Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Catalysis A: Chemical 200 (2003) 157–163

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Micellar effect in hydroformylation of high olefin catalysed by water-soluble rhodium complexes associated with sulfonated diphosphines

Marta Giménez-Pedrós [a], Ali Aghmiz [a], Carmen Claver [a], Anna M. Masdeu-Bultó [a,*], Denis Sinou [b,1]

[a] *Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Pl. Imperial Tàrraco, 1, 43005 Tarragona, Spain*
[b] *Laboratoire de Synthèse Asymétrique associé au CNRS, CPE Lyon, Université Claude Bernard Lyon I, 43, boulevard du 11 novembre 1918, 69622 Villeurbanne Cédex, France*

Received 6 January 2003; accepted 9 January 2003

Abstract

High linear alkenes (1-octene and 1-decene) have been hydroformylated using water-soluble rhodium complexes associated with sulfonated diphosphines in the presence of ionic surfactants or methanol. In all cases, the hydroformylation activities were higher than in experiments without additives. The selectivity in aldehydes was higher when we used cetyltrimethylammonium hydrogensulfate ($CTAHSO_4$) as the surfactant or methanol as the co-solvent.

Keywords: Hydroformylation; Aqueous systems; Sulfonated diphosphines; Micellar effect

1. Introduction

The catalytic hydroformylation of long-chain alkenes is an interesting reaction for transforming alkenes into aldehydes using carbon monoxide and hydrogen [1,2]. The hydroformylation of linear olefins is a well-known industrial process and a key step in the manufacture of oxo alcohols.

Hydroformylation can be carried out in biphasic aqueous systems using a rhodium catalyst associated with the water-soluble ligand sodium trisulfonated triphenylphosphine (TPPTS = $P(C_6H_4$-*m*-$SO_3Na)_3$) [3]. Since this system was first used in 1984 by Rhône-Poulenc/Ruhr-Chemie in the industrial hydroformylation of propene [4–6], research into biphasic catalysis has became very active [7]. However, this process is limited to short-chain alkenes (propene and 1-butene) because a certain solubility of the alkene in water is required [8]. This process is therefore not economically viable for long-chain alkenes, which are not very soluble in water. One way to increase the solubility of the substrates in water is to add surfactants to the system [7]. The amphiphilic nature of these substances drastically lowers the surface tension of water because aggregates such as micelles or vesicles form above the critical micelle concentration (CMC) [9]. These aggregates increase the solubility

* Corresponding author. Tel.: +34-977-559572; fax: +34-977-559563.
[1] Co-corresponding author. Tel.: +33-4-72446263; fax: +33-4-72448160.
E-mail addresses: masdeu@quimica.urv.es (A.M. Masdeu-Bultó), sinou@univ-lyon1.fr (D. Sinou).

1381-1169/03/$ – see front matter
doi:10.1016/S1381-1169(03)00036-0

of hydrophobic substances thus improving the mass transfer [10,11]. This strategy has been used in the hydroformylation of alkenes with rhodium–TPPTS (Rh–TPPTS) systems [12–14]. In the hydroformylation of 1-dodecene, the activity increases in the presence of cationic surfactants such as cetyltrimethylammonium bromide (CTAB). In hydroformylation of ω-alkene carboxylic acids methyl esters up to ω-decene, cationic tensids were the best systems. The hydroformylation of alkenes between C_6 and C_{16} in reverse micellar systems has been studied by Vyve and Renken [15] using sodium dodecylsulfate (SDS) in association with butanol as a co-solvent. Reaction rates were high in the hydroformylation of 1-dodecene with Rh–TPPTS in a microemulsion using nonionic surfactants of alkylpolyglycolether [16].

Another way to increase the solubility of alkenes in water is to add a co-solvent to the system. This was widely studied in catalytic systems using water-soluble rhodium complexes and TPPTS as a ligand. For example, the hydroformylation of 1-octene was studied in the presence of co-solvents such as ethanol, methanol, acetonitrile and acetone [17]. The co-solvents increase the concentration of alkene in water and simultaneously prevent the presence of water in the organic phase. The best result was obtained when ethanol was used as the co-solvent. Adding alcohols as co-solvents was also studied by Bahrmann and Bogdanovic [18], who found that the reaction rate was enhanced when MeOH was added.

