DOI: 10.1002/adsc.200600627

Hybrid Organic-Inorganic Materials Derived from a Monosilylated Hoveyda-type Ligand as Recyclable Diene and Enyne Metathesis Catalysts

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Received: December 6, 2006

Dedicated to the memory of Professor Marcial Moreno-Mañas

Abstract: The synthesis of a monosilylated Hoveyda-type monomer is described as well as the preparation of several organic-inorganic hybrid materials derived from it by sol-gel processes and by anchoring to commercial silica gel and MCM-41. The resulting materials were treated with first and/or second generation Grubbs' catalyst to generate Hoveyda–Grubbs' type alkylidene ruthenium complexes covalently bonded to the silica matrix. These materials are efficient recyclable catalysts for the ring-closing metathesis reaction of dienes and enynes, even for the formation of tri- and tetrasubstituted olefins.

Keywords: catalyst immobilization; metathesis; organic-inorganic hybrid materials; ruthenium; sol-gel process

Introduction

Olefin metathesis is a mild, efficient and selective method for the C=C bond formation, widely used by organic chemists for the preparation of a great variety of compounds.[1] In recent years, ring closing enyne metathesis has also been explored, which provides 1-vinylcycloalkene derivatives from acyclic enynes in an atom economical process.[2] The enormous success of metathesis reactions during the last years is due to the development of several well-defined metal alkylidenes. The second generation Grubbs' ruthenium catalysts[3] **1b** and **c** (Figure 1) and specially the Hoveyda–Grubbs' catalysts[4] **2a** and **b** (Figure 1) show enhanced reactivity, stability and recovery profiles compared to the first generation Grubbs' catalyst **1a** (Figure 1), the chelating styrenic ligands playing a role in such improvements. Several research groups have prepared and tested reusable metathesis catalysts,[5] one of the most used recycling strategies being the immobilization of a robust and stable alkylidene complex on a polymeric insoluble support. Filtration at the end of the reaction allows an easy separation of the product and recovery of the catalyst, avoiding time-consuming chromatography. Anchoring of ruthenium alkylidenes of type **1** and **2** to the polymeric matrix has been performed *via* phosphine exchange,[6] *via* the N-heterocyclic carbene ligand,[7] through halogen exchange,[8] or *via* alkylidene exchange (*boomerang*-type catalysts).[9] The efficiency of *boomerang*-supported catalysts increases notably when Hoveyda-

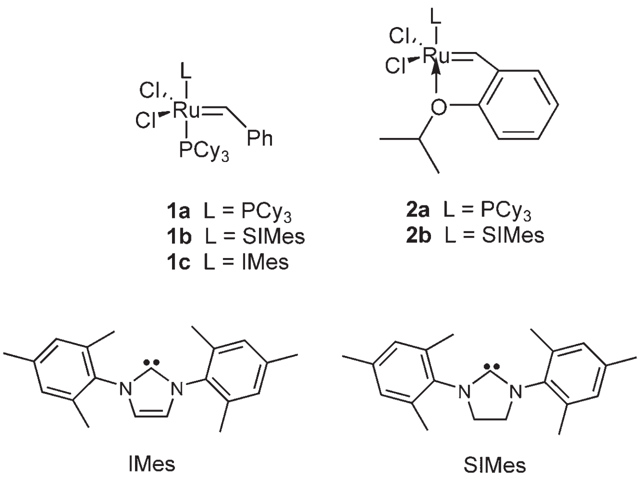


Figure 1. Ruthenium alkylidene metathesis catalysts.

type chelating ligands are used.[10] Insoluble organic polymers are the supports most frequently used, although anchoring to soluble poly(ethylene glycol)[10a–c] and some recent examples of silica-bound alkylidene ruthenium complexes have also been described.[6b, 7c–e,8b–d,10f,g,j,k]

In this context, silica-based inorganic polymers can present high surface areas. Furthermore, the hybrid organic-inorganic materials formed by catalytic species covalently anchored to silica have chemical, mechanical and thermal stability superior to that of organic polymers. Most of the above-mentioned examples about silica-bound catalysts refer to anchoring to porous and non-porous silicas and to non-porous glass monoliths. The sol-gel hydrolytic condensation[11–13] of suitable organoalkoxysilanes is a convenient method to synthesize solid hybrid materials with targeted properties.[14–16] Recently, we have reported[10k] the preparation and the activity as recyclable metathesis catalysts of bridged silsesquioxanes synthesized from a bis-silylated Hoveyda-type monomer *via* the sol-gel process. This was the first example in the literature for the use of a bis-silylated ligand in a sol-gel process for the preparation of reusable metathesis catalysts. As our previous catalyst[10k] did not bear the classical chelating isopropoxy groups present in most of the recyclable Hoveyda-type ligands, which could remain the best choice for activity and recyclability, we have performed further studies with supported catalysts derived from a monosilylated Hoveyda-type monomer featuring this bulkier group which we present in this work. Both strategies for material preparation, grafting and sol-gel co-gelification with TEOS, were tested for comparison. Grafting does not allow the control of either the concentration of the organic groups or their distribution, which depends on the number of surface silanol groups, on the diffusion of reagents through the pores channels, and on steric factors, some organic moieties remaining on the surface of the pores. The co-gelification of a silylated monomer with TEOS would allow a higher and controllable loading of the organic moiety throughout the matrix, which results in a supported catalyst different from those prepared by grafting.

