Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 15 (2004) 495–502

Tetrahedron: *Asymmetry*

Chiral hybrid silica: sol–gel heterogenisation of *trans*-(1*R*,2*R*)-diaminocyclohexane ligands for the rhodium catalysed enantioselective reduction of acetophenone

Anne Brethon, Joël J. E. Moreau* and Michel Wong Chi Man

Laboratoire Hétérochimie Moléculaire et Macromoléculaire (UMR-CNRS 5076), Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'école normale, 34296 Montpellier Cedex 05, France

Received 28 October 2003; accepted 10 November 2003

Abstract—The synthesis of derivatives of *trans*-(1*R*,2*R*)-diaminocyclohexane with different substituents on the nitrogen atoms has been achieved. Rhodium complexes of these chiral ligands were evaluated as homogeneous catalysts for the asymmetric hydride transfer reduction (HTR) of acetophenone leading to moderate selectivities (ee = 0–57%). The silylation of a bromo-aryl derivative was successfully performed by a Heck's coupling reaction with vinyltriethoxysilane in the presence of a palladium catalyst. The immobilisation of this catalyst was then achieved by the sol–gel hydrolysis condensation. The resulting hybrid catalytic materials showed moderate selectivity, although much higher than the related homogeneous catalytic species.

1. Introduction

An increase in demand for the preparation of recoverable catalysts has drawn synthetic chemists' attention to the need to produce heterogeneous catalysts in different ways.[1] The main advantages of heterogeneous catalysts consist in easy separation, simple handling and possible recycling.[2,3] Our current interest in creating new hybrid silicas via the sol–gel process[4] has led us to study the immobilization of catalytic species. Bridged silsesquioxanes prepared by the hydrolysis of organo-bistrialkoxysilanes, $(RO)_3Si–R'–Si(OR)_3$,[5,6] represent a new class of material with a high potential for applications.[7,8] The design of appropriate molecular precursors and their hydrolysis can lead to hybrid materials with specific properties.[9–11] Silica-based materials with catalytic properties have also been prepared by the hydrolysis of organo-trialkoxysilanes.[12–15] Supported chiral catalysts are of particular interest for enantioselective synthesis.[16] We recently reported the incorporation of chiral organic moieties in hybrid silicas and showed that they can be used as chiral heterogeneous catalysts for hydride transfer reduction (HTR) of prochiral ketones.[17] Interestingly the solid heterogeneous catalysts showed selectivities higher than those observed with the corresponding homogeneous catalysts. Lemaire et al. have developed a series of diamine–metal complexes (rhodium, iridium and cobalt) for the reduction of prochiral ketones.[18,19] These catalysts were heterogenized by means of in situ generated polymeric species and revealed even more interesting features with not only inherent selectivities but also for their potential re-use.[20] Herein, we investigated several rhodium complexes of *trans*-(1*R*,2*R*)-diaminocyclohexane derivatives. We investigated the sol–gel hydrolysis of one silylated compound to give new chiral hybrid silica, containing covalently bonded *trans*-(1*R*,2*R*)-diaminocyclohexane bridging units. The complexation of the rhodium species afforded hybrid materials, which were used as heterogeneous asymmetric catalysts.

2. Results and discussion

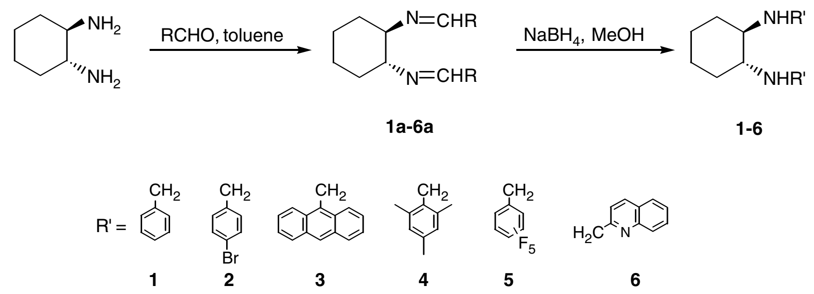
2.1. Synthesis of substituted diaminocyclohexane ligands for catalytic hydrogen transfer reduction

The synthesis of the *trans*-(1*R*,2*R*)-diaminocyclohexane derivatives was achieved in two steps (Scheme 1). The reaction of *trans*-(1*R*,2*R*)-diaminocyclohexane (DACH) with two molar equivalents of the carbonyl compounds gave the corresponding diimines which were

---

* Corresponding author. Tel.: +33-04-6714-7211; fax: +33-04-6714-7212; e-mail: jmoreau@cit.enscm.fr

0957-4166/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2003.11.005



Scheme 1.

subsequently treated with $NaBH_4$ to produce the corresponding benzylic diamines, ligands **1**–**6**.[21–24] The overall yields varied from 50% to 95%.

The aromatic diamine, ligand **7**, was prepared by nucleophilic substitution of *p*-nitrofluorobenzene (Scheme 2).[25]

We then studied the use of these diamine ligands in the rhodium catalysed asymmetric reduction by hydrogen transfer. Although an excess of ligand was shown to increase selectivity in the case of phenanthroline ligands,[26,27] the X-ray crystal structure of a bidentate diamine ruthenium complex showed that only one ligand was necessary for this reaction.[28] Moreover, mechanistic investigations suggested that the active catalytic species was a 1 to 1 diamine/rhodium complex.[18d,e] Based on these observations, we studied the reduction reaction with a 1:1 diamine/rhodium ratio. The diaminocyclohexane ligands **1**–**7** were treated with $[Rh(cod)Cl]_2$ in ethanol (ligand/Rh = 1:1). The formation of the rhodium–ligand complexes was monitored by UV–vis absorption measurements. The UV–vis spectrum of $[Rh(cod)Cl]_2$ exhibited an absorption maximum at 350 nm. A clear shift of this band was observed at 380 nm for the diamine–Rh complexes obtained from compounds **1**, **2** and **4**. Evidence for the formation of complexes **3**, **6** and **7** was not obtained in solution owing to the high absorption of these ligands around 380 nm which masked that of the corresponding Rh complexes. Finally, with the same 1:1 ligand/rhodium ratio, the complexation of ligand **5** in solution was not complete since the absorption band at 350 nm of the starting rhodium dimer persisted in the spectra. This absorption band at 350 nm disappeared upon addition of an excess of ligand. The UV–vis spectra of rhodium complexes of **2** and **5** are given as examples in Figure 1.

