ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 588 (1999) 186–194

Journal of Organometallic Chemistry

New chiral diphosphinites: synthesis of Rh complexes. Heterogenisation on zeolites

A. Fuerte [a], M. Iglesias [a,*], F. Sánchez [b,1]

[a] *Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain*
[b] *Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain*

Received 1 March 1999; received in revised form 20 June 1999

Abstract

New diphosphinite ligands derived from (2*S*,4*R*), (2*S*,4*S*)-1-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)-pyrrolidinylmethanol and (2*S*,4*R*), (2*S*,4*S*)-1-(3-triethoxysilyl)propylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol have been prepared in high yields (60–80%) and reacted with $[RhCl(cod)]_2$ to yield cationic $[Rh(diphosphinite)(cod)]^+$ complexes. Those metal complexes bearing a triethoxysilyl group were covalently bonded to USY-zeolite by controlled hydrolysis and Rh-heterogenised complexes were obtained. A comparative study (homogeneous versus supported) for the catalytic activity and selectivity in hydrogenation and hydroformylation reactions was made, obtaining an enhanced performance for heterogenised catalysts; moreover, those catalysts can be recycled in successive runs, by a simple filtration, without a significant loss of activity.

Keywords: Rhodium; Supported catalysts; Zeolites; Hydrogenation; Hydroformylation

1. Introduction

Asymmetric syntheses with various transition metal complexes as catalysts have attracted much attention in the past two decades. Among them, rhodium(I) chiral diphosphine catalyst complexes have achieved very high stereoselection (up to 99% ee) in asymmetric hydrogenation of carbon–carbon double bonds [1], and some processes based on these catalysts have found industrial applications [2]. In these systems, the access of reactants to chiral ligands was essential for the development of new catalytic systems exhibiting high efficiency and enantioselectivity. In particular, several classes of chiral phosphines have been described and when associated with the rhodium or ruthenium present in the catalytic precursors, they are able to hydrogenate olefins and ketones with almost complete enantioselectivity [1,2]. Up to now less work has been done with less electron-rich ligands such as phosphites, which, on the other hand, are easier to synthesise and are more stable than phosphines. Owing to previous results obtained on Rh complexes supported on inorganic carriers, it can be worth studying supported complexes with phosphite ligands to see whether this introduces any catalytic improvement. Indeed, heterogenised homogeneous catalysts combine the properties of homogeneous catalysts viz. reactivity, controllability and selectivity, and heterogeneous catalysts viz. enhanced stability and reusability [3]. Moreover, we conducted an extensive study of the synthesis of new chiral ligands in order to apply them in asymmetric synthesis. We found that the catalytic activity could be enhanced as a result of such immobilisation on a support. For that purpose, special efforts have been devoted toward the synthesis of easily accessible ligands based on natural amino acids [4]. These ligands have been applied with success in asymmetric catalysis, for example, the addition of diethylzinc to enones [5], hydrogenation [6], cyclopropanation [7], and oxidation of olefins [8]. Hence, we set out to explore the synthesis and application of new, closely related bis(phosphinites) and their corresponding rhodium complexes exhibiting specific constraints and electronic properties in order to improve both the activ-

* Corresponding author. Tel.: +34-913-349-032; fax: +34-913-720-623.
E-mail address: marta.iglesias@icmm.csic.es (M. Iglesias)
[1] Also corresponding author.

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00373-3

ity and selectivity of the hydrogenation and hydroformylation reactions.

In this paper, we report the synthesis of new bis(phosphinite) ligands, the synthesis and spectroscopic characterisation of their corresponding rhodium complexes (homogeneous and heterogenised on USY-zeolite) and their subsequent application in asymmetric hydrogenation and hydroformylation of olefins.

2. Experimental

All organometallic complexes were prepared under dinitrogen by standard Schlenk techniques. The starting complex $[Rh(cod)Cl]_2$ was prepared according to the method reported in the literature [9]. All solvents were carefully degassed before use. The silylating agent $OCN(CH_2)_3Si(OEt)_3$ obtained from Fluka (96% pure), was distilled before use. C, H and N analyses were carried out by the analytical department of the Institute of Materials Science (CSIC) with a Perkin–Elmer 240C apparatus. Metal contents were analysed by atomic absorption using a Unicam Philips SP9 apparatus. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) as KBr pellets; ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers. ^{1}H-NMR chemical shifts are given in ppm using tetramethylsilane as an internal standard; ^{31}P-NMR chemical shifts are downfield from 85% H_3PO_4. Optical rotation values were measured at the sodium-D line (589 nm) with a Perkin–Elmer 241 MC polarimeter. Gas chromatography analysis was performed using a Hewlett–Packard 5890 II with a flame ionisation detector in a cross-linked methylsilicone column.

The inorganic support was an ultrastable Y (USY) zeolite prepared by steam calcination at 1023 K of an 80% ammonium-exchanged NaY (SK40 Union Carbide), followed by treatment with a 1 N citric acid solution at 333 K for 30 min to remove extra-framework species. After this, the zeolite was thoroughly washed and dried at 403 K for 6 h. The final zeolite had a well-developed supermicropore–mesopore system (pore diameter 12–30 Å besides the typical ca. 12 Å micropores). The controlled dealumination promotes destruction of some sodalite units, which allowed direct communication between α-cages generating cavities wider than 12 Å. The formation of supermicropores and large mesopores has been detected by N_2 adsorption–desorption. The main characteristics of the resultant zeolite are: unit cell size, 24.40 Å; bulk SiO_2/Al_2O_3, 4.2; and crystallinity, greater than 95%. The inorganic support was dried at 415 K under 0.01 torr before the anchoring process.

2.1. Synthesis of ligands

The alcohols were prepared according to the method previously described [8].