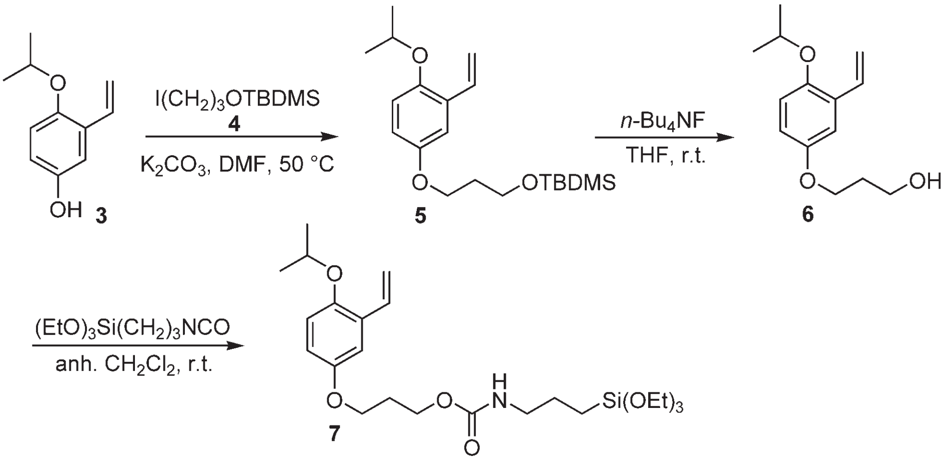
Results and Discussion

Monomer Synthesis

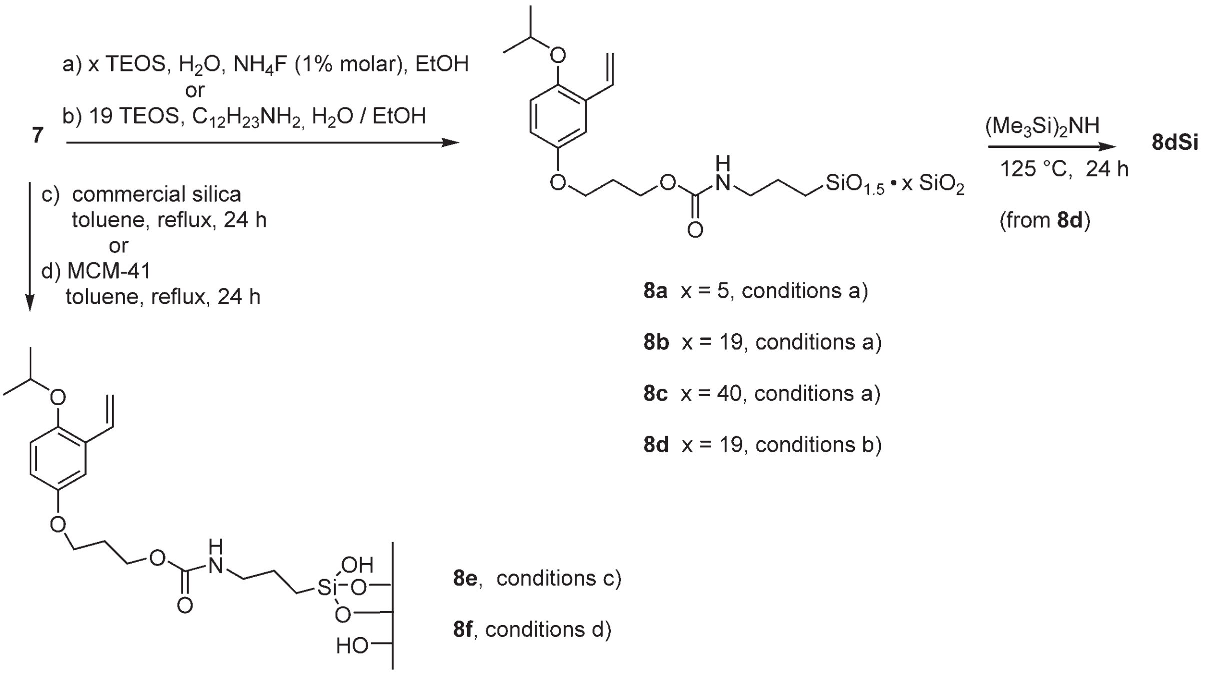
The monosilylated monomer **7** used for the synthesis of hybrid materials was prepared as summarized in Scheme 1. 4-Isopropoxy-3-vinylphenol (**3**)[10a] was reacted with iodide **4** in anhydrous DMF at 50 °C in the presence of potassium carbonate to afford the protected alcohol **5** in 70 % yield. Subsequent deprotection of **5** with tetrabutylammonium fluoride gave the alcohol **6** in 99 % yield, which was treated with commercial 3-(isocyanatopropyl)triethoxysilane in anhydrous dichloromethane at room temperature to afford the desired carbamate **7** in 90 % yield.

Preparation of Hybrid Materials and Catalysts

Several hybrid materials were prepared from the monosilylated carbamate **7** (Scheme 2). Co-gelification with different amounts of tetraethoxysilane (5:1, 19:1 and 40:1 as molar ratios of TEOS:**7**) in ethanol at room temperature under nucleophilic conditions (stoichiometric water, 1 % molar of ammonium fluoride as catalyst) afforded materials **8a–c**. Co-gelification of **7** with TEOS (19:1 as molar ratio of TEOS:**7**) was also performed with dodecylamine acting both as basic catalyst and surfactant,[17,18] giving rise to material **8d.** On the other hand, anchoring of **7** to a commercial silica gel[19] and to a mesostructured silica MCM-41[20] under standard conditions (in refluxing toluene



Scheme 1. Preparation of the monosilylated Hoveyda-type monomer **7.**



Scheme 2. Preparation of hybrid silica materials **8a–f** and **8dSi** from **7.**

for 24 h) afforded materials **8e** and **8f**, respectively. Finally, hydrosilylation of surface hydroxy groups of material **8d** was achieved by heating at 125 °C with excess hexamethyldisilazane, leading to **8dSi**. Capping of the silanol groups was performed in order to test if an improved material could be obtained.

The materials were studied by several techniques (^{29}Si CP-MAS NMR, BET surface area measurements, p-XRD). The ^{29}Si solid state NMR data, some textural properties and the ligand loading of hybrid materials **8** are summarized in Table 1.

^{29}Si CP-MAS NMR of **8b–e** confirmed the covalent bonding of the organic moiety to the matrix by the appearance of T^2 and T^3 signals due to the ligand in addition of the characteristic Q^3 and Q^4 signals due to the condensed TEOS. The ^{29}Si CP-MAS spectrum of **8dSi** showed a signal around 11.9 ppm corresponding to the $-SiMe_3$ unit and the intensity of the Q^3 absorption (−103.1) decreased considerably (Figure 2).

A very low surface area was observed for hybrid material **8a** (5:1). However, increasing the amount of TEOS in the co-gelification process led to highly porous materials, the corresponding BET surface area values for **8b** (19:1) and **8c** (40:1) being 584 and 747 m^2/g, respectively. The use of dodecylamine as catalyst and surfactant[17,18] gave a material **8d** with even a higher porosity (893 m^2/g), a narrower pore size distribution and a worm-like structure observed by transmission electron microscopy (TEM) and powder X-ray diffraction (p-XRD) (Figure 3). The grafted material **8f** has a much higher BET surface area (915 m^2/g) and narrower pore size distribution (20–35 Å) than **8e** (324 m^2/g, 30–150 Å) as expected. The ordered hexagonal structure characteristic of MCM-41 was maintained in **8f** as confirmed by TEM.

The materials **8a–d** prepared by sol-gel show higher loading amount of organic ligand than materials **8e–f** made by anchorage (Table 1). Moreover, the sol-gel

Table 1. Some analytical and textural data of hybrid materials **8**.

8	^{29}Si CP MAS NMR							S_{BET} [m^{2}g^{-1}]	Pore Diam. (Å)	mmol **8** [g]
	Me_3SiO	T^1	T^2	T^3	Q^2	Q^3	Q^4			
8a	-	-	-	-	-	-	-	< 1	-	1.21
8b	-	-	−59.3	−65.4	−90.9	−101.0	−108.7	584	37	0.485
8c	-	-	−59.3	−65.6	−90.9	−100.9	−110.0	747	44	0.349
8d	-	-	−53.7	−65.0	-	−100.7	−109.3	893	18–23	0.557
8dSi	11.9			−66.7		−103.1	−111.2			
8e		-48.8	-56.0		-91.6	-101.0	-110.1	324	30-150	0.271
8f								915	20–35	0.164

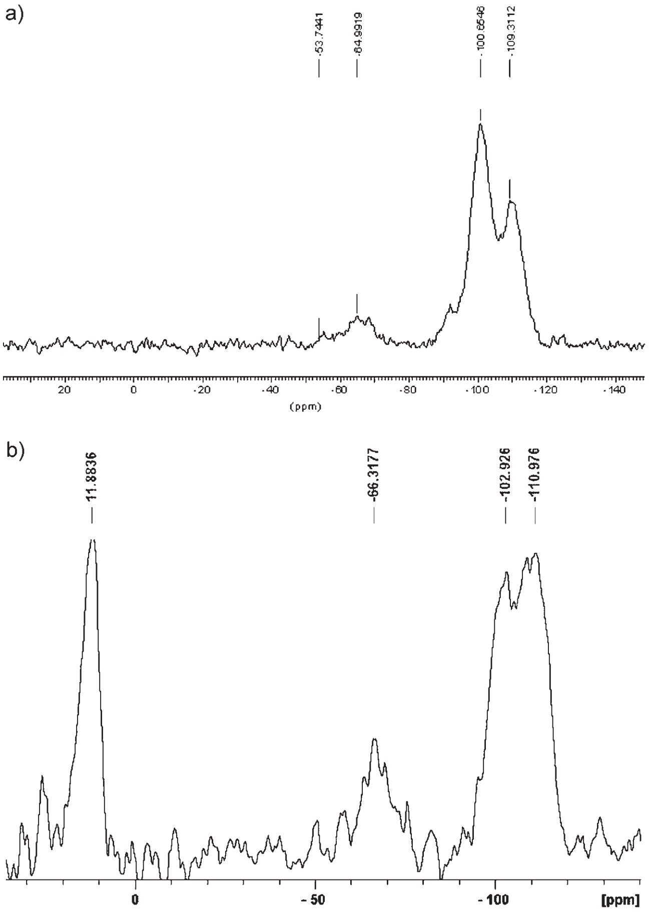


Figure 2. Solid state CP-MAS NMR: a) ^{29}Si of **8d** and b) ^{29}Si of **8dSi**.

