Heterogenization of (η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl and Its Catalytic Application for Cyclopropanation of Styrene Using Ethyl Diazoacetate

Ayyamperumal Sakthivel,[a] Filipe E. Pedro,[a] Anthony S. T. Chiang,[b] Fritz E. Kühn*[a,c]

[a] Lehrstuhl für Anorganische Chemie der Technischen Universität München, Lichtenbergstraße 4, 85747 Garching bei München, Germany
Fax +49(89)28913473; E-mail: fritz.kuehn@ch.tum.de
[b] National Central University, Chung-Li, Taiwan 320, Republic of China
[c] Department of Chemistry, Instituto Tecnológico e Nuclear (ITN), Estrada Nacional 10, 2686-953 Sacavém, Portugal

Abstract: (η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl (**1**) is heterogenized on the surface of mesoporous molecular sieves by direct grafting on mesoporous aluminosilicates or by reaction of an aminosilane-linker-modified silicate surface with the chloride ligand. Elemental analyses reveal that the grafted samples contain 0.2–1.8 wt% Ru. The retaining of long-range ordering of mesoporous MCM-41 and MCM-48 after grafting is evidenced from XRD, N$_2$ adsorption–desorption and TEM analysis. FT-IR, TG-MS, ^{29}Si and ^{1}H CP MAS-NMR spectra confirm the successful grafting of complex **1** on the surface of these mesoporous materials. Mesoporous materials grafted with complex **1** are found to be promising catalysts for the cyclopropanation of styrene with ethyl diazoacetate.

Key words: cyclopropanation, ethyl diazoacetate, ruthenium complex, mesoporous materials

The implementation of organometallic complexes as catalysts for organic synthesis is a continuously developing field. The trends clearly point to a growing demand for efficient, selective, and low-cost catalysts that can be easily separated from the product(s). Ruthenium compounds of the general formula Cp′RuX(PR$_3$)$_2$ have found widespread applications in catalysis.[1,2] The ease of their synthesis, the wide array of ligands available to coordinate with the metal centre and their general high stability makes them a versatile class of catalysts. Recently, various research groups have started to apply this compound family for aldehyde olefination[1–3] and more recently for cyclopropanation reactions.[4] Aldehyde olefination is an important transformation for the production of carbon–carbon double bonds. The catalytic approach is a valid alternative to the Wittig-type reactions since it allows generation of phosphorus ylides in non-basic and generally mild conditions, suitable for base-sensitive substrates.[5] Ruthenium complexes, such as Cp*RuCl(PPh$_3$)$_2$ (**1**) besides displaying a high activity, are among the most selective catalysts for this reaction reported to date.[3] Cyclopropanation of olefinic bonds using diazo compounds as a carbene source is among the best-developed and most useful transformations available to the synthetic organic chemist.[6,7] Cyclopropane derivatives are basic structural elements in a wide range of naturally occurring

and biologically active compounds and they are versatile synthetic intermediates in the synthesis of functionalized cycloalkanes and acyclic compounds. Strained cycloalkanes have also been prepared to test their bonding features and to study enzyme mechanisms and their inhibition. The ruthenium-catalyzed cyclopropanation reaction envisaged an exponential development in recent years. The main reasons for that development lie in the lower price of the ruthenium based catalysts, when compared to rhodium derivatives, and their richer reaction chemistry, providing a wide array of ruthenium complexes.[7]

Catalyst heterogenization, i.e. the immobilization of the catalyst on a supporting material allowing an easy product isolation and catalyst recycling, attracts also considerable industrial attention,[8] since cost-reducing advantages are very important, particularly at industrial-scale production. Among the various supporting materials studied, the mesoporous silicates known as MCM-41 and MCM-48[9] with regular pore size, large surface areas, large number of surface silanol groups, and high chemical and thermal stability, are potential and promising candidates as both catalysts and catalyst supports.[10,11] To the best of our knowledge the only extensive studies published on ruthenium catalyst heterogenization deal with Ru(II) porphyrin and amine derivatives.[12] These particularly effective immobilized catalysts were mainly applied in alkene epoxidation[5,12f] and in a few cases also in intermolecular cyclopropanation.[12f] As a rule, the performance of the immobilized catalysts surpassed, in these cases, that obtained with their homogeneous phase counterparts.