2.1.1. Preparation of (2S,4R)-1-benzyl-4-diphenylphosphinoxy-4-phenyl-2-(1,1-diphenyl-1-diphenylphosphinoxymethyl)pyrrolidine, (2S,4R)-I)

In a typical experiment, (2*S*,4*R*)-1-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol (100 mg, 0.23 mmol) was placed in a 100 ml Schlenk tube (cooled in a ice-water bath) along with diethyl ether (30 ml) and triethylamine (0.073 ml) and was reacted with a solution of chlorodiphenylphosphine (101.4 mg, 0.46 mmol) in diethyl ether (10 ml). The mixture was stirred at room temperature (r.t.) for 24 h. Then the reaction mixture was concentrated in vacuo and ammonium chloride and phosphorus impurities were removed by filtration through a short column of basic alumina (eluted with diethyl ether). The solvents were removed from the filtrate under reduced pressure to afford **(2*S*,4*R*)-I** as a white solid (170 mg, 90% yield). No further attempts were made to purify compound **(2*S*,4*R*-I)** as it was found to be amenable to further reactions. $[\alpha]_D^{25} = +22.3°$ ($c = 1$, CH_2Cl_2). Anal. Calc. for $C_{54}H_{47}NO_2P_2$: C, 80.7; H, 5.9; N, 1.7; P, 7.7. Found: C, 80.2; H, 5.7; N, 1.4; P, 7.2%. ^{1}H-NMR ($CDCl_3$): δ 8.0–6.7 (m, 40H, H phenyl); 4.23–4.20 (dd, 1H, NCH); 3.63–3.55 (AB, 2H, CH_2Ph); 3.1–2.97 (m, 2H, CH_2N); 2.69–2.66 (m, 1H, $CHCH_2$); 2.04–2.00 (m, 1H, $CHCH_2$). ^{13}C-NMR ($CDCl_3$): δ 146.8, 146.1, 143.2, 138.7 (C_{arom}–R); 128.5, 128.3, 128.2, 127.9, 127.1, 127.0. 126.7, 126.6, 125.8, 125.6, 125.3 (C_{arom}–H); 78.2, 78.0 (Ph_2COP, $PhCOP$); 70.6 (CH); 68.6 (CCH_2N); 60.4 ($PhCH_2$); 45.1 (CCH_2CH). ^{31}P-NMR ($CDCl_3$): δ 121.8 ppm.

The phosphinites **(2*S*,4*S*)-II**, **(2*S*,4*R*)-III** and **(2*S*,4*S*)-IV** were prepared through a procedure similar to that given for **(2*S*,4*R*)-I** starting from the corresponding dialcohol.

2.1.2. (2S,4S)-1-benzyl-4-diphenylphosphinoxy-4-phenyl-2-(1,1-diphenyl-1-diphenylphosphinoxymethyl)-pyrrolidine (2S,4S)-II

24 h, 82% yield, white powder. $[\alpha]_D^{25} = +14.19°$ ($c = 1$, CH_2Cl_2). Anal. Calc. for $C_{54}H_{47}NO_2P_2$: C, 80.7; H, 5.9; N, 1.7; P, 7.7. Found: C, 80.4; H, 5.6; N, 1.5; P, 7.5%. ^{1}H-NMR ($CDCl_3$): δ 7.9–6.9 (m, 40H, H phenyl); 5.34–5.24 (dd, 1H, NCH); 4.40–4.36 (m, 1H, CH_2N); 4.00–3.84 (m, 1H, CH_2N); 3.64–3.39 (AB, 2H, CH_2Ph); 2.56–2.36 (m, 2H, $CHCH_2$). ^{13}C-NMR ($CDCl_3$): δ 147.7, 145.7, 143.1, 140.0 (C_{arom}–R); 128.4, 128.3, 128.0, 127.8, 127.0, 126.6, 126.5, 126.4, 125.7, 125.0 (C_{arom}–H); 81.8 (Ph_2COP); 72.3 ($PhCOP$); 66.8

(CH); 61.7 (PhCH$_2$N); 43.8 (CCH$_2$N); 26.9 (CCH$_2$CH). ^{31}P-NMR (CDCl$_3$): δ 118.8 ppm.

2.1.3. (2S,4R)-1-(3-Triethoxysilyl)propylamino-carbonyl-4-diphenylphosphinoxy-4-phenyl-2-(1,1-diphenyl-1-diphenylphosphinoxymethyl)pyrrolidine, ***(2S,4R)-III***

30 h, 67% yield; colourless oil. Anal. Calc. for $C_{57}H_{62}N_2O_6P_2Si$: C, 71.2; H, 6.5; N, 2.9; P, 6.4. Found: C, 70.8; H, 6.4; N, 2.5; P, 6.1%. ^{1}H-NMR (CDCl$_3$): δ 7.98–7.13 (m, 35H, H phenyl); 4.12–4.07 (m, 1H, NCH); 3.85–3.77 (m, 6H, CH$_2$O); 3.76–3.67 (m, 2H, CH$_2$N(CO)); 3.03–2.99 (m, 2H, CH$_2$N); 2.20–2.10 (m, 2H, CHC*H*$_2$); 1.61–1.24 (m, NCH$_2$C*H*$_2$); 1.22 (t, 9H, CH$_3$); 0.65–0.62 (m, 2H, CH$_2$Si). ^{13}C-NMR (CDCl$_3$): δ 158.5 (CO), 145.3, 145.0 (C$_{arom}$–R); 128.4, 128.3, 128.2, 127.4, 127.3, 127.2, 127.0, 124.7 (C$_{arom}$–H); 81.3 (Ph$_2$*C*OP); 79.8 (Ph*C*OP); 67.1 (CH); 63.3 (*C*H$_2$N); 58.4 (CH$_3$*C*H$_2$O); 46.1 (*C*H$_2$CH); 43.5 (*C*H$_2$NHCO); 23.1 (CH$_2$*C*H$_2$CH$_2$); 18.3 (*C*H$_3$CH$_2$O); 7.7 (CH$_2$Si). ^{31}P-NMR (CDCl$_3$): δ 122.1 ppm.

2.1.4. (2S,4S)-1-(3-Triethoxysilyl)propylaminocarbonyl-4-diphenylphosphinoxy-4-phenyl-2-(1,1-diphenyl-1-diphenylphosphinoxymethyl)pyrrolidine, ***(2S,4S)-IV***

32 h, colourless oil, 56% yield. Anal. Calc. for $C_{57}H_{62}N_2O_6P_2Si$: C, 71.2; H, 6.5; N, 2.9; P, 6.4. Found: C, 70.7; H, 6.4; N, 2.8; P, 6.0%. ^{1}H-NMR (CDCl$_3$): δ 7.89–7.09 (m, 35H, H phenyl); 5.24 (m, 1H, NCH); 4.06–4.05 (m, 2H, CH$_2$N(CO)); 3.69–3.56 (q, 6H, CH$_2$O); 2.97–2.93 (m, 2H, CH$_2$N); 2.12–2.07 (m, 2H, CHC*H*$_2$); 1.60–1.40 (m, NCH$_2$C*H*$_2$); 1.20 (t, 9H, CH$_3$); 0.82–0.80 (m, 2H, CH$_2$Si). ^{13}C-NMR (CDCl$_3$): δ 158.8 (CO); 147.8, 145.5, 143.3, 140.0 (C$_{arom}$–R); 128.4, 128.3, 127.8, 127.0, 126.6, 126.4, 125.7, 125.0 (C$_{arom}$–H); 81.5 (Ph$_2$*C*OP); 72.0 (Ph*C*OP); 66.7 (CH); 63.1 (*C*H$_2$N); 58.4 (CH$_3$*C*H$_2$O); 46.4 (*C*H$_2$CH); 43.3 (*C*H$_2$NHCO); 23.0 (CH$_2$*C*H$_2$CH$_2$); 18.5 (*C*H$_3$CH$_2$O); 7.9 (CH$_2$Si). ^{31}P-NMR (CDCl$_3$): δ 119.0 ppm.

