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Journal of Catalysis 217 (2003) 275–283

JOURNAL OF CATALYSIS

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Chiral catalysts confined in porous hosts 2. Catalysis

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Received 11 July 2002; revised 8 November 2002; accepted 12 November 2002

Abstract

The catalytic activities of the dirhodium carboxamide catalysts immobilised in the pores of MCM-41 and on the surface of Aerosil 200 (see preceeding paper) have been investigated. The catalysts were tested in the Si–H insertion reaction of dimethylphenylsilane with methyl phenyl diazoacetate and in the cyclopropanation reaction of styrene with ethyl and *tert*-butyl diazoacetate. Significant improvements in enantioselectivity (Si–H insertion) and in regioselectivity (cyclopropanation) were induced due to the spatial confinement by the carrier.

Keywords: Cyclopropanation; Si–H insertion; Dirhodium; Immobilisation; Catalysis

1. Introduction

Chiral dirhodium carboxamide complexes have attracted considerable interest as enantioselective catalysts for, among other reactions, cyclopropanations and Si–H insertions [1]. In order not only to combine the advantages of homogeneous and heterogeneous catalysts in general, but also to improve selectivity (via synergistic interactions [2] between the catalytic centre and its porous surroundings), we immobilised them on silica (Aerosil 200) surfaces and inside the pores of siliceous MCM-41 [3]. Here, the catalytic behaviour of these immobilised catalysts is presented and a comparison is made with their homogeneous counterparts.

As model reactions the Si–H insertion of methyl phenyldiazoacetate (**1**) with dimethylphenylsilane (**2**) yielding methyl 2-(dimethylphenylsilyl)phenylacetate (**3**) (Fig. 1, reaction (1)) as well as the cyclopropanation of styrene (**4**) with ethyl diazoacetate (**5a**) or *tert*-butyl diazoacetate (**5b**) yielding *cis* and *trans* ethyl or *tert*-butyl 2-phenylcyclopropane carboxylate (**6a/b**) (Fig. 1, reaction (2)) were investigated. Earlier studies [4] showed that in cyclopropanation reactions the interaction of the ester alkyl group with the ligand framework of the chiral catalysts has a strong influence on the orientation of the approaching alkene relative to the carbenic centre. Bulkier ester groups give higher *trans*/*cis* ratios and better enantioselectivities; e.g., *tert*-butyl diazoacetate produces a significant enhancement compared to ethyl diazoacetate in the cyclopropanation of styrene catalysed by $Rh_2(5S\text{-MEPY})_4$. This effect was observed not only for the chiral dirhodium catalysts, but also for the homogeneous Pfaltz and Aratani catalysts [5,6]. Due to confinement effects the immobilised dirhodium catalysts described here might be expected to display this effect in an even more pronounced fashion.

Cyclopropanes are widely used as starting compounds and intermediates in organic synthesis. Several natural and synthetic cyclopropanes display interesting activities [7]. They are essential building blocks for pyrethroid insecticides [8,9] and also in pharmaceuticals a wide variety of active compounds containing cyclopropane rings are known [10–12], e.g., the antidepressant milnacipran [13–15]. In addition to their application in agrochemicals and medicinal chemistry, cyclopropanes are versatile intermediates in organic synthesis. Due to their ring-strain they are readily converted into a large range of interesting compounds [16]. Thus, the enantio- and diastereoselective synthesis of cyclopropanes has attracted considerable attention [17].

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0021-9517/03/$ – see front matter
doi:10.1016/S0021-9517(02)00155-0

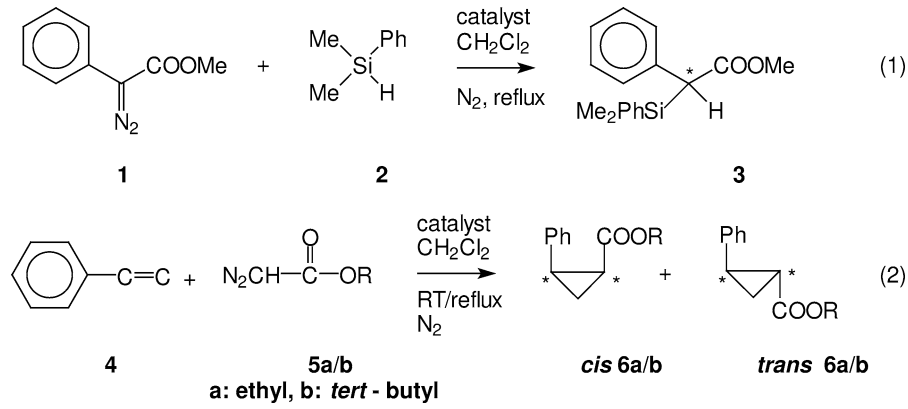

Fig. 1. Catalytic test reactions.

Although α-silyl carbonyl compounds are widely recognised for their utility in organic synthesis [18], there are few general methods for their preparation. Since silanes are excellent scavengers for free carbenes [19], carbene insertion into the Si–H bond of organosilanes is an attractive method for the synthesis of these α-silyl carbonyl compounds [18]. Chiral dirhodium catalysts have proven to be effective catalysts for this transformation. The enantiomerically enriched products are versatile building blocks for the synthesis of a variety of natural products.

Dirhodium tetrakis-methyl-2-pyrrolidone-5-carboxylate (Rh_2(MEPY)$_4$) and dirhodium tetrakis-4-benzyl-2-oxazolidinone (Rh_2(BNOX)$_4$) (Fig. 2) were used as model catalysts. Rh_2(MEPY)$_4$ is a very selective catalyst in intramolecular cyclopropanation reactions [20,21], but is not as selective in intermolecular cyclopropanation. With the immobilisation it was aimed to bring the reagents and the catalyst in such close proximity to each other that an intramolecular reaction analogous to the situation in enzyme catalysis would be mimicked: in enzyme catalysis, reagents are brought close together so that they react in an intramolecular fashion while the noncatalytic reaction is intermolecular. The selectivities are, therefore, much higher than in the normal intermolecular reactions. Rh_2(MEPY)$_4$ and Rh_2(BNOX)$_4$ are normally not used as catalysts for carbene insertions into the Si–H bonds of organosilanes, because they are considered to be less selective, making this a good test case for the immobilised catalysts.