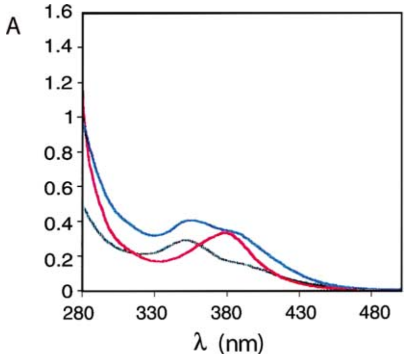
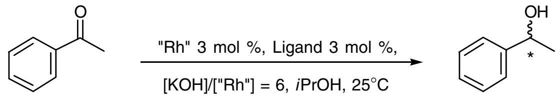
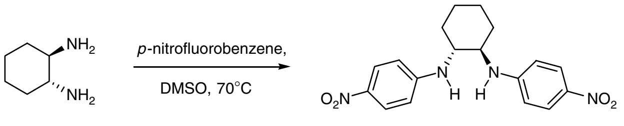


Figure 1. UV–vis spectra of $[Rh(cod)Cl]_2$ (black); **2** complexed with $[Rh(cod)Cl]_2$ (red); **5** complexed with $[Rh(cod)Cl]_2$ (blue).



Scheme 3.



7

Scheme 2.

The resulting solutions of chiral rhodium complexes were then tested as homogeneous catalysts for the hydride transfer reduction of acetophenone (Scheme 3) in order to evaluate their efficiency and to determine the effect of the presence of substituents at the nitrogen atoms on the enantioselectivities of the reduction reaction.

The results are summarised in Table 1.

The simple *trans*-(1*R*,2*R*)-diaminocyclohexane rhodium complex (DACH–Rh) was shown to give a low efficiency (conversion = 5% after 6 days) and selectivity (ee = 12%).[29] In our studies, the yields were appreciably higher (53–96%) with the ee up to 57%. Substituting one hydrogen atom with a benzylic group on the nitrogen atom (ligand **1**) increased both the selectivity (ee = 47%) and the conversion (89%). Compared to the *trans*-(1*R*,2*R*)-diaminocyclohexane containing primary amino groups (DACH), the nitrogen atoms became stereogenic centres when bound to rhodium in ligands **1**–**7**. This may account for the higher selectivity as well as higher activity as already observed for the related *N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine.[18d] Compared to alkyl substituents,[17c] the bulky benzylic group led to higher ee values. The presence of a bromine atom on the benzylic group **2** increased the selectivity (ee = 57%). However, bulkier aromatic substituents **3**–**6**, decreased both the selectivity and activity. Although a high

Table 1. Catalytic activity of the homogeneous catalysts (ligand/Rh 1:1) in the hydrogen transfer reduction of acetophenone by isopropanol (according to Scheme 3)

Entry	Ligand[a]	Reaction time[b] (d)	Conversion (%)	Ee[c] (%)
1	**1**	6	89	47
2	**2**	11	85	57
3	**3**	2	53	7
4	**4**	6	62	0
5	**5**	0.5	96	9
6	**6**	6	84	0
7	**7**	6	92	56

[a] Ligands derived from *trans*-(1*R*,2*R*)-diaminocyclohexane (cf. Schemes 1 and 2).

[b] The reaction was monitored by capillary gas chromatography.

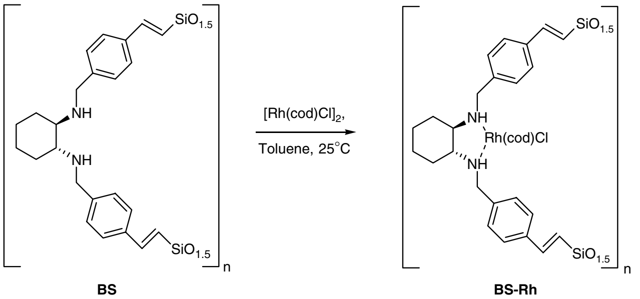
[c] The ees [(*S*)-configuration] were determined by HPLC on a Daicel chiracel OD column.

activity was observed for the perfluorinated aromatic compound **5** (96% in 0.5 day) a low selectivity was found. A phenyl substituent on the nitrogen atom **7** led to activity and selectivity values (ee = 56%) comparable to those already observed for the benzyl derivatives **1** and **2**.

2.2. Synthesis of the heterogeneous hybrid catalysts

We next studied the synthesis of the chiral hybrid catalytic material from the readily available benzyl substituted diaminocyclohexane. The silylation of **2** with vinyltriethoxysilane via a Heck reaction was achieved leading to **8** (Scheme 4). The sol–gel hydrolysis–condensation of the alkoxy groups on silicon allowed the formation of a chiral bridged silsesquioxane, **BS** (Scheme 4), consisting of a siloxane network with (*R*,*R*)-diaminocyclohexane crosslinking units.