2.2. Preparation of [Rh(cod){diphosphinite}]PF$_6$ complexes ***1–4***

Typical procedure for [Rh(cod){(**2*S*,4*R*)-I**}]PF$_6$ (**1**). To a yellow solution of [Rh(cod)Cl]$_2$ (0.4 mmol) in dichloromethane (30 ml) was added a solution of **(2*S*,4*R*)-I** (0.8 mmol), then ammonium hexafluorophosphate (0.8 mmol) was added and the mixture was stirred for 3 h at 40°C, and filtered. The filtrate was evaporated under reduced pressure to 2 ml. Careful addition of diethyl ether caused the precipitation of a yellow–orange solid which was collected by filtration, washed with diethyl ether and dried in vacuo to give the desired cationic complex. Yield 68%. $[\alpha]_D^{25} = +8.65°$ ($c = 0.75$, CH$_2$Cl$_2$). Λ(CH$_3$CN) (Ω^{-1} cm^2 mol^{-1}) = 90. Anal. Calc. for $C_{62}H_{59}F_6NO_2P_3Rh$: C, 64.2; H, 5.1; N, 1.2; P, 8.0; Rh, 8.9. Found C, 63.8; H, 4.8; N, 0.9; P, 7.8; Rh, 8.8%. ^{1}H-NMR (CDCl$_3$): δ 8.0–7.2 (m, 40H, H phenyl); 4.3 (br, 4H, CH=); 4.2 (m, 1H, NCH); 3.6–3.5 (AB, 2H, CH$_2$Ph); 3.1 (m, 2H, CH$_2$N); 2.6 (m, 5H, CHC*H*$_2$, C*H*$_2$–CH=); 2.0 (m, 1H, CHC*H*$_2$); 1.8 (m, 4H, C*H*$_2$–CH=). ^{13}C-NMR (CDCl$_3$): δ 146.8–138.7 (C$_{arom}$–R); 129–125 (C$_{arom}$–H); 81.5–81.0 (=CH$_{cod}$); 78.5–78.0 (Ph$_2$*C*OP, Ph*C*OP); 70.9 (CH); 68.6 (C*C*H$_2$N); 60.8 (Ph*C*H$_2$); 45.1 (C*C*H$_2$CH); 30.4 (CH$_{cod}$). ^{31}P-NMR (CDCl$_3$): δ 126.1 (br); −143.8 (^1J(P–F) = 714 Hz).

Complexes **2**–**4** were prepared following a procedure similar to that given for **1** using 0.4 equivalents of [Rh(cod)Cl]$_2$ and two equivalents of the appropriate ligand (Scheme 1).

*2.2.1. [Rh(cod){**(2S,4S)-II**}]PF$_6$ (**2**)*

Yield 74%. $[\alpha]_D^{25} = +6.09°$ ($c = 0.55$, CH$_2$Cl$_2$). Λ(CH$_3$CN) (Ω^{-1} cm^2 mol^{-1}) = 103. Anal. Calc. for $C_{62}H_{59}F_6NO_2P_3Rh$: C, 64.2; H, 5.1; N, 1.2; P, 8.0; Rh, 8.9. Found C, 63.9; H, 4.7; N, 1.1; P, 8.2; Rh, 9.3%. ^{1}H-NMR (CDCl$_3$): δ 7.7–7.0 (m, 40H, H phenyl); 5.5 (dd, 1H, NCH); 4.3–4.2 (br, 4H, CH=); 4.1, 3.7 (m, 2H, CH$_2$N); 3.6–3.4 (AB, 2H, CH$_2$Ph); 2.6–2.4 (m, 6H, CHC*H*$_2$, C*H*$_2$–CH=); 1.8–1.6 (m, 4H, C*H*$_2$–CH=). ^{13}C-NMR (CDCl$_3$): δ 148.0–140.0 (C$_{arom}$–R); 128.4–125.0 (C$_{arom}$–H); 81.7 (Ph$_2$*C*OP); 79.3–79.0 (=CH$_{cod}$); 72.5 (Ph*C*OP); 66.9 (CH); 61.5 (Ph*C*H$_2$N); 43.8 (C*C*H$_2$N); 28.2 (CH$_{cod}$); 26.9 (C*C*H$_2$CH). ^{31}P-NMR (CDCl$_3$): δ 122.0 (br); −143.8 (^1J(P–F) = 714 Hz).

*2.2.2. [Rh(cod){**(2S,4R)-III**}]PF$_6$ (**3**)*

Yield 55%. $[\alpha]_D^{25} = +13.24°$ ($c = 1.2$, CH$_2$Cl$_2$). Λ(CH$_3$CN) (Ω^{-1} cm^2 mol^{-1}) = 76. Anal. Calc. for $C_{65}H_{74}F_6N_2O_6P_3RhSi$: C, 59.3; H, 5.6; N, 2.1; P, 7.1; Rh, 7.8. Found C, 58.8; H, 6.0; N, 1.7; P, 7.5; Rh, 8.4%. ^{1}H-NMR (CDCl$_3$): δ 7.8–7.1 (m, 35H, H phenyl); 4.2 (br, 4H, CH=); 4.1 (br, m, 1H, NCH); 3.8 (m, 6H, CH$_2$O); 3.7 (m, 2H, CH$_2$N(CO)); 3.0 (m, 2H, CH$_2$N); 2.6 (br, 4 H, C*H*$_2$–CH=); 2.2 (m, 2H, CHC*H*$_2$); 1.8 (m, 4H, C*H*$_2$–CH=); 1.5–1.3 (m, NCH$_2$C*H*$_2$); 1.2 (t, 9H, CH$_3$); 0.55 (m, 2H, CH$_2$Si). ^{13}C-NMR (CDCl$_3$): δ 158.7 (CO), 145.5–145.0 (C$_{arom}$–R); 128.4–124.7 (C$_{arom}$–H); 81.4 (Ph$_2$*C*OP); 80.0 (Ph*C*OP); 79.8–79.3 (=CH$_{cod}$); 67.2 (CH); 63.3 (*C*H$_2$N); 58.5 (CH$_3$*C*H$_2$O); 46.2 (*C*H$_2$CH); 43.4 (*C*H$_2$NHCO); 28.5 (CH$_{cod}$); 23.0 (CH$_2$*C*H$_2$CH$_2$); 18.5 (*C*H$_3$CH$_2$O); 8.0 (CH$_2$Si). ^{31}P-NMR (CDCl$_3$): δ 125.8 (br); −143.6 (^1J(P–F) = 714 Hz).