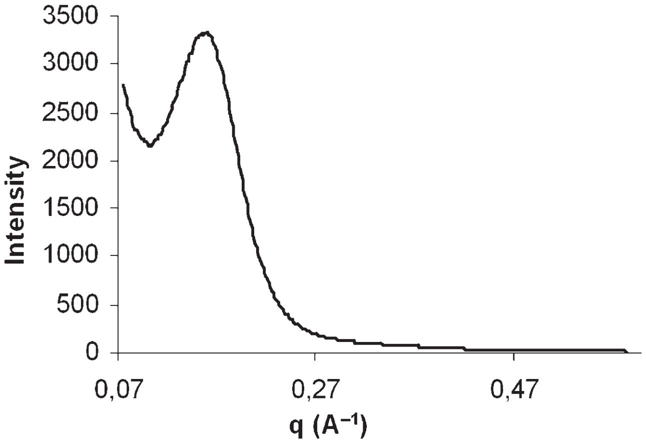
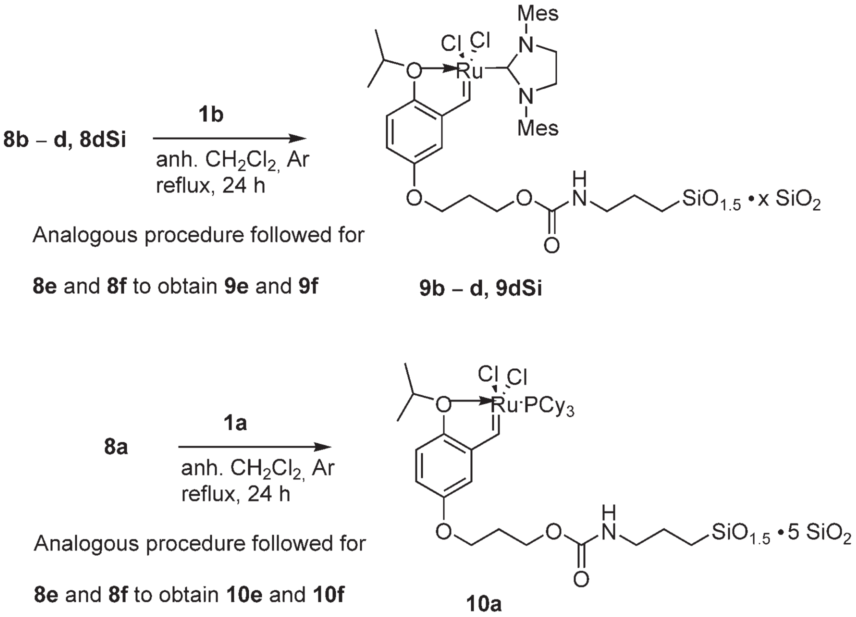


Figure 3. Powder X-ray diffraction of material **8d**.

cogelification allows a higher control of the distribution of organic ligands into the pores and throughout the matrix. With respect to the porosity, the BET surface area increases with the dilution of organic ligand in the co-gelification process and also with the addition of surfactant, achieving for **8d** a value similar to that of **8f**, material derived from grafting to mesostructured MCM-41. A narrower pore size distribution is obtained in organized materials (**8d**, **8f**) as expected (Table 1).

The materials **8b–f** and **8dSi** were charged with the metal by treatment with the second generation Grubbs' catalyst **1b** (0.95–1.06 equivs.) in refluxing anhydrous and degassed dichloromethane for 24 h (Scheme 3). Materials **8a**, **8e** and **8f** were also treated with the first generation Grubbs' catalyst **1a** following



Scheme 3. Preparation of ruthenium heterogeneous catalysts **9a–f, 9dSi, 10a**, **10e** and **10f** from the corresponding materials **8.**

an analogous procedure (Scheme 3). Ruthenium contents in materials **9b–f**, **9dSi**, **10a**, **10e** and **10f** were determined by inductively coupled plasma (ICP) analysis, the results being summarized in Table 2.

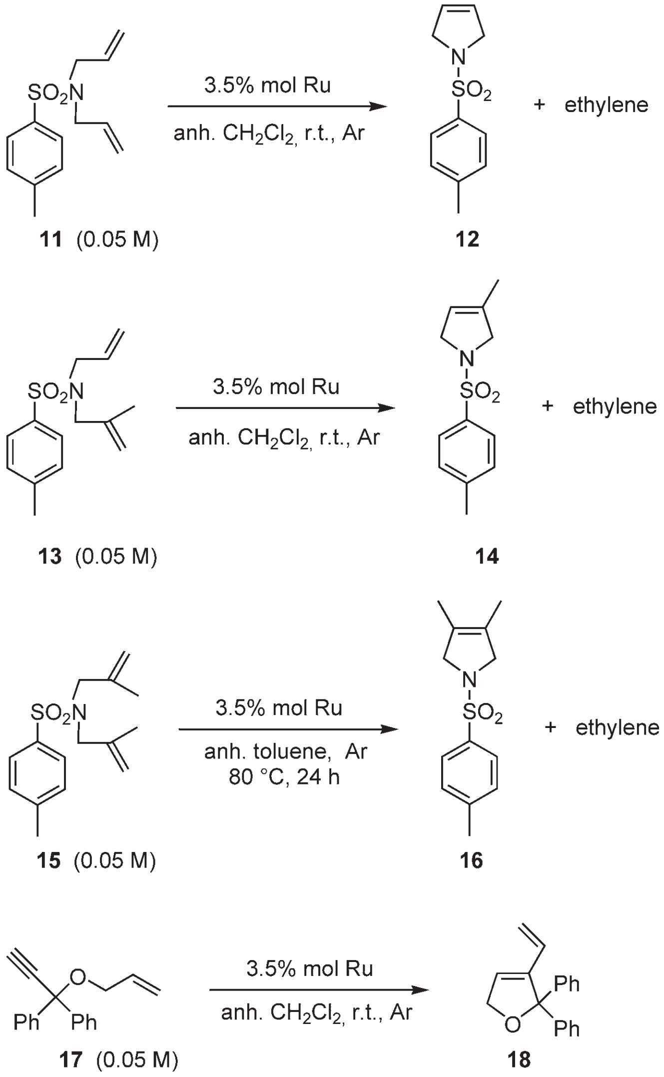
Table 2. Ruthenium contents in hybrid materials **9** and **10**.

9	% Ru	mmol Ru [g]
9b	1.34	0.133
9c	1.41	0.139
9d	2.43	0.240
9dSi	1.71	0.169
9e	0.84	0.083
9f	1.19	0.118
10a	0.37	0.036
10e	0.90	0.089
10f	1.44	0.142

Assay of Supported Catalysts in Diene and Enyne Ring-Closing Metathesis Reactions

Supported catalysts **9b–f**, **9dSi**, **10a**, **10e** and **10f** have been tested in the ring-closing metathesis reaction of *N*,*N*-diallyl-4-methylbenzenesulfonamide (**11**)[21] to give 1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (**12**)[21] (Scheme 4). In all cases the reaction was performed in dichloromethane (0.05 M for **11**) at room temperature under an inert atmosphere, using a 3.5% molar concentration of catalyst for the times indicated in Table 3 (the disappearance of **11** was monitored by GC). Filtration and evaporation of the solvent afforded pure **12**, together with small amounts of **11** in some cases (the molar ratio **12**/**11** was determined by ^{1}H NMR). Heterogeneous catalysts were reused directly in the next run, five cycles being performed for each catalyst. The reaction times were maintained the same in order to follow the efficiency of the catalyst upon recycling.

As we see in Table 3, the activity of catalysts **9** was clearly superior to that of catalysts **10**, as expected. Thus, faster reactions and better recyclability were obtained with supported catalysts **9** prepared with the second generation Grubbs' complex **1b**. For this reason, treatment of the remaining materials **8** with the first generation Grubbs' complex **1a** was not performed.



