warming this reaction gave **6** (R = Ph, R′ = *t*Bu) with 79% *ee*.[19] Other 4-substituted cyclohexanones **5** were converted into the corresponding *cis*-alcohols **6** (R = Ph) and benzylidenecyclohexanes **8** (R = Ph) in 64-84% *ee* (Table 1, entries 1–3). Other diethyl phosphonates **4** (R = 4-ClPh, 1- and 2-naphthyl, vinyl) gave the corresponding alcohol **6** and olefins **8** in 51–90% *ee* (entries 4–7).

The reaction described, which is controlled by external chiral ligands, has the advantage that tedious steps in the synthesis of chiral phosphonate derivatives can be omitted. Furthermore, it may open the way to a catalytic asymmetric HWE reaction.

Experimental Section

A solution of BuLi in hexane (0.81 mL, 1.48 M, 1.2 mmol) was added to a solution of **1** (338 mg, 1.4 mmol) in toluene (6.5 mL) at −78 °C. After the mixtures was stirred for 0.5 h a solution of **4** (274 mg, 1.2 mmol) in toluene (2.0 mL) was added dropwise over 5 min. The solution was stirred for 0.5 h at −78 °C and then for 0.5 h at 0 °C. A solution of **5** (R′ = *t*Bu; 154 mg, 1.0 mmol) in toluene (2.0 mL) was added dropwise over 5 min at −78 °C, and the reaction mixture was stirred for 0.5 h at −78 °C before it was quenched with a saturated solution of aqueous NaCl (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were washed with a saturated solution of aqueous NaCl (20 mL) and dried over sodium sulfate. Concentration followed by column chromatography (silica gel, hexane/ethyl acetate 5/1 then 1/1) gave (*S*)-**6** (R = Ph, R′ = *t*Bu; 340 mg, 89% yield, 82% *ee*) and (*R*)-**7** (R = Ph, R′ = *t*Bu; 18 mg, 5% yield, 12% *ee*) together with recovered **1** (337 mg, 90%).

A mixture of (*S*)-**6** (R = Ph, R′ = *t*Bu; 82% *ee*, 203 mg, 0.67 mmol) and sodium acetate (220 mg, 2.5 mmol) in propionic acid (1.0 mL) was stirred under reflux for 0.5 h. The mixture was allowed to cool to room temperature and then diluted with ethyl acetate (10 mL). The organic layer was washed successively with saturated solutions of sodium hydrogencarbonate (10 mL) and aqueous NaCl (10 mL), and then dried over sodium sulfate. Concentration and purification by column chromatography (silica gel, hexane) gave olefin (*S*)-**8** (R = Ph, R′ = *t*Bu; 156 mg, 85%) with 84% *ee*.

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Methylalumoxane MCM-41 as Support in the Co-Oligomerization of Ethene and Propene with [{C_2H_4(1-indenyl)$_2$}Zr(CH_3)$_2$]**

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With the advent of single-site metallocene catalysts, the field of polymerization of α-olefins has been drastically changed.[1] Next to geometric manipulation of the metallocene structure to induce stereoregular polymerization, substitution or reduction of the excessive amounts of methylalumoxane (MAO) is an important challenge. MAO acts as a weakly coordinating anion and activates the metallocene structure. Heterogenization of the alumoxane structure on support materials like silica and alumina may be a solution to minimize the amounts of MAO. However, after impregnation of MAO or trimethylaluminum (TMA), addition of supple-

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mentary MAO or TMA is still necessary to obtain catalytic activity. Moreover, the obtained polymers show a broadened molecular weight distribution.[2]

We describe a new heterogeneous alumoxane derivative generated by in situ hydrolysis of TMA in the mesopores of the siliceous molecular sieve MCM-41. The spectroscopic and physicochemical features of the solids obtained point to the formation of an MAO phase chemically linked to the pore walls of the support. This MAO phase is accessible for interaction with zirconocene and does not require supplementary MAO for co-oligomerization of ethene and propene. Especially at low concentrations the MAO-MCM-41 is catalytically more active than the corresponding silica-based MAO derivative or the homogeneous system. The molecular weight and physical properties of the co-oligomers are dependent on the pore size of MCM-41, which suggests shape-selective oligomerization. The main advantage of in situ alumoxane synthesis over physisorption is that cluster aggregation is prevented. The subtle balance between anchoring to the MCM-41 surface and delocalization of the negative charge determines the weakly coordinating properties of the alumoxane compound.