*2.2.3. [Rh(cod){**(2S,4S)-IV**}]PF$_6$ (**4**)*

Yield 60%. $[\alpha]_D^{25} = +5.98°$ ($c = 1.2$, CH$_2$Cl$_2$). Λ(CH$_3$CN) (Ω^{-1} cm^2 mol^{-1}) = 68. Anal. Calc. for $C_{65}H_{74}F_6N_2O_6P_3RhSi$: C, 59.3; H, 5.6; N, 2.1; P, 7.1; Rh, 7.8. Found C, 58.9; H, 5.2; N, 2.5; P, 6.6; Rh,

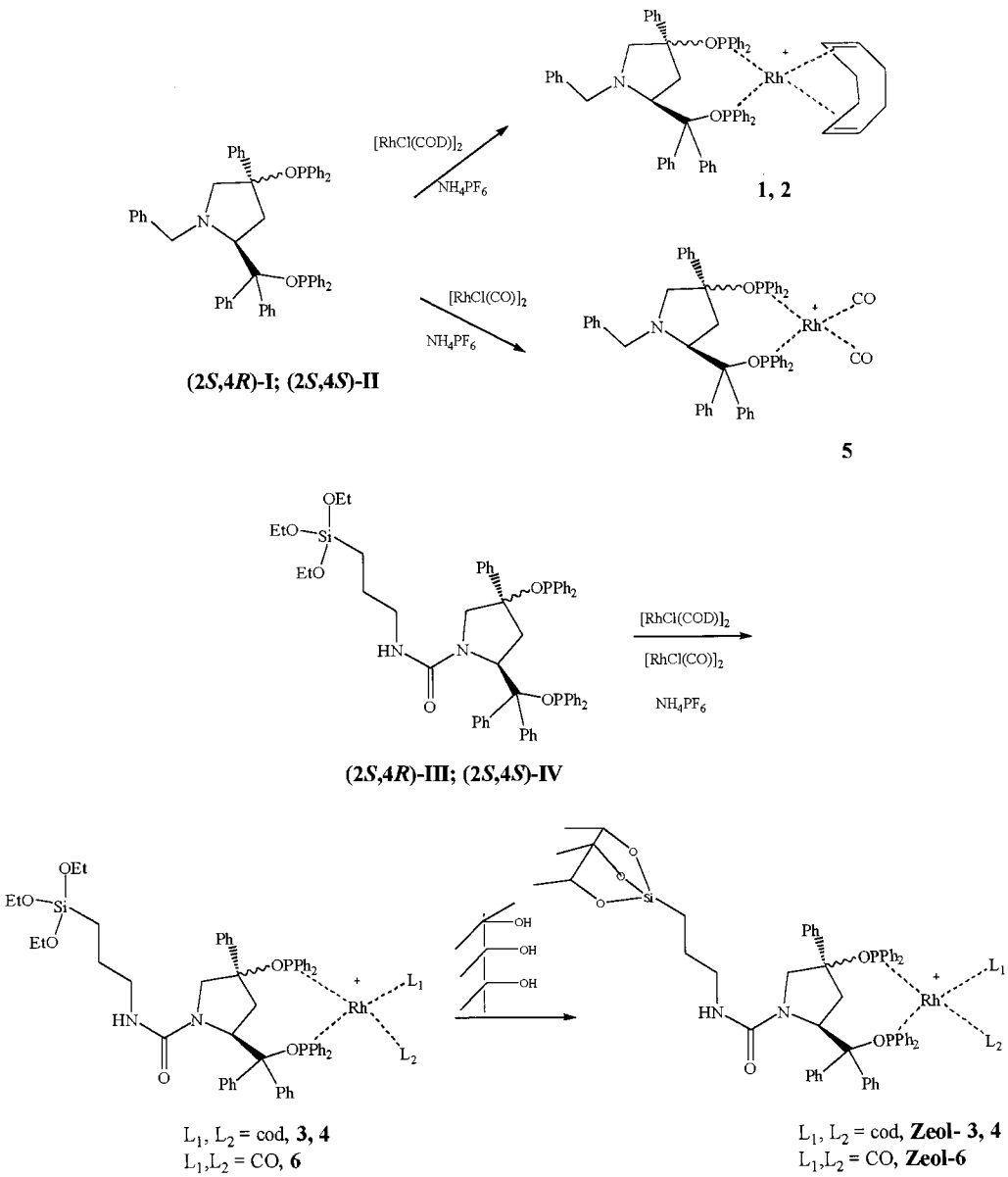
7.5%. ^{1}H-NMR ($CDCl_3$): δ 7.8–7.0 (m, 35H, H phenyl); 5.2 (m, 1H, NCH); 4.2 (br, 4H, CH=); 4.0 (m, 2H, $CH_2N(CO)$); 3.6 (q, 6H, CH_2O); 2.9 (m, 2H, CH_2N); 2.5–2.1 (m, 6H, $CHCH_2$, CH_2–CH=); 1.8 (m, 4H, CH_2–CH=); 1.5 (m, NCH_2CH_2); 1.2 (t, 9H, CH_3); 0.7 (m, 2H, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 158.3 (CO); 148.0–140.0 (C_{arom}–R); 128.4–125.0 (C_{arom}–H); 81.1 (Ph_2COP); 80.6–80.1 (=CH_{cod}); 72.2 (PhCOP); 66.5 (CH); 63.0 (CH_2N); 58.6 (CH_3CH_2O); 46.2 (CH_2CH); 43.1 (CH_2NHCO); 28.5 (CH_{cod}); 23.2 ($CH_2CH_2CH_2$); 18.8 (CH_3CH_2O); 8.0 (CH_2Si). ^{31}P-NMR ($CDCl_3$): δ 122.0 (br); −143.7 (^1J(P–F) = 714 Hz).

