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Hydroformylation of allyl ethers. A study of the regioselectivity using rhodium catalysts

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Abstract

The hydroformylation of different substituted allyl benzyl ethers is studied using the precursor catalytic system $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2 + PR_3$ ($R = Ph$, O-*o*-*t*-BuC_6H_4) in order to obtain γ-, β- and α-hydroxyaldehydes. The influence of the phosphorus auxiliary ligands on the isomerization/hydroformylation processes is analyzed. High yields and low regioselectivities are obtained in the hydroformylation of allyl benzyl ether **1** using both $P(O\text{-}o\text{-}t\text{-}BuC_6H_4)_3$ and PPh_3. 4-Benzyloxy-3-methyl-butanal **8** and 4-benzyloxy-2-methyl-butanal **11** were obtained in good to excellent yields, starting from benzyl-2-metallyl ether **2** and benzyl-2-buthenyl ether **3**, respectively.

Keywords: Hydroformylation; Allyl ethers; Rhodium; Catalysis

1. Introduction

Hydroformylation of propene to obtain butanol by reduction of butanal is a well-known homogeneous catalyzed industrial process [1–4]. The hydroformylation of allyl alcohol or allyl acetate [5,6] has also been the subject of attention because it can provide an alternative route for the manufacture of 1,4-butanediol, a bulk chemical which is used in the synthesis of high performance plastics. In this respect, different works have discussed the influence of the variables on the catalytic reaction. The effect of the different catalysts Co [7] or Rh [8–10], the source of hydrogen [11], and the reaction conditions [12–14] have been studied. All these works focus on the synthesis of the linear aldehyde which provides the 1,4-butanediol by reduction (Scheme 1).

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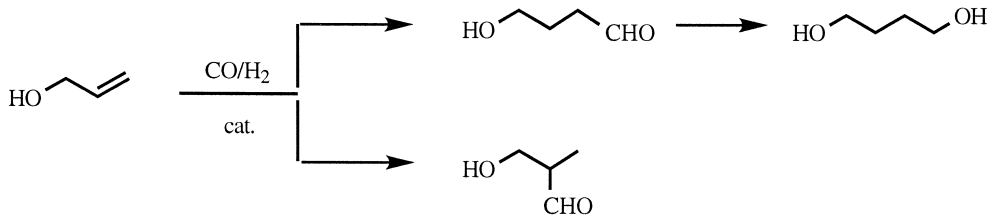


Scheme 1.

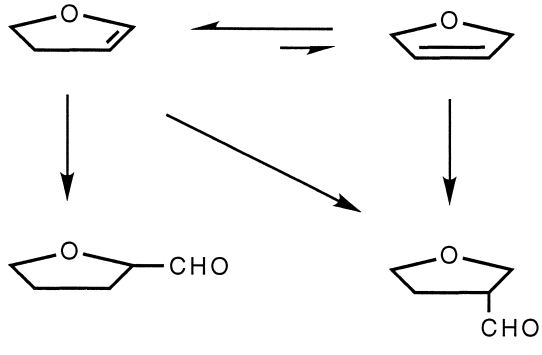
There are much fewer examples about the hydroformylation of allyl ethers [15,16]. We have shown that the hydroformylation of 2,3-dihydrofuran and 2,5-dihydrofuran, vinyl and allyl cyclic ethers respectively, provides the same hydroformylation products when $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2 + P(O\text{-}o\text{-}t\text{-}BuC_6H_4)_3$ was used as catalytic system in appropriate reaction conditions [17]. This is evidence of a consecutive isomerization hydroformylation process, the allyl isomerizing to vinyl ether before the hydroformylation started (Scheme 2).

Using $Rh_4(CO)_{12}$ as catalytic precursor, Lazzaroni [16] has demonstrated, that at a high temperature (100°C), hydroformylation of ethyl allyl ether leads principally to the linear product.