From previous work [22,23], it might be expected that spatial constraints induced by the carrier, and especially by the pores of MCM-41, should increase the influence of the chiral ligands. These studies demonstrated that enantioselective conversions catalysed by a palladium complex immobilised inside the pores of MCM-41 can give a significant increase in *ee* compared to the homogeneous palladium complex (*ee*'s increased from 43 to 96% [23] and from 6 to 17% [22]).

However, this need not always be the case, as can be seen from the following example. Copper bis(oxazoline) catalysts with an alkyl tether were immobilised inside

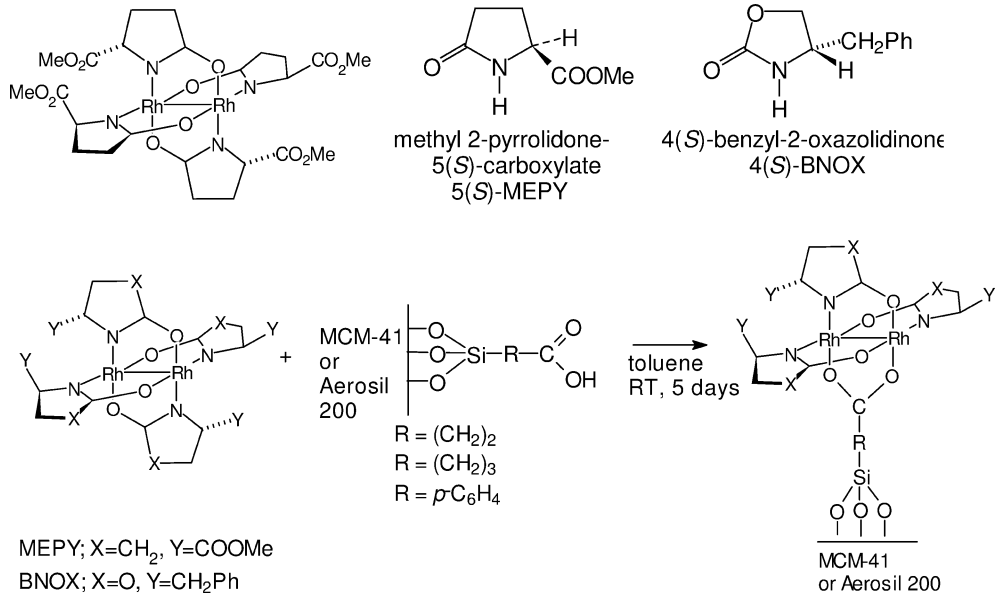

Fig. 2. Homogeneous catalysts and heterogeneous catalysts.

MCM-41 and MCM-48 [24]. In this way highly active catalysts for the cyclopropanation of styrene with ethyl diazoacetate were produced; however, they did not show improved selectivities.

Two previous examples of the immobilisation of the Doyle catalyst are known. In one case [25] oligomer-bound MEPY was prepared from polyethylene oligomers that were esterified with 2-pyrrolidone-5(*S*)-carboxylic acid. By ligand exchange the immobilised catalyst was formed. It displayed behaviour similar to the homogeneous catalysts, but the enantioselectivity and activity for some applications did decrease. More recently, NovaSyn Tentagel and the Merrifield resin were used by the same group for immobilisation of this catalyst [26]. In this case similar or higher selectivities were obtained.

In the second case [27] $Rh_2(5S\text{-MEPY})_4$ was immobilised on graphite. The electrochemical behaviour of this catalyst was tested in the presence and absence of DNA, but no catalytic reactions were performed. In both cases no obvious steric constraints were introduced.

The dirhodium carboxamide catalysts in our study were immobilised by the use of direct covalent anchoring of the catalyst to the carrier surface [3]. Immobilisation took place via ligand exchange of surface-anchored carboxylic acid groups with approximately one ligand per homogeneous chiral catalyst. The steric constraint induced by immobilisation might be expected to partially compensate for the loss of the ligand, which has been replaced by a stabilising carboxylate group.

Next to the steric constraint exercised by the porous carriers, the method of attachment can influence the selectivity and activity of the immobilised catalytic species. To investigate whether there is a significant difference between flexible linkers or more rigid ones, three different nonchiral carboxylate spacer groups were used ($-(CH_2)_2COOH$, $-(CH_2)_3COOH$, and $-p\text{-}C_6H_4COOH$ groups, Fig. 3). These tethers were chosen to generate defined distances between the catalysts and the carrier in order to prevent blocking of the active site by the surface. The $-(CH_2)_2COOH$ and $-(CH_2)_3COOH$ spacer groups are flexible and the catalysts can, therefore, have interactions with the surface of the carrier. The different types of surfaces (with protected or unprotected surface silanol groups) [3] could, therefore, be probed as to whether or not they have an influence on the performance of the catalysts. With the $-p\text{-}C_6H_4COOH$ spacer group these through-space type interactions should be reduced significantly. Protecting the surface silanol groups with dimethoxydimethylsilane modified the polarity of the carrier surface and reduced the pore size [3].

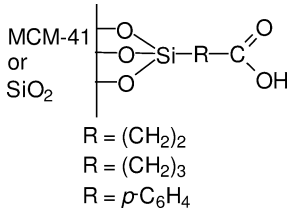

Fig. 3. Spacer groups.