2.3. Preparation of $[Rh(CO)_2\{diphosphinite\}]PF_6$ complexes (**5**, **6**)

To a solution of $[Rh(CO)_2Cl]_2$ (0.4 mmol) in dry dichloromethane (20 ml) the stoichiometric amount of the ligand and NH_4PF_6 was added. The mixture was heated under reflux for 3 h and the NH_4Cl filtered off. The filtrate was evaporated to dryness, diethyl ether was added and the yellow–orange powder thus formed collected, washed with ethyl ether and dried in vacuo.

2.3.1. $[Rh(CO)_2\{$**(2S,4R)-I**$\}]PF_6$ (**5**)

Yield 72%. $[\alpha]_D^{25} = +18.65°$ ($c = 1.3$, CH_2Cl_2).



Scheme 1.

$\Lambda(CH_3CN)$ (Ω^{-1} cm^2 mol^{-1}) = 88. Anal. Calc. for $C_{56}H_{46}F_6NO_4P_3Rh$: C, 60.7; H, 4.3; N, 1.3; P, 8.4; Rh, 9.3. Found C, 60.9; H, 4.4; N, 0.9; P, 8.0; Rh, 8.8%. ^{1}H-NMR ($CDCl_3$): δ 8.0–7.2 (m, 40H, H phenyl); 4.2 (m, 1H, NCH); 3.6–3.4 (AB, 2H, CH_2Ph); 3.0 (m, 2H, CH_2N); 2.5 (m, 3H, CHCH_2); 1.9 (m, 1H, CHCH_2). ^{13}C-NMR ($CDCl_3$): δ 190.5 (br, CO); 147.0–138.5 (C_{arom}–R); 129.0–125.0 (C_{arom}–H); 78.4–78.0 (Ph_2COP, PhCOP); 71.3 (CH); 68.8 (CCH_2N); 60.6 (PhCH_2); 45.3 (CCH_2CH). ^{31}P-NMR ($CDCl_3$): δ 127.1 (br); −143.8 (^1J(P–F) = 714 Hz).

2.3.2. *[Rh(CO)$_2${(2S,4R)-III}]PF$_6$ (6)*

Yield 65%. $[\alpha]_D^{25} = +8.3°$ (c = 1.2, CH_2Cl_2). $\Lambda(CH_3CN)$(Ω^{-1} cm^2 mol^{-1}) = 66. Anal. Calc. for $C_{59}H_{62}F_6N_2O_8P_3RhSi$: C, 56.0; H, 4.9; N, 2.1; P, 7.4; Rh, 8.1. Found C, 56.8; H, 5.0; N, 1.7; P, 7.5; Rh, 8.4%. ^{1}H-NMR ($CDCl_3$): δ 7.8–7.1 (m, 35H, H phenyl); 4.2 (br, m, 1H, NCH); 3.9 (m, 6H, CH_2O); 3.7 (m, 2H, CH_2N(CO)); 3.0 (m, 2H, CH_2N); 2.1 (m, 2H, CHCH_2); 1.5–1.3 (m, NCH_2CH_2); 1.2 (t, 9H, CH_3); 0.57 (m, 2H, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 190.6 (br, CO), 146.0–145.0 (C_{arom}–R); 128.8–124.5 (C_{arom}–H); 81.6 (Ph_2COP); 80.2 (PhCOP); 67.4 (CH); 63.3 (CH_2N); 58.6 (CH_3CH_2O); 46.4 (CH_2CH); 43.5 (CH_2NHCO); 23.2 ($CH_2CH_2CH_2$); 18.7 (CH_3CH_2O); 8.0 (CH_2Si). ^{31}P-NMR ($CDCl_3$): δ 126.5 (br); −143.8 (^1J(P–F) = 714 Hz).

2.4. Heterogenisation of Rh(I) complexes on USY-zeolite

The supported Rh(I) complexes (**Zeol-3**, **Zeol-4**, **Zeol-6**) were prepared as we have previously described [6a,7a]. Thus, a solution of **3** (0.2 mmol) in dry dichloromethane (2 ml) was added to a well-stirred toluene suspension (40 ml) of the inorganic support (modified USY-zeolite dried at 140°C/0.1 mm/Hg for 3–4 h, 1 g) and the mixture was stirred at r.t. for 24 h. The solid was then filtered and Soxhlet-extracted with 1:2 dichloromethane–ethyl ether for 7–24 h to remove the remaining non-supported complex from heterogenised catalyst. The remaining pale-yellow solid was dried in vacuo and analysed.

2.5. Catalytic experiments

The catalytic properties of the above homogeneous and heterogenised Rh complexes were studied under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 ml capacity at temperatures, pressures and Rh/substrate molar ratios indicated below in each particular case. The results were monitored by GLC or HPLC.

2.5.1. Hydrogenation of prochiral olefins

Ethyl (*Z*)-α-acetylaminocinnamate, selected as a model compound, was hydrogenated in a batch reactor at 338 K and 5 atm of dihydrogen pressure. The molar ratio catalyst/substrate was 1/100. The olefin (2 mmol) was added to a solution (homogeneous catalysts) or suspension (heterogenised catalysts) of the catalyst in ethanol (45 ml) and the reactor was purged with nitrogen. The reaction mixture was heated to 338 K, pressurised with dihydrogen and stirred. The results were monitored by HPLC on a C18 reversed phase using 1:1.1 methanol–water as eluent with UV detection at 228 nm. After hydrogenation, the homogeneous catalyst was removed by filtration through a short column of Celite, whilst the heterogenised supported was easily separated by filtration, and used in a new run. Hydrogenation results are shown in Table 1.

Table 1
Asymmetric hydrogenation of *Z*-(α)-ethyl acetamidocinnamate (cat./subs. = 1/100, T = 333 K; P_{H_2} = 5 atm)

Catalyst	Time (h) (% conv.) [a]	TOF [b]	ee (%) [c]
1	7(90)	1654	7
2	3(85)	1667	12
Zeol-3	5(80)	3871	8
Zeol-4	3(90)	3325	14

[a] Total conversion was achieved in 9 h.
[b] mmol substrate/mmol [Rh] h.
[c] *S* configuration, ee measured by optical rotation.