Diphosphines generally provide higher selectivities in hydroformylation in organic media [19,20], but the sulfonated diphosphines have hardly been investigated. This is probably because it is difficult to prepare pure sulfonated ligands.

The sulfonated biphenyl derivative BISBIS-Na [8,21,22] and BINAS-Na [23] associated with the $[Rh(acac)(CO)_2]$ complex (acac = acetylacetonate) has higher activities and selectivities than the rhodium–TPPTS system in the hydroformylation of propene under the same reaction conditions. The BISBIS-Na system is also active in the hydroformylation of higher olefins such as 1-hexene.

Alkyl sulfonated diarylphosphines have hardly been studied in hydroformylation. The system Rh–dppets (dppets: $(C_6H_4\text{-}m\text{-}SO_3Na)P(CH_2)_2P(C_6H_4\text{-}m\text{-}SO_3Na)_2$) [24] gave a low conversion in the hydroformylation of 1-octene. The $[Rh(acac)(CO)_2]$/dppbts system (dppbts: $(C_6H_4\text{-}m\text{-}SO_3Na)P(CH_2)_4P(C_6H_4\text{-}m\text{-}SO_3Na)_2$) has also been studied in the hydroformylation of methyl acrylate but this provided very poor chemo- and regioselectivity [25].

We recently studied the use of chiral sulfonated diphosphines as ligands in the rhodium asymmetric hydroformylation of styrene in a biphasic aqueous system. The conversions in water were low but the enantiomeric excesses were quite similar to those reported for organic solvents [26,27].

In this paper, we describe how adding anionic and cationic surfactants, SDS and cetyltrimethylammonium hydrogensulfate ($CTAHSO_4$), respectively, affects the hydroformylation of long-chain alkenes (1-octene and 1-decene) in the presence of the rhodium complexes $[Rh(\mu\text{-}OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) associated with sulfonated diphosphines 1,3-bis(diphenylphosphino)propane (dpppts) and 1,4-bis(diphenylphosphino)butane (dppbts).

2. Experimental

2.1. General methods

The rhodium catalyst precursors were synthesised using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. All other reagents were used as supplied. The complex $[Rh(\mu\text{-}OMe)(cod)]_2$ [28] and the diphosphines dpppts and dppbts were prepared as previously reported [29,30]. Gas chromatography analyses were performed using a Hewlett–Packard 5890A chromatograph in an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 mm × 0.2 mm ∅) to separate the products. The pH were measured with a pH-meter Crison micro pH 2001.

2.2. Catalysis

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was kept in a teflon vessel. The inside of the cap of the autoclave was also teflon-covered to prevent the solution from coming into direct contact with the stainless steel. An electric heating mantle kept the temperature constant.

2.2.1. Standard hydroformylation experiment

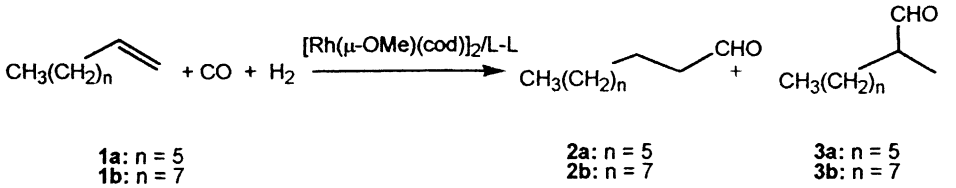
The complex $[Rh(\mu\text{-OMe})(cod)]_2$ (0.05 mmol) and the ligand (0.12 mmol) in water (6 ml) or water/methanol (3 ml/3 ml) were stirred for 1 h at room temperature. NaOH (0.25 M) was then added to adjust the pH to the desired value. The surfactant in the corresponding concentration and the substrate (15 mmol) were added, and the resulting solution was introduced into the evacuated autoclave. The system was pressurised and heated. When thermal equilibrium was reached, more gas mixture was introduced until the desired pressure was attained. After the reaction time, the autoclave was cooled to room temperature and depressurised. The reaction mixture was extracted with dichloromethane (3× 5 ml). In some cases using the anionic surfactant SDS, the final two phases system formed emulsions that were eliminated by addition of sodium chloride. The organic phase was dried over magnesium sulfate and analysed by GC. The products were identified by GC-mass spectrometry.