Scheme 4. Diene and enyne metathesis reactions tested with recyclable catalysts **9** and **10.**

Table 3. Results for the RCM of **11** to **12** with supported catalysts **9** and **10**.

Run	**9b**		**9c**		**9d**		**9dSi**		**9e**		**9f**		**10a**[a]		**10e**		**10f**	
	t [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]
1	5	97	3	96	1.5	94	6	97	3	96	4	97	16	97	24	94	17	>98
2	5	>98	3	>98	1.5	96	6	>98	3	93	4	95	16	96	24	93	16	>98
3	5	97	3	>98	1.5	91	6	97	3	96	4	90	16	89	24	94	16	94
4	5	95	3	>98	1.5	83	6	90	3	85	4	84	16	78	24	88	16	77
5	5	91	3	96	1.5	72	6	84	3	73	4	72	16	60	24	80	16	51
6	24	93	6	95	4	90	24	87	4	90	24	90						

[a] A 2% molar Ru was used.

If we compare catalysts **10**, **10a** prepared by sol-gel was slightly better than **10f** obtained by grafting to mesostructured MCM-41 (note that only a 2% molar of ruthenium was used for **10a**). They react both faster than **10e** but they have no clear advantage over **10e** in terms of recyclability at the fourth and fifth run.

In the case of catalysts **9**, we observe that higher dilution of the organic ligand in the inorganic matrix improves the activity of the catalysts (**9c**$>$**9b**). Ordered materials give also faster reactions (compare **9b** and **9d** with the same 19:1 ratio), although this does not result in better recyclability. Silylation of the Si–OH groups of the material decreases the activity of the catalyst (slower reactions) (compare **9d** and **9dSi**) but it seems to improve the reusability (better yields in the fourth and fifth runs). Catalysts **9e** and **9f** prepared by grafting show similar results. It is worthy of mention that their reusability is worse than that of the material **9c** prepared by sol-gel.

As general trends, we can conclude that the activity and recyclability of the supported catalysts are improved with a higher dilution of the organic ligand in the matrix in the sol-gel derived materials and also with the introduction of some ordering in these materials, both factors increasing the BET surface area and facilitating the diffusion of the reactants. Sol-gel derived materials give better catalytic properties than materials derived from grafting, which must be more related to the intrinsic structural differences between both types of materials than to the properties such as surface area, pore size and pore size distribution.

The ring-closing metathesis reaction to afford **12** has been performed in the literature with several recyclable immobilized catalyst types under different conditions.[9c,e,10a,h,j–m,22] Mauduit[22a] used imidazolium-tagged first and second generation Grubbs' Ru complexes in ionic liquid as immobilizing solvent (2.5% molar Ru, BMIM.PF_6, 60 °C, 45 min) obtaining full conversions up to 5 cycles. In a similar work, Yao[21b] (1% molar Ru, BMIM·PF_6-CH_2Cl_2 1:9, 45 °C, 1 h, 0.2M) achieved 17 cycles with conversions from $>$98% to 90%. Gibson[22c] reported the encapsulation of second generation Grubbs' catalyst in polystyrene (2.5% molar Ru, water/methanol 4:1, 50 °C, 1.5 h) affording 4 cycles with decreasing yields (92% to 40%). Curran[22d] performed the reaction with fluorous versions of first and second generation Grubbs–Hoveyda catalysts (5% molar Ru, refluxing dichloromethane, 2 h) achieving 7 cycles with full conversions or 5 cycles with conversions up to 94%. Recently, Lee[22e] has attached a second generation Grubbs–Hoveyda catalyst on gold clusters, achieving 4 cycles with full conversions (5% molar Ru, dichloromethane, 40 °C, 1.5 h). Yao[10a] described soluble polymers of first generation Grubbs–Hoveyda catalyst anchored to PEG used up to 3 cycles (5% molar Ru, refluxing dichloromethane, 2 h) with slightly decreasing conversions (96 to 92%). Blechert[10h] has used a soluble polymer of second generation Grubbs-Hoveyda catalyst derivative generated by ROMP, achieving 5 cycles with full conversions (1% molar Ru, dichloromethane, room temperature, 1 h). But the simplest method to isolate and recycle the catalyst is by its immobilization in a solid insoluble support. Barrett[9c] has anchored a second generation Grubbs' catalyst to polystyrene by the alkylidene moiety and has described 5 cycles with decreasing conversions (100 to 42%) (2.5% molar Ru, toluene, 50 °C, 2 h). Nolan[9e] has reported the same type of catalysts anchored to polydivinylbenzene resins, performing 3 cycles (5% molar Ru, dichloromethane, room temperature, 1 h) with modest GC yields (30–38%). By anchoring a second generation Hoveyda–Grubbs catalyst to silica gel, Blechert[10j] reported recently 4 cycles with decreasing conversions ($>$99% to 68%) (0.15% molar Ru, dichloromethane, room temperature, 1 h). Bannwarth[10l] performed the reaction in $scCO_2$ (five cycles) with several solid phase-bound Hoveyda-type catalysts (2.5% of catalyst, 40 °C, 150 bar, 24 h) with conversions going from 95% to 84% and 93 to 57% in the best cases. Grela[10m] has very recently achieved a non-covalent immobilization of Hoveyda–Grubbs catalyst to polymeric phases by means of electrostatic binding, performing five cycles of the reaction with gradual loss of activity (5% of catalyst, dichloromethane, room temperature, 24 h; from 85% to 52%). We have recently described[10k] several recyclable organic-inorganic hybrid materials prepared from a bis-silylated Hoveyda-type monomer by sol-gel methologies. Our conditions[10k] for the preparation of **12** were milder than those used in most of the precedent works (percentage of catalyst and/or reaction temperature and/or reaction time), achieving a recyclability better than in most of the aforementioned solid insoluble supports (3.5% molar Ru, dichloromethane, room temperature, 1.5 h, five cycles from $>$98 to 66%). Our present results with materials **9** offer a clear improvement in terms of recyclability. In analogous conditions (3.5% molar Ru, dichloromethane, room temperature, 1.5 h) we obtain a 72% conversion in the fifth run with material **9d**. In other cases, although lower reaction rates are observed, the reusability is better (in the fifth run we achieved 96% conversion in 3 h for **9c** and 91% conversion in 5 h for **9b**). Although some recycling strategies involving the reaction performed under homogeneous conditions[10h,22a,b,d,e] remain superior, the advantage of simplicity in the separation procedure must be taken into account.

Then, we turned our attention to more challenging dienes, **13** and **15**, from which the corresponding trisubstituted and tetrasubstituted olefins, **14** and **16**, could be obtained (Scheme 4). Complete conversion of **13** to 3-methyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole, **14**, with second generation Grubbs' catalyst **1b** under homogeneous conditions (3.5% molar, 0.05 M of **13**, dichloromethane, room temperature) required less than 3 h. This transformation was only tested with the supported catalyst **9c**, which had shown a very good performance for the diene **11**. Excellent results were obtained, outlined in Scheme 4 and Table 4. Complete conversions were achieved in 7 h with only a slight decrease in activity at the fifth cycle (93% conversion).

Table 4. Results for the RCM of **13** to **14** with catalyst **9c**.

Run	**9c**	
	t [h]	Conv. [%]
1	7	94
2	7	>98
3	7	>98
4	7	96
5	7	93
6	15	98

Only Mauduit[22a] has assayed this reaction with immobilized catalysts using imidazolium-tagged Hoveyda-type complexes in room temperature ionic liquids as solvents and immobilizing agents (5% molar Ru, BMI·NTf_2, 40 °C, 4 h; 6 runs, from 98 to 50% conversion in the best case, 74% at the fifth run). The reusability of our catalyst **9c** is superior and the work-up very advantageous.