2.5.2. Hydroformylation reaction, general procedure

Hydroformylation experiments were performed in a 100 ml stainless steel autoclave; toluene or dichloroethane was used as the solvent. Typical reaction conditions were catalyst/substrate molar ratio of 1/700, 50 ml toluene as solvent, temperature of 343 K, 20 bar 1:2 H_2–CO.

The autoclave was charged with the catalyst, solvent and substrate. When thermal equilibrium was reached, the gas mixture was introduced until the desired pressure was reached, and then samples were taken at regular time periods and analysed by GLC. Optical yield was determined by GLC using a cyclodextrine capillary column [10]. The hydroformylation activities are represented by the turnover frequencies (Table 2).

3. Results and discussion

3.1. Synthesis and characterisation of diphosphinite ligands

Phosphinite ligands are generally synthesised by reaction of an amino alcohol with the appropriate chlorophosphine [11]. Accordingly, the diphosphinite ligands were synthesised by following an analogous procedure. The starting alcohols (2*S*,4*R*), (2*S*,4*S*)-*1*-

benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)-pyrrolidinylmethanol and (2*S*,4*R*), (2*S*,4*S*)-1-(3-triethoxysilyl)propylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol were obtained from the corresponding optically active amino acid (L-hydroxyproline) following procedures previously described in the literature [8]. The diols were reacted with two equivalents of chlorodiphenylphosphine in dry diethyl ether, under nitrogen, in the presence of triethylamine (r.t., 24 h) to give the corresponding ligands in 60–80% yields (Scheme 2).

The benzyl pyrrolidine derivatives are white powders, and the ligands with the triethoxysilyl group are colourless oils; they were characterised by microanalysis, and NMR (^{1}H-, ^{13}C-, ^{31}P-) spectroscopy (Section 2). These products are air-sensitive at r.t. and slowly oxidise to give $OP(O)Ph_2$ derivatives. The R–$OP(O)Ph_2$ bonds are prone to hydrolysis and mixtures of composition R–$OPPh_2$·DPA (DPA = diphenyl phosphinic acid, $HOP(O)Ph_2$) were formed by hydrolysis of the partially oxidised products, from which colourless crystals of DPA could be isolated. Totally oxidised and only partially hydrolysed products were also isolated.

^{1}H resonance patterns of the ligands were complex because they are strongly coupled systems. Nevertheless, complete assignment of almost all resonances was possible on the basis of ^{2}D-NMR (^{1}H-, ^{1}H-COSY). The ^{31}P-{^{1}H}-NMR spectra of freshly prepared samples were obtained. The spectrum of **(2*S*,4*R*)-I** exhibits a broad signal at $\delta = 121.8$ ppm while $\delta = 118.8$ ppm for **(2*S*,4*S*)-II**. In all samples, some signals for the oxidised and partially hydrolysed compounds (R–OP(O)PPh_2·DPA) appear at 26.2 ppm for the **(2*S*,4*R*)-I** derivative and 22.5 ppm for **(2*S*,4*S*)-II**, whereas the corresponding signal of DPA is present as a sharp singlet at 28.6 ppm.

Because of their sensitivity to hydrolysis **(2*S*,4*R*)-V** and **(2*S*,4*R*)-VI**, could not be fully characterised. IR spectra of freshly prepared samples were obtained. The most characteristic IR bands are those of the 1200–950 cm^{-1} region, and the characteristic band of free diphenylphosphinic acid at 955 cm^{-1} is of medium intensity. The ^{31}P-NMR shows the signals mentioned before (a broad signal at 26.2 (**V**), 22.5 (**VI**) ppm) and a sharp singlet at 28.64 ppm corresponding to DPA).

3.2. Synthesis of rhodium complexes

The dimeric $[Rh(cod)Cl]_2$, two equivalents of NH_4PF_6 and two equivalents of freshly prepared ligands (**I**–**IV**) were reacted (CH_2Cl_2, 313 K, 3 h) leading to the corresponding complexes **1**–**4** (Scheme 2). The complexes were isolated as yellow and relatively air-stable solids. Microanalytical, conductivity, IR, ^{1}H- and ^{31}P-NMR spectroscopic data given in Section 2 confirm the proposed structures. Some precautions, i.e. low temperatures and the exclusion of water and hydroxylic solvents, have to be taken, especially in the case of triethoxysilane derivatives, in order to avoid hydrolysis and subsequent polymerisation. Since no suitable crystals could be obtained for carrying out the X-ray work, the structures of the complexes were determined by IR and NMR spectroscopy and elemental analyses.

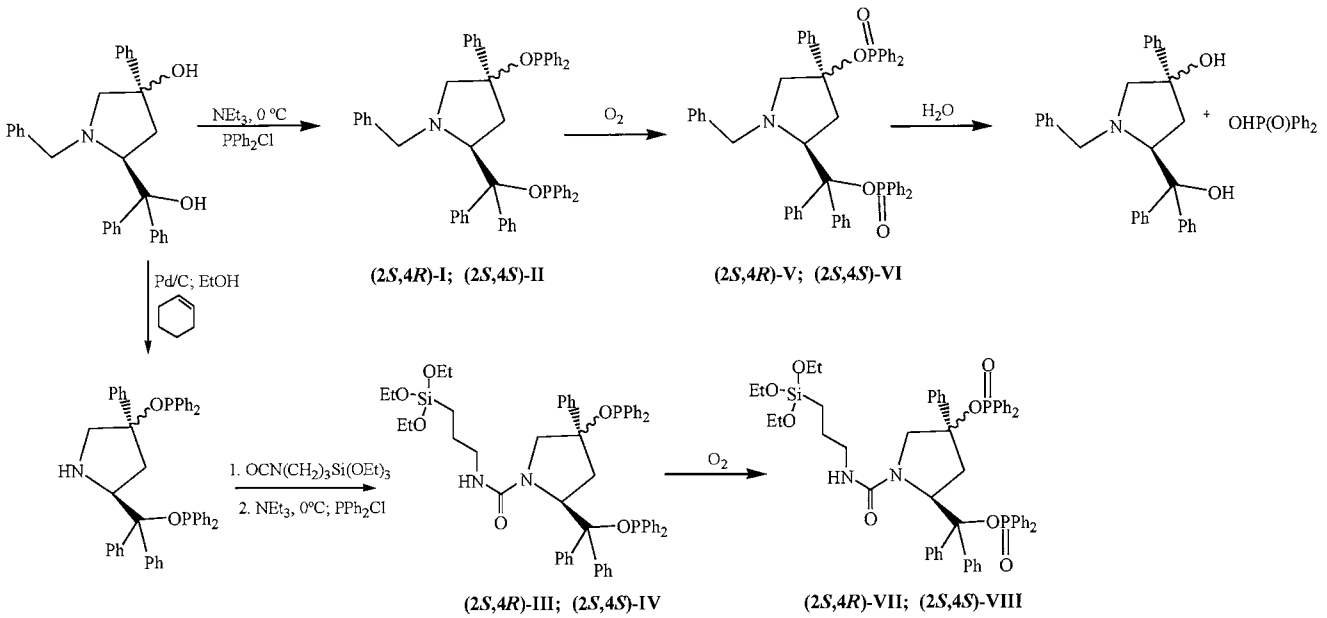
The elemental analyses are in agreement with the stoichiometry proposed for bidentate structures with 1:1 Rh–P-donor ratio. The IR spectra show bands for a coordinated diene (cod) and for the P-donors that appear at their expected frequencies. A band at ~845 cm^{-1} that corresponds to ν(P–F) was also present.