2.2.2. Recycling experiments

In the case of the recycling experiments, the separation was performed under nitrogen. The pH of the aqueous solution was readjusted to the desired value. Fresh substrate was added and the mixture was introduced again into the autoclave following the standard procedure.

3. Results and discussion

We studied the hydroformylation of 1-octene (**1a**) and 1-decene (**1b**) to obtain the corresponding linear (**2**) and branched aldehydes (**3**) (Eq. (1)) in aqueous systems. We prepared the catalyst precursors in situ by adding the sulfonated diphosphines dppbts (dppbts: tetrasulfonated 1,4-bis(diphenylphosphinobutane) (**4**) or dpppts (dpppts: tetrasulfonated 1,3-bis(diphenylphosphinopropane) (**5**) to the rhodium complex $[Rh(\mu\text{-OMe})(cod)]_2$.



(1)

We adjusted the initial pH of the aqueous phase to 11 because in the literature, activity was reported to be higher in basic medium than in neutral medium in the hydroformylation of 1-octene catalysed by $[Rh(\mu\text{-Cl})(cod)]_2$/TPPTS [31]. At the end of the reaction generally the pH decreased.

In this study, we chose an anionic surfactant, SDS, and a cationic surfactant, $CTAHSO_4$. The CMC values for these surfactants in water at 25 °C are 8×10^{-3} M (SDS) and 9.2×10^{-4} M ($CTAHSO_4$), respectively. To test how the concentration of the surfactants affect the conversion, we used three concentrations of surfactants ($C_1 = 6.3 \times 10^{-3}$ M, $C_2 = 1.8 \times 10^{-2}$ M, and $C_3 = 3.0 \times 10^{-2}$ M).

3.1. Hydroformylation of 1-octene in aqueous systems

Table 1 shows the results of 1-octene hydroformylation in water using $[Rh(\mu\text{-OMe})(cod)]_2$/dppbts as the precursor (entries 1–6). For comparison purposes, the results without surfactant are also given. In the conditions we studied, the products formed were the isomeric aldehydes *n*-nonanal and *iso*-nonanal, and the isomerization products 2-*trans*-octene, 2-*cis*-octene, and 3-*trans*-octene. No hydrogenation product was observed. Table 1 also shows, therefore, the selectivity in isomerization products.

The aldehyde conversion and selectivity in aldehydes of the catalyst $[Rh(\mu\text{-OMe})(cod)]_2$/dppbts were

Table 1
Hydroformylation of 1-octene (**1a**) in aqueous systems using $[Rh(\mu\text{-OMe})(cod)]_2$/L (L = dppbts (**4**) and dpppts (**5**)) as the catalyst precursors[a]

Entry	Ligand	[Surfactant][b]	P (bar) H_2/CO	T (°C)	Conversion (%)[c]	S_{ald} (%)[d]	**2/3**	S_{isom} (%)[e]
1	**4**	–	7/7	80	5	40	72/28	55
2	**4**	SDS (C_2)	7/7	80	8	38	72/28	50
3	**4**	SDS (C_3)	7/7	80	98	31	65/35	62
4	**4**	SDS (C_3)	7/7	65	5	55	72/28	45
5	**4**	$CTAHSO_4$ (C_1)	7/7	80	24	96	79/21	1
6[f]	**4**	$CTAHSO_4$ (C_3)	7/7	80	95	79	75/25	12
7	**5**	–	7/7	80	5	80	75/25	<1
8	**5**	SDS (C_2)	7/7	80	33	25	73/27	73
9	**5**	SDS (C_3)	7/7	80	66	12	75/25	79
10	**5**	SDS (C_2)	25/25	80	30	60	69/31	30
11	**5**	SDS (C_2)	17/33	80	13	62	71/29	31
12	**5**	$CTAHSO_4$ (C_1)	7/7	80	17	82	58/42	12