In our hands, treatment of *N,N*-bis(2-methylallyl)-4-methylbenzenesulfonamide (**15**) with second generation Grubbs' catalyst **1b** under homogeneous conditions (3.5% molar Ru, 0.05 M of **15**, toluene, 80 °C, 7 h) gave 90% conversion to 3,4-dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (**16**). Supported catalysts **9c** and **9d** were also assayed under analogous conditions. Catalyst **9c** afforded an 88% conversion (^{1}H NMR) after 24 h (Scheme 4 and Table 5). The conversion decreased to 29% after the same reaction time in the second cycle. The catalytic material **9d** provided better results, giving complete conversion after 22 h. The attempted recycling gave 93 and 31% conversion in the second and third cycles. Structuring of the hybrid material seems to offer an advantage in the recycling for a challenging tetrasubstituted olefin.

Table 5. Results for the RCM of **15** to **16** with catalysts **9c** and **9d**.

Run	**9c**		**9d**	
	t [h]	Conv. [%]	*t* [h]	Conv. [%]
1	24	88	22	>98
2	24	29	22	93
3	–	–	22	31

We should mention that very few reports appear in the literature about this challenging ring closing metathesis reaction. Grela[10e] found a 45% conversion in a homogeneous process with a modified Hoveyda–Grubbs second generation catalyst (5% molar Ru, refluxing dichloromethane, 16 h), describing also a failed attempt to obtain **16** with a supported catalyst (0% conversion in the second cycle, 5% molar Ru, refluxing dichloromethane, 16 h). Mauduit[22a] describes this reaction using imidazolium-tagged ruthenium complexes in room temperature ionic liquids, but no recycling could be achieved (5% molar Ru, BMI·PF_6/toluene, 60 °C, 7 h, 65% conversion in the first cycle, 0% conversion in the second cycle). We have recently reported[10k] this reaction with silica-based hybrid materials derived from a bis-silylated Hoveyda-type monomer, with very poor conversions at the second cycle. The use of monomer **7** featuring an isopropoxy group improves, as we have mentioned before, the recyclability properties of the sol-gel derived materials. Thus, our results with tetrasubstituted olefin **15** constitute the first successful example of recycling for the obtention of **16**. Few reports can be found about the recyclability of ruthenium catalysts in the preparation of other tetrasubstituted alkenes, such as (*Z*)-4,5-dimethyl-1-tosyl-2,3,6,7-tetrahydro-1*H*-azepine[10b,22b] and diethyl 3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate.[9e] For the first substrate, Yao[10b] described 3 cycles using a soluble second generation Grubbs–Hoveyda carbene complex immobilized on poly(ethylene glycol) (5% molar Ru, 0.4 M, refluxing dichloromethane, 18 h, 82% conversion at the third cycle) and the same author[22b] performed 2 cycles with an imidazolium-tagged second generation Hoveyda–Grubbs catalyst (4% molar Ru, BMIM·PF_6-CH_2Cl_2, 1:1, 45 °C, 16 h, 79% and 78% conversion). For the second substrate, Nolan[9e] achieved 4 cycles with modest yields with a second generation Grubbs' catalyst anchored to a cross-linked polystyrene through the alkylidene ligand (5% molar Ru, toluene, 80 °C, 3 h, GC yields between 36 and 22%).

On the other hand, the ring-closing enyne metathesis was successfully performed on 1-allyloxy-1,1-diphenyl-2-propyne (**17**) to give 2,2-diphenyl-3-vinyl-2,5-dihydrofuran (**18**) with our heterogeneous catalysts **9c**, **9d** and **9dSi** (Scheme 4 and Table 6). Good conversions (*ca.* 100%) were obtained in short reaction times (2 to 4.5 h) with 3.5% molar of catalyst in anhydrous dichloromethane (0.05 M of **17**) at room temperature, and up to three or five cycles were performed with only slightly decreasing conversions. Under analogous homogeneous conditions with the second generation Grubbs' catalyst **1b** we obtained full conversion in 1 h.

Table 6. Results for the RCM of **17** to **18** with catalysts **9c, 9d** and **9dSi**.

Run	**9c**		**9d**		**9dSi**	
	t [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]
1	4.5	>98	3	>98	2	>98
2	4.5	81	3	94	2	>98
3	4.5	92	3	92	2	>98
4	4.5	93	3	91		
5	4.5	90	3	88		
6	24	100				

This enyne ring-closing metathesis process has been described in the literature[23,24] using several catalysts and homogeneous conditions, but there is no report about recycling and about using polymer-supported catalysts for the obtention of **18** except our own recent work[10k] and the report of Grela,[10m] which do not mention the recycling with this enyne substrate.

A blank test suggested by one referee has been performed with catalyst **9e** in the RCM reaction of diene **11**. A suspension of **9e** in anhydrous dichloromethane was stirred at room temperature under inert atmosphere for three hours. Then the solid was filtered and **11** was added to the filtrate. The solution was stirred at room temperature under nitrogen atmosphere for 3 h and the solvent was evaporated. The ^{1}H NMR analysis of the residue showed a mixture of **11** and **12** in a molar ratio 97:3. This small percentage of conversion must be due to a homogeneous process derived from some leaching of the heterogeneous catalyst. However, we must take into account that, due to the release-return mechanism[9,10] operating in these Hoveyda–Grubbs *boomerang*-type catalysts, the reaction takes place in homogeneous phase with the soluble ruthenium carbenic species released from the supported catalyst after the addition of the substrate, which are then recaptured by the polymer. In this respect, another experiment was performed with catalyst **9b** in the RCM reaction of the same diene **11**. A mixture of **11** (0.132 mmol) and **9b** (0.00456 mmol Ru) in anhydrous dichloromethane (2.5 mL) was stirred at room temperature under inert atmosphere for 15 min. The insoluble catalyst was filtered under nitrogen and the resulting filtrate containing an 18% of **12** (^{1}H NMR monitoring) was left under stirring at room temperature for 5 h. The solvent was evaporated and the residue was analysed by ^{1}H NMR, showing a 23% of **12**. The small increase in the conversion is due to the expected soluble catalytic species remaining in solution after the filtration.

Conclusions

In summary, we have described the synthesis of a monosilylated Hoveyda-type monomer **7**, the preparation of several hybrid organic-inorganic materials **8** by sol-gel co-gelification with TEOS and by anchorage to commercial and mesostructured MCM-41, then the obtention of the corresponding Grubbs–Hoveyda-type ruthenium complexes **9** and **10**, and their evaluation as recyclable catalysts in the ring-closing metathesis reactions of dienes **11**, **13** and **15** and enyne **17**. As expected, supported catalysts **9** prepared from the second generation Grubbs' complex **1b** gave much higher reaction rates than catalysts **10** prepared from the first generation Grubbs' complex **1a** in the RCM on *N,N*-diallyl-4-methylbenzenesulfonamide (**13**). They offer milder conditions and better recyclability than other previous works based on catalysts anchored to insoluble solid supports. The RCM on more challenging substrates, *N*-allyl-*N*-(2-methylallyl)-4-methylbenzenesulfonamide (**13**). and *N,N*-bis(2-methylallyl)-4-methylbenzenesulfonamide (**15**) gave rise to trisubstituted and tetrasubstituted alkenes **14** and **16**, respectively, good yields and recyclability being achieved for the trisubstituted olefin. Two very successful runs have been performed for the tetrasubstituted one, constituting the first report of recycling for this substrate. Our materials are also good recyclable catalysts for the ring-closing enyne metathesis performed on 1-allyloxy-1,1-diphenyl-2-propyne (**17**). This is the second case described in the literature about recycling in this ring-closing enyne metathesis reaction, the first one being recently reported by us.[10k] In all cases, materials prepared from sol-gel are superior to those coming from anchorage to commercial silica or mesostructured MCM-41. Further investigations are underway with other structurally modified ligands in order to get improved activity and reusability.