In the present work, complex **1** is grafted on the surface of mesoporous materials by direct reaction with mesoporous aluminosilicate (H-AlMCM-41 and H-AlMCM-48) or with aminosilane-linker-modified mesoporous silicate materials (designated as SM-41SNH, and SM-48SNH) (Scheme 1). Complex **1** grafted in H-AlMCM-41, H-AlMCM-48, SM-41SNH, and SM-48SNH samples are designated as HAM-41RuG, HAM-48RuG, SM-41SNHRuG, and SM-48SNHRuG, respectively. The grafted materials obtained from the heterogenization of compound **1** were systematically characterized by powder X-ray diffraction (XRD), N$_2$ adsorption–desorption (BET), TEM analysis, thermogravimetry coupled with mass spectroscopy (TG-MS), FT-IR and NMR spectro-
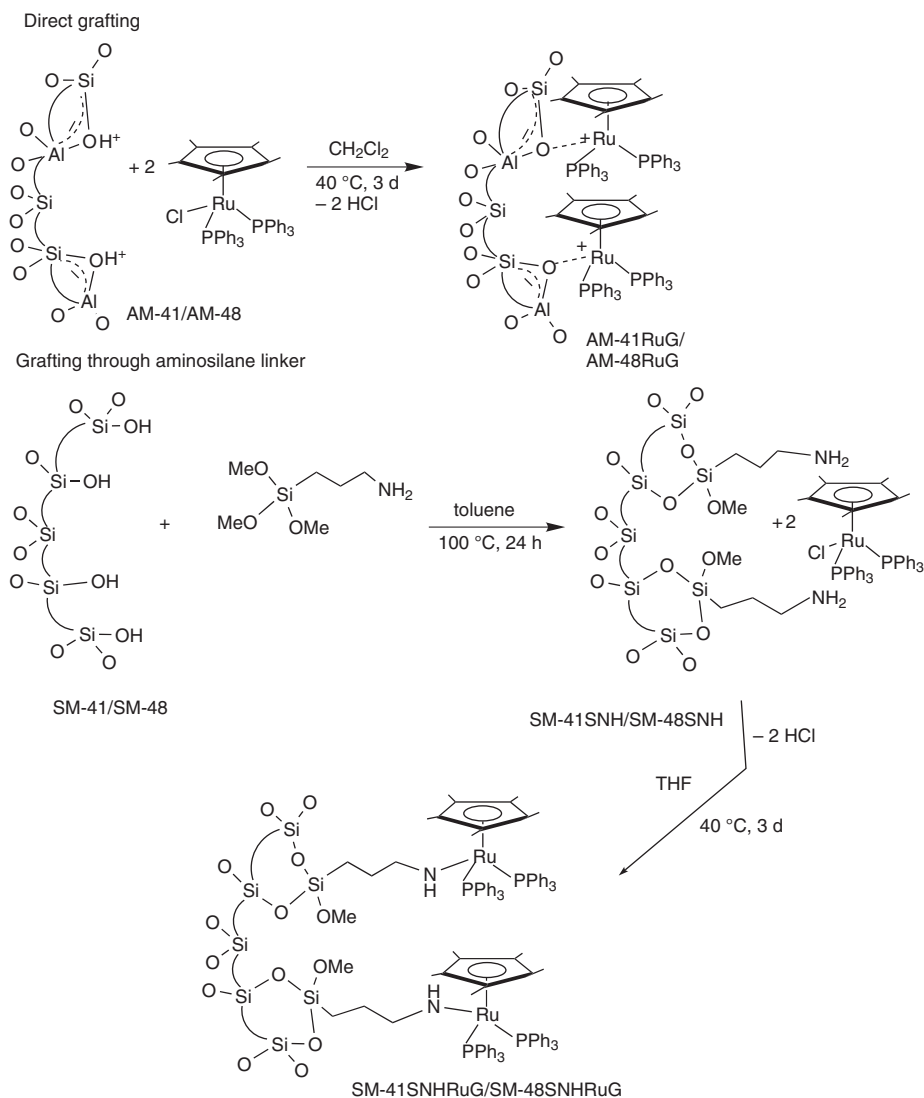
Scheme 1

scopic methods. The grafted samples are applied in the catalytic styrene cyclopropanation (Scheme 2).
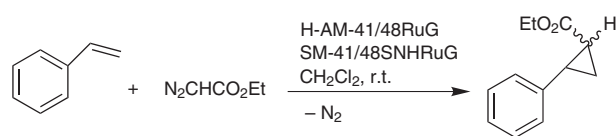
Scheme 2

