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From homogeneous to heterogeneous catalysis: zeolite supported metal complexes with C_2-multidentate nitrogen ligands. Application as catalysts for olefin hydrogenation and cyclopropanation reactions

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Abstract

The fixation of the preformed rhodium and copper complexes, {[Rh(*N*,*N*′-bis[(*S*)-prolyl-*N*-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)(THF)]X, [Rh((*N*,*N*′-bis[(*S*)-benzyl prolyl]-*N*-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine)(cod)]X, X = PF_6}, {[Cu(*N*,*N*′-bis[(*S*)-prolyl-*N*-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)]X, [Cu((*N*,*N*′-bis[(*S*)-benzylprolyl]-*N*-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine)(CH_3CN)]X, X = ClO_4} on zeolites (USY, MCM41) and their use, under heterogeneous conditions, for the hydrogenation and cyclopropanation reactions are reported. The catalytic activity and selectivity are higher to that observed under homogeneous conditions, as a consequence of the complex—and/or reagents—to-support interaction. The strength of such interactions allows the recovery and recycling of the supported catalysts for a number of cycles. Atomic absorption analysis of the reaction solutions shows that there is no rhodium or copper leaching into the solutions. © 2002 Published by Elsevier Science B.V.

Keywords: Rhodium; Copper; Enantioselective hydrogenation; Cyclopropanation; Zeolites

1. Introduction

In recent years, the synthesis of optically pure important chiral pharmaceuticals and agrochemical gained significant and potential. Heterogeneous catalytic enantioselective reaction, being a tool for asymmetric synthesis, has a special importance taking into account the industrial applications [1]. Recently, due to environmental considerations and safety concerns, there is an accelerating tendency to substitute the waste productive homogenous methods to heterogeneous ones. As a consequence, supported metal catalysts play a crucial role in many industrial important chemical processes. These industrial requirements initiate growing efforts concerning catalyst preparation [2,3].

Spectacular enantioselectivity and efficiency are now currently reported for phosphine-based metal complexes as homogeneous catalysts. Nevertheless, only a few examples have been developed to an industrial scale. Several reasons can be put forward to explain this relative lack of success, among which the metal price (noble metals are usually used) and the cost of the ligands, which is often much higher than that of the metal itself. In addition, difficulties encountered in the separation and recycling of homogeneous catalysts have considerably decreased and sometimes suppressed the potential interest of enantioselective catalysis. Moreover, most of the efforts are still concentrated on the synthesis and evaluation of new homogeneous catalysts in view of improving efficiency, selectivity and scope of applications. This orientation leads generally to the conception of more sophisticated phosphine-based complexes as catalysts (often more expensive and unstable), which suffer from the same problems at the development step. One possible solution to such drawbacks is

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heterogeneous catalysis, which allows easy separation of the product(s) and the catalyst [4]. It could be assumed that the introduction of heterogeneous asymmetric catalysis might have a crucial importance in the development of chirotechnology [5]. The results obtained by several groups have demonstrated the feasibility of, but also the difficulties encountered in, heterogenisation of chiral phosphine-based complexes as catalysts.

We looked into the development of another class of ligands, that would be cheaper, easily accessible and with greater stability than phosphines and potentially more suitable for heterogenisation purposes. Nitrogen-containing compounds seemed to fit with such a definition and we oriented our efforts towards this family of ligands, and we have already some promising results [6].

In this paper, we describe the successful use of C_2-multidentate nitrogen-containing ligands in asymmetric homogeneous catalysis and how efficient and selective heterogeneous zeolite systems involving this type of ligands could be designed.

2. Experimental

2.1. General

All preparations of organometallic complexes were carried out under dinitrogen by conventional schlenk-tube techniques. The starting complexes $[Rh(cod)Cl]_2$ and $[Cu(NCCH_3)_4]ClO_4$ were prepared according to the literature methods [7,8]. Solvents were carefully degassed before use. The silylating agent *N*-(2-aminoethyl-3-aminopropyl)triethoxysilane was obtained as described in the literature [9]. C, H and N analysis 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 and plasma ICP Perkin–Elmer 40. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets; ^1H-NMR, ^{13}C-NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers. Chemical shifts being referred to tetramethylsilane (internal standard). High resolution ^{13}C MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence, in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6 μs 90° pulse width, 2 ms contact time and five to ten recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44′) was 4 KHz. 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.

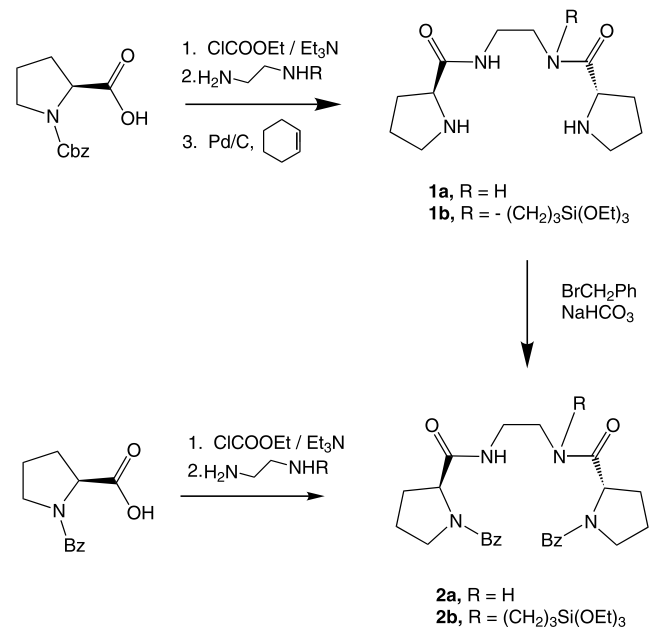
The inorganic support for anchoring was an ultrastable Y zeolite (USY) prepared by steam calcination at 1023 K of an 80% ammonium-exchanged NaY (SK40 Union Carbide), followed by treatment with a 1 N citric acid solution at 333 K for 30 min to remove extra-framework species. After this, the zeolite was 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; crystallinity: greater than 95%. A detailed synthesis procedure for purely siliceous MCM-41 with an exhaustive characterisation has been described [10].

2.2. Synthesis of ligands

The ligands *N*,*N*′-bis[(*S*)-prolyl]ethylenediamine (**1a**), *N*,*N*′-bis[(*S*)-benzylprolyl]ethylenediamine (**2a**) were synthesised according to our previously published methods [11] as depicted in Scheme 1.

2.2.1. *N*,*N*′-bis[(*S*)-prolyl]-*N*-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine (**1b**)

2.2.1.1. N,N′-bis[(S)-N-benzyloxycarbonylprolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine. To a solution of (*S*)-*N*-benzyloxycarbonylproline (3.7 g, 14.8 mmol) and triethylamine (1.5 g, 2.07 ml, 14.8 mmol) in tetrahydrofurane (80 ml) ice-cooled, ethyl chloroformate (1.6 g, 14.8 mmol) was added dropwise with vigorous stirring, when the addition is finished, the pasty reaction mixture is stirred for 30 min (temperature 5–10 °C), obtaining a very reactive mixed anhydride. To the anhydride solution, *N*-(2-aminoethyl-3-aminopropyl)triethoxysilane (1.96 g, 2.03 ml, 7.4 mmol) in tetrahydrofurane (5 ml), was added dropwise for 15 min and the mixture was stirred at 0 °C for 1 h, and filtered. The solvent was evaporated and the residue extracted with ethyl acetate and washed successively with water, aqueous $NaHCO_3$ and brine. The organic layer was dried over magnesium sulphate and evaporated in vacuo to give 5.17 g (96%) of product. $[\alpha]_D^{20} = -30$ (0.8, EtOH). $C_{37}H_{54}N_4O_9Si$ (768): Calc. C, 61.0; H, 7.5; N, 9.1. Found: C, 60.7; H, 7.1; N, 9.3%. IR (film, cm^{-1}): $\nu = 3321$ (NH); 1730 ($C{=}O_{Cbz}$); 1700 ($C{=}O_{amide}$); 1534 (N–C=O); 1104(C–Si). ^1H-NMR ($CDCl_3$, 50 °C) δ (ppm): 7.32–7.25 (m, 10H, Ph); 5.20–5.02 (m, 4H, OCH_2Ph); 4.27–4.06 (m, 2H, H_2); 3.69 (q, 6H, 6,4 Hz,



Scheme 1. Synthesis of ligands.