The ^{1}H- and ^{13}C-NMR spectra show the signals corresponding to pyrrolidine protons and carbons slightly downfield shifted with respect to the free ligands. The signals of the atoms close to the metal are remarkably broadened due to metal interactions and to

Table 2
Styrene hydroformylation using diphosphinite–rhodium catalysts [a]

Catalyst	t (h)	Conv. (%) [b]	Aldehydes (%)		TOF [d]
			Branched [c]	Normal	
1	94	83	36	63	838
	72 [e]	10	77	32	24
2	96	78	43	57	933
5	80	75	45	55	2104
Zeol-3	36	87	51	40	7336
Zeol-4	96	78	53	42	2188
Zeol-6	86	80	49	51	2620

[a] Conditions: cat./substrate = 1/700, P, 20 bar CO/H_2, $T = 343$ K.
[b] Conversion into aldehydes.
[c] ee < 10% in all cases.
[d] mmol substrate/mmol [Rh] h.
[e] $T = 313$ K.



Scheme 2.

the conformational non-rigidity on the NMR time scale. The cyclooctadiene and aromatic rings give rise to resonances in the expected positions. ^{31}P-NMR spectra showed a broad signal centred at 126 ppm for **1** and 122 ppm for **2**. The signal for the PF_6 anion appears at -143.8 ppm with $^1J(P–F) = 714$ Hz.

Partially oxidised compounds react with $[RhCl(cod)]_2$ to yield complexes with phosphine oxide ligands (**7**, **8**). IR for these compounds show ν(P=O) at 1200 cm^{-1}. In the case of R–$OP(O)Ph_2$ the peak at 26.2 ppm in the ^{31}P-NMR of the free ligand is shifted to 32.1 ppm when the Rh complex was formed. The shift indicates a coordination of the ligand with the rhodium through the phosphine oxide. These compounds could not be fully characterised due to the presence of diphenylphosphinic acid as contaminant.

The same form, starting from binuclear rhodium complex $[\{Rh(CO)_2Cl\}_2]$ and ligands (2*S*,4*R*)-*1*-benzyl-4-diphenylphosphinoxy-4-phenyl-2-(1,1-diphenyl-1-diphenylphosphinoxymethyl)pyrrolidine **(2*S*,4*R*)-I**, or (2*S*,4*R*)-*1*-(3-triethoxysilyl)propylaminocarbonyl-4-diphenylphosphinoxy-4-phenyl-2-(1,1-diphenyl-1-diphenylphosphinoxymethyl)pyrrolidine **(2*S*,4*R*)-III**, in CH_2Cl_2 and in the presence of NH_4PF_6, mononuclear complexes $[Rh(CO)_2(ligand)]PF_6$ (**5**, **6**) were obtained in good yield. The compounds synthesised were characterised by elemental analysis, IR and ^{1}H- and ^{13}C-NMR spectroscopies. IR spectra show two intense ν(CO) bands at 2072 and 1998 cm^{-1}, assigned to two *cis*-dicarbonyl vibrations and bands corresponding to diphosphinite and anion that appear in the expected positions. The ^{1}H- and ^{13}C-NMR spectra show the signals corresponding to pyrrolidine protons and carbons slightly downfield shifted as well as broadened signals for the atoms spacially close to the metal. The two carbonyl ligands appear as a sharp single resonance at $\delta = 190.6$ ppm.

3.3. Heterogenisation of Rh(I) complexes on USY-zeolite

Preparations of zeolite heterogenised complexes for complexes **3**, **4**, and **6** bearing a triethoxysilylpropyl group were carried out by controlled hydrolysis of Si–OEt bonds and reaction with the free silanol (Si–OH) on the surface of a USY-zeolite. The resulting catalytic material is very stable and the species are covalently bonded to the surface. IR and UV–vis spectroscopy confirmed the fact that structures of the starting complexes are maintained when attached to the surface. The elemental analysis of C, H, N and Rh also confirm the 1:1 Rh–ligand stoichiometry. It is unlikely that the nature of the complex is substantially altered under the relatively mild conditions of the anchoring reaction [12]. The loading of metal is always ca. ~ 1–2% (± 0.1%) measured by atomic absorption of metal of the digested samples. These values have been used for calculating the ratio catalyst/substrate in the reaction tests.

4. Reactivity

4.1. Hydrogenation of dehydroaminoacid derivatives

The homogeneous and heterogenised Rh catalysts (**1**, **2** and **Zeol-3**, **Zeol-4**, respectively) were tested for enantioselective hydrogenation of ethyl (*Z*)-α-acetamido- and α-benzamidocinnamates (1/100 catalyst/substrate ratio) in mild conditions yielding the corresponding phenylalanine derivatives with quantitative conversion and up to 14% ee (Table 1). For the two substrates tested the homogeneous complexes present an induction period due to slow formation of catalytic active species. On the contrary, when complexes were supported on a modified USY-zeolite, using the same amount of rhodium as homogeneous catalysts, no induction period can be detected, probably as a consequence of the known strong capability of zeolites to absorb H_2 on their surfaces, which increases the local concentration of hydrogen. This behaviour was found in other zeolite supported Rh complexes [6b,13]. When transition metal complexes have been supported on carriers such as polymers or silica, etc. it is generally accepted that a moderate to strong reduction in the reactivity has been observed; however, in our case the turnover numbers for hydrogenation increase slightly indicating the cooperative effect of the support. The enantioselectivities obtained were low and close to the results for homogeneous catalysts. The low enantioselectivity is presumably due to the loss of the bidentate coordination of the ligand with the metal because of the opening of the seven–membered ring.