The powder XRD pattern of complex **1** grafted MCM-41 and MCM-48 samples are in full agreement with reported patterns,[8–10] indicating the samples to be well ordered[9,10] (Figure 1). Several distinct Bragg peaks are observed in the $2\theta = 2–8°$ region, which can be indexed to different hkl reflections for a hexagonal unit cell (using the strongest reflection, d_{100}) and a cubic unit cell (using the strongest reflection, d_{211}), respectively. Even after grafting bulky complex **1** on mesoporous surfaces (Figure 1) the higher 2θ peaks are still observed, indicating the retention of long-range hexagonal and cubic symmetry. Compared to parent MCM-41 and MCM-48,[10e] the grafted samples

show a decrease in the relative intensities of the XRD reflections and there is a clear shift to higher 2θ values (for the decrease in inter-planar distances and unit-cell parameters, see Table 1). These changes originate from the immobilization of the bulky organometallic Ru complexes inside the channels of MCM-41 and MCM-48.[9–11]
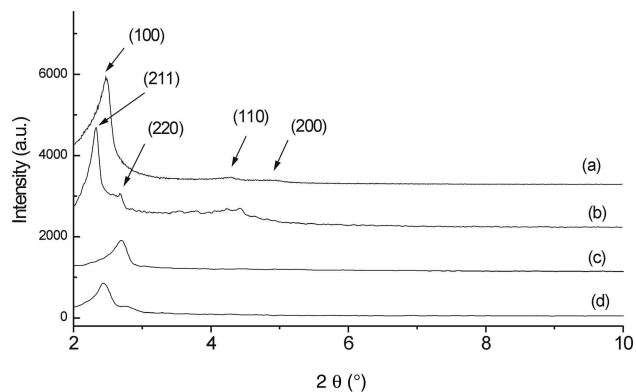

Figure 1 XRD pattern of (a) HAM-41RuG, (b) HAM-48RuG, (c) SM-41SNHRuG, and (d) SM-48SNHRuG

Table 1   Textural Properties of MCM-41/MCM-48 and the Samples Grafted with the Cp*Ru Complexes

| Sample	Ru wt. (%)	Interplane Distance (nm)[a]	Unit cell Parameter $\bar{a}$ (nm)[b]	BET Surface Area (m^2g^{-1})	Pore Diameter (nm)
MCM-41	–	3.80	4.39	839	2.74
MCM-48	–	3.97	9.72	1043	2.41
H-AM-41RuG	0.2	3.59	4.14	770	2.1–3.0
H-AM-48RuG	0.35	3.78	9.28	680	2.1–3.5
SM-41SNHRuG	0.9	3.26	3.76	211	1.5–5.0
SM-48SNHRuG	1.8	3.60	8.82	200	1.4–5.1

[a] d_{100} for MCM-41 and d_{211} for MCM-48.
[b] $\bar{a} = 2d_{100}/\sqrt{3}$ for MCM-41; $\bar{a} = d_{hkl} (h^2 + k^2 + l^2)^{1/2}$ for MCM-48.

Figure 2 depicts the FT-IR spectra of parent calcined mesoporous MCM-41 and of the grafted samples. The bands at 1206, 1060, and 794 cm^{-1} are attributed to stretching vibrations of the mesoporous framework (Si–O–Si). New, comparatively weak bands around 3000, 2957, and 2927 cm^{-1} can be assigned to cyclopentadienyl-(Cp), and triphenylphosphine-group vibrations of the grafted compounds. Additional bonds appear for SM-41SNHRuG and SM-48SNHRuG samples in the range of 2853 cm^{-1} due to C–H stretching vibrations, originating from the CH$_2$ groups present in the silane ligand. Additional bands appear at 690 and 745 cm^{-1}, due to C–C bending vibration from the phenyl ring.[13] Elemental analyses indicate (Table 1) that aluminum-containing MCM-41/48 show a relative low Ru content (0.2–0.4 wt%) when compared to the amino silane linker modified MCM-41/48 (0.9–1.8 wt%). The presence of more Ru in the amino silane linker containing mesoporous samples compared to pure aluminum samples is attributed to the ease of the reaction of the Ru complex with the amino functional group of the linker (0.12–0.25 mol% of linker on the surface based on C, H, N elementary analysis), as shown in Scheme 1.