2. Experimental section

All reactions and manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk-type techniques. Dry solvents were purchased from Aldrich and used without further purification. Styrene was obtained from Aldrich and was vacuum-distilled before use. Methyl phenyldiazoacetate [28] and *t*-butyl diazoacetate [29] were prepared according to literature procedures. All other reagents were purchased from Aldrich, Acros, or Baker and used without further purification. For column chromatography silica gel 60 (particle size 0.063–0.2 mm, Fluka) was used. NMR spectra were obtained on a Varian Inova 300 MHz or a Varian VXR 400s spectrometer, relative to TMS. *Trans*/*cis* ratios for **6a**/**b** were determined using GC analysis on a Varian Star 3400 CX GC with a CP wax 52 CB column ($l = 50$ m, od $= 0.70$ mm, df $= 2.0$ μm) and on-column injection (retention times: **6a**: 41.5 min (*cis*), 42.6 min (*trans*), **6b**: 43.6 min (*cis*), 44.3 min (*trans*). Chiral GC analysis for *cis* and *trans* **6a**/**b** was performed using a B-DA [30] ($l = 40$ m, $Ø = 0.25$ mm, split injection) (methylesters of **6a**, 110 °C, 129.4 ($1R, 2S$), 133.0 ($1S, 2R$) min (*cis*), 157.6 ($1S, 2S$), 159.1 ($1R, 2R$) min (*trans*)) or B-PH ($l = 40$ m, $Ø = 0.25$ mm, split injection) (**6b**, 100 °C, 85.4, 87.7 min (*cis*), 119.7, 122.6 min (*trans*)) column. HPLC analysis for Si–H insertions was performed using a literature procedure [31]. Rhodium elemental analysis was performed using ICP-OES on a Perkin–Elmer Optima 4300DV after the solid samples were dissolved in 1% v/v HF and 1.3% v/v H_2SO_4 in water. The Rhodium leaching was determined by analysing the reaction filtrates with graphite AAS on a Perkin–Elmer 4100ZL. All yields are isolated yields.

2.1. Typical Si–H insertion procedure

Dichloromethane, 1 ml, was added to the catalyst (SiO_2–C_6H_4COO–$Rh_2(4R\text{-BNOX})_3$, 0.176 g, 8.41×10^{-6} mol Rh) and the mixture was stirred. Subsequently methyl phenyldiazoacetate (0.188 g, 1.07 mmol) in 0.5 ml dichloromethane and dimethylphenylsilane (0.196 g, 1.45 mmol) in 1 ml dichloromethane were added. The resulting mixture was refluxed overnight. After evaporation of the solvent in vacuo, the reaction mixture was chromatographed on silica gel using 19/1 light petroleum/ethyl acetate. Yield: 67%, *ee*: 28% (*R*-major product). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): 173.1 (C=O), 135.9, 135.5, 134.0 (2 *C*'s), 129.6, 128.3 (2 *C*'s), 128.0 (2 *C*'s), 127.7 (2 *C*'s), 125.7 (aromatic *C*'s), 51.2 ($COOCH_3$), 46.0 (C–$SiPhMe_2$), −4.1 (Si–CH_3), −4.5 (Si–CH_3). ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.4–7.1 (m, 10 H, Ar–*H*), 3.602 (s, 1 H, C–*H*), 3.532, (s, 3 H, $COOCH_3$),

0.348 (s, 3 H, Si–CH_3), 0.319 (s, 3 H, Si–CH_3). ^{29}Si NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.157 (R_2CHSi).

2.2. Reuse following typical Si–H insertion procedure

The Si–H insertion reaction was performed following the typical procedure described above, using SiO_2–$(CH_2)_2$COO–Rh_2(4*S*-BNOX)$_3$ (0.324 g, 1.78×10^{-6} mol Rh), methyl phenyldiazoacetate (0.242 g, 1.38 mmol), dimethylphenylsilane (0.205 g, 1.52 mmol, and 1,2-dichlorobenzene (0.2229 g) as the internal standard). After refluxing overnight, the catalyst was allowed to settle. The solution was transferred to another vial through a syringe filter to remove traces of immobilised catalyst. In this solution 2.9×10^{-7} mol rhodium was present (determined by AAS). The *ee* of the product and the conversion were determined by chiral HPLC. The remaining solid was washed with dichloromethane and dried. It was then used again following the same procedure. After three cycles, the rhodium content of the catalyst was determined by ICP-OES. After the third cycle, the catalyst was again separated from the solution and to this solution 1,2-dichlorobenzene (0.181 g), dimethylphenylsilane (0.166 g, 1.23 mmol), and methyl phenyldiazoacetate (0.199 g, 1.13 mmol) were added. Samples were taken after 4 min and 20 h and were analysed by chiral HPLC to determine the activity of the filtrate. In the first cycle 79% conversion (after 20 h) was reached, while after the third cycle only 19% conversion (after 20 h) was observed. No catalytic activity was observed in the liquid phase that was removed after the third cycle. The *ee*'s were approximately 35% (the *S* product was the major product) in the first two cycles. In the third cycle the *ee* decreased to 11%. The rhodium content before reaction was 0.0055 mmol/g, while after three cycles no rhodium could be detected anymore on the carrier.

2.3. Typical cyclopropanation procedure

Dichloromethane, 3 ml, styrene (0.490 g, 4.70 mmol), and chlorobenzene (0.2435 g) as the internal standard were added to the catalyst (SiO_2–$(CH_2)_2$COO–Rh_2(4*R*-BNOX)$_3$, 0.077 g, 4.36×10^{-6} mol Rh) and the mixture was stirred at room temperature. Over a period of 3–5 h a solution of ethyl diazoacetate (0.052 g, 0.453 mmol) in 3 ml dichloromethane was added. After stirring overnight at room temperature, the solvent was evaporated in vacuo and the residue was chromatographed on silica gel using 9/1 hexane/ethyl acetate. Yield: 84%, *trans*/*cis*: 60/40, ee_{cis}: 33% (1*S*, 2*R*), ee_{trans}: 35% (1*S*, 2*S*). Before chiral GC analysis, the products were converted into the corresponding methyl esters by reaction with 0.1 molar solution of NaOH in MeOH [30].