4.2. Hydroformylation of styrene

Hydroformylation of styrene with a 2:1 mixture of carbon monoxide and hydrogen was carried out making use of the zeolite–metal complexes (**Zeol-3**, **Zeol-4**, **Zeol-6**). The results were compared with those obtained with homogeneous metal complexes (**1**, **2**, **5**). We have studied the influence of the different parameters on the reaction, especially the role of the support on the intrinsic activity of the heterogenised catalysts, as well as the surface concentration effect and the geometrical constraints.

In the following, chemical yield, selectivity and optical yield obtained with varying parameters such as nature of the solvent, reaction temperature and catalyst type, are given.

The nature of the solvent is critical to the rate and selectivity of the hydroformylation results. Solvents such as acetone with medium rated polarity ($Z = 65.7$ kcal mol^{-1}) and coordinating properties gave low conversions to aldehydes, while very polar protic solvents (e.g. methanol) ($Z = 83.6$ kcal mol^{-1}) led to medium conversions of olefin to aldehydes. Only non-coordinating solvents of low polarity such as CH_2Cl_2 and toluene ($Z = 54.0$ kcal mol^{-1}) gave high conversions to aldehydes with medium branched/linear ratio (c.f. the same behaviour observed in some other hydroformylation systems [14]).

The temperature has a remarkable effect on reaction rate and selectivity. The rate of hydroformylation increases when increasing the reaction temperature, but the selectivity strongly decreases [15]. Optimal results were obtained at 343 K and therefore this was chosen as the standard temperature in most of our experiments. The reaction can be performed at r.t. in excellent selectivity but the reaction rate is too low (Table 2). Thus, the selected conditions for testing the catalysts for hydroformylation are 70°C and 20 bar, and a ratio of 14:6 $CO–H_2$. In these conditions high conversion ($>75\%$) and a branched/linear ratio near unity was obtained (Table 2).

An examination of Table 2 shows that in all cases high conversions and yields of oxo products, low regioselectivities and poor enantioselectivities ($<10\%$), were obtained. The racemization phenomena probably take place during the long time required to obtain high substrate conversion.

When transition metal complexes have been supported on USY-zeolite, no induction period was observed and the turnover numbers for hydroformylation increases. With these rhodium systems, ethylbenzene, the hydrogenation product of styrene was not detected. These catalysts can be recovered and reused retaining most of their catalytic activity.

5. Conclusions

A facile procedure for the synthesis of bis-phosphinites has been found. The new rhodium–phosphinite complexes are active for the hydrogenation and hydroformylation of olefins. Heterogenisation on USY-zeolite (containing supermicropores and a large quantity of silanol groups) increases the activity of the homogeneous catalysts for different substrates. The heterogenised complexes are significantly more stable than their corresponding homogeneous complexes over prolonged reaction times.

To summarise, zeolite-supported complexes show interesting catalytic properties in hydrogenation and hydroformylation reactions and these properties are related to the changes in the microenvironment of the ligand metal-complex, caused by the support. These catalysts can be recovered and reused, retaining most of their catalytic activity.

Acknowledgements

The authors are grateful for the financial support from Dirección General de Investigación Científica y Técnica of Spain (Project MAT97-1016-c02-02).

References

[1] Reviews: (a) H. Takaya; T. Ohta; R. Noyori, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, Ch. 1. (b) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994, p. 16. (c) J.M. Brown, Chem. Soc. Rev. (1993) 25. (d) H. Brunner, in: E.L. Eliel, S.H. Wilen (Eds.), Topics in Stereochemistry, vol. 18, Wiley, New York, 1988, p. 129. (e) I. Ojima, N. Clos, C. Bastos, Tetrahedron 45 (1989) 6901.

[2] S. Akutagawa in: A.N. Collins, G.N. Sheldrake, J. Crosby (Eds.), Chirality in Industry, Wiley, Chichester, UK, 1992, p. 325. (b) S. Kohta, Tetrahedron 50 (1994) 3639. (C) S. Akutagawa, Appl. Catal. A: Gen. 128 (1995) 171.

[3] U. Nagel, E. Kinzel, J. Chem. Soc. Chem. Commun. (1986) 1089.

[4] S.M. Laurie, in: G. Wilkinson, R.R. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987, p. 739.

[5] A. Corma, M. Iglesias, M.V. Martín, J. Rubio, F. Sánchez, Tetrahedron: Asymmetry 3 (1992) 845.

[6] (a) A. Corma, A. Carmona, M. Iglesias, A. San José, F.Sánchez, J. Organomet. Chem. 492 (1995) 11. (b) A. Corma, M. Iglesias, C. Del Pino, F. Sánchez, J. Organomet. Chem. 431 (1992) 233.

[7] (a) A. Corma, A. Carmona, M. Iglesias, F. Sánchez, Inorg. Chim. Acta 244 (1996) 239. (b) A. Corma, A. Carmona, M. Iglesias, F.Sánchez, Inorg. Chim. Acta 244 (1996) 79.

[8] A. Corma, A. Fuerte, M. Iglesias, F. Sánchez, J. Mol. Catal. A: Chem. 107 (1996) 225.

[9] (a) J. Chatt, L.M. Venanzi, J. Chem. Soc. (1957) 4715. (b) D. Drew, J.R. Doyle, Inorg. Synth 13 (1972) 48. (c) G. Giordano, R.H. Crabtree, Inorg. Synth 28 (1990) 88.

[10] E. Miranda, F. Sánchez, J. Sanz, M.I. Jimenez, I. Martinez-Castro, J. High Resol. Chromatogr. 21 (1998) 225.

[11] A. Mortreux, F. Petit, G. Buono, G. Peiffer, Bull. Soc. Chim. Fr. 4 (1987) 631.

[12] L.L. Murrell, in: J.J. Burton, R.L. Garten (Eds.), Advanced Materials in Catalysis, Academic Press, New York, 1977, Ch. 8.

[13] A. Corma, M. Iglesias, F. Sánchez, Catal. Lett. 32 (1995) 313.

[14] I. Amer, H. Alper, J. Am. Chem. Soc. 112 (1990) 3674.

[15] R. Lazzaroni, G. Ucello-Barretta, M. Benetti, Organometallics 8 (1989) 2323.