$\mathrm{OC}H_2\mathrm{CH}_3$); 3.57–3.49 (m, 4H, H_5); 3.47–3.31 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_2Si}$); 3.30–3.16 (m, 4H, $\mathrm{C}H_2$–NH); 2.17–1.96 (m, 4H, H_3); 1.96–1.82 (m, 4H, H_4); 1.66–1.57 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2Si}$) 1.19 (t, 9H,6.4 Hz, $\mathrm{OCH_2C}H_3$); 0.55–0.49 (m, 2H, $\mathrm{CH_2Si}$). ^{13}C-NMR ($\mathrm{CDCl_3}$, 50 °C) δ (ppm): 172.5 ($\mathrm{C{=}O_{amide}}$); 158.2 ($\mathrm{C{=}O_{Cbz}}$); 136.5 ($\mathrm{C_{arom}}$–R); 128.3–127.7 ($\mathrm{C_{arom}}$–H); 66.9 ($\mathrm{CH_{2Cbz}}$); 59.2 (C_2); 58.3 ($C\mathrm{H_2CH_3}$); 47.2–46.3 ($C\mathrm{H_2CH_2CH_2Si}$, $C\mathrm{H_2CH_2NH}$,C_5); 30.8 ($\mathrm{CH_2}C\mathrm{H_2NH}$); 26.4 ($C_3$); 23.4 ($C_4$); 18.1 ($\mathrm{CH_3}$); 13.9 ($C\mathrm{H_2CH_2Si}$); 7.5 ($\mathrm{CH_2Si}$).

2.2.1.2. N,N′-bis[(S)-prolyl]N-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine. A mixture of *N*,*N′*-bis[(*S*)-*N*-benzyloxycarbonylprolyl]-*N*-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine (1 g, 1 mmol), cyclohexene (0.31 g, 3.8 mmol) and 130 mg of commercial Pd–C (10%) in 20 ml of ethanol was heated under reflux for 1 h in argon, cooled and filtered over celite. The catalyst was washed with ethanol, and filtrate and wash liquids were evaporated under reduced pressure to give 620 mg of **1b**. Yield: (98%). $[\alpha]_D^{20} = -64.3$ (1, EtOH). $\mathrm{C_{21}H_{42}N_4O_5Si}$ (459): Calc. C, 54.9; H, 9.1; N, 12.2. Found: C, 54.7; H, 9.4; N, 11.9%. IR (KBr, $\mathrm{cm^{-1}}$): $\nu = 3428$, 3342 (NH); 1692 (amide I); 1521 (amide II); 1099 (C–Si). ^{1}H-NMR ($\mathrm{CDCl_3}$, 50 °C) $\delta = 7.87$–7.80 (s br, 1H, NH); 5.54–5.27 (s br, 1H, NH); 4.18–4.08 (m, 2H, H_2); 3.70 (c, 6H, 8.3 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.49–3.20 (m, 4H, H_5); 3.35–2.95 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_2Si}$); 2.97–2.88 (m, 4H, $\mathrm{C}H_2$–NH); 2.17–1.991 (m, 2H, H_3); 1.97–1.41 (m, 8H, $H_{3'}$, H_4, $\mathrm{C}H_2\mathrm{CH_2Si}$); 1.19 (t, 9H, 8.3 Hz, $\mathrm{OCH_2C}H_3$); 0.68–0.38 (m, 2H, $\mathrm{CH_2Si}$). ^{13}C-NMR ($\mathrm{CDCl_3}$, 50 °C) δ (ppm): 166.3 ($\mathrm{C{=}O_{amide}}$); 61.3 (C_2); 58.1 ($C\mathrm{H_2CH_3}$); 47.0–46.5 ($C\mathrm{H_2CH_2CH_2Si}$, $C\mathrm{H_2CH_2NH}$); 45.1 (C_5); 27.6 ($\mathrm{CH_2}C\mathrm{H_2NH}$); 26.4 ($C_3$); 23.2 ($C_4$); 18.3 ($\mathrm{CH_3}$); 14.6 ($C\mathrm{H_2CH_2Si}$); 7.8 ($\mathrm{CH_2Si}$). $\mathrm{MS^+}$(m/z): 460 ($\mathrm{M^+}$); 254 (M–$\mathrm{Si(OCH_2CH_3)_3}$).

*2.2.2. N,N′-bis[(S)-benzylprolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine (**2b**)*

2.2.2.1. Procedure A. To a solution of (*S*)-*N*-benzylproline (2 g, 10.4 mmol) and triethylamine (1.05 g, 1.45 ml, 10.4 mmol) in tetrahydrofurane (80 ml) ice-cooled, ethyl chloroformate (1.1 g, 10.4 mmol) was added dropwise with vigorous stirring, when the addition is finished the pasty reaction mixture is stirred for 30 min (temperature 5–10 °C), obtaining a very reactive mixed anhydride. To the anhydride solution, *N*-(2-aminoethyl-3-aminopropyl)triethoxysilane (1.37 g, 1.42 ml, 5.2 mmol) in tetrahydrofurane (5 ml), was added dropwise for 15 min and the mixture was stirred at 0 °C for 1 h, and filtered. The solvent was evaporated and the residue extracted with ethyl acetate and washed successively with water, aqueous $\mathrm{NaHCO_3}$ and brine. The organic layer was dried over magnesium sulphate and evaporated in vacuo to give 6.01 g (90%) of product. $[\alpha]_D^{20} = -50.3$ (1, EtOH). $\mathrm{C_{35}H_{54}N_4O_5Si}$ (639): Calc. C, 64.1; H, 8.2; N, 8.5. Found: C, 63.7; H, 8.4; N, 8.9%. IR (KBr, $\mathrm{cm^{-1}}$): $\nu = 3400$ (NH); 1700 (amide I); 1530 (amide II); 1098 (C–Si). ^{1}H-NMR ($\mathrm{CDCl_3}$, 40 °C) $\delta = 7.70$–7.50 (d, br, 1H, NH); 7.40–7.28 (m, 10H, Ph); 3.91 (d, 2H, $\mathrm{CH_2Ph}$); 3.80 (q, 6H, 8.3 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.50 (d, 2H, $\mathrm{CH_2Ph}$); 3.45 (m, 3H, $\mathrm{CH_2N}$, $H_{5'}$); 3.34–3.26 (m, 2H, $\mathrm{CH_2N}$); 3.20–2.95 (m, 5H, $\mathrm{C}H_2\mathrm{CH_2CH_2Si}$, $H_{5'}$, $H_{2'}$); 2.50–2.25 (m, 2H, H_5); 2.23–2.05 (m, 2H, $H_{3'}$); 1.85–1.74 (m, 2H, H_3); 1.76–1.50 (m, 4H, H_4); 1.55 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2Si}$); 1.19 (t, 9H, $\mathrm{CH_3}$); 0.52–0.44 (m, 2H, $\mathrm{CH_2Si}$). ^{13}C-NMR ($\mathrm{CDCl_3}$, 40 °C) δ (ppm): 175.16 (C=O); 138.36, 138.32 ($\mathrm{C_1Ph}$); 128.69, 128.54, 128.43, 128.40, (C_o–Ph); 127.24, 127.16, (C_p–Ph); 67.16 ($C_{2'}$); 62.44 ($C_{2'}$); 59.87 ($\mathrm{Ch_2Ph}$); 58.42 ($\mathrm{OCH_2}$); 57.78 ($\mathrm{Ch_2Ph}$); 54.10 ($C_{5'}$); 52.90 (C_5); 50.28 ($C\mathrm{H_2CH_2CH_2Si}$), 45.58, 38.77, 37.33 ($\mathrm{CH_2N}$); 30.74 ($C_{3'}$); 29.48 (C_3); 24.14 ($C_{4'}$); 23.94 (C_4); 22.90 ($\mathrm{CH_2}C\mathrm{H_2CH_2Si}$); 18.27 ($\mathrm{CH_3}$); 7.70 ($\mathrm{CH_2Si}$). $\mathrm{MS^+}$(m/z): 639 ($\mathrm{M^+}$); 435 (M–$\mathrm{Si(OCH_2CH_3)_3}$).