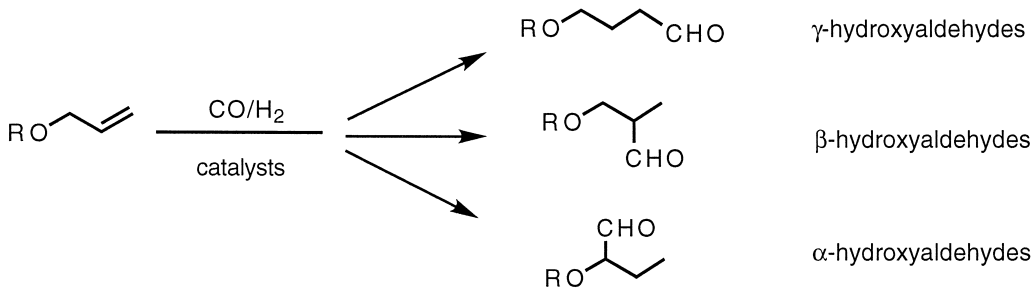
However, β-elimination of the alkyl–metal complex produces a considerable amount of *Z* and *E* vinyl ethers, which need more drastic reaction conditions to be hydroformylated. Nozaki et al. [18] have recently used a chiral phosphite–phosphine rhodium complex to show that the regioselectivity and the enantioselectivity can be rationalized by the degree of reversibility of alkyl–rhodium formation.

The allyl ethers are much more simple to synthesise than the vinyl ethers. It is known that the hydroformylation of vinyl ethers and esters mainly provides the product with the formyl group next to the oxygen [17]. Therefore, if it is possible to isomerize the allyl to vinyl ether in the hydroformylation conditions, α-hydroxyaldehydes will be principally obtained. The main problem of this consecutive isomerization–hydroformylation process is the lower reactivity of the internal olefin, which requires more drastic conditions than the terminal ones.

In this context, we believed it would be interesting to study the hydroformylation of differently substituted allylic alcohols with the aim of obtaining γ-, β- and α-hydroxyaldehydes (Scheme 3), which after oxidation will provide the corresponding γ-, β- and α-hydroxyacids. In this work, we



Scheme 2.



Scheme 3.

present the results obtained from the hydroformylation of compounds **1**–**3** using the catalytic precursor $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2$ and PR_3.

2. Experimental section

2.1. General methods

The catalyst precursor $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2$ was prepared using a previously described method [15]. Solvents were distilled and deoxygenated before use. Phosphorus reactants were of commercial origin and used without further purification. Tris (*o-tert*-butylphenyl)phosphite was prepared as previously described [19]. All other reagents were commercial samples and were used as purchased. Gas chromatography was performed on a Hewlett–Packard 5840A chromatograph with flame ionization detector using an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm Ø) capillary column (Ultra 2). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 MHz spectrophotometer and chemical shifts are quoted in ppm downfield from internal TMS.

2.2. Preparation of the substrates

Substrates were prepared by the conventional methods of reacting the corresponding sodium salt of benzyl alcohol with the allyl halide or reacting the sodium salt of the allyl alcohol with benzyl bromide.

*2.2.1. Allyl benzyl ether **1***

Boiling point: 205–210°C. NMR ($CDCl_3$): ^1H δ 7.33 (m, Ph), 5.95 (m,–CH=), 5.20, 5.30 (m, $=CH_2$), 4.51 (s, O–CH_2–Ph), 4.02 (m, O–CH_2–C=); ^{13}C δ 138.38 (C, Ph), 134.83 (–CH=), 127.50–129.50 (CH, Ph), 117.16 ($=CH_2$), 72.00 (O–CH_2–Ph), 71.02 (O–CH_2–C=).