The preparation of the chiral hybrid rhodium catalysts was envisaged by two routes: (i) The complexation of rhodium species was performed via treatment of **BS** with $[Rh(cod)Cl]_2$ in refluxing toluene to afford the post Rh-complexed hybrid catalyst **BS-Rh** (Scheme 5). Using this approach, rhodium atoms were expected to react only with accessible diamine ligands in the solid material, **BS**. (ii) **8** was first treated with $[Rh(cod)Cl]_2$ in ethanol yielding **8-Rh**. The latter was then hydrolysed, leading to the in situ Rh-complexed hybrid catalyst, **Rh-BS** (Scheme 6). In this case, the rhodium species was only partially embedded in the chiral matrix.

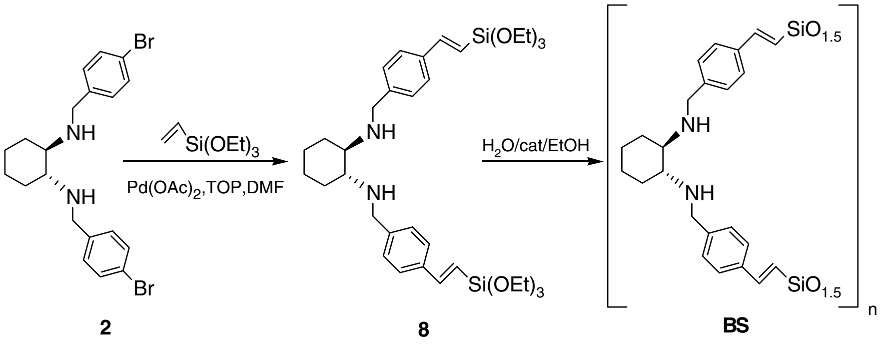


Scheme 5.

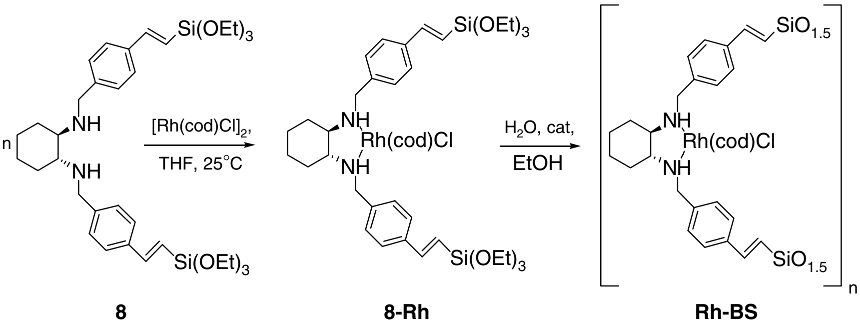
The chiral hybrid materials **BS**, **Rh-BS** and **BS-Rh** were analysed by NMR spectroscopy. In all cases, the solid state ^{29}Si NMR spectra showed only T substructures with a predominant T^3 substructure $[CSi–(OSi)_3]$ at −75 to −78 ppm indicating that no Si–C bond cleavage occurred during the hydrolysis–condensation step and the formation of a highly condensed siloxane network. The ^{29}Si spectrum of **BS** is given as an example in Figure 2.

The ^{13}C NMR spectrum of **BS** (Fig. 3a) exhibited signals at chemical shifts characteristic of the organic fragment at 25.7 and 30.9 (cyclic CH_2), 52.6 and 59.4 (NCH, NCH_2, residual OCH_2) and 120–150 (C_{Ph} and C_{vin}). An additional signal centred at 68 ppm was found in the spectra of the hybrid **Rh-BS** and **BS-Rh** attributable to the C sp^3 (CH_2) of the cyclo-octadiene (Fig. 3b), which remained in the coordination sphere of the incorporated rhodium atom.[18d,e]

The formation of rhodium complexes within the solid material was confirmed by solid UV–vis spectroscopy, with an absorption maximum centred at 380 nm. Elemental analyses showed that 30% and 40% of the expected amount of rhodium was incorporated in **Rh-BS** and **BS-Rh** respectively. These hybrid solids proved to be materials with low porosity; **BS** and **BS-Rh** having specific surface areas quite close to zero whereas **Rh-BS** exhibited a higher surface area of 5 m^2 g^{-1}.



Scheme 4.



Scheme 6.

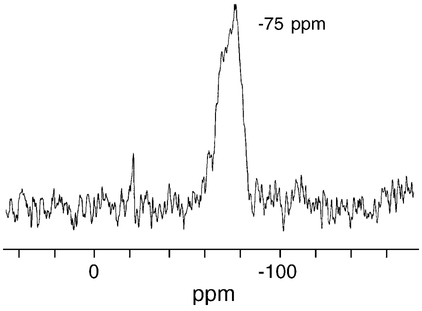


Figure 2. Solid state ^{29}Si CP-MAS NMR of **BS**.

The rhodium catalysed hydrogen transfer reduction of acetophenone was used to evaluate the catalytic material. The HTR reactions were performed with the soluble **8-Rh** homogeneous catalyst along with the derived chiral hybrid solids, **Rh-BS** and **BS-Rh**. The results are summarised in Table 2.