2.2.2.2. Procedure B. To a solution of *N*,*N′*-bis[(*S*)-prolyl]*N*-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine **1b** (2 mmol) and triethylamine (1 mmol) in ice-cooled THF (25 ml), benzyl bromide (1 mmol), was added dropwise with vigorous stirring. When the addition was finished the reaction mixture was stirred for 6 h at 0 °C. The solvent was evaporated and the residue extracted with chloroform and washed successively with water, aqueous $\mathrm{NaHCO_3}$ and brine. The organic layer was dried over magnesium sulphate and evaporated in vacuo to give **2b**. The product was purified by flash chromatography with 1:1 hexane–ethyl acetate.

2.3. Preparation of rhodium and copper complexes (**I–IV**)

The complexes $[Rh(\mathbf{1a})]^+$, $[Rh(\mathbf{2a})(cod)]^+$, $[Cu(\mathbf{1a})]^+$, $[Cu(\mathbf{2a})]^+$ were synthesised previously [12].

2.3.1. Rhodium complexes

General method: Silver hexafluorophosphate (0.2 mmol) in THF (40 ml) was added to $[Rh(cod)Cl]_2$ (0.1 mmol) in THF (10 ml) and the mixture was stirred vigorously at room temperature (r.t.) for 30 min. Precipitated silver chloride was filtered off and the yellow solution was treated with the ligand (0.2 mmol) in THF. The mixture was stirred for 6 h under reflux. The solvent 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 vacuum (10^{-3} mm Hg) to give the cationic complex.

2.3.1.1. [Rh(N,N′-bis[(S)-prolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)]PF$_6$. $[Rh(\mathbf{1b})(THF)]PF_6$.THF. Yield: 113 mg (70%). m.p. = 166–173 °C. $C_{29}H_{58}F_6N_4O_7PRhSi$ (851): Calc: C, 40.9; H, 6.9; N, 6.6; Rh, 12.1. Found: C, 41.1; H, 6.9; N, 6.4; Rh, 11.8%. IR (KBr, cm^{-1}): $\nu = 3400$ (N–H); 1670, 1610 (amide I); 1560 (amide II); 1120 (C–Si); 840 (P–F). ^{13}C-NMR (solid) δ (ppm) = 170.8, 156.0 (C=O); 73.5 (C_2); 61.1 ($\mathit{C}H_2CH_3$); 59.4–40.1 ($\mathit{C}H_2CH_2CH_2Si$, $\mathit{C}H_2CH_2NH$, C_5); 38.5–20.9 ($CH_2\mathit{C}H_2NH$, C_3, C_4, CH_3); 14.6 ($\mathit{C}H_2CH_2Si$); 7.5 (CH_2Si). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) = 376 nm (2.3), 292.5 (2.8). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) = 143–155. MS$^+$(*m*/z): 669 $[Rh(\mathbf{1b})]PF_4$, 562 $[Rh(1b)]^+$. TG analysis: 0.838 mg weight loss (16.7% of 5.01 mg; expected loss 16.9%) at 60–95 °C.

2.3.1.2. [Rh(N,N′-bis[(S)-benzylprolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)]PF$_6$. $[Rh(\mathbf{2b})(cod)]PF_6$. Yield: 82 mg (65%). m.p. = > 268 °C. $C_{43}H_{66}F_6N_4O_5PRhSi$ (995): Calc: C, 51.9; H, 6.6; N, 5.3; Rh, 10.4. Found: C, 51.4; H, 6.9; N, 5.4; Rh, 10.8%. IR (KBr, cm^{-1}): $\nu = 3330$ (N–H); 1650, 1610 (amide I); 1578 (amide II); 1128 (C–Si); 836 (P–F). ^{13}C-NMR (solid) δ (ppm) = 181.3, 175.5 (C=O); 129.2 (Ph); 81.8 ($C=C_{cod}$); 67.7 (C_2); 64.8 ($\mathit{C}H_2CH_3$); 57.4 ($\mathit{C}H_2CH_2CH_2Si$, $\mathit{C}H_2CH_2NH$, C_5); 31.2 ($CH_2\mathit{C}H_2NH$, C_3, C_4, CH_3); 12.6 ($\mathit{C}H_2CH_2Si$); 7.5 (CH_2Si). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) = 346.0 nm (3.27), 290.0 (3.70). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) = 95. MS$^+$(*m*/z): 1035 $[Rh(\mathbf{2b})(cod)]PF_6$+$CH_3CN$ (carrier), 850 $[Rh(\mathbf{2b})(cod)]^+$. TG analysis: 0.930 mg weight loss (18.9% of 4.93 mg; expected loss 19.3%) at 110–125 °C.

2.3.2. Copper complexes

General method: To a solution of $[Cu(CH_3CN)_4]ClO_4$ (1 mmol) in dry acetonitrile (20 ml) was added a solution of the ligand (1 mmol); the mixture was stirred for 3 h at r.t. and the crystalline precipitate filtered. The filtrate was evaporated under reduced pressure to a volume of 5 ml and a careful addition of diethyl ether caused the precipitation of a microcrystalline blue solid, which was collected by filtration, washed and dried in vacuo (10^{-3} mmHg/8 h) to give the desired complex.

2.3.2.1. [Cu(N,N′-bis[(S)-prolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)]ClO$_4$. $[Cu(\mathbf{1b})]ClO_4 \cdot 2H_2O$. Yield: 66%. m.p. = 225–230 °C. Λ_M (10^{-3} M, Ω^{-1}cm^{2}mol^{-1}, CH_3CN) = 154–168. $C_{15}H_{34}ClCuN_4O_{11}Si$ (574): Calc. (with $Si(OCH_2CH_3)_3$ as $Si(OH)_3$): C, 31.4; H, 6.0; N, 9.8; Cu, 11.1. Found: C, 31.1; H, 5.8; N, 10.0; Cu, 11.4%. UV–vis (10^{-3} M, DMF): λ nm (log ϵ) = 637.5 (w); 290.0 (3.5). IR (KBr, cm^{-1}): $\nu = 3460$, 3300 (N–H); 1680 (C=O), 1620; 1590 (N–C=O); 1100 (C–Si); 1090 (Cl–O). TG analysis: 0.820 mg weight loss(18.98% of 4.32 mg complex; expected weight loss 19.5%) at 95–133 °C ($5H_2O$).

2.3.2.2. [Cu(N,N′-bis[(S)-benzylprolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)]ClO$_4$. $[Cu(\mathbf{2b})(CH_3CN)]ClO_4$. Yield: 56%. M.p. > 250 °C. Λ_M (10^{-3} M, Ω^{-1} cm^2 mol^{-1}, CH_3CN) = 122–125 $C_{37}H_{57}ClCuN_5O_9Si$ (843): Calc.: C, 52.7; H, 6.8; N, 8.3; Cu, 7.5. Found: C, 52.3; H, 6.8; N, 8.0; Cu, 7.4%. UV–vis (10^{-3} M, DMF): λ nm (log ϵ) = 617.5 (w); 355.5 (2.43); 288.50 (3.5). IR (KBr, cm^{-1}): ν = 3772, 3542 (OH); 3300 (N–H); 1670 (C=O), 1621; 1592 (N–C=O); 1100 (C–Si); 1090 (Cl–O). MS$^+$(*m*/z): 742 $[Cu(\mathbf{2b})(CH_3CN)]^+$, 700 $[Cu(2b)]^+$. TG analysis: 0.660 mg weight loss (14.8% of 4.60 mg complex; expected weight loss 14.8%) at 102–126 °C.

2.4. Heterogenisation of M-complexes (**Zeol–Rh, Zeol–Cu**)

2.4.1. Anchoring on USY and MCM-41-zeolite: route A

The supported M-complexes (MCM-Rh**1b**, USY-Cu**1b**, MCM-Cu**1b**) were prepared as we have previously described [13,14]. Thus, a solution of metal complex (0.5 mmol) in ethanol (2 ml) was added to a well-stirred toluene suspension (40 ml) of the inorganic support (modified USY-zeolite or MCM-41 dried at 140 °C/0.1 mmHg 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 for 7–24 h to remove the remaining non-supported complex from heterogenised catalyst. The resulting solid was dried in vacuo and analysed.

2.4.1.1. MCM-Rh1b. Elemental analysis indicated 0.72 mass%. Rh. IR (KBr, cm^{-1}): $\nu = 3410$ (O–H, N–H);

1660, 1600 (amide I); 1560 (amide II); 1237 (vs, support); 1120 (C–Si); 1080 (vs, support); 840 (P–F). ^{13}C-NMR (solid): δ (ppm) = 170.6, 157.0 (C=O); 73.7 (C_2); 61.1 (CH_2CH_3); 59.0–40.3 ($CH_2CH_2CH_2Si$, CH_2CH_2NH, C_5); 39.5–21.0 (CH_2CH_2NH, C_3, C_4, CH_3); 14.7 (CH_2CH_2Si); 7.8 (CH_2Si).). UV–vis (solid) (nm): 296.

