme 1). The higher activity of the TPPTS system might be attributed to the less crowded rhodium active species than the BISBIS system, which was favorable for the coordination of olefin dissolved in micelle with the rhodium active species on the interface of micelle.

3.2. Effect of molar ratio of BISBIS to rhodium

The molar ratio of phosphine to rhodium was one of the important factors to affect the activity and re-

gioselectivity of the hydroformylation. The results are summarized in Table 2. The ratio of linear to branched aldehyde increased and the hydrogenation and isomerization of 1-dodecene were suppressed when the molar ratio of BISBIS to rhodium increased. The same trend was observed in the change of TPPTS/Rh ratio [27]. The optimum activity was reached at [BISBIS]/Rh = 3. The regioselectivity for the linear aldehyde increased with increasing ratio of [BISBIS]/[Rh] and the break appeared at [BISBIS]/[Rh] = 3 (Entry 3 in Table 2). When RhCl(CO)(TPPTS)₂ was converted to HRh(CO)(TPPTS)₂ in the presence of syngas, there was a ligand exchange equilibrium between TPPTS in rhodium complexes and BISBIS (Eq. (1)). HRh(CO)₂(TPPTS)₂ was the main active species and would be responsible for the low regioselectivity when the molar ratio of BISBIS to Rh was low. The concentration of HRh(CO)₂(BISBIS) increased with the addition of BISBIS, and its formation would be favorable for the high regioselectivity at higher molar ratio of BISBIS to Rh.



3.3. Effect of reaction temperature

As shown in Table 3, both the activity and regioselectivity increased when the reaction temperature rose

Table 2

Influence of molar ratio of BISBIS to Rh on 1-dodecene hydrofomylation catalyzed by RhCl(CO)(TPPTS)₂-BISBIS

Entry	[BISBIS]/[Rh]	Aldehydes (%)	L/B	Dodecane (%)	Isomerization (%)	TOF (h ⁻¹)
1	1	13.1	5.3	3.5	1.9	150
2	2	14.7	4.8	5.7	3.0	169
3	3	27.8	24.7	1.7	–	319
4	4	19.5	31.2	1.7	1.2	224
5	6	10.4	35.9	0.8	1.0	119

Reaction conditions: CTAB: 2.75×10^{-3} mol/l, the others are the same as in Table 1.

Table 3

Influence of the temperature on 1-dodecene hydroformylation catalyzed by RhCl(CO)(TPPTS)₂-BISBIS in two-phase catalytic system

Entry	Temperature (°C)	Aldehydes (%)	L/B	Dodecane (%)	Isomerization (%)	TOF (h ⁻¹)
1	90	11.4	17.4	2.8	2.2	131
2	100	27.8	24.7	1.7	–	319
3	110	48.1	26.2	2.8	1.2	552
4	120	64.5	27.8	4.3	2.7	740
5	130	76.8	12.5	9.6	5.2	882

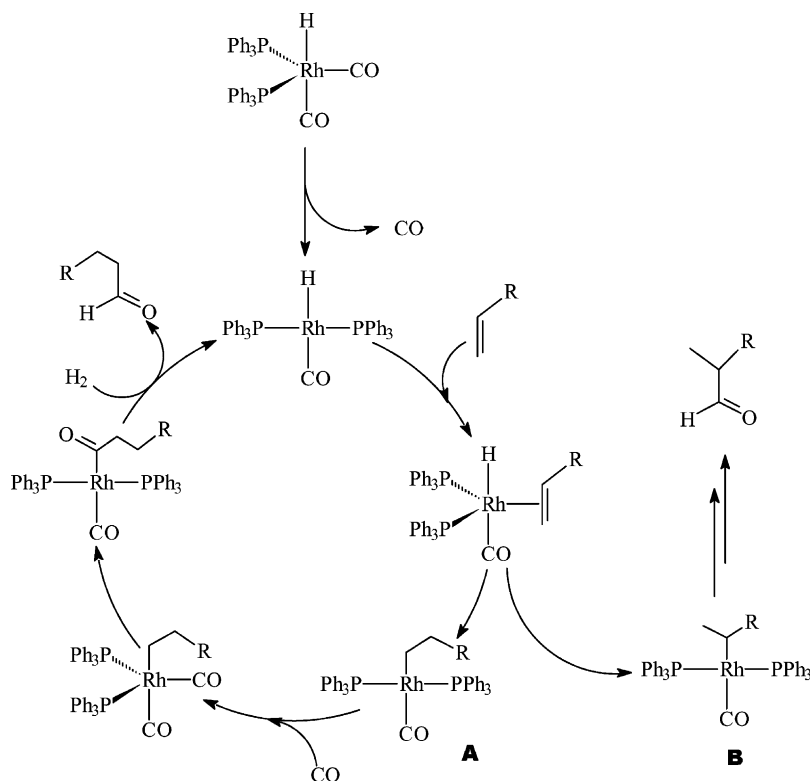
Reaction conditions: [BISBIS]/[Rh] = 3, CTAB: 2.75 × 10⁻³ mol/l, the others are the same as in Table 1.