The siliceous mesoporous molecular sieves MCM-41 were synthesized according to published procedures with different quaternary ammonium compounds as surfactant.[3, 4] If $C_nH_{2n+1}(CH_3)_3N^+X^-$ with $n = 10$, 14, or 16 are used, d_{100} spacings of 2.89, 3.50 and 3.99 nm, respectively, result. Various silica sources (Ludox, Cab-O-Sil, and TEOS) were used for the synthesis. The alumoxane-MCM-41 materials were prepared by controlled in situ hydrolysis of TMA in a continuously stirred, cooled reactor at 273 K. During TMA treatment the OH overtone at 6900 cm^{-1} and the combination band at 5208 cm^{-1} of the water-containing MCM-41 disappear, while a CH overtone and a combination band appear at 5952 and 4386 cm^{-1}, respectively.[5] At the same time a charge transfer band (Al→O), characteristic for an alumoxane-type structure,[6] shows up as a broad band around 300 nm in the diffuse reflectance spectrum. ^{13}C *c*ross-*p*olarized (CP) *m*agic *a*ngle *s*pinning (MAS) NMR spectrum of alumoxane-MCM-41 reveals the presence of a broad band at $\delta = -7.4$, assigned to the methyl group of the alumoxane compound. No sharp signal of associated TMA ($\delta = -5.3$) is superimposed on this broad band, indicating complete conversion of TMA into alumoxane.[7] The fate of the silanol groups is followed by ^{29}Si CP-MAS NMR (Figure 1). The CP mode selectively highlights the Si atoms with bound hydroxyl groups, such as $[Si(OSi)_2(OH)_2]$ (Q_2, $\delta = -91.6$) and $[Si(OSi)_3(OH)]$ (Q_3, $\delta = -100.6$).[8] Si atoms with four neighboring Si atoms (Q_4) are silent in the CP mode. The disappearance of the Q_2 and Q_3 resonances after treatment with TMA clearly demonstrates the covalent bonding of the alumoxane to the silanol groups of the MCM-41. The ^{27}Al MAS NMR spectrum of the alumoxane-MCM-41 (Figure 2) displays a broad resonance between $\delta = 0$ and 80 due to the interaction of the Lewis acidic Al center of the alumoxane with the O bridging atoms of the mesoporous support. Different Al environments with tri-, tetra-, penta-, or hexacoordinated Al may contribute to this band. The ^{27}Al MAS NMR spectrum of the MAO-physisorbed system as well as of pure MAO does not reveal these particular coordinations, because of strong internal clustering of the alumoxane structure (Figure 2).

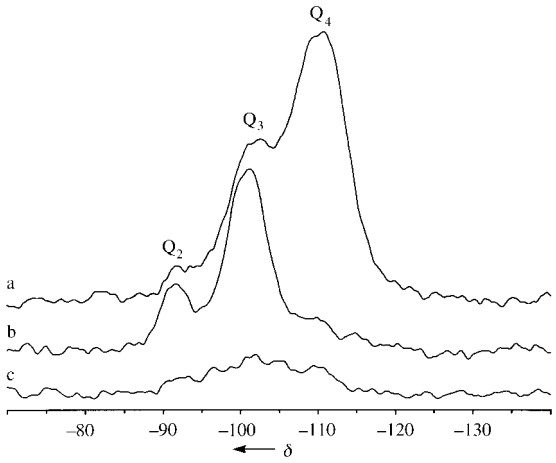

Figure 1. a) ^{29}Si MAS NMR spectrum of hydrated MCM-41 synthesized with Ludox. b) ^{29}Si CP-MAS NMR spectrum of hydrated MCM-41 and c) of alumoxane-MCM-41.

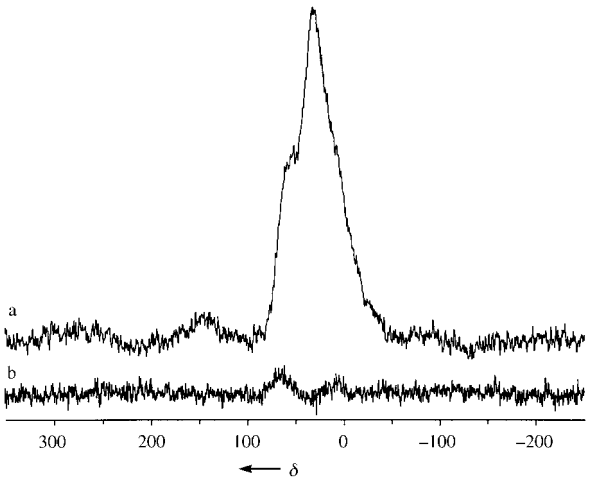

Figure 2. ^{27}Al MAS NMR spectrum of a) alumoxane-MCM-41 (3000 accumulations) and of b) MAO physisorbed onto MCM-41 (10000 accumulations).