The low temperature N$_2$ adsorption–desorption isotherm is of type IV according to the IUPAC[14] and characteristic for mesoporous solids. However, compared to parent mesoporous samples (Table 1),[10e] the samples bearing grafted Ru complex (Figure 3) exhibit a drastic decrease in N$_2$ uptake and surface area (10–70%, Table 1) due to both the presence of quite large amounts of the comparatively bulky organometallic molecules and to bridging silane moieties on the surface of the mesoporous channels. The parent MCM-41 and MCM-48 samples exhibit narrow pore-size distributions with average pore diameters of 2.7 and 2.4 nm, respectively. The grafted materials exhibit a broader pore size distribution (1.4–3.0 nm) and also display a decrease in surface area and unit cell parameter (see Table 1) compared to parent MCM-41 and MCM-48.[10e] The decrease of the unit-cell value and the broad pore-size distribution evidences that the organometallic complexes in the grafted mesoporous samples are mainly located on internal surfaces of the mesoporous materials.[9–11] The TEM images (see Figure 4) of the grafted samples (SM-41SNHRuG, and SM-48SNHRuG) provide strong evidence that the mesoporous structure of the support retains its long-range ordering[9,10] throughout the grafting process and that the channels remain accessible. The ED pattern of the grafted samples shows the reflection of the (100) plane, which further supports the presence of long-range ordering in the samples, even after blocking of some pores by linker molecules and Ru complexes.
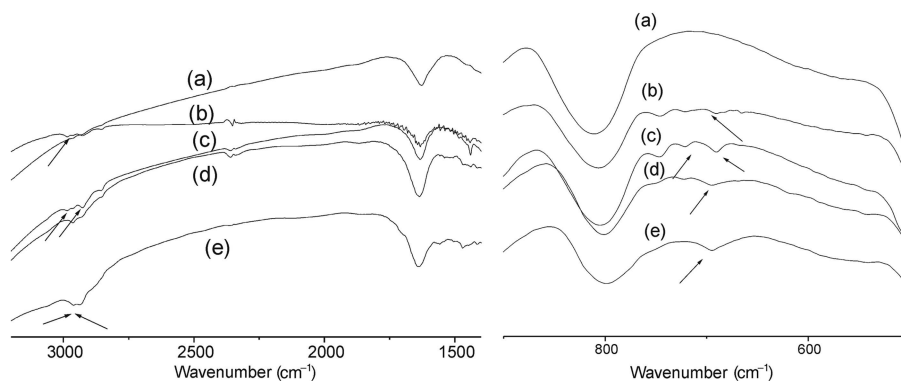
Figure 2   FT-IR spectra of (a) MCM-41, (b) HAM-41RuG, (c) HAM-48RuG, (d) SM-41SNHRuG and (e) SM-48SNHRuG
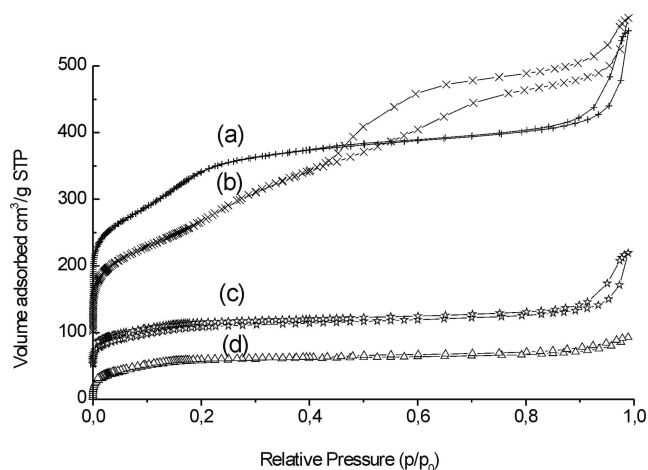
Figure 3 N_2 adsorption–desorption isotherms of (a) HAM-41RuG, (b) HAM-48RuG, (c) SM-41SNHRuG, and (d) SM-48SNHRuG.
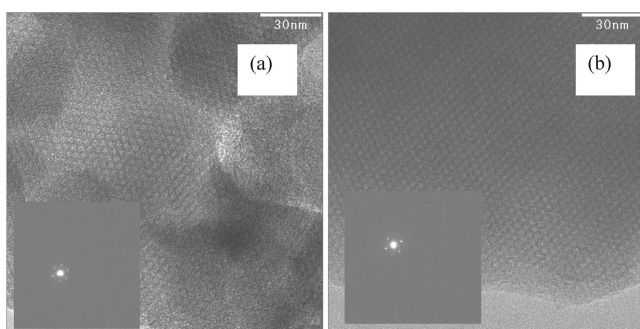
Figure 4 TEM image and electron-diffraction pattern of (a) SM-41SNHRuG and (b) SM-48SNHRuG