2.4.1.2. MCM-Rh2b. Elemental analysis indicated 0.52 mass% Rh. IR (KBr, cm^{-1}): ν = 3550 (O–H); 3335 (N–H); 1659, 1628 (amide I); 1525 (amide II); 1214 (vs, support); 1122 (C–Si); 1071 (vs, support); 838 (P–F). ^{13}C-NMR (solid) δ (ppm) = 181.0, 175.2 (C=O); 129.5 (Ph); 81.1 (C=C_{cod}); 67.3 (C_2); 64.4 (CH_2CH_3); 57.3 ($CH_2CH_2CH_2Si$, CH_2CH_2NH, C_5); 31.2 (CH_2CH_2NH, C_3, C_4, CH_3); 12.8 (CH_2CH_2Si); 7.6 (CH_2Si). UV–vis (solid) (nm): 360, 310.

2.4.1.3. USY-Cu1b. Elemental analysis indicated 0.86 mass% Cu. IR (KBr, cm^{-1}): ν = 3440–3300 (O–H, N–H); 1670, 1600 (C=O); 1236 (vs, support); 1100–1083 (C–Si, support); 1080 (Cl–O). UV–vis (solid) (nm): 598, 305.

2.4.1.4. MCM-Cu1b. Elemental analysis indicated 0.92 mass% Cu. IR (KBr, cm^{-1}): ν = 3440–3300 (O–H, N–H); 1670, 1600 (C=O); 1236 (vs, support); 1100–1083 (C–Si, support); 1080 (Cl–O). UV–vis (solid) (nm): 594, 300.

2.4.1.5. MCM-Cu2b. Elemental analysis indicated 0.82 mass% Cu. ν = 3440–3300 (O–H, N–H); 1670, 1600 (C=O); 1236 (vs, support); 1100–1083 (C–Si, support, Cl–O). UV–vis (solid) (nm): 356, 310.

2.4.2. Anchoring on USY and MCM-41-zeolite: route B

The supported Cu-complex (MCM-**1b**Cu) was prepared as follows. A solution of *N*,*N*′-bis[(*S*)-prolyl]-*N*-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine (**1b**) (0.5 mmol) in ethanol (2 ml) was added to a well-stirred toluene suspension (40 ml) of the zeolite MCM-41 (dried at 140 °C/0.1 mmHg 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 for 7–24 h to remove the remaining non-supported product from heterogenised ligand. The resulting white solid was dried in vacuo and analysed. To a solution of $[Cu(CH_3CN)_4]ClO_4$ (1 mmol) in dry acetonitrile (20 ml) was added a suspension of the heterogenised ligand (1 mmol); the mixture was stirred for 6 h at r.t. and the pale blue solid filtered, washed with acetonitrile, and dried in vacuo (10^{-3} mmHg/8 h) to give the heterogenised Cu-complex. Elemental analysis indicated 0.65 mass% Cu. IR (KBr, cm^{-1}): ν = 3460–3300 (O–H, N–H); 1665, 1600 (C=O); 1230 (vs, support); 1100–1090 (C–Si, support); 1090 (Cl–O). UV–vis (solid) (nm): 600, 304.

2.5. Catalytic experiments

2.5.1. Hydrogenation of prochiral alkenes

The catalytic properties, in hydrogenation reactions, of the Rh-complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 ml capacity at 40 °C temperature, 4 atm dihydrogen pressure and 1/500 of metal–substrate molar ratio. The evolution of the reaction and optical purity (ee) of hydrogenated product were monitored by gas chromatography with a chiral glass capillary column (mixture of methylsilicone (OV-1701) and methylsilicone-heptakis-[2,3-dipentyl-6-(*t*-butyldimethylsilyl)]-β-cyclodextrin as stationary phase) [15].

2.5.2. Cyclopropanation of styrene

To a stirred mixture of styrene (3 mmol) and a catalyst (0.02 mmol), alkyl diazoacetate (alkyl = ethyl, *t*-butyl) (4.12 mmol) was added dropwise with a syringe over a period of 2 h in an N_2 atmosphere at 50 °C. After the evolution of N_2 ceased, a mixture of ethyl *cis–trans*-2-phenylcyclopropanecarboxylates was obtained. Chemical yield, selectivity and the enantiomeric excesses of cyclopropanes were measured by gas chromatography with a chiral glass capillary column (mixture of methylsilicone (OV-1701) and methylsilicone-heptakis-[2,3-dipentyl-6-(*t*-butyldimethylsilyl)]-β-cyclodextrin as stationary phase) [15].

2.5.3. Recovery and recycling of catalysts

At the end of the hydrogenation or cyclopropanation process, the mixture of reaction was filtered; the residue of zeolite-containing catalyst was washed with CH_2Cl_2 or acetonitrile to completely remove the remains of products and/or reactants and used again.

3. Results and discussion

3.1. Synthesis of metal-complexes

The complexes [M(ligand)(L′)]X (M = Rh, Cu; L′ = H_2O, THF, cod; X = ClO_4, PF_6) **I**–**IV**, have been prepared as we have reported [16]. The coordinating solvents have been verified by the appropriate losses in their thermogravimetric (TG) analyses.

The mononuclear complexes $[Rh(\mathbf{L})(L')]PF_6$ (**I**, **II**) were prepared in good yield (> 60%) by ligand exchange of **L** with $[Rh(cod)(THF)_2]PF_6$ in THF. The complexes were isolated as yellow, microcrystaline, and air-stable solids. The IR spectra of show ν(N–H) bands at ~3400 cm^{-1}, shifted to higher frequencies respect to free ligand, due to Rh-coordinated NH of pyrrolidine ring.

The amide I band appears at 1660 and 1600 cm^{-1}. The amide II band appears in the same position as the free ligand. The ν(P–F) frequency appears at 840 cm^{-1}. The complexes are almost insoluble in organic solvents and we have obtained the ^{13}C MAS and CP/MAS NMR spectra of powdered samples. The spectra display two separate resonances at 170.8, 156.0 ppm (**I**) and 181.3, 175.5 ppm (**II**) indicating the presence of two inequivalent C=O moieties. The signals are downfield shifted compared with free amide as a consequence of the Rh–N–C=O coordination.