*2.2.2. Benzyl-2-metallyl ether **2***

Boiling point: 215–220°C. NMR ($CDCl_3$): ^1H δ 7.33 (m, Ph), 4.96 (m, $=CH_2$), 4.48 (s, O–CH_2Ph), 3.92 (s, O–CH_2–C=), 1.76 (s, CH_3); ^{13}C δ 142.27 (–C=), 138.51 (C, Ph), 127.50–129.00 (CH, Ph), 112.36 ($=CH_2$), 74.00 (O–CH_2Ph), 71.69 (O–CH_2–C=), 19.30 (CH_3).

*2.2.3. Benzyl-2-buthenyl ether **3***

Boiling point: 205–210°C. NMR ($CDCl_3$): ^1H δ 7.32 (m, Ph), 5.65 (m, =CH–), 4.49 (s, O–CH_2–Ph), 3.95 (m, O–CH_2–C=), 1.71 (m, CH_3); ^{13}C δ 138.46 (C, Ph), 131.80 (=CH–), 126.88–129.55 (=CH–, Ph), 71.90 (O–CH_2–Ph), 70.87 (O–CH_2–C=).

2.3. Catalysis

Low-pressure hydroformylation experiments (5 and 35 bar) were carried out in a specially designed autoclave with magnetic stirring. The catalytic solution was contained in a glass vessel. Constant temperature was maintained by circulating water through a double jacket. The gas mixture was introduced at constant pressure from a gas ballast. The pressure drop in the ballast was monitored using a pressure transducer connected to an electronic measurement and printing unit.

High-pressure hydroformylation experiments (80 bar) were carried out in a Berghof autoclave, and the reaction mixtures were magnetically stirred and electrically heated. These experiments were not performed at constant pressure, but for the amount of substrate used, the drop in pressure was never more than 3 bar.

2.4. Standard catalysis experiment

A solution of the substrate (20 mmol) previously stirred with alumina for 24 h, the catalyst (0.05 mmol) and the phosphorus co-catalyst were introduced into the evacuated autoclave and heated with stirring. Once the system reached thermal equilibrium, the gas mixture was introduced to reach the working pressure. After each run, the solution was removed from the autoclave, and analyzed by gas chromatography and ^1H and ^{13}C NMR spectroscopy.

Products **5–7**, obtained from alkene **1**, were identified by ^1H NMR spectroscopy of the products mixture. Thus, in the ^1H NMR spectrum appeared three signals at 9.75 ppm (triplet), 9.70 ppm (doublet) and 9.64 ppm (doublet) attributed to formyl protons of compounds **5**, **6**, and **7**, respectively. Signals of compounds **6** and **7** were attributed by double resonance experiments.

Compound **8**: ^1H NMR δ 9.75 (s, 1H, $J=2.2$ Hz, CHO), 4.47 (s, 2H, $PhCH_2O$), 3.33 (m, 2H, OCH_2C) 2.20–2.60 (m, 4H, CH_2–CH_2), 0.97 (d, 3H, $J=6.7$ Hz, CH_3). ^{13}C NMR δ 202.7, 128.8–127.6 (Ph), 74.8, 72.9, 48.3, 28.9, 16.8.

Signal of aldehyde proton of compound **10** was overlapped with signal of compound **8**, and their presence in the mixture was proposed taken into account the absence of singlets in the methyl signals.

In the case of substrate **3** products were assigned by preparation and isolation of the 2,4-dinitrophenylhydrazone derivatives.

Conversions and selectivities into aldehydes were determined by GC. Integrations in the ^1H NMR spectrum were in agreement with GC data.

2.5. Preparation of the 2,4-dinitrophenylhydrazone derivatives of the products from the hydroformylation of benzyl-2-butenyl ether (3)

A solution of 2,4-dinitrophenylhydrazine in methanol 95% was prepared (1 mmol hydrazine to 30 ml methanol) and heated until the solid completely dissolved. A solution of aldehydes in methanol was added (ratio aldehydes/hydrazine 1/1) and the mixture reaction was refluxed for 1 h. Some drops of hydrochloric acid were added and a red solid appeared when the solution was cooled.