[a] Reaction conditions: substrate = 15 mmol, $[Rh(\mu\text{-OMe})(cod)]_2 = 5 \times 10^{-3}$ M, substrate/precursor = 500, solvent = H_2O (6 ml), P/Rh ratio = 4 (L/$[Rh(\mu\text{-OMe})(cod)]_2$ molar ratio = 4), time = 24 h, pH 11.
[b] Concentration: $C_1 = 6.3 \times 10^{-3}$ M, $C_2 = 1.8 \times 10^{-2}$ M, $C_3 = 3.0 \times 10^{-2}$ M.
[c] Aldehyde conversion measured by gas chromatography.
[d] Selectivity in aldehydes defined as percent aldehyde conversion/percent total conversion.
[e] Selectivity in isomerised products defined as percent isomerization products/percent total conversion.
[f] Loss of catalyst in the organic layer.

very low both without any additive (Table 1, entry 1) and with the addition of SDS at low concentration (Table 1, entry 2). Adding anionic surfactant SDS at a higher concentration (Table 1, entry 3) increased the activity (complete conversion was observed at the same reaction time). However, the selectivity was low and similar to the one obtained without additive. Regioselectivity was the same in water as at a low concentration of SDS (Table 1, entry 2), but a higher concentration of surfactant increased the amount of *iso*-nonanal.

To prevent the formation of isomerization products by β-elimination, we performed one experiment at 65 °C. Decreasing the temperature of the reaction effectively enhanced the selectivity in aldehydes; unfortunately the conversion was very low (Table 1, entry 4).

Adding cationic surfactant $CTAHSO_4$ increased the conversion and selectivity in aldehydes (Table 1, entries 5 and 6). This could be due to two factors: the substrate is efficiently dissolved in the micellar system, or the cationic micelle has a positive charged surface that attracts the catalytic rhodium species to the micelle surface through the sulfonated groups, which are negatively charged [12]. This promotes the contact between the substrate and catalyst. However, high concentrations of surfactant can lead to a loss of catalyst in the organic phase. This can be easily observed because the organic phase became coloured.

In fact, when we used the highest concentration of cationic surfactant, which was above CMC (Table 1, entry 6), there was a loss of catalyst in the organic phase. At concentrations above CMC, there is an equilibrium between the free surfactant and the micellar species. Electrostatic interaction between anionic species of the rhodium complex and cationic surfactant-free species may have been responsible for the loss of catalyst in the organic phase. At a lower concentration of surfactant (Table 1, entry 5), which is closer to CMC this phenomenon did not occur and there was a slight increase in conversion and a higher selectivity. The regioselectivity was better than that of the system without additive (with cationic surfactant, regioselectivity in nonanal was around 80%).

Table 1 shows the results when the precursor $[Rh(\mu\text{-OMe})(cod)]_2$/dpppts was used (entries 7–12). If we compare the different systems, we can see that the Rh/dpppts system was more selective in aldehydes than the Rh/dppbts system when no additive was added (Table 1, entry 7 versus entry 1).

Adding SDS to the Rh/dpppts system had the same effect as in the Rh/dppbts system. Conversion increased but selectivity decreased when we raised the concentration of the surfactant. To improve the selectivity, we increased the pressure to 50 bar (Table 1, entries 10 and 11). When the hydrogen:carbon monoxide ratio was 1:1, selectivity improved but conversion remained the same (Table 1, entry 10 versus entry 8). On the other hand, when the H_2:CO ratio was changed to 1:2, there was a drop in conversion (Table 1, entry 11). The regioselectivities obtained in the presence of SDS were similar to those obtained without additive.

Adding $CTAHSO_4$ had the same effect as the system that used dppbts as the ligand (Table 1, entry 12), i.e. both the activity and the selectivity increased. Note that regioselectivity in nonanal was lower than that of the system that used dppbts as the ligand (Table 1, entry 12 versus entry 5).