The reaction was first performed with **8-Rh** in solution. Complete conversion was attained after 7 days with this homogeneous catalyst. Surprisingly, the selectivity proved to be very low (ee = 6%) when compared with the previously related benzylic ligands **1** and **2** (Table 1). The use of chiral material as heterogeneous catalysts is more interesting. A much higher enantioselectivity was obtained with the two hybrid solids, **Rh-BS** and **BS-Rh**, giving identical enantiomeric excesses (ee = 39%). Furthermore, a higher activity was obtained from **Rh-BS** (conversion = 90% in only 2 days) when compared to that of **BS-Rh** (conversion = 94% in 6 days). The reactivity difference between these two hybrid catalytic materials may be due to the higher (although moderate) surface area of the in situ Rh-complexed catalyst **Rh-BS** ($5.2\,m^2\,g^{-1}$) whereas the **BS-Rh** featured a completely non porous solid ($0.4\,m^2\,g^{-1}$). The selectivity observed with the two hybrid solids was higher than that of the homogeneous catalyst probably due to the 3D chiral network of the solid support, which contributes to the chiral environment of the catalytic system. We have already observed a related chiral matrix effect.[17] Interestingly, the two solid catalysts could easily be recovered by filtration and washing with water and ethanol and then recycled for a further HTR reaction by adding KOH again. The in situ Rh-complexed catalyst, **Rh-BS**, gave similar activity in the second run (90% vs 91%) whereas an important loss of activity was observed with the post Rh-complexed catalyst, **BS-Rh**, in the second run (22% vs 94%). This loss in catalytic properties is probably due to a degradation of the catalytic species, which are most likely located at the external surface of

Table 2. Catalytic activity of **8-Rh** and related hybrid materials (ligand/Rh 1:1) in the hydrogen transfer reduction of acetophenone by isopropanol (according to Scheme 3)

Entry	Catalyst	Reaction time[a] (d)	Conversion (%)	Ee[b] (%)
1	**8-Rh**	7	100	6
2	**Rh-BS**	2	90	39
3	**Rh-BS**[c]	6	91	37.5
4	**BS-Rh**	6	94	39
5	**BS-Rh**[c]	6	22	37

[a] The reaction was monitored by capillary gas chromatography.
[b] The ees [(*S*)-configuration] were determined by HPLC on a Daicel chiracel OD column.
[c] Recycled catalyst (2nd run).

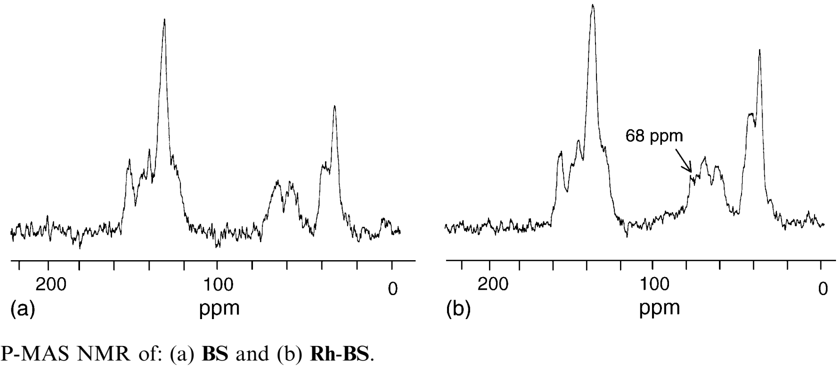


Figure 3. Solid state ^{13}C CP-MAS NMR of: (a) **BS** and (b) **Rh-BS**.

BS-Rh. Conversely, the embedded catalytic species in the porous matrix of the in situ Rh-complexed sol–gel hybrid **Rh-BS** appeared stable.

3. Conclusions

N,*N*′-Substituted *trans*-(1*R*,2*R*)-diaminocyclohexane derivatives have been synthesised and used as chiral ligands for the asymmetric hydrogen transfer reduction of acetophenone. Simple benzylic substituents on nitrogen allowed a significant increase in selectivity when compared to the non-substituted derivative, DACH. The silylation and the heterogenisation of chiral *trans*-(1*R*,2*R*)-*N*,*N*′ dibenzyl diaminocyclohexane moieties were successfully achieved. Two routes were used to form heterogeneous chiral hybrid catalysts, to give **Rh-BS** (the in situ Rh-complexed catalyst) where the catalytic species was embedded within the chiral matrix, and **BS-Rh** (the post Rh-complexed catalyst), where the catalytic species was likely to lie at the outer surface of the material. Increased selectivity and stability arose from embedding the catalytic species in a chiral three-dimensional network. This approach seems particularly relevant to generating selective, re-usable catalytic materials.

4. Experimental

4.1. General

The syntheses of the chiral ligands were carried out under a nitrogen atmosphere using a vacuum line and schlenk techniques or round-bottom flasks. Diamine ligands **1**,[21] **4**[23] and **7**[25] as well as the Schiff bases **3a**[23] and **6a**[24] were synthesised as described in literature. *trans*-(1*R*,2*R*)-Diaminocyclohexane was resolved according to literature[30] from a commercial *cis*/*trans* mixture of (1,2)-diaminocyclohexane. Commercial acetophenone was distilled before use and kept at −30 °C. All other chemicals were purchased from ACROS, Aldrich, Avocado, Fluka, Gelest, Lancaster and Strem Chemicals and used without further purification. Molecular sieves (3 Å) were dried under vacuum (10^{-2} Torr) at 100 °C for 12 h. Solvents were distilled under nitrogen over P_2O_5 (CH_2Cl_2), magnesium turnings (ethanol and propan-2-ol), KOH pellets (triethylamine) and from sodium/benzophenone (THF, diethylether and toluene). Melting points were determined on an electrothermal apparatus (IA9000 series) and are uncorrected. Optical rotations were measured using a Perkin–Elmer (Norwalk, CT) 241 polarimeter with solutions in a 1 dm cell in $CHCl_3$. UV–vis spectra in solution were obtained from a Hewlett–Packard 8453 spectrophotometer. IR data were obtained on a Perkin–Elmer 1000 FT-IR spectrophotometer. Elemental analyses were carried out by the 'Service Central d'Analyse du CNRS' in Vernaison, France. ^1H, ^{13}C and ^{29}Si NMR in solution were recorded on Bruker AC-200 and AC-250 spectrometers at room temperature using deuterated chloroform as solvent and TMS as the internal reference. ^{13}C and ^{29}Si solid state NMR spectra were obtained from Bruker FT-AM 200 or FT-AM 400 spectrometers using cross-polarization and magic-angle spinning techniques (CP-MAS) with TMS as a reference for the chemical shifts. Mass spectra were measured on a JEOL MS-DX 300 mass spectrometer. BET measurements for the determination of the surface areas of the solid hybrids were performed with a Micromeritics Gemini 2375 apparatus. Enantiomeric excesses (ee) were determined by HPLC analyses on a Waters 515 apparatus equipped with a Daicel chiracel OD column, hexane/isopropanol (9:1) as eluent with a flow of 0.5 mL/min and the UV detection was performed at 254 nm.