Quantitative yields of the three 2,4-dinitrophenylhydrazone derivatives were obtained. Products were separated by flash chromatography using hexane/ethyl acetate 8:1 as eluent.

The only pure isolated derivative was 4-benzyloxy-2-methyl-butiraldehyde (as 2,4 dinitrophenylhydrazone).

^{1}H RMN (300 MHz, $CDCl_3$), δ (ppm): 10.91 (s, 1H, NH), 9.11 (d, 1H, $J_{3'5'} = 2.1$ Hz, H-3′), 8.25 (d, 1H, $J_{5'-6'} = 12$ Hz), 7.90 (d, 1H, H-6′), 7.42 (d, 1H, $J_{CH=N3} = 4.5$ Hz, CH = N), 7.29 (m, 5H, ArH), 4.49 (s, 2H, H-6), 3.60 (m, 2H, H-4), 2.80 (m, 1H, H-2), 1.90 (m, 2H, H-3), 1.20 (d, 3H, $J_{1,2} = 6.9$ Hz, H-1).

^{13}C RMN (75.4 MHz, $CDCl_3$), δ (ppm): 156.5 (CH = N), 129.9, 128.3, 127.6, 127.5, 123.5, 116.5 (Ar), 73.1 (CH_2O), 67.8 (CH_2O), 34.5 (CH_2), 34.4 (CH), 17.6 (CH_3).

3-benzyloxy-2-ethyl-propionaldehyde (as 2,4-dinitrophenylhydrazone) was not isolated. An elimination process took place during the reaction.

Finally, 2-benzyloxy-pentaldehyde (as 2,4-dinitrophenylhydrazone) was not identified due to the low regioselectivity in this product during the hydroformylation reaction.

3. Results and discussion

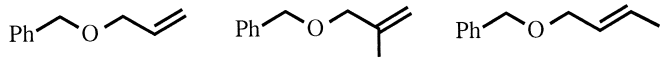
To perform the study, we selected a series of different substituted allyl benzyl ethers (**1**–**3**), which can be considered to be allyl alcohols protected with the benzyl group. A greater tendency to isomerize to the thermodynamically stable enol ether can be expected when the substitution in the terminal carbon, compound **3**, is increased (Fig. 1).

Compounds **1** and **2** were prepared from the benzyl alcohol and allyl bromide and metallyl chloride, respectively in basic medium through a typical etherification reaction. In a similar way, compound **3** was obtained from benzyl bromide and crotyl alcohol.

We have shown that in the hydroformylation of dihydrofuran (Scheme 2) the catalytic precursor system $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2 + PPh_3$ working at high pressures leads exclusively to the 3-formyl derivative. When $P(O\text{-}o\text{-}t\text{-}BuC_6H_4)_3$ was used as auxiliary ligand, however, the system isomerizes the 2,5 to the 2,3-dihydrofuran leading to the 2-formyltetrahydrofuran as the main hydroformylation product. Therefore, $P(O\text{-}o\text{-}t\text{-}BuC_6H_4)_3$ produced a fast isomerization allowing the vinyl olefin to be hydroformylated.

In order to find out how the phosphorus ligands affect the isomerization/hydroformylation processes, $P(O\text{-}o\text{-}t\text{-}BuC_6H_4)_3$ (cone angle = 175°) and PPh_3 (cone angle = 145°) were used as auxiliary ligands.

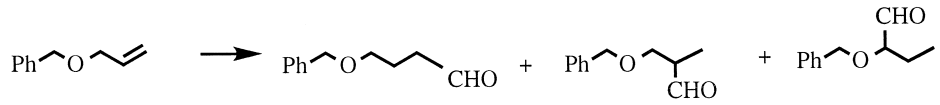
The hydroformylation of **1** (Table 1) was carried out with $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2$ as catalytic precursor in the temperature range 80–120°C and at a total pressure 2–30 atm ($CO:H_2$ 1:1) for 24 h. Conversion and regioselectivity of the allylic substrate to aldehydes was determined by GC analysis and the products were identified by ^{1}H NMR spectroscopy. As shown in Table 1, using either tris(*o-tert*-butylphenyl)phosphite or tryphenylphosphine as the auxiliary ligand, conversions into



1 **2** **3**

Fig. 1.