2.3.1. Trans **6a**

^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): 173.4 (*C*=O), 140.1, 128.5 (2 *C*'s), 126.5, 126.1 (2 *C*'s), (aromatic *C*'s), 60.7 (COO*C*H_2CH$_3$), 26.2 (Ph–*C*HCH$_2$CH), 24.2 (Ph–CHCH$_2$*C*H), 17.0 (Ph–CH*C*H$_2$CH), 14.3 (COOCH$_2$C*H*$_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.3–7.0 (m, 5H, Ar–*H*), 4.16 (q, $^3J = 7.2$ Hz, 2 H, COOC*H*$_2$CH$_3$), 2.5 (ddd, 1 H, $^3J_{H1–H2} = 4.2$ Hz, $^3J_{H1–H3} = 6.6, 9.2$ Hz CH$_2$C*H*COOEt), 1.90 (ddd, 1 H, $^3J_{H2–H1} = 4.2$ Hz, $^3J_{H2–H3} = 5.3, 8.4$ Hz, PhC*H*CH$_2$), 1.60 (ddd, 1 H, $^3J_{H2–H3} = 9.2$ Hz, $^3J_{H3–H2} = 5.3$ Hz, $^3J_{H3–H3} = 4.7$ Hz, PhCHC*H*$_2$CH), 1.35 (m, 1 H, PhCHC*H*$_2$CH), 1.27 (t, $^3J = 7.2$ Hz, 3 H, COOCH$_2$C*H*$_3$).

2.3.2. Cis **6a**

^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): 171.0 (*C*=O), 136.6, 129.3 (2 *C*'s), 127.9 (2 *C*'s), 126.6, (aromatic *C*'s), 60.2 (COO*C*H_2CH$_3$), 25.5 (Ph–*C*HCH$_2$CH), 21.8 (Ph–*C*HCH$_2$CH), 14.0 (Ph–CH*C*H$_2$CH), 11.1 (COOCH$_2$*C*H$_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 7.3–7.1 (m, 5 H, Ar–*H*), 3.8 (q, $^3J = 7.2$ Hz, 2 H, COOC*H*$_2$CH$_3$), 2.6 (ddd, 1 H, $^3J_{H1–H2} = 7.7$ Hz, $^3J_{H1–H3} = 9.0, 7.7$ Hz CH$_2$C*H*COOEt), 2.10 (ddd, 1 H, $^3J_{H2–H1} = 7.7$ Hz, $^3J_{H2–H3} = 5.5, 9.2$ Hz, PhC*H*CH$_2$), 1.70 (ddd, 1 H, $^3J_{H3–H1} = 7.7$ Hz, $^3J_{H3–H2} = 5.5$ Hz, $^3J_{H3–H3} = 5.1$ Hz, PhCHC*H*$_2$CH), 1.3 (m, 1 H, PhCHC*H*$_2$CH), 0.95 (t, $^3J = 7.2$ Hz, 3 H, COOCH$_2$C*H*$_3$).

If *tert*-butyl diazoacetate (0.089 g, 0.62 mmol), styrene (0.476 g, 4.57 mmol), chlorobenzene (0.490 g) and MCM-41-$(CH_2)_2$COO–Rh_2(4*R*-BNOX)$_3$ (0.018 g, 3.21×10^{-6} mol Rh) were used, the reaction was performed under reflux. The following results were obtained: yield: 51%, *trans*/*cis*: 72/28, ee_{cis}: 21%, ee_{trans}: 14%.

2.3.3. Trans **6b**

^{13}C NMR (400 MHz, $CDCl_3$, δ (ppm)): 172.5 (*C*=O, *trans*), 140.5, 128.4 (2 *C*'s), 126.3, 126.1 (2 *C*'s), (aromatic *C*'s), 80.5 (*C*(CH$_3$)$_3$), 28.2 (C(*C*H$_3$)$_3$), 25.7 (Ph–*C*HCH$_2$CH), 25.3 (Ph–CHCH$_2$*C*H), 17.0 (Ph–CH*C*H$_2$CH). ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.3–7.0 (m, 5H, Ar–*H*), 2.43 (ddd, 1 H, $^3J_{H1–H2} = 4.2$ Hz, $^3J_{H1–H3} = 6.3$, 9.2 Hz, CH$_2$C*H*COO*tert*-Bu), 1.83 (ddd, 1 H, $^3J_{H2–H1} = 4.2$ Hz, $^3J_{H2–H3} = 5.3, 8.4$ Hz, PhC*H*CH$_2$), 1.53 (m, 1 H, PhCHC*H*$_2$CH), 1.46 (s, 9H, COOC(C*H*$_3$)$_3$), 1.22 (m, 1 H, PhCHC*H*$_2$CH).

2.4. Leaching test

The cyclopropanation reaction was performed following the typical procedure described above for ethyl diazoacetate, using SiO_2–$(CH_2)_3$COO–Rh_2 (4*R*-BNOX)$_3$ (0.325 g, 4.23×10^{-6} mol Rh), ethyl diazoacetate (0.211 g, 1.85 mmol), styrene (1.999 g, 0.0192 mol) and chlorobenzene (0.4484 g). Two minutes after the addition of ethyl diazoacetate (**5a**) was complete, no diazo compound could be detected by GC anymore. After stirring overnight at room temperature, the solid catalyst was allowed to settle. The solution was transferred to another vial through a syringe filter to remove traces of immobilised catalyst. After 30 min a GC sample was taken of this solution as a baseline sample. Then ethyl diazoacetate (0.220 g, 1.92 mmol) was added and two minutes later

a GC sample was taken. Hardly any changes were observed. The mixture was left to stir. Samples were taken after 16 h and 87.5 h. From GC analysis it was shown that 66% of **5a** was consumed after 16 h. After 87.5 h, 11% of **5a** were still present. This is approximately equivalent to 0.5% of the activity of the immobilised catalyst. From this we can conclude that only a very small amount of catalytically active material leached during the reaction.

2.5. Reuse following typical cyclopropanation procedure

The cyclopropanation reaction was performed following the typical procedure described above, using SiO_2–C_6H_4COO–$Rh_2(5S\text{-MEPY})_3$ (0.185 g, 1.67×10^{-5} mol), ethyl diazoacetate (0.111 g, 0.968 mmol), styrene (1.017 g, 9.76 mmol), and chlorobenzene (0.3071 g). After stirring overnight at room temperature, the solid catalyst was allowed to settle. The solution was transferred to another vial through a syringe filter to remove traces of immobilised catalyst. The conversion was determined by GC. The solution contained 3.20×10^{-8} mol rhodium (determined by AAS). The remaining solid was washed with dichloromethane and dried. It was then used again following the same procedure. After three cycles, the rhodium content of the catalyst was determined by ICP OES. In all three cycles complete conversion was observed after 16 h. Before reaction the rhodium content was 0.090 mmol/g, and after three cycles 0.041 mmol/g was left on the carrier.