4.2. (1*R*,2*R*)-*N*,*N*′-Di(4′-bromobenzylidene)-1,2-diaminocyclohexane 2a

Molecular sieves 3 Å (5 g), *trans*-(1*R*,2*R*)-diaminocyclohexane (4 g, 35 mmol), *p*-bromobenzaldehyde (13 g, 70 mmol) and CH_2Cl_2 (80 ml) were introduced in a Schlenk tube under nitrogen atmosphere. The mixture was stirred for 20 h, filtered and then washed with CH_2Cl_2 (three times). After evaporation of the solvent, the title compound (14.9 g, 95%) was obtained as a pale yellow solid. mp = 124–125.5 °C; $[\alpha]_D = -266.5$ (*c* 1.23, $CHCl_3$); ν_{max} (KBr, cm^{-1}) 3048, 2936, 2852, 1646, 1587, 1483, 1372, 1065, 933, 822; ^{1} H NMR ($CDCl_3$, δ) 1.5 (2H, m), 1.8 (6H, m), 3.4 (2H, m), 7.4 (8H, s), 8.1 (2H, s); ^{13}C NMR ($CDCl_3$, δ) 24.4, 32.8, 73.7, 124.7, 129.3, 131.6, 135.1, 159.7; mass spectrum: *m*/*z* [FAB^+] (%): 447, 449 (100, M^+); Anal. Calcd for $C_{20}H_{20}N_2Br_2$: C, 53.6; H, 4.5; N, 6.25; Br, 35.6. Found: C, 53.4; H. 4,5; N, 6.45 Br, 35.1.

4.3. (1*R*,2*R*)-*N*,*N*′-di(2′,3′,4′,5′,6′-pentafluorobenzylidene)-1,2-diaminocyclohexane 5a

trans-(1*R*,2*R*)-Diaminocyclohexane (1 g, 8.8 mmol), pentafluorobenzaldehyde (3.45 g, 17.6 mmol) and dry toluene (60 mL) were introduced in a 2-neck round bottom flask (100 mL) equipped with a Dean–Stark's apparatus and reflux condenser. The mixture was stirred and refluxed in order to eliminate water through the azeotropic distillation of water–toluene. After 20 h, toluene was removed in vacuo and the resulting crude product crystallised in cyclohexane affording the title compound (2 g, 48%) as an off-white solid. mp = 115–118 °C; $[\alpha]_D = -172$ (*c* 1.03, CH_2Cl_2); ^1H NMR ($CDCl_3$, δ) 1.5 (2H, m), 1.9 (6H, m), 3.5 (2H, m), 8.3 (2H, s); ^{13}C NMR ($CDCl_3$, δ) 24.1, 32.3, 75.3, 112, 135.1, 139.3, 143.1, 148.1, 149; mass spectrum: *m*/*z* [FAB^+] (%): 471(100, M^+).

4.4. (1*R*,2*R*)-*N*,*N*′-Di(quinoline-2′-methylidene)-1,2-diaminocyclohexane 6a

Yield: 77%; mp = 205–208 °C; $[\alpha]_D = +90.3$ (*c* 1, CH_2Cl_2); ν_{max} (KBr, cm^{-1}) 3062, 2926, 2857, 1640, 1595, 1560, 1500, 1427, 830, 753; ^{1}H NMR ($CDCl_3$, δ) 1.6 (2H, m), 3.6–3.7 (2H, m), 7.4–7.8 (6H, m), 8–8.1 (6H, m), 9.5 (2H, s), 1.9 (6H, m); ^{13}C NMR ($CDCl_3$, δ) 24.4, 32.7, 73.9, 118.5, 127.1, 127.6, 128.7, 129.4, 136.3, 147.6, 154.9, 161.8; mass spectrum: m/z [FAB$^+$] (%): 393 (100, M$^+$).

4.5. General procedure for the synthesis of the diamino ligands 2, 3, 5, 6

Typically, to a cool solution (0 °C) of **2a** (14.96 g, 33.4 mmol) in methanol (150 mL), $NaBH_4$ (3 g, 79.3 mmol) was added portionwise over a period of 30 min and the reaction mixture, then left to stir overnight at room temperature. Water was then added and the resulting milky solution extracted (three times) with CH_2Cl_2. The solution was dried over K_2CO_3, filtered and the solvent then removed in vacuo.

4.5.1. (1*R*,2*R*)-*N*,*N*′-Di(4′-bromobenzyl)-1,2-diaminocyclohexane 2. Colourless oil; Yield: 87% (13.1 g); $[\alpha]_D = -39.6$ (c 1.12, $CHCl_3$); ν_{max} (KBr, cm^{-1}) 3297, 3022, 2927, 2853, 1591, 1486, 1457, 1403, 1357, 1240, 1116, 1070, 1011, 974, 858, 834, 796; ^{1}H NMR ($CDCl_3$, δ) 1.2–1.01 (4H, m), 1.7–1.8 (2H, m), 1.8 (2H, s), 2.1–2.2 (4H, m), 3.6 (2H, d), 3.8 (2H, d), 7.2 (4H, d), 7.4 (4H, d); ^{13}C NMR ($CDCl_3$, δ) 120, 24.9, 31.5, 50.2, 60.9, 129.7, 131.4, 140.1; mass spectrum: m/z [FAB$^+$] (%): 453, 451(100, M$^+$); Anal. Calcd for $C_{20}H_{24}N_2Br_2$: C, 53.1; H, 5.35; N, 6.2; Br, 35.34. Found: C, 53.1; H, 5.59; N, 6.37; Br, 35.06.