up. However, the hydrogenation and isomerization of 1-dodecene also increased at higher temperature. According to the literatures [28,29], the hydroformylation in the two-phase system still followed the generally accepted mechanism proposed by Wilkinson (shown in Scheme 2) [2]. In this mechanism, the regioselectivity of the hydroformylation was determined by the difference value of the activation energies (ΔE) between the alkyl complexes **A** and **B** in the reaction

course as listed in Scheme 1, that is

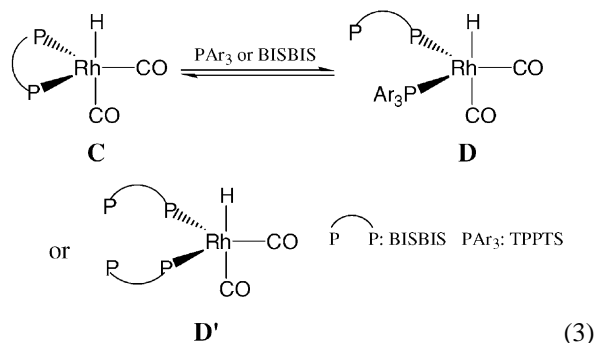
$$\frac{L}{B} = A e^{-(E/RT)} \quad (2)$$

According to Eq. (2), the ratio of linear to branched aldehyde (*L/B* ratio) would be lower at higher temperature. However, the inverse trend was observed when BISBIS was used. In this catalytic system, there was equilibrium as shown in Eq. (1); both



Scheme 2.

HRh(CO)₂(TPPTS)₂ and HRh(CO)₂(BISBIS) would exhibit different contribution to the formation of linear aldehyde in the hydroformylation, but the later played the predominant role compared with the former as shown for the Entry 8 in Table 1. At higher temperature, the stable chelated species HRh(CO)₂(BISBIS) would become more active and would induce the increase in the ratio of linear to branched aldehydes; the *L/B* ratio increased from 17.4 to 27.8 when the reaction temperature was raised from 90 to 120 °C. At 130 °C, HRh(CO)₂(BISBIS) could become unstable and the reversible dissociation of a phosphorus atom in BISBIS could partly occur to give a monodentate trigonal bipyramidal complex **D** or **D'** (Eq. (3)) under the reaction conditions (the molar ratio of BISBIS to TPPTS was 3:2). Both the formation of less selective species **D** or **D'** and the rise in temperature were responsible for the decrease in the regioselectivity, but the former should be the main reason for the large drop of *L/B* ratio (Entry 5 in Table 3), although, there was no experimental evidence to support the hypothesis due to the difficulty in direct inspection of **D** or **D'** by ³¹P NMR in situ at high temperature.



4. Conclusions

The reaction rate could be greatly accelerated by the addition of CTAB for the hydroformylation of 1-dodecene in the two-phase system catalyzed by water-soluble RhCl(CO)(TPPTS)-BISBIS, and the high regioselectivity forming linear aldehyde could be obtained by using BISBIS as a ligand. Under the

optimum conditions, the turnover frequency and the regioselectivity for linear aldehyde attained 740 h⁻¹ and 96.5%, respectively. The results showed that the combinatory system of BISBIS and the cationic surfactant was superior to the related BISBI-type ligands bearing surface active groups [19–21].

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