Experimental Section

General Remarks

When required, experiments were carried out with standard high-vacuum and Schlenk techniques. Solvents were dried and distilled just before use. Ammonium fluoride and *N,N*-bis(trimethylsilyl)amine were purchased from Aldrich, 3-(triethoxysilyl)propyl isocyanate was purchased from Lancaster, tetraethyl orthosilicate, potassium *tert*-butoxide and tetrabutylammonium fluoride were purchased from Acros. The second generation Grubbs' catalyst has been purchased from Aldrich and also from Acros. IR data were obtained in the following spectrophotometer: Bruker Tensor 27 with ATR Golden Gate. The solution NMR spectra were recorded on a Bruker AC-250 (^{1}H and ^{13}C). Chemical shifts (δ, ppm) were referenced to Me_4Si (^{1}H, ^{13}C). The abbreviations used are s for singlet, d for doublet, dd for double doublet, t for triplet, q for quartet, quint for quintuplet, sept for septet and m for multiplet. The CP-MAS ^{29}Si solid state NMR spectra were recorded on a Bruker FT-AM 400. The repetition time was 5 seconds with contact times of 5 milliseconds. Surface areas were determined by Brunauer-Emmett-Teller

(BET) method on a Micromeritics Gemini III 2375 analyzer, and the average pore diameter was calculated by the BJH method. ESI mass spectra were acquired using a Navigator quadrupole instrument, operating in the positive ion mode (ES+) at a probe tip voltage of 3 kV. HR-MS have been determined at SCAI-Unidad de Espectrometría de Masas at the Universidad de Córdoba. Elemental analysis have been performed at the Servei d'Anàlisi Química of the Universitat Autònoma de Barcelona or at the Serveis Científico-Tècnics of the Universitat de Barcelona. The content of ruthenium was determined at the Serveis Científico-Tècnics of the Universitat de Barcelona by inductively coupled plasma (ICP) techniques.

1-(*tert*-Butyldimethylsiloxy)-3-iodopropane (**4**)[25] was prepared in two steps from 3-chloro-1-propanol as reported.[26] Mesostructured silica MCM-41 was prepared following the standard procedure.[20] Methyltriphenylphosphonium iodide was synthesized from methyl iodide and triphenylphosphine. 4-Isopropoxy-3-vinylphenol, **3**, was prepared as reported.[10a] The dienes **11** and **15**, and enyne **17** were prepared as previously described by us.[10k] The diene **13**[27] was synthesized from *N*-allyl-*p*-toluenesulfonamide[28] and 3-bromo-2-methyl-1-propene.

Synthesis of 2-Isopropoxy-5-(3-*tert*-butyldimethylsiloxypropoxy)styrene (5)

Potassium carbonate (1.940 g, 14.04 mmol) was added to a stirred solution of 4-isopropoxy-3-vinylphenol (**3**; 1.0 g, 5.62 mmol) and 1-(*tert*-butyldimethylsiloxy)-3-iodopropane (**4**; 1.687 g, 5.62 mmol) in DMF (44 mL). The mixture was stirred overnight at 40 °C under argon. Upon cooling at room temperature water was added (30 mL) and the solution was extracted with petroleum ether (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was chromatographed through silica gel (hexane/dichloromethane, 3:1, as eluent) to afford **5** as an oil; yield: 1.37 g (70 %). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.10–6.97$ (m, 2 H), 6.82 (d, 1 H, $J = 8.8$ Hz), 6.75 (dd, 1 H, $J = 8.8$, 2.8 Hz), 5.72 (dd, 1 H, $J = 18.0$ Hz, 1.2 Hz), 5.27 (dd, 1 H, $J = 11.25$, 1.2 Hz), 4.40 (sept, 1 H, $J = 6.1$ Hz), 4.03 (t, 2 H, $J = 6.2$ Hz), 3.80 (t, 2 H, $J = 6.2$ Hz), 1.97 (quint, 2 H, $J = 6.2$ Hz), 1.33 (d, 6 H, $J = 6.1$ Hz), 0.93 (s, 9 H), 0.09 (s, 6 H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 153.2$, 149.1, 131.7, 129.1, 116.8, 114.5, 113.7, 111.8, 72.0, 64.8, 59.4, 32.3, 25.7, 22.0, 18.1, −5.6; IR (ATR): $\nu = 2953$, 2928, 2856, 1488, 1471, 1253, 1208, 1100, 834, 774 cm^{-1}; MS: $m/z = 351$ ($M^+ + 1$) (13), 350 (M^+) (3), 293 ($M^+ - [C_4H_9]$) (23), 251 (72), 235 ($M^+ - [C_6H_{15}Si]$) (11), 233 (20), 193 ($M^+ - [C_6H_{15}Si] - [C_3H_6]$) (100), 177 (74), 167 (86), 96 (10), 88 (8), 73 (28), 59 (10), 43 (11).

Synthesis of 3-(4-Isopropoxy-3-vinylphenoxy)propan-1-ol (6)

A solution of tetrabutylammonium fluoride (4.314 g, 14 mmol) in anhydrous THF (15 mL) was added under argon to a stirred solution of 2-isopropoxy-5-(3-*tert*-butyldimethylsiloxypropoxy)styrene (**5**; 2.322 g, 6.62 mmol) in anhydrous THF (20 mL). The mixture was stirred for 2 h at room temperature under argon. Water was added (50 mL) and extractions with distilled diethyl ether (3 × 50 mL) were performed. The combined organic layers were washed with water (2 × 40 mL) and saturated aqueous NaCl (30 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum to afford **6** as a yellow oil; yield: 1.55 g (99 %). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.11–7.00$ (m, 2 H), 6.85 (d, 1 H, $J = 8.9$ Hz), 6.78 (dd, 1 H, $J = 8.9$, 2.9 Hz), 5.73 (dd, 1 H, $J = 17.7$, 1.4 Hz), 5.26 (1 H, $J = 11.1$, 1.4 Hz), 4.41 (sept, 1 H, $J = 6.1$ Hz), 4.13 (t, 2 H, $J = 5.9$ Hz), 3.86 (t, 2 H, $J = 5.9$ Hz), 2.23 (s, 1 H), 2.04 (quint, 2 H, $J = 5.9$ Hz), 1.33 (d, 6 H, $J = 6.1$ Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 152.9$, 149.4, 131.6, 129.1, 116.8, 114.6, 113.9, 111.8, 72.1, 66.1, 60.2, 31.9, 22.0; IR (ATR): $\nu = 3334$, 2973, 1575, 1488, 1425, 1383, 1282, 1207, 1108, 1058, 995, 954, 907, 851, 807 cm^{-1}; MS: $m/z = 236$ (M^+) (21), 194 (38), 136 (100), 107 (21), 91 (5), 77 (12), 65 (4), 43 (12), 41 (12); HR-MS: $m/z = 236.1412$ (calcd. for $C_{14}H_{20}O_3$: 236.1395).

Synthesis of *O*-{3-[(3-vinyl-4-isopropoxy)phenoxy]-propyl} *N*-(3-Triethoxysilylpropyl) Carbamate (7)

Freshly distilled 3-(triethoxysilyl)propyl isocyanate (1.9 mL, 0.99 g mL^{-1}, 7.22 mmol) was added dropwise *via* syringe under argon to **6** (1.18 g, 4.99 mmol) in anhydrous dichloromethane (7 mL). The mixture was stirred under argon at room temperature for 5 days (^{1}H NMR monitoring). The solvent was removed under vacuum and excess isocyanate was distilled off (100 °C, 1.7 mbar). Anhydrous diethyl ether (4 mL) was added to the residue, the solution was filtered under nitrogen atmosphere and the solvent was evaporated, to give **7** as a pale yellow oil; yield: 2.17 g (90 %). ^{1}H NMR (250 MHz $CDCl_3$): $\delta = 7.03–6.98$ (m, 2 H), 6.82 (d, 1 H, $J = 8.8$ Hz), 6.75 (dd, 1 H, $J = 8.8$, 2.8 Hz), 5.71 (dd, 1 H, $J = 17.9$, 1.4 Hz), 5.24 (dd, 1 H, $J = 11.1$, 1.4 Hz), 5.02 (m, 1 H), 4.37 (sept, 1 H, $J = 5.9$ Hz), 4.24 (t, 2 H, $J = 6.1$ Hz), 4.01 (t, 2 H, $J = 6.3$ Hz), 3.82 (q, 6 H, $J = 7.0$ Hz), 3.17 (apparent q , 2 H, $J = 6.4$ Hz), 2.06 (m, 2 H), 1.63 (m, 2 H), 1.31 (d, 6 H, $J = 6.1$ Hz), 1.22 (t, 9 H, $J = 7.0$ Hz), 0.63 (t, 2 H, $J = 8.0$ Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 156.3$, 152.9, 149.3, 131.6, 129.1, 116.7, 114.6, 113.8, 111.7, 72.0, 64.7, 61.2, 58.1, 43.1, 28.9, 23.0, 21.9, 18.0, 7.4; IR (ATR): $\nu = 3341$, 2973, 2927, 2883, 1704, 1525, 1489, 1426, 1385, 1371, 1279, 1243, 1209, 1165, 1101, 1074, 997, 953, 852, 772 cm^{-1}; HR-MS: $m/z = 483.2650$ (calcd. for $C_{24}H_{41}NSiO_7$: 483.2652).