4.5.2. (1*R*,2*R*)-*N*,*N*′-Di(anthracenyl-9′-methylene)-1,2-diaminocyclohexane 3. Yield: 80%; $[\alpha]_D = +242.9$ (c 1.144, $CHCl_3$); ν_{max} (KBr, cm^{-1}) 3280, 3043, 2963, 2852, 1444, 1260, 1090, 1019, 799, 724. ^{1}H NMR ($CDCl_3$, δ) 1.7 (10H, m)2.8 (2H, m), 4.3 (2H, d), 4.7 (2H, d), 8.4–6.8 (18H, m); ^{13}C NMR ($CDCl_3$, δ) 49, 69.7, 24.7; mass spectrum: m/z [FAB$^+$] (%): 494 (100, M$^+$).

4.5.3. (1*R*,2*R*)-*N*,*N*′-Di(2′,3′,4′,5′,6′-pentafluorobenzyl)-1,2-diaminocyclohexane 5. Yield: 50%; $[\alpha]_D = -55$ (c 1.04, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, δ) 1.0 (2H, m,), 1.2 (2H, m), 1.7–2.2 (8H, m), 3.8 (2H, d), 3.9 (2H, d); ^{13}C NMR ($CDCl_3$, δ) 24.8, 31.4, 37.9, 60.7, 113.8, 134.9, 137.8, 139.8, 142.7, 147.7; mass spectrum: m/z [FAB$^+$] (%): 475 (100, M$^+$); Anal. Calcd for $C_{20}H_{16}N_2F_{10}$: C, 50.64; H, 3.40; N, 5.91; F, 40.01. Found: C, 50.86; H, 3.42; N, 6.15; F, 39.06.

4.5.4. (1*R*,2*R*)-*N*,*N*′-Di(quinoline-2′-methylene)-1,2-diaminocyclohexane 6. Yield: 50% mp = 90.5–92.3 °C; $[\alpha]_D = -42.7$ (c 1.1, CH_2Cl_2); ν_{max} (film, cm^{-1}) 3300, 3057, 2926, 2853, 1600, 1504, 1450, 1260, 1095, 1019, 799; ^{1}H NMR ($CDCl_3$, δ) 2.9 (4H, m), 3.4 (2H, m), 3.9 (2H, m), 4.1 (2H, m), 4.4 (2H, m), 5.7 (2H, d), 5.95 (2H, d); ^{13}C NMR($CDCl_3$, δ) 25, 31.7, 53.2, 61.7, 120.8, 125.9, 127.5, 128.9, 129.2, 136.2, 147.7, 161.2; m/z [FAB$^+$] (%): 475 (100, M$^+$); Anal. Calcd for $C_{26}H_{28}N_4$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.44; H, 7.11; N, 14.1.

4.6. Synthesis of the silylated hybrid catalysts

4.6.1. (1*R*,2*R*)-*N*,*N*′-bis(4′-(Triethoxysilylethenyl)benzyl)-1,2-diaminocyclohexane 8. Diamine **2** (1 g, 2.2 mmol), $Pd(OAc)_2$ (10 mg, 0.044 mmol) and tris *o*-tolylphosphine (82 mg, 0.26 mmol) were introduced in a Schlenk tube and dried under vacuum for 1 h. Vinyltriethoxysilane (0.95 g, 4.95 mmol), NEt_3 (1 mL, 6.8 mmol) and DMF (5 mL) were added under nitrogen atmosphere and the mixture heated overnight at 105 °C. Cooling resulted in the formation of white needle-like crystals of $NHEt_3Br$. DMF was then removed in vacuo and the crude product dissolved in dry toluene. Diaminocyclohexane was added to precipitate any further ammonium bromide salt. The mixture was filtered, toluene was evaporated leading to an orange viscous oil. Yield: 60% (0.92 g); $[\alpha]_D = -30.3$ (c 0.33, THF); ν_{max} (film, cm^{-1}) 3300, 2970, 2927, 1606, 1567, 1509, 1450, 1390, 1166, 1077, 960, 826, 790; ^{1}H NMR ($CDCl_3$, δ) 1.3 (18H, q), 1.7 (4H, m), 2.1–2.2 (4H, m), 3.6 (2H, d), 3.8–3.9 (12H, q, +2H, d), 6.2 (2H, d), 7.4–7.1 (8H, m); ^{13}C NMR($CDCl_3$, δ) 18.325, 31.5, 50.6, 58.6, 60.8, 117, 128.6, 126.8, 136.3, 141.8, 148.9; Anal. Calcd for $C_{36}H_{58}N_2O_6Si_2$: C, 64.44; H, 8.71; N, 4.17; Si, 8.37. Found: C, 63.94; H, 8.62; N, 4.3; Si, 8.62.

4.6.2. Synthesis of the hybrid bridged silsesquioxane, BS. In a schlenk tube, water (69 µL, 3.8 mmol) and NH_4F (6.4 µL of a 1 M solution, 0.5 mol%) were added to a stirred mixture of **8** (0.85 g, 1.27 mmol) in ethanol (1.6 mL) and the mixture then left under static conditions. After 3 days, a white gel formed. This was aged for 7 days and then powdered, washed with ethanol and dried under vacuum for 12 h to give a white powder (0.4 g). ν_{max} (KBr, cm^{-1}) 3627, 3294, 2925, 2853, 1605, 1509, 1450, 1198, 1080, 827, 789; ^{13}C CP-MAS NMR (δ, ppm) 25.7,30.9, 47.8, 52.6, 59.4, 122.2, 127.6, 136.4, 148.4; ^{29}Si CP-MAS NMR (δ, ppm) broad signal centred at −75 (T^3 unit); N_2 BET surface area: 0.5 m^2 g^{-1}.