Table 1
Hydroformylation of allyl benzyl ether (**1**) using $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2 + nPR_3$



1 **5** **6** **7**

Run	PR_3	*P* (atm)	*T* (°C)	$\%C_{ald}$	% **5**	% **6**	% **7**
1	20P∗	5	80	99	43	37	20
2[a,b]	20P∗	5	80	99	45	35	20
3	4P∗	2	80	92	46	34	20
4	20P∗	30	80	86	48	43	9
5	20P∗	5	120	87	50	32	18
6	$20PPh_3$	5	80	89	59	40	1
7	$20PPh_3$	35	80	99	48	52	–
8	$4PPh_3$	5	80	94	56	40	4

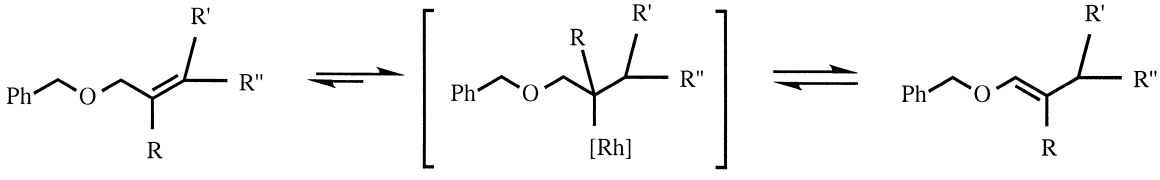
Reaction conditions: Solvent: Toluene, $CO/H_2 = 1$, ([a]1/2), $[cat] = 6.6 \times 10^{-7}$ M, reaction time: 24 h ([b]48 h).
P∗: tris-(*o-tert*-butylphenyl) phosphite.

aldehydes were between 86–99%. Polymerization and hydrogenation products of olefins or aldehydes were not observed.

At 5 atm and 80°C (run 1) using tris (*o-tert*-butylphenyl)phosphite as auxiliary ligand, the substrate isomerizes to internal olefin (Scheme 4) by β-hydride elimination during the reaction and aldehyde **7** (2-benzyloxybutiraldehyde) is formed together with the expected aldehydes **5** and **6** (Table 1). The regioselectivity is in favor of the linear isomer (**5**:**6**:**7** = 43:37:20). The aldehyde **7** content is not affected either by the change in CO/H_2 ratio 1:2 (run 2) or by changing the total pressure (2 atm, run 3 or 30 atm, run 4). At higher temperatures (120°C, run 5) higher β-hydride elimination would be expected [5–7] but there was a slight decrease in aldehyde **7** together with a lower conversion into aldehydes.

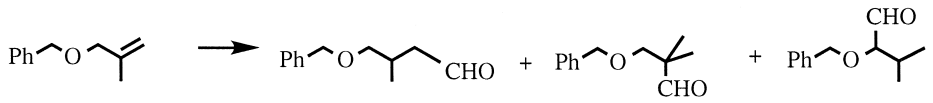
When triphenylphosphine, a less hindered auxiliary ligand, was used, only the aldehydes **5** and **6** were formed and no isomerization of the substrate was observed. No major changes in regioselectivities were observed when total pressure was increased (5 atm, run 6 to 30 atm, run 7) and the linear aldehyde **5** was mainly obtained.