3. Results and discussion

3.1. Si–H insertion

In the Si–H insertion reaction (Fig. 1, reaction 1) very clear differences can be observed between the different homogeneous and immobilised catalysts (Table 1). The homogeneous catalysts (entries 1, 7) are active, but only the MEPY system displays chiral induction. The catalysts immobilised on Aerosil 200 showed similar activity; moreover the BNOX systems (entries 2–4, 6) showed more than a 10-fold increase in enantioselectivity. This is clear evidence that, although one chiral ligand was lost due to the method of immobilisation, the spatial confinement can lead to a significant improvement of enantioselectivity. In contrast to the catalysts immobilised on silica, none of the catalysts immobilised inside the pores of MCM-41 showed significant activity. Even after refluxing overnight, large amounts of unmodified diazo starting compound remained. Possibly there is not enough space inside the pores of MCM-41 for the reaction to take place. Indeed, the average pore diameter (19 Å)[3] is only slightly larger than the catalyst size (between 19 and 13 Å). A transition state requiring a space-demanding conformation of the catalyst might, therefore, be impossible under these circumstances.

We also tested if the immobilised catalyst could be recycled in the Si–H insertion reaction (Fig. 1, reaction 1). SiO_2–$(CH_2)_2COO$–$Rh_2(4S\text{-BNOX})_3$ was used as the catalyst. Since all catalysts were immobilised in the same manner it can be assumed that these results are representative for all the different immobilised catalysts described here. These experiments show significant deactivation of the immobilised catalysts. In the first cycle 79% conversion was reached, while after the third cycle only 19% conversion was observed. After the third cycle, the liquid phase was removed from the catalyst and to this solution an additional amount of dimethylphenylsilane and methyl phenyldiazoacetate was added. No catalytic activity was observed in the resulting mixture. The *ee*'s were approximately 35% (the *S* product was the major product) in the first two cycles. In the third cycle the *ee* decreased to 11%.

3.2. Cyclopropanation

For the cyclopropanation reaction (Fig. 1, reaction 2), the immobilisation of the catalyst gave an increase of the

Table 1
Comparison of different rhodium catalysts used in the Si–H insertion reaction immobilised on different supports via different tethers

Entry	Catalyst	Yield (%)[a]	*ee* (%)[b]
1	$Rh_2(4R\text{-BNOX})_4$[c]	73	2
2	SiO_2–$(CH_2)_2COO$–$Rh_2(4R\text{-BNOX})_3$	88	20
3	SiO_2–$(CH_2)_3COO$–$Rh_2(4R\text{-BNOX})_3$	61	26
4	SiO_2–C_6H_4COO–$Rh_2(4R\text{-BNOX})_3$	67	28
5	MCM-41-$(CH_2)_2COO$–$Rh_2(4R\text{-BNOX})_3$	Only traces of product detected	–
6	SiO_2–$(CH_2)_2COO$–$Rh_2(4S\text{-BNOX})_3$ [d]	79	33
7	$Rh_2(5S\text{-MEPY})_4$[e]	70	37
8	SiO_2–$(CH_2)_2COO$–$Rh_2(5S\text{-MEPY})_3$	78	2
9	SiO_2–C_6H_4COO–$Rh_2(5S\text{-MEPY})_3$	65	1
10	MCM-41-$(CH_2)_2COO$–$Rh_2(5S\text{-MEPY})_3$	Only traces of product detected	–

[a] All reported yields are isolated yields.
[b] Analysis was performed according to Ref. [31], where the second eluted product was determined to be the *S*-product by correlation to methyl-(*S*)-(+)-mandelate.
[c] The reactions using *R*-BNOX as the ligand gave the *R* product as the major isomer.
[d] The reactions using *S*-BNOX as the ligand gave the *S* product as the major isomer.
[e] The reactions using *S*-MEPY as the ligand gave the *S* product as the major isomer.

Table 2
Comparison of EDA (**5a**) and TBDA (**5b**) in the cyclopropanation reaction (Fig. 1, reaction 2)

Entry	Catalyst	Diazo compound	Yield (%)[b]	*trans*/*cis* ratio[c]	ee_{cis} (%)[d]	ee_{trans} (%)[d]
1	$Rh_2(5S\text{-MEPY})_4$[a]	**5a**	59	56/44	33	58
2	SiO_2–$(CH_2)_2$COO–$Rh_2(5S\text{-MEPY})_3$	**5a**	73	59/41	29	35
3	MCM-41-$(CH_2)_2$COO–$Rh_2(5S\text{-MEPY})_3$	**5a**	65	60/40	19	22
4	$Rh_2(5S\text{-MEPY})_4$	**5b**	50	60/40	66	14
5	SiO_2–$(CH_2)_2$COO–$Rh_2(5S\text{-MEPY})_3$	**5b**	62	71/29	30	27
6	MCM-41-$(CH_2)_2$COO–$Rh_2(5S\text{-MEPY})_3$	**5b**	50	74/26	55	14
7	$Rh_2(4R\text{-BNOX})_4$	**5a**	79	46/54	2	17
8	SiO_2–$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	**5a**	84	60/40	33	35
9	MCM-41-$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	**5a**	51	70/30	29	36
10	$Rh_2(4R\text{-BNOX})_4$	**5b**	64	59/41	34	9
11	SiO_2–$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	**5b**	53	66/34	19	9
12	MCM-41-$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	**5b**	51	72/28	21	14

[a] Literature value [20].
[b] All reported yields are isolated yields.
[c] Determined by GC.
[d] The *ee*'s for the ethyl esters were determined by chiral GC after conversion to the corresponding methyl esters [30], the *ee*'s for *tert*-butyl esters were determined by chiral GC. The main enantiomer for *cis* **6a** using *S*-MEPY or *R*-BNOX as the ligand is $1S, 2R$; the main enantiomer for *trans* **6a** using *S*-MEPY or *R*-BNOX as the ligand is $1S, 2S$ [30]. For **6b**, the same enantioselectivity is assumed.

trans/*cis* ratios when ethyl diazoacetate (**5a**) was used as the diazo compound, and even more (from 56/44 to 76/24) for *tert*-butyl diazoacetate (**5b**) (Table 2). While the *trans*/*cis* ratios were modified significantly due to the spatial confinement, some enantioselectivity was lost, probably due to the spatial confinement in this case not fully compensating for the loss of one of the chiral ligands per complex. All immobilised catalysts listed in Table 2 have protected surfaces [3].