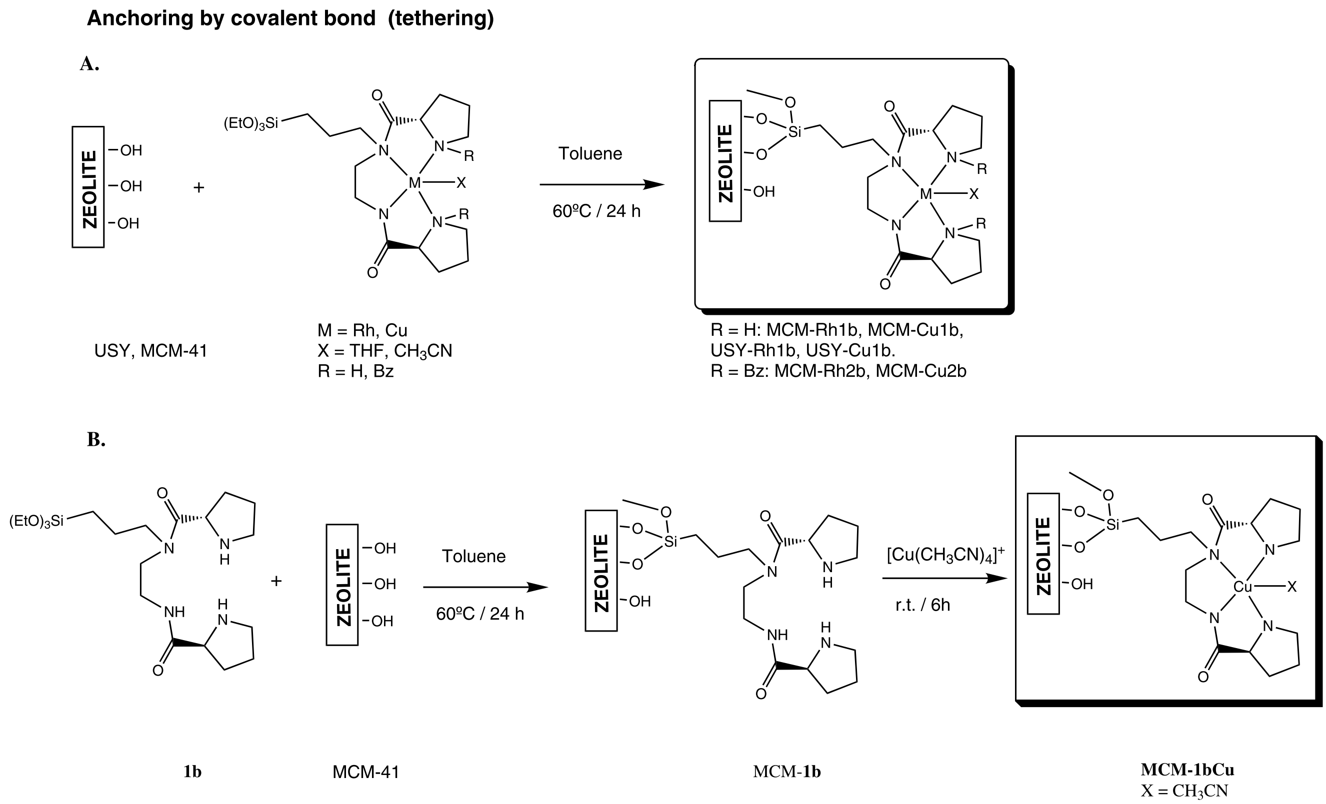
The Cu-complexes **III**, **IV** were formed according to a simple substitution reaction starting from $[Cu(NCCH_3)_4]ClO_4$. The Cu-complexes described herein involve the ligand functioning as a neutral, multidentate chelate through its amine, amide groups. The complexes were characterised analytical and spectroscopically. The IR spectra of Cu-complex show ν(N–H) bands, shifted to higher frequencies than free ligand bands, due to Cu-coordinated NH of pyrrolidine ring and a broad band at 3300 cm^{-1} shifted to lower frequencies that corresponds to ν(N–H) amide band. The amide I band appears at 1680 and 1620 cm^{-1} is attributed to the uncoordinated keto function. The amide II band appears in the same position as the free ligand. The ν(Cl–O) frequency appears at 1100 cm^{-1}. No splitting or broadening of ν_3 or ν_4 was observed in the spectrum of complexes containing ClO_4 anions, which excludes M–O–Cl bonds. The ^{13}C-MAS spectra show broad signals due to paramagnetic Cu(II) nuclei.

The FAB, ESIMS and APCIMs mass spectra of complexes were recorded. All the complexes examined provided nice quality ionspray mass spectra and the molecular weight of the complexes have been confirmed in all cases.

3.2. *Heterogenisation of complexes*

The solids employed in the present study as supports of the active chiral complexes were modified USY-zeolite and purely siliceous MCM-41. The two solids were selected to compare topologies. Modified USY-zeolite was prepared by steam calcination at 1300 K of an 80% NH_4^+ exchanged NaY-zeolite, followed by treatment with a 0.33 mol dm^{-3} citric acid solution at 403 K, the final zeolite presented a well developed supermicropore (pore diameter 12–30 Å) system. These zeolitic materials were formed by a controlled dealumination that breaks some sodalite units, and allowed direct communication between several α-cages, generating cavities wider than 12 Å. Thus, the dealumination process gives rise to the formation of mesopores (pore diameter >15 Å) on the surface and in the interior of the crystallites as has been observed by transmission electron microscopy (TEM). the steam calcination of the zeolite produces the supermicropores and mesopores which are 'cleaned' of extra framework aluminium basic species, which would obstruct the pores, by treatment with a citric acid solution. The formation of supermicropores and large mesopores has been determined by N_2 adsorption–desorption. At the same time a large quantity of silanol groups inside mesopores were produced in the dealumination process, as detected by IR spectroscopy, which are suitable for anchoring the complex. In the case of MCM-41 the complex would be presumably located in the interior of the mesoporous channels (40 Å of diameter).

The heterogenisation of homogeneous catalysts is a field of continuing interest: indeed, although some of these organometallic complexes exhibit remarkable catalytic properties (activities and selectivity), they are difficult to separate, intact, from the reaction medium. Thus, unless the activity of the homogeneous catalysts is exceptionally high, their heterogenisation is still currently and economical, but also a toxicological and environmental challenge. We have considered one strategy for heterogenisation, which preserve as much as possible the coordination sphere of the metal. This is achieved: by anchoring the homogeneous catalyst to an inorganic support (USY or MCM-41 zeolite) via covalent bonds between the solid (silanol groups –Si–OH) and one ligand that have appropriate groups (–$Si(OEt)_3$) at a position remote to the metal center (Scheme 2a). Preparations of zeolite heterogenised materials of complexes 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 or MCM-41 zeolite. The resulting catalytic material is very stable and the species are covalently bonded to the surface showing only minor frequency shifts from those of the corresponding 'neat' complex. IR and UV–vis spectroscopy confirmed the fact that structures of the starting complexes are maintained when attached to the surface and show only minor frequency shifts from those of the corresponding complex. The elemental analysis of C, H, N and M also confirm the M–ligand (1:1) stoichiometry. It is unlikely that the nature of the complex is substantially altered under the relatively mild conditions of the anchoring reaction [17]. Thermogravimetric analysis shows that the total weight loss is associated with the metal complex content corresponding to composition of the organic ligands. The loading of metal was 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. IR and electronic spectra (diffuse reflectance) of heterogenised complexes are coincident with that recorded for homogeneous complexes (Fig. 1). The IR spectra of the zeolite-supported catalyst show bands that corresponds to the complexes and support. Peaks due to the zeolite dominate the spectra. These include



Scheme 2. Preparation of heterogenised complexs: Route A or B.

the O–H vibration in the range 3700–3300 cm^{-1}. Some of the bands characteristic of the complexes could, however, be distinguished. Major zeolite framework bands appeared around 1140, 1040, 960, 785 and 740 cm^{-1}. Vibrational bands due to N–H, C=O and P–F, Cl–O occur around 3300, 1670, 840 and 1100 cm^{-1}, respectively, broadly similar to those of the neat complex. The UV–vis electronic spectra data are given in Section 2. **Zeol–Cu1b** and **Zeol–Cu2b** exhibit a medium band with a maximum at 594.1, 617.5 nm. This band is due to d→d transition ($d_{xy} \rightarrow d_{x^2-y^2}$, d_{z^2}). The band maximum is not significantly altered on zeolite heterogenised complex. The positions and relative intensities of these bands are similar to those of the free complexes.

Also, we have obtained the zeolite-supported complex by anchoring the ligand to the support (Scheme 2b) and reaction of this heterogenised ligand with the starting complex to give **MCM-1bCu**. This product shows analytical and spectroscopical properties similar to that obtained via route A.

3.3. Catalytic experiments

3.3.1. Hydrogenation of alkenes

Rh-complexes were evaluated as catalysts in the hydrogenation of prochiral alkenes. Prochiral alkenes were used as substrates to research multifunctional recognition such that chirality and size can be distinguished simultaneously (Fig. 2). In the presence of 1 mol% of catalysts in ethanol at 40 °C under a pressure of 4 bar H_2, the substrate was fully converted to the alkane in less than 30 min. The results are summarised in Table 1, Fig. 3a and b.

In all experiments with the homogeneous catalyst we observed an induction period, depending of the substrate, from 5 min for less bulky derivatives and 30 min for diethyl mesaconate. On the contrary when complexes were supported on a 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 [18]. 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 (except with the bulky citraconic anhydride), indicating the cooperative effect of the support. The enantioselectivities obtained were low and close to the results for homogeneous catalysts. The maximum rate of hydrogenation of the olefins was shown to be in the order: citraconic anhydride ~ ethyl tiglate > diethyl citraconate > diethyl mesaconate > > diethyl 2-benzylidenesuccinate.