Electron probe microanalysis (EPMA) reveals an average Si/Al ratio of 0.88, with a deviation as small as 0.11. Thus 72 mol% of the added TMA is incorporated as alumoxane, which is homogeneously distributed in the mesoporous host. The alumoxane formation reduces the average pore diameter of MCM-41 from 2.75 to 2.40 nm and its surface area from 880 to 470 $m^2 g^{-1}$. Capillary condensation within the pores of the alumoxane-MCM-41 disappears, which illustrates that the uniform pores are narrowed from mesoporous to microporous dimensions.

To obtain the final catalyst, *rac*,*meso*-ethylenebis(1-indenyl)dimethylzirconium ($[\{C_2H_4(ind)_2\}Zr(CH_3)_2]$) was added to a vigorously stirred suspension of in situ prepared alumoxane-MCM-41 in toluene. Table 1 shows representative activities for the co-oligomerization of ethene and propene with $[\{C_2H_4(ind)_2\}Zr(CH_3)_2]$/alumoxane-MCM-41 with various

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Table 1. Co-oligomerization of ethene and propene with the *ansa*-metallocene $[\{C_2H_4(ind)_2\}Zr(CH_3)_2]$ on alumoxane-MCM-41 at 343 K in toluene.

Entry	Support components[a]	Al/Zr[b]	Activity[c]	M_n[d]	M_w/M_n[d]	P [mol %][e]
1	Ludox, C_{16}	180	4.12	1280	1.99	55.8
2	Ludox, C_{14}	180	3.85	1730	1.94	54.6
3	Ludox, C_{16}	360	4.37	830	1.97	58.0
4	Cab-O-Sil, C_{10}	360	4.32	880	2.00	57.9
5	Ludox, C_{16}	90	3.55	1890	1.99	53.5
6	TEOS, C_{16}	360	4.45	790	1.87	56.4
7	TEOS, C_{16}	180	4.34	830	2.08	55.9
8	TEOS, C_{16}	90	4.30	940	2.13	55.8
9	TEOS, C_{16}	40	3.88	1280	1.94	55.3
10	Ludox, C_{16}[f]	90	2.43	5590	–	56.7
11	Ludox, C_{16}[f]	90	2.43	960	2.46	45.1

[a] The MCM-41 samples were synthesized from Ludox, Cab-O-Sil, or TEOS as silica source with C_{16}TMACl, C_{14}TMABr, or C_{10}TMABr as surfactant. [b] The Al/Zr ratio was determined based on the Al content of the alumoxane-MCM-41. [c] Co-oligomerization activity (10^6 g(per mol Zr) h^{-1}) of the zirconocene after 75 min reaction time. [d] The number-average molecular weight (M_n) in g mol^{-1} and polydispersity (M_w/M_n) of the co-oligomer were correlated to polystyrene standards and determined on a GPC Chrompack Microgel 3 Mix column with a refractive index detector. [e] P = overall mol % propene incorporated in the co-oligomer chain, based on GC conversion after 75 min. [f] The oligomerization temperature of reactions 10 and 11 was 308 K and 373 K, respectively.

Al/Zr ratios. The polydispersity of the co-oligomer is always around 2, pointing to the occurrence of single-site catalysis.

There is, however, a clear pore size effect. Narrowing the pore size by altering the surfactant chain length during synthesis (entries 1–4) results in an increase of the molecular weight and alters the physical properties of the product from liquid (pour point 253 K) to wax (pour point 265 K). The effect of the pore size on the molecular weight is more pronounced at a lower Al/Zr ratio (entries 1 and 2). A smaller pore diameter of the alumoxane-MCM-41 is expected to lower the incorporation of metallocene molecules into the tubular pores of the host, which is reflected in a decreased oligomerization activity.

Generally, at a smaller Al/Zr ratio, the activity decreases and the molecular weight increases, because less propene is incorporated in the co-oligomer chain (entries 1, 3, and 5). Increasing the reaction temperature from 308 K (entry 10) to 343 K (entry 5) has a positive effect on the oligomerization activity and decreases the molecular weight. A further increase of the reaction temperature to 373 K (entry 11) has a negative influence on the activity and increases the molecular weight. At such high temperatures, the decreased solubility of propene in the reaction solvent becomes a limiting factor.