Although in this work the complex $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2$ in presence of PPh_3 has been used as catalyst precursor, simultaneous studies showed that $RhH(CO)_2(PPh_3)_2$ is considered to be the main species during the hydroformylation reaction, in rapid equilibrium via CO and PPh_3 dissociation steps with other related species [20–22]. This behaviour is different from the bulk ligand tris-(*o-tert*-butylphenyl)phosphite in which $RhH(CO)_3P*$ has been proposed as the predominant species during the catalysis. The presence of only one phosphite coordinated to the rhodium centre is attributed to the large cone angle of the P∗ [23,24].



Scheme 4.

Table 2
Hydroformylation of benzyl metallyl ether (**2**) using $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2 + nPR_3$



2 **8** **9** **10**

Run	PR_3	*P* (atm)	*T* (°C)	$\%C_{ald}$	% **8**	% **9**	% **10**
9	20P∗	5	80	56	93	–	7
10	20P∗	5	120	21	90	–	10
11	$20PPh_3$	5	80	37	100	–	–
12	$20PPh_3$	30	80	91	100	–	–

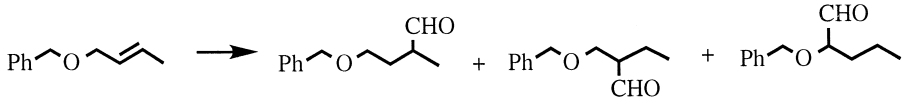
Reaction conditions: Solvent: Toluene, $CO/H_2 = 1$, $[cat] = 6.6 \times 10^{-7}$ M, reaction time: 24 h.
P∗: tris-(*o-tert*-butylphenyl) phosphite.

When PPh_3 was used, a high P:Rh ratio could stabilize the formation of alkylic species in front of β-hydride elimination process due to the fact that triphenylphosphine is less hindered than tris-(*o-tert*-butylphenyl)phosphite and enables a higher number of phosphorus ligands to be coordinated to the metal center. When the P:Rh ratio was decreased, a small amount of isomerization product **7** was observed (run 8).

Therefore, in the case of the allyl benzyl ether, due to the steric effects, the linear aldehyde is mainly formed as is to be expected for olefins containing different substitution. Although there is some β-hydride elimination for P∗ and PPh_3, the rate is lower than in for cyclic allyl ethers [5,6].

Hydroformylation of **2** was carried out under the same conditions used for **1**. Linear aldehyde **8** was the major product (Table 2). Using the P∗, however, the substrate can isomerize to olefin

Table 3
Hydroformylation of benzyl-2-buthenyl ether (**3**) using $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(cod)]_2 + nPR_3$



3 **11** **12** **13**

Run	PR_3	*P* (atm)	*T* (°C)	$\%C_{ald}$	% **11**	% **12**	% **13**
13	4P∗	5	80	0	–	–	–
14[a]	4P∗	30	80	11	38	4	–
15[a]	4P∗	80	120	27	47	26	–
16	20P∗	80	60	100	35	62	3
17	20P∗	80	80	100	37	55	8
18	20P∗	80	120	100	61	14	25
19	$4PPh_3$	5	80	0	–	–	–
20[a]	$4PPh_3$	80	120	7	9	8	–
21	$20PPh_3$	80	80	98	38	57	5

Reaction conditions: solvent: Toluene, $CO/H_2 = 1$, $[cat] = 6.6 \times 10^{-7}$ M, reaction time: 24 h.
P∗: tris-(*o-tert*-butylphenyl) phosphite.
[a]Non-identified secondary products were observed.

(Scheme 4) and aldehyde **10** is formed in the reaction mixture although only in low amounts. At low pressure (5 atm, run 9, 10, and 11), conversions into aldehydes were lower. The effect of the auxiliary ligand on the β-elimination process is similar to the one observed for substrate **1**.