The parent MCM-48 and the grafted samples were examined by solid-state ^{29}Si CP MAS NMR spectroscopy. The parent MCM-48 exhibits two broad elaborate resonances (Figure 5a) in the ^{29}Si CP MAS NMR spectrum at δ = –113.0 and –103.8, assigned to Q_4 and Q_3 species of the silica framework, respectively, $[Q_n = Si(OSi)_n(OH)_{4-n}]$.[9–11] A weak shoulder is also observed at δ = –94.5 for the Q_2 species. After grafting of complex **1** (Figure 5b) there is an increase of Q_4 and Q_3 intensities and a corresponding Q_2 species decrease, which indicates the successful grafting of complex **1** on AlMCM-41/48. The grafting of aminopropyltrimethoxysilane $[(MeO)_3Si(CH_2)_3NH_2]$ also results in the reduction of the Q_2 and Q_3 resonances, and a concurrent increase of the Q_4 resonance. The changes of the Q_4 resonances are more pronounced due to the higher loading. This is consistent with an esterification of the isolated silanol groups (single and geminal) by nucleophilic substitution at the silicon atoms in the organic ligand.[10] The ^{29}Si CP MAS NMR spectra also exhibit two additional signals at δ = –61.4 and –67.4 assigned to T_2 and T_3 organosilica species, respectively, $[T_m = RSi(OSi)_m(OR)_{3-m}]$. However, as expected, the silylated but not Ru-containing and the Ru-grafted samples show (nearly) identical ^{29}Si CP MAS NMR signals, thus indicating that during the in situ grafting process there is no significant change in

the silicon environment. The observed changes in the ^{29}Si CP MAS NMR spectra arise during the silylating procedure using the aminosilane. The ^{1}H MAS NMR spectra of all the samples show signals at δ = 7.7, 7.2, 6.8 and 1.92, characteristic for the Cp, phenyl and methyl groups of complex **1**. The additional peak at 3.30 for SM-41SNHRuG, and SM-48SNHRuG samples is due to the residual OMe groups attached to silane. All the above-described studies support the successful grafting of complex **1** in the mesoporous channels of MCM-41 and MCM-48.
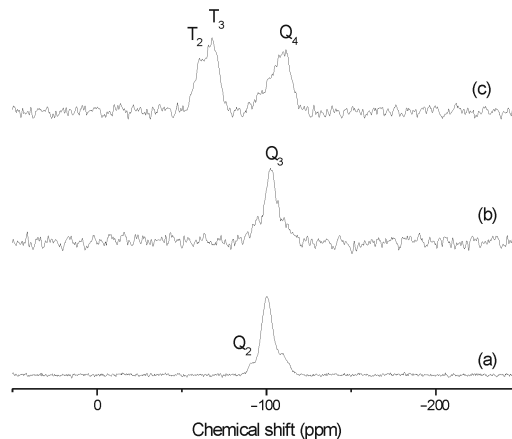

Figure 5 ^{29}Si CP MAS NMR spectra of (a) MCM-48, (b) HAM-48RuG, and (c) SM-48SNHRuG.

The TG-MS spectra of HAM-41RuG and SM-41SNHRuG (Figure 6) show about 2.5% and 8.5% weight loss up to 1000 °C, due to decomposition of the $Cp^*Ru(PPh_3)_2$ moiety. The observed mass values $m/z^+ = 77$ and 15 correspond to a phenyl and methyl group of complex **1**, which once again confirms the presence of Ru-complexes in the mesoporous channels. In addition, the presence of mass values $m/z^+ = 14$ and 31 in the SM-41SNHRuG sample are characteristic of methylene (CH_2) and residual methoxy groups of silane.

Applying materials with the grafted complex **1** to benzaldehyde olefination with ethyl diazoacetate (EDA) and triphenylphosphine (PPh_3) (Scheme 3) shows two different types of behavior: SM-41SNHRuG and SM-48SNHRuG display almost no catalytic activity with only trace amounts of (*E*)-**2** being formed, with azine **3** as the major product along with traces of **4**; HAM-41RuG and HAM-48RuG afford olefin yields of 15–20% with an *E/Z* ratio of 99:1. The reaction profiles for the latter materials follow a similar trend: a steady olefin formation until ca. one hour after the start of the reaction followed by no further olefin yield improvement during the rest of the reaction time with concomitant build-up of azine **3**.