When tetraethyl orthosilicate (TEOS) is used as Si source instead of Ludox in the MCM-41 synthesis, the oligomerization activity increases and the molecular weight decreases for all Al/Zr ratios studied (compare entries 3, 1, and 5 with 6, 7, and 8, respectively). The surfactant chain length was identical in both series of samples. The ^{29}Si MAS NMR spectrum of the hydrated MCM-41 synthesized with TEOS shows a clear decrease in silanol content, as reflected by lower Q_2/Q_4 and Q_3/Q_4 ratios of 6.6×10^{-2} and 4.2×10^{-1} respectively, relative to the Ludox sample ($Q_2/Q_4 = 9.2 \times 10^{-2}$ and $Q_3/Q_4 = 4.4 \times 10^{-1}$). A decrease in the Q_2 and Q_3 concentrations is expected to provide less docking points for the alumoxane on the mesoporous support. This may increase the charge delocalization in the alumoxane structure, hereby producing a more weakly coordinating anion and a higher activity.

In Table 2 the alumoxane-MCM-41 is compared with homogeneous MAO and different alumoxane derivatives under identical reaction conditions. The oligomerization activity of the optimal alumoxane-MCM-41 sample (Table 1, entries 6, 7, and 8) exceeds that of the homogeneous system (Table 2, entries 1, 2, and 3) at all Al/Zr ratios tested. The alumoxane-MCM-41 (Table 1, entry 9) even retains a high activity at a reduced Al/Zr ratio of 40, where the homogeneous system is catalytically inert. A lower activity was also observed when alumoxane was formed on an amorphous, pyrogenic silica (Aerosil; Table 2, entry 4). The higher accessible surface area for the metallocene catalyst in the alumoxane-MCM-41 than in the alumoxane-Aerosil reduces the possibility of deactivation by binuclear complex formation, which is reported as the most probable way to form inactive sites after immobilization.[9] Physisorption of commercial MAO on MCM-41 results in a heterogeneous support with a much higher Si/Al ratio (3.27 ± 0.42 by EPMA measurement) than that for the in situ formed alumoxane. With such a physisorbed system lower activities than with the homogeneous system have been observed in the isotactic polymerization of propene with *rac*-$[\{C_2H_4(ind)_2\}ZrCl_2]$.[10] Moreover, in our oligomerization setup no significant activity is observed for the MAO-physisorbed system at an Al/Zr ratio of 90 (Table 2, entry 5). It seems therefore more appropriate to anchor and to finely distribute the alumoxane structure onto the silanol groups of the mesoporous material by in situ hydrolysis.

Table 2. Comparison of the co-oligomerization of ethene and propene with $[\{C_2H_4(ind)_2\}Zr(CH_3)_2]$ on different alumoxane derivatives at 343 K in toluene.

Entry	Support	Al/Zr	Activity	M_n	M_w/M_n	P [mol %]
1	MAO[a]	360	4.34	840	2.05	58.1
2	MAO[a]	180	4.14	1110	2.14	57.8
3	MAO[a]	90	4.15	1150	2.06	57.9
4	Aerosil[b]	360	2.81	2170	1.91	47.6
5	MAO on MCM-41[c]	90	–	–	–	–

[a] Reference experiment under homogeneous conditions. [b] Alumoxane-Aerosil is synthesized by in situ hydrolysis of TMA. [c] MAO is physisorbed on MCM-41 synthesized with Ludox as silica source and C_{16}TMACl as surfactant. (see footnote [e] of Table 1 for definition of P).

Experimental Section

Support syntheses: Typically, MCM-41 was synthesized from a gel with the molar composition of SiO_2:TEAOH:C_{16}TMACl:H_2O 1.00:0.21:0.30:44.81. The silica source was Ludox AS 40, and the templating agent tetraethylammonium hydroxide (TEAOH) and hexadecyltrimethylammonium chloride (C_{16}TMACl). After heating at 383 K for 24 hours in an autoclave, washing with water and ethanol, the sample was dried and calcined at 813 K for 10 hours. X-ray diffraction (Siemens D5000, $Cu_{K\alpha}$ source with $\lambda =$

0.1542 nm) showed the four peaks of MCM-41 between 1° and 12° (2θ) A d_{100} spacing of 3.99 nm was observed after calcination. In the synthesis of MCM-41 with C_{14}TMABr, a similar gel composition was made. A d_{100} spacing of 3.50 nm was observed after calcination. In the synthesis of MCM-41 with C_{10}TMABr as surfactant, the molar composition of the gel was SiO_2:TMAOH:C_{10}TMABr:Na_2O:H_2O 1.00:0.09:0.32:0.09:63.45. A d_{100} spacing of 3.03 nm was observed after calcination. In the same way MCM-41 was obtained with TEOS as Si source with the following composition: TEOS:C_{16}TMACl:NaOH:H_2O = 1.00:0.11:0.49:54.09.