A method to enhance the effects of the immobilisation is to add a weak inhibitor. In the presence of an inhibitor, the speed of the reaction decreases and differences in selectivity become more evident. Because of the coordinative unsaturation of the active metal catalyst, Lewis bases that can associate with the metal inhibit diazo decomposition. Amines, sulphides, and nitriles are generally effective inhibitors for dirhodium(II)-catalysed diazo decomposition, but alkenes and alkylbenzenes can also play this role. Halogenated hydrocarbons are known not to coordinate with dirhodium(II) complexes and, therefore, they serve as useful solvents for the reactions catalysed by these complexes [32]. In the reactions described in Table 3, dichloromethane was the solvent. In most reactions the noncoordinating chlorobenzene was added as the internal standard. In some cases this was replaced by toluene, which then served as both the internal standard and the inhibitor. The catalysts described in Table 3 were immobilised on carriers with free silanol groups. The outer surface of the MCM-41 carriers was protected in order to make sure that the catalyst was immobilised inside the pore. Selectivities are expected to be higher at lower conversions. Indeed, while the yields decrease significantly in the presence of toluene (Table 3), the *trans*/*cis* ratios and *ee*'s (especially of the *cis* product) are higher in its presence.

The above results show that, as predicted, modification of the regioselectivity of the immobilised catalysts can be observed for the cyclopropanation reaction (Fig. 1, reaction 2). In this reaction the ratio between the *trans* and *cis* product formed is determined by the steric repulsion between the phenyl group of the styrene and the ester group of the carbene. As can be seen in Figs. 4a and 4b, in the homogeneous reaction, the ligand does not significantly restrict the incoming styrene, and, thus, the difference in

Table 3
Influence inhibitor in the reaction of ethyl diazoacetate (**5a**) and styrene (Fig. 1, reaction 2)

Catalyst	Toluene	Yield (%)[a]	*trans*/*cis*[b]	ee_{trans} (%)[c]	ee_{cis} (%)[c]
1. $Rh_2(4S\text{-BNOX})_4$	yes	32	45/55	43	19
2. $Rh_2(4S\text{-BNOX})_4$	no	85	49/51	34	8
3. MCM-41-C_6H_4COO–$Rh_2(4S\text{-BNOX})_3$	yes	14	66/34	26	24
4. MCM-41-C_6H_4COO–$Rh_2(4S\text{-BNOX})_3$	no	30	60/40	27	16
5. SiO_2–$(CH_2)_3$COO–$Rh_2(4S\text{-BNOX})_3$	yes	10	65/35	37	36
6. SiO_2–$(CH_2)_3$ COO–$Rh_2(4S\text{-BNOX})_3$	no	58	59/41	39	27

[a] All reported yields are isolated yields.
[b] Determined by GC.
[c] The *ee*'s for the ethyl esters were determined by chiral GC after conversion to the corresponding methyl esters [30]. The main enantiomer for *cis* **6a** using *S*-MEPY or *R*-BNOX as the ligand is $1S, 2R$; the main enantiomer for *cis* **6a** using *R*-MEPY or *S*-BNOX as the ligand is $1R, 2S$; the main enantiomer for *trans* **6a** using *R*-MEPY or *S*-BNOX as the ligand is $1R, 2R$; the main enantiomer for *trans* **6a** using *S*-MEPY or *R*-BNOX as the ligand: $1S, 2S$ [30].

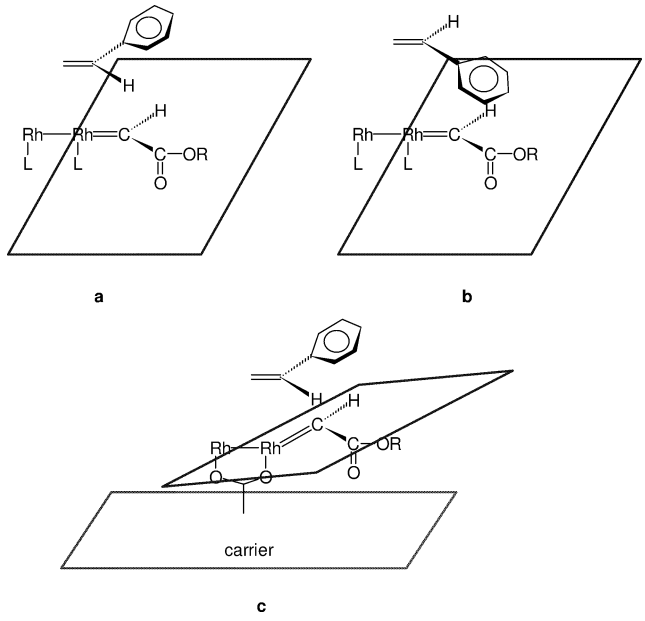

Fig. 4. Transition state of the homogeneous reaction (a *trans* orientation, b *cis* orientation) and heterogeneous reaction (c).

the formation of the *trans* and *cis* products is not large. In Fig. 4c, the transition state of the heterogeneous reaction is shown. In this case, steric hindrance by the bulky carrier surface forces the carbene upwards, away from the surface. The carbene then directs, due to the bulk of the ester group, the incoming styrene in such a way that more *trans* compound is formed than in the homogeneous reaction. If the more bulky *tert*-butyl diazoacetate is used, both effects are even more pronounced. If the catalysts are immobilised on Aerosil 200, the effect is smaller than if the catalysts are immobilised inside MCM-41. This can be explained by the predicted steric confinement within the pores, which restricts the incoming styrene even more.