Preparation of Hybrid Material 8a

A solution of ammonium fluoride (60 μL of a 1 M solution, 0.060 mmol of fluoride, 3.33 mmol of water) and distilled and deionized water (0.414 mL, 23 mmol) in anhydrous ethanol (6 mL) was added to a solution of **7** (0.483 g, 1.0 mmol) and TEOS (1.040 g, 5.0 mmol) in anhydrous ethanol (6 mL). The mixture was stirred manually for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation ocurred after few minutes and the gel was allowed to age for 2 days, after which it was powdered and washed successively several times with water and then with ethanol. The solid was dried under vacuum (10^{-2} mmHg, room temperature, overnight), affording **8a** as a white powder; yield: 0.620 g. $S_{BET} < 1$ m^2 g^{-1}; elemental analysis found: C 25.22, H 4.05, N 1.70, Si 24.50.

Preparation of Hybrid Material 8b

A solution of ammonium fluoride (100 μL of a 1 M solution, 0.100 mmol of fluoride, 5.56 mmol of water) and distilled and deionized water (0.7 mL, 38.9 mmol) in anhydrous ethanol (5 mL) was added to a solution of **7** (0.240 g, 0.5 mmol) and TEOS (1.997 g, 9.6 mmol) in anhydrous ethanol (5 mL). The mixture was stirred manually for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation ocurred after few minutes and the gel was allowed to age for 5 days, after which it was powdered and washed successively several times with water and then with ethanol. The solid was dried under vacuum (1 mmHg, room temperature, overnight), affording **8b** as a white powder; yield: 0.751 g. $S_{BET}=584\ m^2g^{-1}$; IR (KBr): $\nu=3428$, 2982, 1699, 1538, 1492, 1086, 957, 801 cm^{-1}; ^{29}Si CP-MAS NMR: $\delta=-59.3$ (T^2), -65.4 (T^3), -90.9 (Q^2), -101.0 (Q^3), -108.7 (Q^4); elemental analysis found: N 0.68.

Preparation of Hybrid Material 8c

A solution of ammonium fluoride (200 μL of a 1 M solution, 0.200 mmol of fluoride, 11.1 mmol of water) and distilled and deionized water (1.0 mL, 55.6 mmol) in anhydrous ethanol (10 mL) was added to a solution of **7** (0.241 g, 0.50 mmol) and TEOS (4.183 g, 20.1 mmol) in anhydrous ethanol (10 mL). The mixture was stirred manually for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation ocurred after few minutes and the gel was allowed to age for 5 days, after which it was powdered and washed successively several times with water and then with ethanol. The solid was dried under vacuum (1 mmHg, room temperature, overnight), affording **8c** as a white powder; yield: 1.501 g. $S_{BET}=747\ m^2g^{-1}$; IR (KBr): $\nu=3215$, 2981, 2901, 1700, 1490, 1222, 1035, 956, 801 cm^{-1}; ^{29}Si CP-MAS NMR: $\delta=-59.3$ (T^2), -65.6 (T^3), -90.9 (Q^2), -100.9 (Q^3), -110.0 (Q^4); elemental analysis found: C 11.26, H 2.55, N 0.49, Si 33.10.

Preparation of Hybrid Material 8d

A solution of dodecylamine (0.40 g, 2.16 mmol) in ethanol (10 mL) was added to distilled and deionized water (30 mL) and stirred for 30 min. Compound **7** (0.239 g, 0.5 mmol) and TEOS (1.981 g, 9.62 mmol) were added. The mixture was stirred at room temperature for 24 h. The formed solid was filtered and left to dry at air overnight. Then it was powdered and extracted with ethanol in a Soxhlet for 48 h. The solid was washed with ethanol and dried at atmospheric pressure, affording **8d** as a white powder; yield: 0.763 g. $S_{BET}=893\ m^2g^{-1}$; IR (KBr): $\nu=3430$, 2982, 1701, 1491, 1205, 1079, 957, 797 cm^{-1}; ^{29}Si CP-MAS NMR: $\delta=-53.7$ (T^2), -65.0 (T^3), -100.7 (Q^3), -109.3 (Q^4); elemental analysis found: C 14.96, H 2.37, N 0.78, Si 28.0.

Preparation of Hybrid Material 8dSi

A suspension of **8d** (0.254 g) in *N,N*-bis(trimethylsilyl)amine (12 mL) was heated under argon at 125 °C for 24 h. After cooling, the solid was filtered and washed with ethanol (3 times), acetone (3 times) and diethyl ether (3 times), then it was dried under vacuum (1 mm Hg, 70 °C, overnight), affording **8dSi** as a white powder; yield: 0.259 g; IR (KBr): $\nu=3444$ (residual), 2962, 1717, 1492, 1095, 847, 758, 457 cm^{-1}; ^{29}Si CP-MAS NMR: $\delta=11.9$ (Me_3SiO), -66.7 (T^3), -103.1 (Q^3), -111.2 (Q^4); elemental analysis found: C 19.31, H 3.55, N 0.84.

Preparation of Hybrid Material 8e

Activated silica gel (silicagel ultrapure, 60–200 μm, 60 Å, ref: 36006 ACROS, 4.024 g, 67.1 mmol SiO_2) was added to a solution of **7** (0.650 g, 1.34 mmol) in toluene (30 mL). The mixture was refluxed for 24 h. The solid was filtered and washed successively with toluene, ethyl acetate (twice) and dichloromethane (twice), and dried under vacuum (1 mmHg, room temperature, overnight), affording **8e** as a slightly yellow powder; yield: 4.332 g. $S_{BET}=324\ m^2g^{-1}$; ^{29}Si CP-MAS NMR: $\delta=-48.8$, -56.0, -91.6, -101.0, -110.1; elemental analysis found: C 6.00, H 1.26, N 0.38.

Preparation of Hybrid Material 8f

Mesostructured MCM-41 (0.443 g, 7.38 mmol SiO_2) was added to a solution of **7** (0.0713 g, 0.148 mmol) in toluene (20 mL). The mixture was refluxed for 24 h with a Dean–Stark apparatus. The solid was filtered and washed with acetone, then it was placed in a Soxhlet and extracted with acetone for 4 h., filtered and dried under vacuum (10^{-2} mmHg, room temperature, overnight), affording **8f** as a white powder; yield: 0.380 g. $S_{BET}=915\ m^2g^{-1}$; elemental analysis found: C 5.33, H 1.74, N 0.23, Si 37.26.

Preparation of Hybrid Catalyst 9b

Anhydrous and degassed dichloromethane (15 mL) was added under argon to a stirred mixture of **8b** (0.298 g, 0.485 mmol ligand/g, 0.145 mmol) and Grubbs' second generation catalyst **1b** (0.128 g, 0.151 mmol, 1.05 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **9b** as a green powder; yield: 0.292 g; elemental analysis found: C 17.80, N 1.31, Ru (ICP) 1.34.