If we compare the two systems $[Rh(\mu\text{-OMe})(cod)]_2$/dppbts and $[Rh(\mu\text{-OMe})(cod)]_2$/dpppts, we can conclude that the system with dpppts is more selective in aldehydes with no additive. Adding SDS enhanced the total conversion, but not the selectivity in aldehydes. On the other hand, adding $CTAHSO_4$ enhanced both total conversion and selectivity but conversion was still low. Finally, regioselectivities in nonanal were higher when dppbts was used as the ligand and $CTAHSO_4$ was used as the surfactant.

3.2. Hydroformylation of 1-decene in aqueous systems

Table 2 shows the results of the hydroformylation of 1-decene. Interestingly, when $[Rh(\mu\text{-OMe})(cod)]_2$/dppbts was used as the precursor (Table 2, entries 13–17), the conversion observed in the hydroformylation of 1-decene was higher than that of 1-octene in water (Table 1, entry 1). However, the selectivity in aldehydes was low, and the main products obtained were isomerization products.

Adding SDS to the system $[Rh(\mu\text{-OMe})(cod)]_2$/dppbts (Table 2, entries 14 and 15, versus Table 1, entries 2 and 3) has the same effect than in the case of 1-octene. The conversion increased with increasing amount of surfactant, but the selectivity in aldehydes and the regioselectivity in nonanal decreased.

Adding $CTAHSO_4$ (Table 2, entry 16) improves both the conversion and the selectivity; it is to be noted that they are even higher than those obtained in the case of 1-octene. A conversion of 63% with selectivity in aldehydes of up to 97% was achieved. Additionally, we were able to recycle the system, the conversion and selectivity in aldehydes being maintained (Table 2, entry 17).

When the system Rh–dpppts was used no conversion was detected. Adding SDS resulted in a high increase of the conversion in the highest concentration studied. However, the selectivity was low and

Table 2
Hydroformylation of 1-decene (**1b**) in aqueous systems using $[Rh(\mu\text{-OMe})(cod)]_2$/L (L = dppbts (**4**) and dpppts (**5**)) as the catalyst precursors[a]

Entry	Run	Ligand	[Surfactant][b]	Conversion (%)[c]	S_{ald} (%)[d]	**2/3**	S_{isom} (%)[e]
13	1	**4**	–	15	20	73/20	80
14	1	**4**	SDS (C_2)	48	31	75/25	69
15	1	**4**	SDS (C_3)	88	25	65/35	75
16	1	**4**	$CTAHSO_4$ (C_1)	63	97	78/22	3
17	2	**4**	$CTAHSO_4$ (C_1)	72	96	69/31	4
18	1	**5**	–	–	–	–	–
19	1	**5**	SDS (C_2)	–	–	–	–
20	1	**5**	SDS (C_3)	68	21	74/26	76
21	1	**5**	$CTAHSO_4$ (C_1)	3	86	55/45	13

[a] Reaction conditions: substrate = 15 mmol, $[Rh(\mu\text{-OMe})(cod)]_2 = 5 \times 10^{-3}$ M, substrate/precursor = 500, solvent = H_2O (6 ml), P/Rh ratio = 4, P = 14 atm, H_2/CO = 7/7, T = 80 °C, time = 24 h, pH 11.
[b] Concentration: $C_1 = 6.3 \times 10^{-3}$ M, $C_2 = 1.8 \times 10^{-2}$ M, $C_3 = 3.0 \times 10^{-2}$ M.
[c] Aldehyde conversion measured by gas chromatography.
[d] Selectivity in aldehydes.
[e] Selectivity in isomerised products.

the main products were isomerized products (Table 2, entry 20).

Adding $CTAHSO_4$ improved the activity only very slightly (Table 2, entry 21). If we compare this result with those from the same system in the hydroformylation of 1-octene (Table 1, entry 12, versus Table 2, entry 21) we can see that the regioselectivity in nonanal was very low when dpppts was used as the ligand.