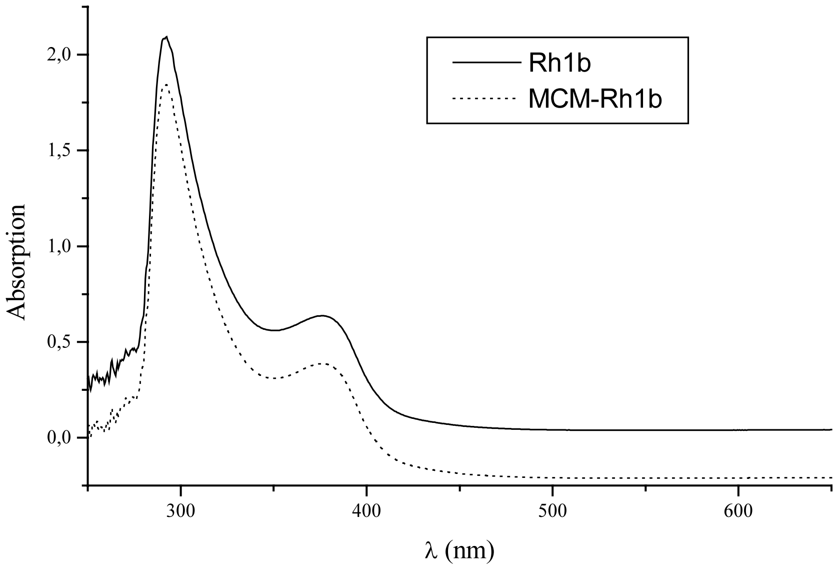


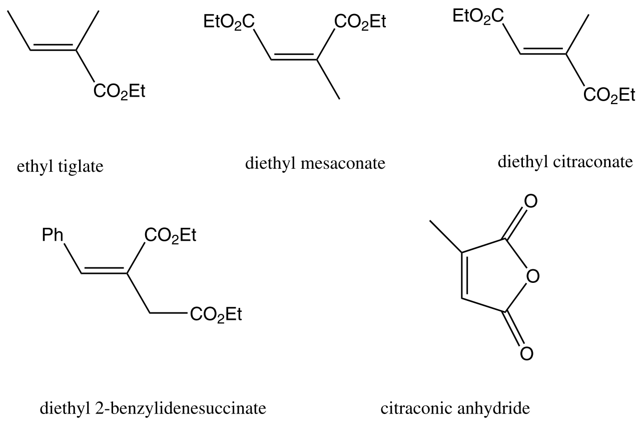
Fig. 1. UV–vis diffuse reflectance spectra of Rh1a and Rh1b.

Soluble complexes could be used only once, because of they deteriorate completely by the end of the first catalytic run. Zeolite-complexes could be recovered for recycling, and reused retaining most of their catalytic activity (Table 2, Fig. 4). After each cycle, the liquid phase that was separated from the reaction mixture was examined for catalytic activity in the hydrogenation of alkenes under the same conditions used with the solid catalyst. The results show that the liquid phases are inactive for hydrogenation. Moreover, atomic emission analyses did not detect rhodium the liquid phases from the first, second and third cycles. Based on the lower detection limit of the instrument, the amount of rhodium leaching into the liquid phases must be less than 0.2% of the Rh on the catalyst. IR analysis of the used catalyst isolated from the reaction mixture showed a new band at 2060 cm^{-1}. This spectrum suggests that during the hydrogenation a new Rh–H species be formed. The conversion increases faster with the increase of the cycle due to this previously formed active Rh–H species.

The comparative analysis between Rh**1a** and Rh**2a** shows that the reactivity increases when the pyrrolidine ring is protected as benzyl derivative (Fig. 5).

For the homogeneous catalyst, the selectivity varied from 5 to 31% ee depending on the substrate, where the highest selectivity was obtained when citraconic anhydride was employed. Comparing soluble and heterogenised materials we can see that the heterogenisation of the catalyst did not cause a significant decrease of asymmetric induction, a problem commonly reported in the literature.

The comparative analysis between these heterogenised complexes and their respective monomer–ligand–Rh complexes ([Rh(L)(cod)]PF_6, where L represents an *N*,*N′*-bidentate ligand, (*S*)-2-*t*-butylaminocarbonylpyrrolidine) [11], shows that the dimer–ligand complexes reported here presents, in general, a higher activity and enantioselectivity.



ethyl tiglate
diethyl mesaconate
diethyl citraconate
diethyl 2-benzylidenesuccinate
citraconic anhydride

Fig. 2. Prochiral olefins for the catalytic hydrogenation.

Table 1
Asymmetric hydrogenation of alkenes with rhodium-catalyst (cat./subs. = 1/500, T = 40 °C; PH_2 = 4 atm.)

Substrate	Rh1a		MCM-Rh1b	
	TOF [a]	ee(%) [b]	TOF [a]	ee(%) [b]
Diethyl mesaconate	304	5.5	2003	16
Diethyl citraconate	4960	19.0	6267	14.3
Ethyl tiglate	5680	19.2	7652	18
Citraconic anhydride	4642	31	4195	28
Diethyl 2-benzylidenesuccinate [c]	31	23	371	18

[a] Mmol subs./mmol cat min.

[b] Optical yield was determined by GLC using a cyclodextrine capillary column.

[c] Cat./substr. = 1/100.

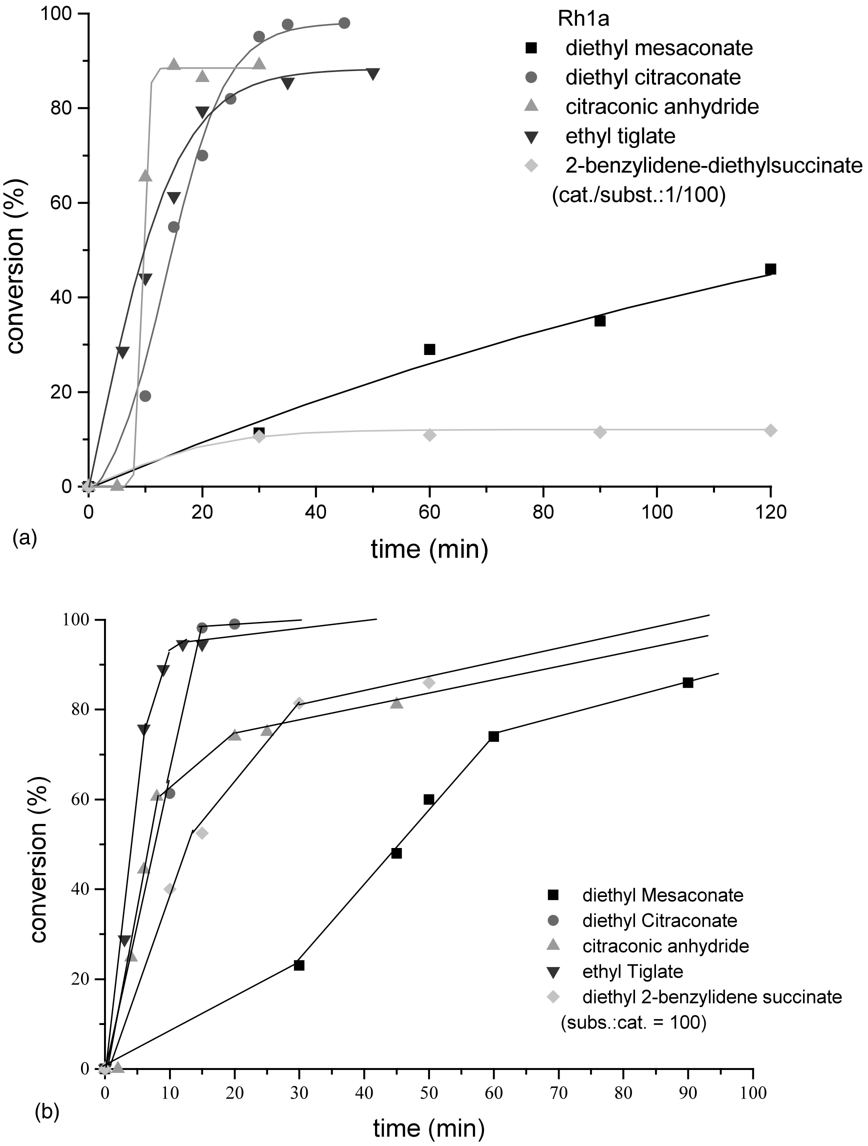


Fig. 3. (a) Catalytic activity of the complex MCM-Rh1a in the asymmetric hydrogenation of prochiral alkenes (cat./subs. = 1/500; T = 313K,pH_2 = 4 atm). (b) Catalytic activity of the complex MCM-Rh1b in the asymmetric hydrogenation of prochiral alkenes (cat./subs. = 1/500; T = 313K, pH_2 = 4 atm).