According to Scheme 3, the pores of the grafted materials have to accommodate not only the quite bulky complex **1**, bearing two PPh_3 ligands, but an extra PPh_3 for oxygen abstraction of the aldehyde and the resulting triphenylphosphine oxide. The N_2 adsorption–desorption data show that in the case of SM41-SNHRuG and SM48-SN-
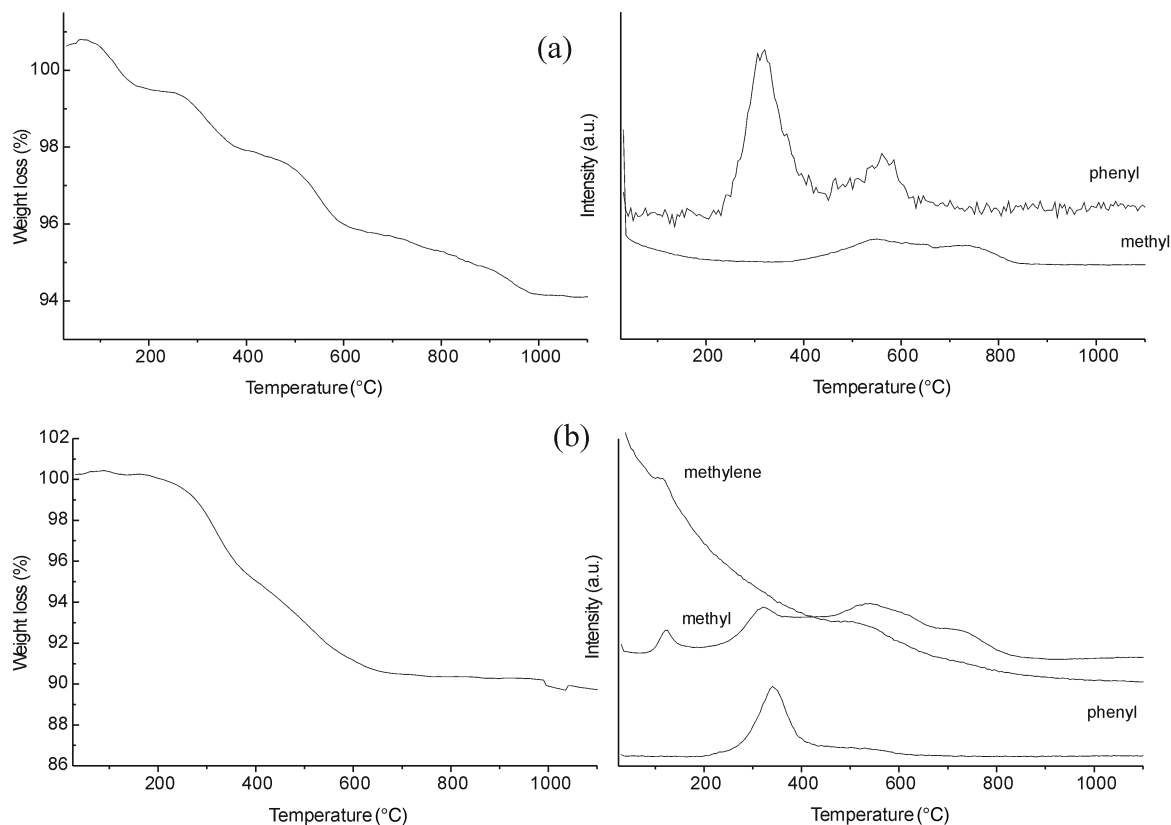
Figure 6   TG-MS spectra of (a) HAM-41RuG and (b) SM-41SNHRuG

HRuG with complex loadings of 0.9% and 1.8%, respectively, already 75% of the pores are occupied, thus preventing the incoming PPh3 to reach the catalytic center and blocking any catalytic activity. Materials HAM-41RuG and HAM-48RuG, having much lower Ru complex loadings (0.2% and 0.35%, respectively) are initially catalytically active, but after a while (ca. 1 hour of reaction time) the pores are also blocked, preventing the olefination reaction to further proceed. To overcome these problems it is essential to use supporting materials with bigger pore dimensions and to keep the catalyst loading at low levels to avoid complete pore blocking.

The grafted MCM-41 and MCM-48 materials were additionally applied in the styrene cyclopropanation with EDA at room temperature (Scheme 2) and the results are displayed in Table 2. The grafted materials show medium to good activity in the cyclopropanation reaction, when compared to their homogeneous phase counterpart, with prevailing *E*-selectivity, as expected. The three-dimensional pore structure of MCM-48 is beneficial to the reaction, since these grafted materials achieve better performances than the ones grafted on the one-dimensional MCM-41, regarding both activity and *E*-selectivity, for both immobilization techniques. The yields are considerably higher when complex **1** is grafted through the aminosilane linker, especially for SM-48SNHRuG, rather than when immobilized by direct grafting. The higher catalyst loadings might be the cause for these activity differences. The fact that SM-48SNHRuG is considerably more active and selective than complex **1**, when used in homogeneous catalysis conditions, led to its reuse for two additional runs. There is a slight decrease of activity during the second run, but the fact that it remains active for the third run shows that the grafted compound **1** is stable on the surface and remains active for several catalytic cycles. The slight decrease in activity and selectivity in the recycled catalyst is possibly due to some adsorption of organic molecules on the channels of the mesoporous materials. The inexistence of Ru in the filtrate, as well as the absence of catalytic conversion in the filtrate, indicate that the catalyst is stable and the leaching of complex **1** is insignificant. The
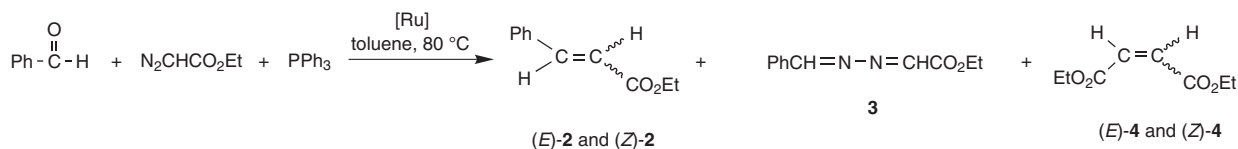
Scheme 3