4.6.3. Synthesis of the post Rh-complexed hybrid catalyst, BS-Rh. In a Schlenk tube under nitrogen atmosphere, $[Rh(cod)Cl]_2$ (0.165 g, 0.35 mmol) was added to a suspension of **BS** (0.3 g) in dry ethanol (5 mL). After stirring for 3 days, the mixture was filtered. The solid was washed with THF in a soxhlet apparatus and then dried under vacuum to give a yellow powder (0.195 g). ν_{max} (KBr, cm^{-1}) 3278, 2925, 2854, 1605, 1560, 1509, 1450, 1198, 1108, 828, 790; ^{13}C CP-MAS NMR (δ, ppm) 25.7, 30.9, 52.9, 59.3, 68, 128.3, 136.9, 147.5; ^{29}Si CP-MAS NMR (δ, ppm) broad signal centred at −77.9 (T^3 unit); N_2 BET surface area: 0.4 m^2 g^{-1}; Anal. Calcd $C_{32}H_{40}O_3N_2Si_2RhCl$: Si, 8.06; N, 4.03; Rh, 14.83; Cl, 5.11. Found: Si, 7.2; N, 4.01; Rh, 5.2; Cl, 2.54.

4.6.4. Synthesis of the in situ Rh-complexed hybrid catalyst, Rh-BS. A mixture of **8** (0.76 g, 1.15 mmol), $[Rh(cod)Cl]_2$ (0.278 g, 0.565 mmol) and ethanol (3 mL) was stirred in a schlenk for 2 h. A solution of NH_4F (27 μL of a 1 M solution, 0.1 mol%) and water (35 μL, 1.5 mmol) in ethanol (0.8 mL) was then added and the mixture kept under static conditions at room temperature. A gel then appeared after 8 h. After ageing for 7 days, it was crushed, washed with THF for 1 day in a soxhlet apparatus and then dried under vacuum. A yellow powder (0.49) was obtained. $\nu_{\max}$ (KBr, cm^{-1}) 3272, 2927, 2854, 1656, 1606, 1566, 1510, 1450, 1200, 1134, 828, 784; ^{13}C CP-MAS NMR (δ, ppm) 25.6, 31.7, 53.1, 59.2, 68, 128, 136.9, 147.9; ^{29}Si CP-MAS NMR (δ, ppm) broad signal centred at −77.0 (T^3 unit); N_2 BET surface area: 5.2 $m^2\,g^{-1}$; Anal. Calcd $C_{32}H_{40}O_3N_2Si_2$-RhCl: Si, 8.06; N, 4.03; Rh, 14.83; Cl, 5.11. Found: Si, 9.9; N, 5.27; Rh, 4.35; Cl, 2.39.

4.7. General procedure for the rhodium-catalysed reduction of acetophenone with the homogeneous catalysts

The diamine ligand (0.06 mmol), $[Rh(cod)Cl]_2$ (14.8 mg, 0.03 mmol), KOH (20 mg, 0.36 mmol) and freshly distilled isopropanol were stirred for 1 h in a Schlenk tube under nitrogen atmosphere. Acetophenone was then added (0.24 g, 2 mmol) to the mixture and the reaction monitored by capillary gas chromatography. After the reaction was complete, the solvent was evaporated. The ee was measured by HPLC on a Daicel chiracel OD column, eluent: hexane/*i*-PrOH 9:1, 0.5 mL min^{-1}.

4.8. General procedure for the rhodium-catalysed reduction of acetophenone with the heterogeneous hybrid catalysts

The solid catalyst containing 3 mol% of rhodium is mixed with KOH (20 mg, 0.36 mmol) and freshly distilled isopropanol (10 mL) in a Schlenk tube. The mixture was then stirred under nitrogen atmosphere for 4 h. Acetophenone (240 mg, 2 mmol) was then added and the reaction monitored by capillary gas chromatography. At the end of the reaction, the heterogeneous mixture was centrifuged and the solution mixed with pentane and then filtered on a silica column. The ee was measured by HPLC technique equipped with a chiral column (Daicel chiracel OD). The solid catalyst was washed with pentane, dried under vacuum and then re-used for a second run.