The influence of the polarity of the surface was investigated in the cyclopropanation of styrene with *tert*-butyl diazoacetate (Fig. 1, reaction 2). The *trans*/*cis* ratios (vide supra) increase if the catalysts are immobilised; however, if the surfaces are protected, the increases are even higher for both Aerosil 200 and MCM-41 immobilised catalysts (Table 4). The results indicate that, if no polar interactions are possible between the surface and the catalyst, this has a positive influence on the selectivity. Alternatively, it is possible that the increased spatial restrictions, due to the surface protection, are causing these improvements. Additionally, polar interactions can also have a positive effect on the catalyst, as can be concluded from the fact that in the case of catalysts immobilised on unprotected carriers, the observed *ee*'s are moderately higher than with the protected surfaces. Molecular modelling studies are under way to probe these effects more deeply.

The influence of the spacer group in the reaction of styrene with ethyl diazoacetate does not show a clear pattern (Fig. 1, reaction 2). Contrary to expectation, its influence seems rather small (Table 5). Although entries 4, 5, and 6 indicate that shorter and, especially, rigid spacer groups improve the *trans*/*cis* ratios significantly, entries 9, 10, and 11 do not support this trend. Even if it is taken into account that some of the surfaces were protected and others not, there is no clear pattern.

We also immobilised $Rh_2(4R\text{-BNOX})_4$ on MCM-41 with free internal and external silanol groups and on fully protected MCM-41 (protected with dimethoxydimethylsilane) [3]. The immobilisation on unprotected MCM-41 gave a blue solid after Soxhlet extraction. This solid was active in the cyclopropanation of styrene (**4**) with ethyl diazoacetate (**5a**) (Table 6, entry 2). The results were similar to those for the homogeneous catalyst (Table 6, entry 1). This clearly demonstrates that the fine tuning of the catalyst in the pore is essential. Without a tether and surface protection, the pore is larger and, therefore, does not induce any additional selectivity. Hölderich and co-workers [33] reported similar results when they immobilised complexes inside the pores of MCM-41 via ionic interactions. The immobilisation on protected MCM-41 was not successful. The resulting solid was white and was not active in the cyclopropanation of styrene (**4**) with ethyl diazoacetate (**5a**). We also compared the selectivity of $Rh_2(4R\text{-BNOX})_4$ immobilised on protected MCM-41-$(CH_2)_3$COOH in dichloromethane (Table 6, entry 5) and of $Rh_2(4R\text{-BNOX})_4$ immobilised on protected MCM-41-$(CH_2)_3$CN in toluene (Table 6, entry 4). The catalyst immobilised via the CN tether behaved as the homogeneous catalyst, while the catalyst immobilised via the COO tether gave the increased selectivity that was observed for all the other examples in this paper. From these results we assume that the CN tether immobilises the catalyst via the axial position and, therefore, the catalyst behaves as if it was homogeneous.

Table 4
Influence surface polarity on the cyclopropanation reaction of styrene with *tert*-butyl diazoacetate (**5b**) (Fig. 1, reaction 2)

Entry	Catalyst	Protected	Yield (%)[a]	*trans*/*cis*[b]	ee_{trans} (%)[c]	ee_{cis} (%)[c]
1	$Rh_2(4R\text{-BNOX})_4$	–	64	59/41	9	34
2	MCM-41-$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	yes	51	72/28	14	21
3	MCM-41-$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	no	45	56/44	18	27
4	SiO_2–$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	yes	53	66/34	9	19
5	SiO_2–$(CH_2)_2$COO–$Rh_2(4R\text{-BNOX})_3$	no	61	64/36	16	21

[a] All reported yields are isolated yields.
[b] Determined by GC.
[c] *ee*'s for *tert*-butyl esters were determined by chiral GC.

Table 5
Influence spacer length on the reaction of styrene with ethyl diazoacetate (**5a**) (Fig. 1, reaction 2)

Catalyst	Protected	Yield (%)[b]	*trans*/*cis*[c]	ee_{cis} (%)[d]	ee_{trans} (%)[d]
1. $Rh_2(5S\text{-MEPY})_4$[a]	–	59	56/44	33	58
2. MCM-41-C_6H_4COO–$Rh_2(5S\text{-MEPY})_3$	no	27	52/48	24	20
3. MCM-41-$(CH_2)_2COO$–$Rh_2(5S\text{-MEPY})_3$	yes	65	60/40	19	22
4. SiO_2–C_6H_4COO–$Rh_2(5S\text{-MEPY})_3$	no	51	94/6	15	37
5. SiO_2–$(CH_2)_2COO$–$Rh_2(5S\text{-MEPY})_3$	yes	73	59/41	29	35
6. SiO_2–$(CH_2)_3COO$–$Rh_2(5S\text{-MEPY})_3$	no	53	53/47	21	29
7. $Rh_2(4S\text{-BNOX})_4$	–	85	49/51	8	34
8. MCM-41-C_6H_4COO–$Rh_2(4S\text{-BNOX})_3$	no	30	60/40	16	27
9. SiO_2–C_6H_4COO–$Rh_2(4S\text{-BNOX})_3$	no	50	66/34	17	18
10. SiO_2–$(CH_2)_2COO$–$Rh_2(4S\text{-BNOX})_3$	yes	71	82/18	35	40
11. SiO_2–$(CH_2)_3COO$–$Rh_2(4S\text{-BNOX})_3$	no	58	59/41	27	39
12. $Rh_2(4R\text{-BNOX})_4$	–	79	46/54	2	17
13. MCM-41-C_6H_4COO–$Rh_2(4R\text{-BNOX})_3$	no	70	48/52	16	39
14. MCM-41-$(CH_2)_2COO$–$Rh_2(4R\text{-BNOX})_3$	yes	51	70/30	29	36
15. SiO_2–C_6H_4COO–$Rh_2(4R\text{-BNOX})_3$	no	75	40/60	15	36
16. SiO_2–$(CH_2)_2COO$–$Rh_2(4R\text{-BNOX})_3$	yes	84	60/40	33	35
17. SiO_2–$(CH_2)_3COO$–$Rh_2(4R\text{-BNOX})_3$	yes	63	56/44	38	45