3.3. Hydroformylation in aqueous–methanolic systems

To compare the strategies for improving the mass transfer between the two phases, we also studied the effect of a co-solvent such as methanol. When methanol was used as the co-solvent, $[Rh(\mu\text{-OMe})(cod)]_2$/dppbts or $[Rh(\mu\text{-OMe})(cod)]_2$/dpppts as the catalyst precursor, and 1-octene as the substrate (Table 3, entries 22 and 23), activities were higher than those obtained in water (Table 1, entries 1 and 7), while the regioselectivities in nonanal were lower. When Rh–dppbts was used as the ligand (Table 3, entry 22), selectivity in aldehydes was 90%. When 1-octene was used as the substrate, the results for both total conversion and selectivity in aldehydes were highest when methanol was used as the co-solvent. However, regioselectivity in nonanal was low with this system.

In the hydroformylation of 1-decene, adding methanol considerably increased conversion when the Rh–dpppts system was used (Table 3, entry 25). When dppbts was used as the ligand (Table 3, entry 24), activity did not improve and only selectivity in aldehydes improved. Regioselectivities with both ligands dppbts and dpppts were similar to those obtained when water was the only solvent.

Table 3
Hydroformylation of 1-octene (**1a**) and 1-decene (**1b**) in aqueous–methanolic systems using $[Rh(\mu\text{-OMe})(cod)]_2$/L (L = dppbts (**4**) and dpppts (**5**)) as catalyst precursors[a]

Entry	Ligand	Substrate	Conversion (%)[b]	S_{ald} (%)[c]	**2/3**	S_{isom} (%)[d]
22	**4**	**1a**	60	90	58/42	3
23	**5**	**1a**	67	57	68/32	42
24	**4**	**1b**	14	79	74/26	11
25	**5**	**1b**	60	23	71/29	60

[a] Reaction conditions: substrate = 15 mmol, $[Rh(\mu\text{-OMe})(cod)]_2 = 5 \times 10^{-3}$ M, substrate/precursor = 500, solvent = H_2O/MeOH (3 ml/3 ml), P/Rh ratio = 4, time = 24 h, pH 11, T = 80 °C, P = 14 atm (CO/H_2 = 1/1).
[b] Aldehyde conversion measured by gas chromatography.
[c] Selectivity in aldehydes.
[d] Selectivity in isomerised products.

4. Conclusions

In the Rh-sulphonated diphosphine hydroformylation of 1-octene and 1-decene, selectivities and total conversions are modified when surfactants are added or a co-solvent is used.

In the hydroformylation of 1-octene, the results for conversion and selectivity in aldehydes were best when methanol was the co-solvent and dppbts was the ligand, but regioselectivities in nonanal were lower. Adding surfactants increased the conversion with the systems Rh–dpppts and Rh–dppbts. However, selectivity in aldehydes did not improve when SDS was added. Adding $CTAHSO_4$ increased both the total conversion and the selectivity, and there was a slight improvement in regioselectivity in nonanal. However, a high concentration of surfactant led to a loss of the catalyst in the organic phase.

For 1-decene hydroformylation, the results were best when $CTAHSO_4$ was used as the surfactant and dppbts was used as the ligand: conversion was 63% and selectivity in aldehydes was 97%. Moreover, we could recycle the system maintaining the same activity and selectivity in aldehydes. Adding SDS increased activity, but unfortunately selectivity in aldehydes did not improve. When methanol was used as the co-solvent with the system Rh–dppbts, selectivity increased but the activity was similar to the activity in water.

Acknowledgements

We thank the Ministerio de Educación, Cultura y Deporte (PB97-04070CO5-01), the Generalitat de Catalunya (ACI-96) and the Commission for the European Communities (COSTD10 Action01) for their financial support.