In the case of internal olefin **3**, a molar ratio P∗/precursor = 20 and 80 bar of CO/H_2 are required to obtain total conversion into aldehydes. Low pressures, 5 to 30 atm (Table 3), do not provide considerable conversions either for P∗ or PPh_3. Non-identified secondary products were observed in some cases. Runs 16 to 18 corroborate the effect of the temperature on the β-elimination process. Thus, increasing the temperature from 60 to 120°C decreases the percentage of compound **12** and increases **13**, which arises from the enol ether, and **11**. It should be noted that the regioselectivity obtained in the branched aldehydes **11** and **12** (runs 18 and 16, respectively) depends on the reaction conditions.

In conclusion, although the use of bulky phosphite P∗ or PPh_3 affects the different products obtained, no regiocontrol was obtained like it was for cyclic ethers. High yield and low regioselectivity is obtained in the hydroformylation of allyl ether **1** using both P∗ or PPh_3, although up to 20% of α-benzyloxypropanal is obtained using P∗ as auxiliary ligand. 4-Benzyloxy-3-methyl-butanal and 4-benzyloxy-2-methyl-butanal were obtained in good to excellent yields, starting from olefin **2** and **3**, respectively. Depending on the reaction conditions, significant regioselectivities were obtained in 4-benzyloxy-2-methyl-butanal **11** and 2-benzyloxymethyl-butanal starting from compound **3**.

References

[1] R. Kummer, German Patent 2401553 to BASF, 1975.
[2] W.E. Smith, German Patent 2453671, 1975.
[3] D.F. Aycock, German Patent 2429768, 1975.
[4] T.H. Johnson, Shell Oil, US 4584411, 1985.
[5] C. Rasp, G. Sharfe, J. Grolig, German Patent 2430082, 1975.
[6] W.E. Smith, Netherland Patents 7407237 and 7407242, and German Patents 2425653, 1974, and 2425844, 1975.
[7] A. Matsuda, Bull. Chem. Soc. Jpn. 41 (1968) 1876.
[8] C.U. Pittman Jr., W.D. Honnick, J. Org. Chem. 45 (1980) 2132.
[9] V.B. Fell, M. Barl, Chem. Zeit. 101 (1977) 343.
[10] C. Botteghi, R. Ganzerla, M. Lenarda, G. Moretti, J. Mol. Catal. 40 (1987) 129.
[11] M.M. Taqui Khan, S.B. Halligudi, S.H.R. Abdi, J. Mol. Catal. 48 (1988) 7.
[12] R.M. Deshpande, R.V. Chaudhari, J. Catal. 115 (1989) 326.
[13] R.M. Deshpande, S.S. Divekar, R.V. Gholap, R.V. Chaudhari, Ind. Eng. Chem. Res. 30 (1991) 1389.
[14] R.M. Deshpande, S.S. Divekar, B.M. Bhanage, R.V. Chaudhari, J. Mol. Catal. 75 (1992) L19.
[15] M. Matsumoto, M. Tamura, J. Mol. Catal. 16 (1982) 195.
[16] R. Lazzaroni, R. Sttambolo, G. Uccello-Barretta, Organometallics 14 (1995) 4644.
[17] A. Polo, C. Claver, S. Castillón, A. Ruiz, J.C. Bayón, J. Real, C. Mealli, D. Masi, Organometallics 11 (1992) 3525.
[18] T. Horiuchi, E. Shirakawa, K. Nozaki, H. Takaya, Organometallics 16 (1997) 2981.
[19] P.W.N.M. van Leeuwen, C.F. Roobeck, J. Organomet. Chem. 258 (1983) 343.
[20] R.L. Pruett, Adv. Organomet. Chem. 17 (1979) 1.
[21] J.M. Brown, A.G. Kent, J. Chem. Soc., Perkin Trans. II (1987) 1597.
[22] W.R. Moser, C.J. Papile, D.A. Brannon, R.A. Druwell, J. Mol. Catal. 41 (1987) 271.
[23] T. Jongnsma, G. Challa, P.W.N.M. van Leeuwen, J. Organomet. Chem. 421 (1991) 121.
[24] A. van Rooy, N.E. Orij, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 14 (1995) 34.