Table 2
Recycling of MCM-Rh**1b**

Substrate	1 Run	2 Run	3 Run	3 Run
Diethyl mesaconate	2003	682	474	582
Diethyl citraconate	6267	6396	8406	9250
Ethyl tiglate	7652	8116	9629	11375
Citraconic anhydride	4195	3803	2767	2800
Diethyl 2-benzylidenesuccinate [a]	371	323	320	381

[a] Cat./substr. = 1/100.

3.3.2. Cyclopropanation of styrene

The soluble and heterogenised catalysts were tested in the benchmark reaction of styrene with alkyl diazoacetate (Scheme 3). Table 3 shows the results obtained in these reactions. In the reaction of styrene with ethyl diazoacetate the main product is ethyl *cis–trans*-2-phenylcyclopropanecarboxylate. In this reaction two new asymmetric centres are generated, which cause a total of four stereoisomers. Also, diethyl maleate and diethyl fumarate are formed as by-products.

In the standard cyclopropanation reaction, ethyl diazoacetate is added to styrene in 2 h using a syringe pump. The reactions are carried out in the absence of a solvent. The complexes are dissolved o suspended in styrene prior to the addition of ethyl diazoacetate. After dissolution of the catalyst, the dropwise addition of ethyl diazoacetate is started, the beginning of the reaction is indicated by a spontaneous evolution of N_2.

To compare the activity of zeolite-supported complexes with that of unsupported two sets were simultaneously run. With soluble complexes the formation of

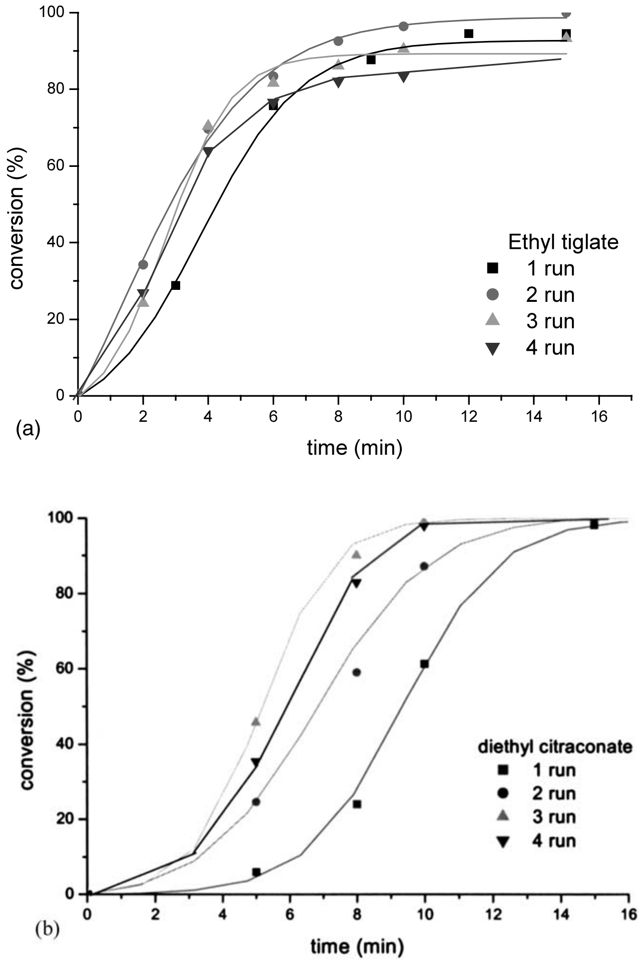


Fig. 4. (a) Recycling exeperiment of catalyst MCM-Rh1b; hydrogenation of ethyl tiglate. (b) Recycling exeperiment of catalyst MCM-Rh1b; hydrogenation of diethyl citroconate.

by-products was observed. These compounds consisted exclusively of (ethoxycarbonyl)carbene residues, as was shown by ^{1}H-NMR spectroscopy. We think that polymer formation occurred by reaction of ethyl diazoacetate with diethyl maleate and diethyl fumarate. Polymer formation inside the zeolite would probably lead to a gradual deactivation of the zeolite due to pore blocking by the polymers. It was observed that the reaction involving zeolite-supported catalyst give rise to relatively low amounts of polymeric side-products which is assumed to be formed at the outer zeolite surface.

Zeolite catalysts lead, in general, to higher selectivities with regard to styrene and diazoacetate. Heterogeneous catalysts also lead to similar or higher conversions than their homogeneous counterparts, in spite of the use of an equal styrene–copper ratio (1 mmol of copper per 150 mmol of styrene), which indicates that the support does not impose diffusional limitation to the reaction. As previously described with other Cu-heterogenised catalysts [9,19] a lower *trans* preference is observed.

All complexes were found to induce asymmetric cyclopropanation of styrene. It must be noted that the stereoselectivity in the reaction products is small but outside error. The magnitude of the small enantioselectivity observed was generally greater with *trans* than the *cis* isomer. In general the asymmetric induction for unsupported and zeolite-supported-Cu-complexes is similarly directed. The heterogeneous catalysts lead to higher enantioselectivities than soluble catalysts (**Cu1a**, < 5%; **USY-Cu1b**, 8%; **MCM-Cu1b**, 15%; **MCM-1bCu**, 10%).

The changes in *trans–cis* selectivity are not easy to explain. We speculate that these changes may be due to

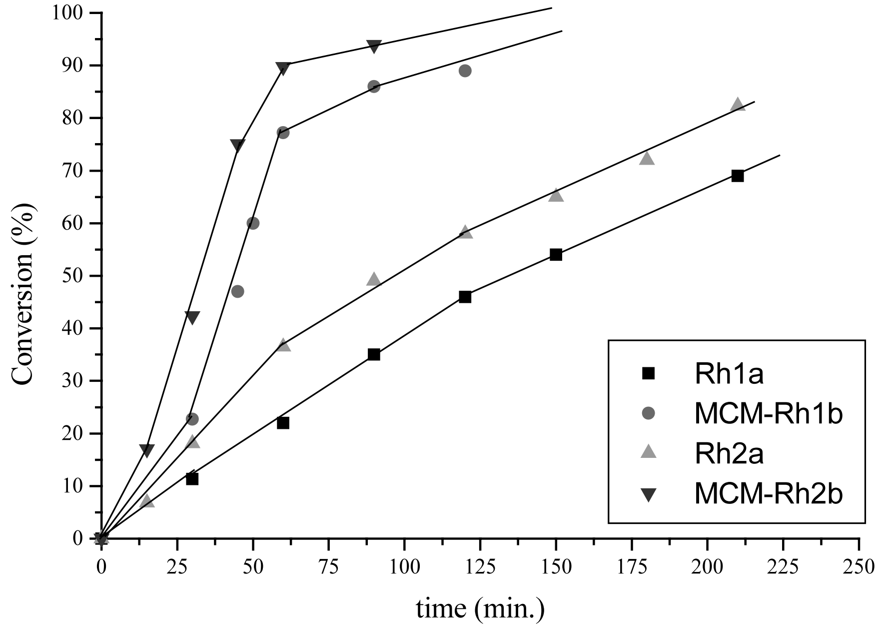
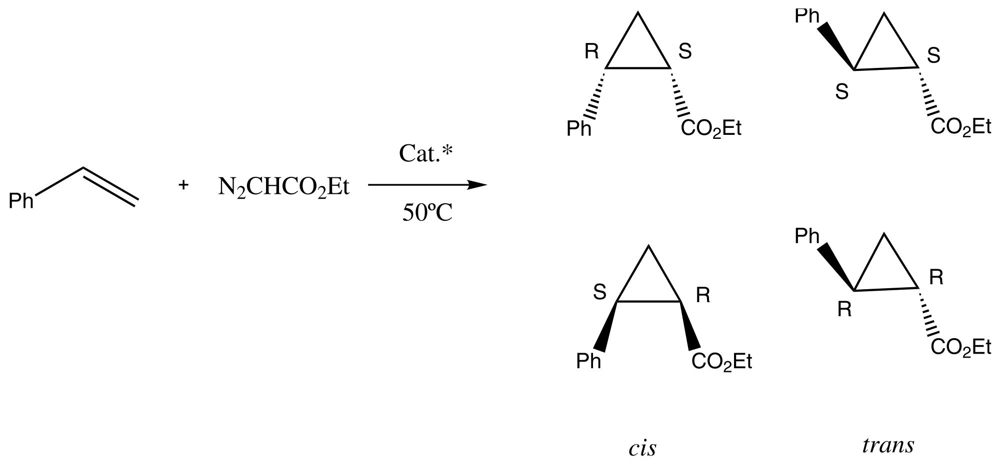


Fig. 5. Ligand influence in the hydrogenation of diethyl mesaconate.