References

[1] C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with

Organometallic Compounds, VCH, Weinheim, 1996, Chapter 2.1, p. 29.
[2] P.W.N.M. van Leeuwen, in: P.W.N.M. van Leeuwen, C. Claver (Eds.), Rhodium Catalyzed Hydroformylation, 2000, Chapter 1, p. 1.
[3] E.G. Kuntz, Chemtech 17 (1987) 570.
[4] E.G. Kuntz, Rhône-Poulene Recherches, Fr 2.314.910, 1975.
[5] B. Cornils, E.G. Kuntz, J. Organomet. Chem. 502 (1995) 177.
[6] B. Cornils, E. Wiebus, Recl. Trav. Chim. Pays-Bas 115 (1996) 211.
[7] B. Cornils, in: W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, VCH, Weinheim, 1998, Chapter 6, p. 271.
[8] E. Wiebus, B. Cornils, Chem. Eng. Technol. 66 (1994) 916.
[9] K. Tsujii, Surface Activity Principles, Phenomena, and Applications, Academic Press, New York, 1998, Chapter 2, p. 45.
[10] G. Oehme, I. Grassert, S. Ziegler, R. Meisel, H. Furhrmann, Catal. Today 42 (1998) 459.
[11] F. Robert, G. Oehme, I. Grassert, D. Sinou, J. Mol. Catal. A: Chem. 156 (2000) 127.
[12] B. Fell, C. Schobben, G. Papadogianakis, J. Mol. Catal. A: Chem. 111 (1995) 179.
[13] H. Chen, H. Liu, Y. Li, P. Cheng, X. Li, Chin. J. Mol. Catal. A: Chem. 9 (1995) 145.
[14] H. Chen, Y. Li, J. Chen, P. Cheng, Y. He, X. Li, J. Mol. Catal. A: Chem. 149 (1999) 1.
[15] F.V. Vyve, A. Renken, Catal. Today 48 (1999) 237.
[16] M. Haumann, H. Koch, P. Hugo, R. Schomäcker, Appl. Catal. A 255 (2002) 239.
[17] F. Monteil, R. Queau, P. Kalck, J. Organomet. Chem. 480 (1994) 177.
[18] H. Bahrmann, S. Bogdanovic, in: B. Cornils, W.A. Hermann (Eds.), Aqueous-Phase Organometallic Catalysis, VCH, Weinheim, 1998, p. 306.
[19] D.W. Mee, in: L.H. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, 1983, p. 257.
[20] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpainter, J. Mol. Catal. A: Chem. 104 (1995) 17.
[21] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrmann, H. Kottmann, J. Mol. Catal. A: Chem. 97 (1995) 65.
[22] W.A. Herrmann, C.W. Kohlpaintner, H. Bahrmann, W. Konkol, J. Mol. Catal. 73 (1992) 191.
[23] H. Bahrmann, H. Bach, C.D. Frohning, H.J. Kleiner, P. Lappe, D. Peters, D. Regnat, W.A. Herrmann, J. Mol. Catal. A: Chem. 116 (1997) 49.
[24] T. Bartik, B.B. Bunn, B. Bartik, B.E. Hanson, Inorg. Chem. 33 (1994) 164.
[25] G. Fremy, E. Monflier, J.F. Carpentier, Y. Castanet, A. Mortreux, Angew. Chem. Int. Ed. Engl. 34 (1995) 1474.
[26] M.D. Miquel-Serrano, A. Aghmiz, M. Diéguez, A.M. Masdeu-Bultó, C. Claver, D. Sinou, Tetrahedron: Asymmetry 10 (1999) 4463.
[27] A. Aghmiz, A. Orejón, M. Diéguez, M.D. Miquel-Serrano, C. Claver, A.M. Masdeu-Bultó, D. Sinou, G. Laurenczy, J. Mol. Catal. A: Chem., in press.
[28] R. Usón, L.A. Oro, J. Cabeza, Inorg. Synth. 23 (1985) 126.
[29] Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Toth, B. Heil, Organometallics 8 (1989) 542.
[30] L. Lecomte, D. Sinou, Phosphorus, Sulfur Silicon Relat. Elem. 53 (1990) 239.
[31] R.M. Desphande, Purwanto, H. Delmas, R.V. Chaudhari, J. Mol. Catal. A: Chem. 126 (1997) 133.