reaction can be conveniently performed in CH_2Cl_2 avoiding the use of styrene itself as solvent for the reaction, which is favorable regarding both starting materials usage and product isolation. There are also no C–H insertion side products, which were observed in homogeneous catalysis.[4b] These features are obvious advantages over the homogeneous catalysis system.

Table 2 Cyclopropanation of Styrene over Cp*Ru Complex Grafted Samples[a]

Samples	Yield (%)[b]	Product Distribution	
		cis	*trans*
Compound **1**	56.3	31.3	68.7
H-AM-41RuG	28.1	39.4	60.6
H-AM-48RuG	36.0	34.8	65.2
SM-41SNHRuG	49.2	22.4	77.6
SM-48SNHRuG 1st run	68.5	8.4	91.6
SM-48SNHRuG 2nd run	56.8	27.0	73.0
SM-48SNHRuG 3rd run	55.5	26.9	72.1

[a] Catalyst/styrene = 1:250.
[b] Isolated yield based on EDA conversion; time = 16 h; r.t.

Further work is currently in progress in our group to immobilize this and other ruthenium complexes in mesoporous materials with larger pore dimensions in order to avoid pore blocking during the reactions as observed for the aldehyde olefination.

In summary, a ruthenium complex of formula (η^5-C_5Me_5)Ru(PPh$_3$)$_2$Cl (**1**) was successfully grafted on the surface of mesoporous MCM-41 and MCM-48 either by direct grafting or by an aminosilane linker. The obtained materials are stable and the structures of the supporting materials remain intact. The heterogenized catalysts are active in the cyclopropanation of styrene with EDA, especially SM-48SNHRuG whose activity and selectivity are both higher than in homogeneous catalysis. This catalyst is active even after several recycling cycles, with just a slight activity decrease.

IR spectra were recorded on a PerkinElmer FT-IR spectrometer using KBr pellets as IR matrix. Thermogravimetric analyses were performed using a Netzsch TG209 system at a heating rate of 10 K min^{-1} under argon. Elemental analyses were measured at the Mikroanalytisches Labor of the TU München (M. Barth). Powder XRD data were collected with a Philips X'pert diffractometer using Cu-Kα radiation filtered by Ni. N$_2$ adsorption–desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41/48 samples were degassed at 723 K overnight to a residual pressure of ca. 10–24 mbar. A degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume (VP) was estimated from the N$_2$ uptake at p/p$_0$ = 0.95, using the liquid N$_2$ density of

0.8081 g cm^{-3}. The pore-size-distribution curves (PSD, the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using the method based on the area of the pore walls. Transmission electron microscopy (TEM) was recorded on a Jeol JEM2010 operated at 120 kV. ^{29}Si CP MAS NMR spectra were recorded at 59.627 MHz, with a (7.05 T) Bruker Avance 300 spectrometer, with 5.5 μs ^{1}H 90° pulses, 8 ms contact time, and a spinning rate of 5 kHz and 4 s recycle delays. ^{1}H MAS NMR spectra were recorded at 300 MHz using a Bruker Avance 300 spectrometer with 3.0 s ^{1}H 90° pulses and a spinning rate of 8 kHz.

The following materials, colloidal silica (SiO$_2$), fumed silica (SiO$_2$), hexadecyltrimethylammonium bromide (CTABr), polyoxyethylene(4)laurylether (Brij-30), tetramethylammonium hydroxide (TMAOH, 25 wt%), aluminum nitrate nonahydrate [Al(NO$_3$)$_3$·9H$_2$O] and NaOH were used without purification for the synthesis of the mesoporous materials.

Na-AlMCM-41
Na-AlMCM-41 with a Si/Al (molar) ratio of 100 was synthesized as described in the literature,[10d] having a typical molar gel composition of 1 SiO$_2$:0.2 NaOH:0.27 TMAOH:0.27 CTABr:60 H$_2$O:0.005 Al$_2$O$_3$ as follows: First TMAOH was dissolved in H$_2$O and stirred for 5 min. To this solution fumed silica was slowly added (the resulting solution is designated as A). Another solution, B, was prepared by mixing CTABr and NaOH in distilled H$_2$O and stirred for about 30 min. Both these solutions, A and B, were mixed together and a gel formed. Aluminum nitrate was then added to the resulting clear solution and the mixture was stirred for 1 h. The pH of the resulting gel was adjusted to 11.0 with dilute H$_2$SO$_4$, and was aged for 16 h. The gel was transferred into a polyethylene bottle and kept in an oven under air for crystallization at 373 K for 3 d. The obtained solid product was washed repeatedly, filtered, and dried at 353 K for 12 h. The thus synthesized sodium form of the material (Na-AlMCM-41) was calcined at 823 K for 2 h in N$_2$ followed by drying under air for 6 h.