Scheme 3. Cyclopropanation reaction.

Table 3
Catalytic results for the cyclopropanation reaction involving styrene and alkyl diazoacetates [a]

N_2CHCO_2R	Catalyst	Selectivity [b] (% yield [c], h)	*Trans–cis*
R = Et	**Rh1**a	**100(65, 23)**	2.32
	MCM-Rh**1b**	100(60, 20)	1.80
	Cu**1a**	49(74, 2)	2.0
	USY-Cu**1b**	100(32, 20)	1.88
	MCM-Cu**1b**	100(60, 21)	2.0
	MCM-**1b**Cu	100(20, 20)	1.89
R = *t*-Bu	**Rh1**a	100(34, 24)	2.38
	MCM-Rh**1b**	100(60, 23)	1.89
	Cu**1a**	48(74, 4)	2.08
	USY-Cu**1b** [d]	100(23, 19)	2.13
	MCM-Cu**1b**	100(57, 19)	2.04
	MCM-**1b**Cu	85(37, 21)	2.17

[a] All reactions were run at 50 °C. Cat./subs. = 1/150. Analysis was made by GC.

[b] Amount of cyclopropanes/amount of diazoacetate consumed.

[c] Yield is the percentage of cyclopropanes formed relative to the theoretical maximum expected for 100% diazoacetate conversion.

[d] Conv. = 69% for cat./subs. = 1/50.

the isolation of the catalytic sites or to the changes in the dimensionality that take place on changing from a homogeneous to a heterogeneous phase.

3.3.2.1. Nature of the support. Other point that is also clear from the results is that the activity and ee values for the heterogenised complexes depend on a small but significant extent on the support. These results are a reflection of the differences in the structure of the solid (topology, surface and silanol nests). A higher activity and asymmetric induction is obtained when MCM-41 was used as support, in comparison with the modified USY-zeolite.

3.3.2.2. The impact of the catalyst preparation procedure on catalysis. The method of catalyst immobilisation appeared to affect its performance in catalysis. When the catalyst was synthesised via route B the catalyst showed a low selectivity in the cyclopropanation of styrene (Table 3) whereas the route A catalyst is highly reactive. If the copper complex is prepared prior the anchoring (route A) no ligand-free copper is attached to the support. This approach gives rise to a well-defined, very selective catalyst.

Also, when we compared these materials with the respective [Cu((*S*)-2-*t*-butylaminocarbonylpyrrolidine)$(NCCH_3)_2$]ClO_4 [14], we have found a higher stability, activity and enantioselectivity when multitopic-pyrrolidine ligand complexes were used as catalysts for cyclopropanation reactions.

3.3.2.3. Nature of the recovered materials. One of the main advantages of the heterogeneous catalysts is the possibility for their recovery and reuse. This possibility was explored with **MCM-Cu1b**. The results obtained indicate (Table 4) that after the first reaction, the recovered catalyst does not show a significant degree of leaching of copper. The spectral data for recovered **zeol-Cu** are essentially the same before and after the cyclopropanation reaction.

Table 4
Recycling of MCM-Cu1b

N_2CHCO_2R	Run	Selectivity [a] (% yield)	*Trans–cis*	% ee
R = Et	1	100(50)	2.0	15
	2	100(57)	2.02	15
	3	100(53)	2.03	14
	4	100(52)	2.0	13
R = *t*-Bu	1	100(37)	2.04	< 5
	2	100(47)	2.13	< 5
	3	100(41)	2.02	< 5
	4	100(39)	2.04	< 5

[a] Amount of cyclopropanes/amount of diazoacetate consumed.

4. Conclusions

The new metal complexes heterogenised on zeolites are excellent catalysts for enantioselective hydrogenation and cyclopropanation of olefins. Heterogenisation on USY-zeolite (containing supermicropores and a large quantity of silanol groups) and MCM41 increases the activity of the homogeneous catalysts for different substrates. These catalysts can be recovered and reused, retaining most of their catalytic activity. Moreover, the heterogenised complexes are significantly more stable than the corresponding homogeneous complexes over prolonged reaction times and were handled without special care in standard conditions. Zeolite-supported complexes show interesting catalytic properties in different reactions which are related to the changes in the microenvironment (solvent, site isolation, dimensionality) of the metal-complex, mediated by the support. These materials are a real alternative to homogeneous catalysts for preparative applications.

Acknowledgements

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References

[1] G. Jannes, V. Dubois (Eds.),Chiral Reactions in Heterogenous Catalysis, Plenum Press, New York, London, 1995.

[2] (a) H.U. Blaser, B. Pugin, in: G. Jannes, V. Dubois (Eds.), Chiral Reactions in Heterogenous Catalysis, Plenum Press, New York, London, 1995, p. 33;
(b) D.E. Vos, I.F.K. Vankelecom, P.A. Jacobs (Eds.),Chiral Catalyst Inmobilization and Recycling, Wiley-VCH, Weinheim, 2000.

[3] (a) H.U. Blaser, Tetrahedron: Asymmetry 3 (1991) 843;
(b) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994, p. 346;
(c) T. Ohkuma, M. Kitamura, R. Noyori, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis (Ch. 1), Wiley-VCH, New York, 2000.

[4] R.A. Sheldon, H. van Bekkum (Eds.),Fine Chemicals Through Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2001.

[5] R.A. Sheldon, Chirotechnology: Industrial Synthesis of Optically Active Compounds, Dekker, New York, 1993.

[6] (a) A. Corma, C. del Pino, M. Iglesias, F. Sánchez, J. Chem. Soc. Chem. Commun. 1253 (1991).;
(b) A. Corma, M. Iglesias, M.V. Martín, J. Rubio, F. Sánchez, Tetrahedron: Asymmetry 3 (1992) 845;
(c) A. Corma, A. Fuerte, M. Iglesias, F. Sánchez, J. Mol. Catal. A: Chem. 107 (1996) 225 (and references cited herein).

[7] (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.

[8] I. Csöregh, P. Kierkegaard, R. Norestam, Acta Crystallogr. Sect. B 31 (1975) 314.

[9] (a) J.W. Ryan, G.K. Menzie, J.L. Speier, J. Am. Chem. Soc. 82 (1960) 3601;
(b) J.L. Speier, C.A. Roth, J.W. Ryan, J. Org. Chem. 36 (1971) 3120.

[10] (a) C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710;
(b) J.S. Beck, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, K.H. Olson, E. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenk, J. Am. Chem. Soc. 114 (1992) 10834.

[11] M.J. Alcón, M. Iglesias, F. Sánchez, I. Viani, J. Organomet. Chem. 601 (2000) 284.

[12] (a) M.J. Alcón, M. Iglesias, F. Sánchez, J. Organomet. Chem. 601 (2000) 284;
(b) M.J. Alcón, M. Iglesias, F. Sánchez, Inorg. Chim. Acta 306 (2000) 116.

[13] A. Corma, A. Carmona, M. Iglesias, A. San José, F. Sánchez, J. Organomet. Chem. 492 (1995) 11.

[14] A. Corma, A. Carmona, M. Iglesias, F. Sánchez, Inorg. Chim. Acta 244 (1996) 239.

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

[16] (a) M.J. Alcón, M. Iglesias, F. Sánchez, J. Organomet. Chem. 601 (2000) 284;
(b) M.J. Alcón, M. Iglesias, F. Sánchez, Inorg. Chim. Acta 306 (2000) 116.

[17] L.L. Murrell, in: J.J.B.urton R.L. Garten (Ed.), Advanced Materials in Catalysis (Chap. 8), Academic Press, New York, 1977.

[18] (a) A. Corma, M. Iglesias, C. Del Pino, F. Sánchez, J. Organomet. Chem. 431 (1992).;
(b) A. Corma, M. Iglesias, F. Sánchez, Catal. Lett. 32 (1995) 313.

[19] (a) J.M. Fraile, J.I. García, J.A. Mayoral, Chem. Commun. (1996) 1319.;
(b) J.M. Fraile, J.I. García, J.A. Mayoral, T. Tarnai, Tetrahedron Asymmetry 8 (1997) 2089.