References and notes

1. Gladysz, J. A. *Chem. Rev.* **2002**, *102*, 3215–3216.
2. Rechavi, D.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 3467–3494.
3. Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385–3466.
4. Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*; Academic: London, 1990.
5. (a) Shea, K. J.; Loy, D. A.; Webster, O. W. *Chem. Mater.* **1989**, *1*, 512–513; (b) Shea, K. J.; Loy, D. A.; Webster, O. W. *J. Am. Chem. Soc.* **1992**, *114*, 6700–6710; (c) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431–1442; (d) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *19*, 3306–3319.
6. (a) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217–1224; (b) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed.* **1996**, *35*, 1432–1455; (c) Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1376–1398.
7. Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007–1047.
8. (a) *Organic/inorganic Hybrid Materials, MRS Symp.*; Laine, R. M., Sanchez, C., Brinker, C. J., Giannelis, E., Eds.; 1998; (b) *Organic/inorganic Hybrid Materials, MRS Symp.*; Laine, R. M., Sanchez, C., Brinker, C. J., Eds.; 2000; (c) *Organic/inorganic Hybrid Materials, MRS Symp.*; Laine, R. M., Sanchez, C., Brinker, C. J., Eds.; 2002.
9. (a) Moreau, J. J. E.; Wong Chi Man, M. *Coord. Rev.* **1998**, *178–180*, 1073–1084; (b) Adima, A.; Moreau, J. J. E.; Wong Chi Man, M. *Chirality* **2000**, *12*, 411–420; (c) Ameduri, B.; Boutevin, B.; Moreau, J. J. E.; Moutaabbid, H.; Wong Chi Man, M. *J. Fluorine Chem.* **2000**, *104*, 185–194; (d) Bourg, S.; Broudic, J.-C.; Conocar, O.; Moreau, J. J. E.; Meyer, D.; Wong Chi Man, M. *Chem. Mater.* **2001**, *13*, 491–499.
10. (a) Oviatt, H. W.; Shea, K.; Kalluri, S.; Shi, Y.; Steier, W. H.; Dalton, L. R. *Chem. Mater.* **1995**, *7*, 493; (b) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, K.-Y. A.; Shea, K. *Chem. Mater.* **1995**, *7*, 1060.
11. (a) Corriu, R. J. P.; Hesemann, P.; Lanneau, G. F. *Chem. Commun.* **1996**, 1845–1846; (b) Boury, B.; Ben, F.; Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2853–2856; (c) Cerveau, G.; Corriu, R. J. P.; Framery, E.; Ghosh, S.; Nobili, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 594–596; (d) Corriu, R. J. P.; Lancelle-Beltran, E.; Mehdi, A.; Reyé, C.; Brandès, S.; Guilard, R. *J. Mater. Chem.* **2002**, *12*, 1355–1362.
12. Schubert, U. *New J. Chem.* **1994**, *18*, 1049–1958.
13. (a) Lindner, E.; Schneller, T.; Auer, F.; Mayer, H. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2154–2174; (b) Lu, Z.-I.; Lindner, E.; Mayer, H. A. *Chem. Rev.* **2002**, *102*, 3543–3578.
14. (a) Abu-Reziq, R.; Avnir, D.; Blum, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4132–4134; (b) Abu-Reziq, R.; Avnir, D.; Blum, J. *J. Mol. Catal. A., Chem.* **2002**, *187*, 277–281.
15. Duchateau, R. *Chem. Rev.* **2002**, *102*, 3225–3542.
16. Song, C. E.; Lee, S.-G. *Chem. Rev.* **2002**, *102*, 3495–3524.
17. (a) Adima, A.; Moreau, J. J. E.; Wong Chi Man, M. *J. Mater. Chem.* **1997**, *7*, 2331–2333; (b) Adima, A.; Moreau, J. J. E.; Wong Chi Man, M. *Chirality* **2000**, *12*, 411–420; (c) Hesemann, P.; Moreau, J. J. E. *Tetrahedron: Asymmetry* **2000**, *11*, 2183–2194; (d) Brethon, A.; Hesemann, P.; Moreau, J. J. E.; Réjaud, L.; Wong Chi Man, M. *J. Organomet. Chem.* **2001**, *627*, 239–248; (e) Bied, C.; Gauthier, D.; Moreau, J. J. E.; Wong Chi Man, M. *J. Sol–Gel Sci. Technol.* **2001**, *20*, 313–320.
18. (a) Gamez, P.; Fache, F.; Mangeney, P.; Lemaire, M. *Tetrahedron Lett.* **1993**, *34*, 6897–6898; (b) Gamez, P.; Fache, F.; Lemaire, M. *Tetrahedron: Asymmetry* **1995**, *6*, 705–718; (c) ter Halle, R.; Bréhéret, A.; Schulz, E.; Pinel, C.; Lemaire, M. *Tetrahedron: Asymmetry* **1997**, *8*, 2101–2108; (d) Gamez, P.; Fache, F.; Mangeney, P.; Lemaire, M. *J. Organomet. Chem.* **1998**, *567*, 133–136; (e) Bernard, M.; Guiral, V.; Delbecq, F.; Fache, F.; Sautet, P.; Lemaire, M. *J. Am. Chem. Soc.* **1998**, *120*, 1441–1446.
19. Zassinovich, G.; Mestroni, G. *Chem. Rev.* **1992**, *92*, 1051–1069.

20. Gamez, P.; Dunjic, B.; Fache, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1417–1418.
21. Bennani, Y. L.; Hanessian, S. *Tetrahedron* **1996**, *52*, 13837–13866.
22. Desimoni, G.; Faita, G.; Righetti, P.; Sardone, N. *Tetrahedron* **1996**, *52*, 12019–12030.
23. Krasik, P.; Alper, H. *Tetrahedron* **1994**, *50*, 4347–4354.
24. Abu-Surrah, A. S.; Laine, T.; Repo, T.; Fawzi, R.; Steimann, M.; Rieger, B. *Acta Cryst., Section C* **1997**, *C53*, 1458–1459.
25. Smith, H. E.; Cozart, W. I.; de Paulis, T.; Chen, F.-M. *J. Am. Chem. Soc.* **1979**, *101*, 5186–5193.
26. Botteghi, C.; Chelucci, G.; Chessa, G.; Delogu, G.; Soccolini, F. *J. Organomet. Chem.* **1986**, *304*, 217–225.
27. Gladiali, S.; Pinna, L.; Delogu, G.; De Martin, S.; Zassinovich, G.; Mestroni, G. *Tetrahedron: Asymmetry* **1990**, *1*, 635–648.
28. Haack, K. J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 285–290.
29. Dunjic, B.; Gamez, P.; Fache, F.; Lemaire, M. *J. Appl. Polym. Sci.* **1996**, *59*, 1255–1262.
30. (a) Whitney, T. A. *J. Org. Chem.* **1980**, *45*, 4214–4219; (b) Larrow, J. F.; Jacobsen, E. N. *J. Org. Chem.* **1994**, *59*, 1939–1942.