Preparation of Hybrid Catalyst 9c

Anhydrous and degassed dichloromethane (20 mL) was added under argon to a stirred mixture of **8c** (0.500 g, 0.349 mmol ligand/g, 0.174 mmol) and Grubbs' second generation catalyst **1b** (0.157 g, 0.185 mmol, 1.06 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, romm temperature, overnight) to obtain **9c** as a green powder; yield: 0.491 g; elemental analysis found: C 14.66 %, H 2.13 %, N 0.87, Ru (ICP) 1.41.

Preparation of Hybrid Catalyst 9d

Anhydrous and degassed dichloromethane (20 mL) was added under argon to a stirred mixture of **8d** (0.350 g, 0.557 mmol ligand/g, 0.195 mmol) and Grubbs' second generation catalyst **1b** (0.162 g, 0.185 mmol, 0.95 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **9d** as a green powder; yield: 0.381 g; elemental analysis found: C 21.73, H 3.16, N 1.38, Ru (ICP) 2.43.

Preparation of Hybrid Catalyst 9dSi

Anhydrous and degassed dichloromethane (14 mL) was added under argon to a stirred mixture of **8dSi** (0.219 g, 0.603 mmol ligand/g, 0.132 mmol) and Grubbs' second generation catalyst **1b** (0.111 g, 0.131 mmol, 0.98 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **9dSi** as a green powder; yield: 0.221 g; elemental analysis found: C 21.37 %, H 3.31 %, N 1.25, Ru (ICP) 1.71.

Preparation of Hybrid Catalyst 9e

Anhydrous and degassed dichloromethane (7.5 mL) was added under argon to a stirred mixture of **8e** (0.386 g, 0.271 mmol ligand/g, 0.105 mmol) and Grubbs' second generation catalyst **1b** (0.088 g, 0.103 mmol, 0.98 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 5 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **9e** as a green powder; yield: 0.367 g; elemental analysis found: C 10.26, H 1.62, N 0.63, Si 34.5, Ru (ICP) 0.84.

Preparation of Hybrid Catalyst 9f

Anhydrous and degassed dichloromethane (4.5 mL) was added under argon to a stirred mixture of **8f** (0.126 g, 0.164 mmol ligand/g, 0.0207 mmol) and Grubbs' second generation catalyst **1b** (0.018 g, 0.021 mmol, 1.02 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 5 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **9f** as a green powder; yield: 0.117 g; elemental analysis found: C 9.78, H 1.82, N 0.52, Ru (ICP) 1.19.

Preparation of Hybrid Catalyst 10a

Anhydrous and degassed dichloromethane (20 mL) was added under argon to a stirred mixture of **8a** (0.195 g, 1.21 mmol ligand/g, 0.161 mmol) and first generation Grubbs' catalyst **1a** (0.153 g, 0.186 mmol, 1.15 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **10a** as a brown powder; yield: 0.155 g; elemental analysis found: C 27.55, H 3.92, N 1.94, Si 23.1 Ru (ICP) 0.37.

Preparation of Hybrid Catalyst 10e

Anhydrous and degassed dichloromethane (12 mL) was added under argon to a stirred mixture of **8e** (0.743 g, 0.168 mmol ligand/g, 0.125 mmol) and first generation Grubbs' catalyst **1a** (0.121 g, 0.150 mmol, 1.2 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 12 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **10e** as a brown powder; yield: 0.691 g; elemental analysis found: C 10.72, H 1.87, N 0.50, Si 26.6 Ru (ICP) 0.90.

Preparation of Hybrid Catalyst 10f

Anhydrous and degassed dichloromethane (5 mL) was added under argon to a stirred mixture of **8f** (0.170 g, 0.164 mmol ligand/g, 0.028 mmol) and first generation Grubbs' catalyst **1a** (0.028 g, 0.034 mmol, 1.2 equivs.) and the mixture was refluxed under argon for 24 h. The solid was filtered, washed several times with portions of 5 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, overnight) to obtain **10f** as a brown powder; yield: 0.156 g; elemental analysis found: C 10.48, H 2.24, N 0.27, Si 36.27 Ru (ICP) 1.44.

Ring-Closing Metathesis Reaction on *N*,*N*-Diallyl-4-methylbenzenesulfonamide (11) with Supported Catalysts 9 and 10. Synthesis of 1-[(4-Methylphenyl)-sulfonyl]-2,5-dihydro-1*H*-pyrrole (12). Typical Procedure

A solution of **11** (0.1004 g, 0.399 mmol) in anhydrous and degassed dichloromethane (8 mL) was added under nitrogen to **9b** (0.1051 g, 0.133 mmol Ru/g, 0.0140 mmol Ru) and the mixture was stirred under argon at room temperature for 5 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed 4 times with 8 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **12**[21] (0.084 g, the molar ratio **12**/**11** by ^{1}H NMR was 32.7/1, 97 % conversion). The solid catalyst **9b** was dried and reused in the next run.

The same conditions were adopted for the other catalysts **9c–d**, **9dSi** and also for catalysts **10a**, **10e** and **10f**, except the reaction times that are summarized in Table 3 together with the attained conversions.

Ring-Closing Metathesis Reaction on *N*-Allyl-*N*-2-methylallyl-4-methylbenzenesulfonamide (13) with Supported Catalyst 9c. Synthesis of 3-Methyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (14)

A solution of **13** (0.0535 g, 0.202 mmol) in anhydrous and degassed dichloromethane (4 mL) was added under nitrogen to **9c** (0.0508 g, 0.139 mmol Ru/g, 0.00706 mmol Ru) and the mixture was stirred under argon at room temperature for 7 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed 4 times with 4 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **14**[29]

(0.0466 g, the molar ratio **14/13** by ^{1}H NMR was 16.1/1, 94% conversion). The solid catalyst **9c** was dried and reused in the next run.

Ring-Closing Metathesis Reaction on *N,N*-Bis(2-methylallyl)-4-methylbenzenesulfonamide (15) with Supported Catalysts 9. Synthesis of 3,4-Dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (16). Typical Procedure

A solution of **15** (0.0996 g, 0.356 mmol) in anhydrous and degassed toluene (7 mL) was added under nitrogen to **9d** (0.052 g, 0.240 mmol Ru/g, 0.0125 mmol Ru) and the mixture was stirred under argon at 80 °C for 22 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed 4 times with 7 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **16** (0.0862 g, the molar ratio **16/15** by ^{1}H NMR was 66.7/1, >98% conversion). ^{1}H and ^{13}C NMR of **16** were coincident with that described for this compound in the literature.[30] The solid catalyst **9d** was dried and reused in the next run.

The same conditions were adopted for catalyst **9c** except the reaction time (see Table 5).

Ring-Closing Metathesis Reaction on 1-Allyloxy-1,1-diphenyl-2-propyne (17) with Supported Catalysts 9. Synthesis of 2,2-Diphenyl-3-vinyl-2,5-dihydrofuran (18). Typical Procedure

A solution of **17** (0.076 g, 0.306 mmol) in anhydrous and degassed dichloromethane (6 mL) was added under nitrogen to **9c** (0.0769 g, 0.139 mmol Ru/g, 0.0107 mmol Ru) and the mixture was stirred under argon at room temperature for 4.5 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed 4 times with 6 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **18** (0.0732 g, the molar ratio **18/17** by ^{1}H NMR was 81.2/1, >98% conversion), whose spectroscopic data were coincident with that reported in the literature.[23] The solid catalyst **9c** was dried and reused in the next run.

The same conditions were adopted for the other catalysts **9d** and **9dSi** except the reaction times (see Table 4).

Acknowledgements

Financial support from the Ministry of Science and Technology of Spain, Generalitat de Catalunya and Universitat Autònoma de Barcelona (Projects 2002BQU-04002, CTQ2005–01254/BQU and CTQ2006–04204/BQU, SGR2001–00181, SGR2005–00305, PNL2005–10), from the French Ministry of Research and Technology and from the CNRS is gratefully acknowledged.

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