In situ hydrolysis of TMA: The calcined MCM-41 samples and Aerosil 380 (Degussa) were equilibrated against a relative humidity of 79.3% at room temperature; thereafter they contained 16–27 wt% of sorbed water. The water-saturated sample was suspended in 270 mL toluene in the reactor, which was flushed with nitrogen and cooled to 273 K under continuous stirring for 1 h. TMA (2.0 M solution in toluene) was diluted in 20 mL toluene and added slowly to the suspension to give a water/Al ratio of 1. The alumoxane-MCM-41 was filtered, washed with toluene, and dried under inert atmosphere. Diffuse reflectance measurements were performed on a Varian Cary 05 UV/Vis/NIR spectrophotometer. Nitrogen sorption isotherms were recorded at 77 K with an Omnisorp 100 CX from Coulter. EPMA measurements were obtained on a JEOL JXA 733 scanning electron microscope using pure SiO_2 and Al_2O_3 as standards. ^{29}Si MAS NMR was performed on a BRUKER AMX 300 spectrometer operating at 59.62 MHz with excitation pulses of 3.5 μs and a spinning frequency of 4 kHz. ^{29}Si CP-MAS NMR was measured with a contact time of 1 ms. ^{27}Al MAS NMR measurements were carried out on a BRUKER MSL 400 with a resonance frequency of 104.26 MHz for Al, excitation pulses of 0.61 μs, and a spinning frequency of 12 kHz.

Catalyst preparation: [{C_2H_4(ind)$_2$}Zr(CH_3)$_2$] (0.036 mmol), obtained from the dichloride [{C_2H_4(ind)$_2$}ZrCl_2] by alkylation with TMA, was added under nitrogen atmosphere to the suspension of in situ prepared alumoxane-MCM-41 (Al/Zr ratios of samples were 360, 180, 90, and 40). Physisorption of MAO (85 g of a 10 wt% solution in toluene, Witco) on the calcined MCM-41 sample (0.77 g) was performed for 3 h at room temperature under inert atmosphere. The suspension was filtered and washed several times with toluene. Chemical analysis of the support shows that only 2.5 mol% of the added Al is anchored to the MCM-41 structure.

Co-oligomerization reactions: The reactions were performed for 75 min in a 600 mL water-cooled batch reactor (Parr) continuously fed with a flow of methane (491 mL min^{-1}), ethene (700 mL min^{-1}), propene (1400 mL min^{-1}), nitrogen (40 mL min^{-1}) and hydrogen (500 mL min^{-1}) at an overall pressure of 0.7 MPa. The solvent and the gases used were carefully dried over a molecular sieve (5 Å, Merck). The gas outlet was monitored by GC to calculate the conversion (methane as internal standard).

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Iterative Nucleophilic and Electrophilic Additions to Coordinated Cyclooctatetraene: An Efficient Route to *cis*-5,7-Disubstituted 1,3-Cyclooctadienes**

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Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday

Hitherto, cyclooctatetraene (cot) played only a minor role as a starting material in the stereocontrolled synthesis of *cyclo*-C_8 compounds.[1, 2] From the point of view of synthetic chemistry, cot became more interesting as a complexing ligand.[3] It is usually functionalized by electrophilic substitution[4] and addition,[5] and more recently by photochemical reactions;[6] however, nucleophilic addition has seldom been used thus far despite its synthetic potential.[7, 8] With an iterative method involving nucleophilic and electrophilic additions, *cis*-5,7-difunctionalized 1,3-cyclooctadiene has now been prepared for the first time by a very simple route. These kinds of cyclooctadienes containing two stereogenic centers are representatives of a rare,[9] but remarkable class of compounds that show great synthetic potential with regard to terpenoid *cyclo*-C_8 compounds.

The starting material for our studies of the stereo- and regioselective functionalization of cot is [Ru(Cp)(η^6-cot)]$^+$ (**1**, Cp = cyclopentadienyl), which can be recovered after completion of the reaction cycle (Scheme 1). The first nucleophilic addition of the dimethyl malonate anion to **1** occurs *exo* to the metal center[10] and leads initially, as expected,[11] to the 1,2,3,4,5-η-cyclooctatrienyl complex **2a**, which gradually rearranges to the 1,2,3-η:6,7-η-haptomer **2b**.[12] The thermal stability of **2a** is sufficient, however, to allow, for the most part, its separation from **2b** by chromatographic methods. The stereochemistry of both haptomers can

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