[a] Literature value [20].
[b] All reported yields are isolated yields.
[c] Determined by GC.
[d] The *ee*'s for the ethyl esters were determined by chiral GC after conversion to the corresponding methyl esters [30]. The main enantiomer for *cis* **6a** using *S*-MEPY or *R*-BNOX as the ligand is $1S, 2R$; the main enantiomer for *cis* **6a** using *R*-MEPY or *S*-BNOX as the ligand is $1R, 2S$; the main enantiomer for *trans* **6a** using *R*-MEPY or *S*-BNOX as the ligand is $1R, 2R$; the main enantiomer for *trans* **6a** using *S*-MEPY or *R*-BNOX is the ligand: $1S, 2S$ [30].

3.3. Leaching test

In order to evaluate whether any of the rhodium leaches into solution during the reaction, the activity of the filtrate of a cyclopropanation reaction of styrene (**4**) with ethyl diazoacetate (**5a**) catalysed by SiO_2–$(CH_2)_2COO$–$Rh_2(4R\text{-BNOX})_3$ was determined. One minute after the addition of ethyl diazoacetate (**5a**) was complete, no diazo compound could be detected by GC anymore; i.e., 100% had been converted. To the filtrate of this reaction **5a** was added. From GC analysis it was shown that 66% of **5a** was consumed after 16 h. After a further three days, 11% of **5a** was still present. This behaviour corresponds to a conversion of, after 2 min, less than 0.5%, whereas in the homogeneous case after 2 min full conversion was reached. Therefore, only traces of catalyst leach during the reaction.

Recycling experiments were performed for the cyclopropanation of styrene (**4**) with ethyl diazoacetate (**5a**) in dichloromethane with chlorobenzene as an internal standard, with SiO_2–C_6H_4COO–$Rh_2(5S\text{-MEPY})_3$ as the catalyst at room temperature (Fig. 1, reaction 2). The conversions were determined by GC. In the second cycle a decrease in activity by 20% was observed, which remained stable in the third cycle. In all cases complete conversion was observed after 16 h.

4. Conclusion

By immobilising the chiral dirhodium complexes on Aerosil 200 and inside the pores of MCM-41, we demonstrate that it is possible to achieve better selectivities using this strategy:

In the Si–H insertion reactions a significant increase of enantioselectivity was obtained with the BNOX catalysts immobilised on silica. Earlier work in this area described an increase in *ee* from 6 to 17% for a reduction and from 43

Table 6
Variation of immobilisation mechanisms in the cyclopropanation of styrene and ethyl diazoacetate (**5a**) (Fig. 1, reaction 2)

Catalyst	Protected	Yield (%)[a]	*trans*/*cis*[b]	ee_{cis} (%)[c]	ee_{trans} (%)[c]
1. $Rh_2(4R\text{-BNOX})_4$	–	79	46/54	2	17
2. MCM-41-OH–$Rh_2(4R\text{-BNOX})_4$	no	74	47/53	7	32
3. MCM-41-SiMe2–$Rh_2(4R\text{-BNOX})_4$	yes	–	–	–	–
4. MCM-41-$(CH_2)_3CN$–$Rh_2(4R\text{-BNOX})_4$	yes	63	47/53	13	30
5. MCM-41-$(CH_2)_3COO$–$Rh_2(4R\text{-BNOX})_3$	yes	65	63/37	37	37

[a] All reported yields are isolated yields.
[b] Determined by GC.
[c] The *ee*'s for the ethyl esters were determined by chiral GC after conversion to the corresponding methyl esters [30]. The main enantiomer for *cis* **6a** using *R*-BNOX as the ligand is $1S, 2R$; the main enantiomer for *trans* **6a** using *R*-BNOX is the ligand: $1S, 2S$ [30].

to 96% for an allylic amination [22,23]. This is to say, the selectivity of the reactions was improved. Our conversion of an essentially unselective reaction (*ee* 2%) into a selective reaction (*ee* 28%) in the case of the Si–H insertion reaction is, thus, another step forward.

In the case of the cyclopropanation reactions, we observed a significant improvement of the *trans*/*cis* ratios. This is a general result for both catalysts, immobilised on a variety of different supports. However, we have to note that in this case the enantioselectivity of the reaction did not improve. Leaching experiments showed that only traces of catalytically active material leached during the cyclopropanation reaction. We also proved that with protected carrier surfaces, the catalyst was immobilised via the tether. With unprotected carrier surfaces, the immobilisation can proceed via ligand exchange with the tether or via adsorption to the surface silanol groups. In this case the influence of the spatial confinement is less pronounced.

With the above experiments, we have shown that our synthesis method gives us the opportunity to fine-tune the pore size in such a way that we can increase the selectivity of the test reactions. By changing the pore size of the carrier materials (using silica or MCM-41) we can increase the selectivity for the cyclopropanation reaction, while by immobilising the catalysts on Aerosil 200 we can do the same for the Si–H insertion reaction.

The deactivation that occurrs during recycling of the immobilised catalysts is caused by rhodium leaching and probably also by clogging of the pores. The deactivation is higher at a higher temperature. Tests of the filtrate demonstrated that the rhodium that leaches is not active. Despite the leaching, we were still able to obtain full conversion in the cyclopropanation reaction. In the Si–H insertion reactions a loss of activity was observed; however, the *ee*'s remained.

In short, we have shown that immobilisation of the homogeneous dirhodium catalysts on Aerosil 200 surfaces and inside MCM-41 affords a significant improvement in regioselectivity (cyclopropanation reaction) and enantioselectivity (Si–H insertion). The improvement is attributed to the confinement resulting from immobilisation.

Acknowledgments

The Royal Netherlands Academy of Arts and Sciences (U.H.) and the Netherlands Research School Combination Catalysis (H.M.H.) are acknowledged for financial support.

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