Na-AlMCM-48
Na-AlMCM-48 was prepared[10a] by the following procedure with a molar gel composition of 5.0 SiO$_2$:2.5 NaOH:0.87 CTABr:0.13 Brij-30:0.025 Al$_2$O$_3$:400 H$_2$O. First, a surfactant solution mixture was prepared by dissolving both CTABr (7.74 g) and Brij-30 (1.35 g) simultaneously in distilled H$_2$O (60 mL). Then, aq NaOH solution (2.5 g in 5 mL of H$_2$O) was added to the surfactant solution and stirred for 0.5 h. The silica solution was then added to the solution described above and the mixture was shaken vigorously for 0.5 h. The resulting gel was kept at 373 K for crystallization. After 2 d, the mixture was cooled to r.t. (298 K) and the pH of the solution was adjusted to 10 with AcOH. This procedure was repeated twice. Then, aluminum nitrate was added to the gel and the mixture was kept at 373 K for 7 d. The resulting final product was filtered and washed with EtOH–H$_2$O mixture and dried in an oven at 373 K, followed by calcination in air at 823 K for 6 h.

Protonated Forms of Na-AlMCM-41 and Na-AlMCM-48
The calcined sample (ca. 1 g) was treated with aq 1 M NH$_4$NO$_3$ solution (30 mL) and refluxed at 343 K for 6 h. The process was repeated thrice to obtain maximum exchange and then washed, filtered and dried at 373 K. It was then calcined at 773 K in air for 6 h to obtain H-AlMCM-41 and H-AlMCM-48.

Aminosilanes on Siliceous Mesoporous Materials
First siliceous mesoporous materials were prepared by a similar procedure as Na-AlMCM-41 and Na-AlMCM-48 without addition of aluminum salt. The SiMCM-41 and SiMCM-48 (1 g) were preactivated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove phy-

sisorbed H_2O. The physisorbed H_2O-free SiMCM-41 and SiMCM-48 (1 g) was silylated with aminopropyltrimethoxysilane ($[(MeO)_3Si(CH_2)_3NH_2]$, 2 mmol) using anhyd toluene (30 mL) as solvent under argon at 383 K for 24 h. Then excess of silane was removed by filtration followed by washing several times with CH_2Cl_2. The resulting solid was dried under vacuum at r.t. The samples silylated with aminopropyltrimethoxysilane were designated as SM-41SNH, and SM-48SNH, respectively.

Grafting Experiments

These were carried out using standard Schlenk techniques under argon as follows: (η^5-C_5Me_5)RuCl(PPh$_3$)$_2$ (1) was synthesized as described earlier.[4] The mesoporous molecular sieves H-AlMCM-41, H-AlMCM-48 and aminosilane modified molecular sieves SM-41SNH, and SM-48SNH (1 g) were again pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove any physisorbed H_2O. Then, the samples (each 1 g) were treated with complex 1 (0.6 mmol) in anhyd THF (30 mL) under argon. The mixtures were stirred at 313 K for 3 d. The resulting solutions were filtered and the white solids were repeatedly washed with THF until all physisorbed complexes were removed from the surfaces. The washed samples were dried under vacuum at r.t.

Benzaldehyde Olefination

Benzaldehyde (0.318 g, 3 mmol), Ph$_3$P (0.865 g, 3.3 mmol), catalyst (0.01 mmol, based on Ru content), and fluorene (0.2 g, used as internal standard) were dissolved in toluene (15 mL). The mixture was heated to 80 °C and EDA (0.410 g, 3.6 mmol) was added all at once. The reaction was monitored by GC-MS. Yields were determined by GC using a previously recorded calibration curve.

Styrene Cyclopropanation

EDA (0.114 g, 1.0 mmol) in CH_2Cl_2 (2.0 mL) was slowly added (addition time 1 h) to a CH_2Cl_2 (4 mL) solution of styrene (0.520 g, 5.0 mmol) and catalyst (0.02 mmol, based on Ru content). The reaction was followed by GC-MS. After completion of the reaction, the products were identified by GC-MS and isolated by flash chromatography. Yields were determined based on EDA.

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