DOI: 10.1002/adsc.200505447

Hybrid-Bridged Silsesquioxane as Recyclable Metathesis Catalyst Derived from a Bis-Silylated Hoveyda-Type Ligand

Xavier Elias,[a] Roser Pleixats,[a,*] Michel Wong Chi Man,[b,*] Joël J. E. Moreau[b]

[a] Chemistry Department, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Spain
Fax: (+34)-93-581-1265, e-mail: roser.pleixats@uab.es
[b] Hétérochimie Moléculaire et Macromoléculaire (UMR-CNRS 5076), Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier cédex 5, France
Fax: (+33)-4-6714-7212, e-mail: michel.wong-chi-man@enscm.fr

Received: November 17, 2005; Accepted: February 2, 2006

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: The synthesis of a bis-silylated Hoveyda-type monomer is described as well as the preparation of several organic-inorganic hybrid materials derived from it by a sol-gel process (with and without tetraethyl orthosilicate) and by anchoring to MCM-41. The resulting materials were treated with second generation Grubbs' catalyst to generate second generation Hoveyda–Grubbs-type alkylideneruthenium complexes covalently bonded to the silica matrix. These materials are recyclable catalysts for the ring-closing metathesis reaction of dienes and enynes.

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

Introduction

Olefin metathesis constitutes a very powerful, mild, efficient and selective method for the rupture and reformation of C–C double bonds, widely used by organic chemists for the synthesis of a great variety of compounds.[1] Ring-closing enyne metathesis has also been explored in recent years, providing 1-vinylcycloalkene derivatives from acyclic enynes in an atom economical process.[2] The enormous success of metathesis reactions during the last decade is due to the development of several well-defined metal alkylidenes. The second-generation Grubbs ruthenium catalysts[3] **1b**, **c** (Figure 1) and specially the Hoveyda–Grubbs catalysts[4] **2a**, **b** (Figure 1) show enhanced reactivity, stability and recovery profiles compared to the first generation Grubbs catalyst **1a** (Figure 1), chelating styrenic ligands playing a role in such improvements. In the last years several research groups have dedicated their efforts to the preparation and testing of 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-type chelating ligands are used.[10] Insoluble organic polymers are the supports most frequently found in the literature, 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]

The above-mentioned examples about silica-bound catalysts refer to anchoring to porous and non-porous silicas and to glass non-porous monoliths. The sol-gel hydrolytic-condensation[11–13] of suitable organo-alkoxysilanes is a convenient method to synthesize solid hybrid materials with targeted properties.[14–16] Several organometallic complexes have been immobilized according to this process to generate heterogeneous hybrid catalysts[17–19] and among these, bridged silsesquioxanes[20,21] appeared as an efficient route to produce these catalysts with a high and controlled loading of the organics due to the preserved covalent Si–C bonds during the mild hydrolysis-condensation reactions.[22] We want to present here our results concerning the preparation, the activity and the recycling of hybrid organic-inorganic silicas containing second-generation Grubbs-Hoveyda-type ruthenium complexes, in the ring-closing metathesis

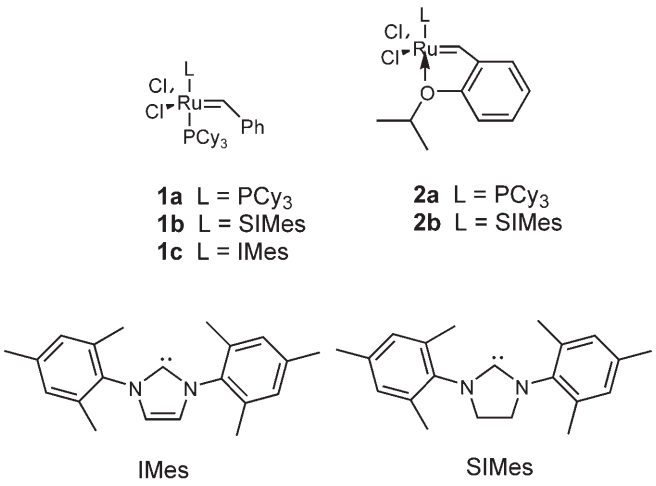


Figure 1. Ruthenium-alkylidene metathesis catalysts.

(RCM) reaction. These heterogeneous catalysts are obtained as bridged silsesquioxanes from a bis-silylated Hoveyda-type monomer *via* the sol-gel process and also by anchoring this monomer to a mesostructured MCM-41.[23]

To our knowledge there is no example in the literature reporting the use of a bis-silylated ligand in a sol-gel process for the preparation of re-usable metathesis catalysts. Grafting does not allow the control of either the loading of organic groups or their distribution, which depends on the number of the surface silanol groups, on the diffusion of reagents through the pore channels, and on steric factors, with some organic moieties remaining on the surface of the pores. The co-gelification of the bis-silylated monomer with TEOS would allow the organic moiety to be integrated in the matrix, which could result in a supported catalyst different from those prepared by grafting. Moreover, the hydrolysis of this bis-silylated ligand alone (without TEOS) can also afford a hybrid material with a regular and stoichiometric distribution of the organics throughout the silicate network.

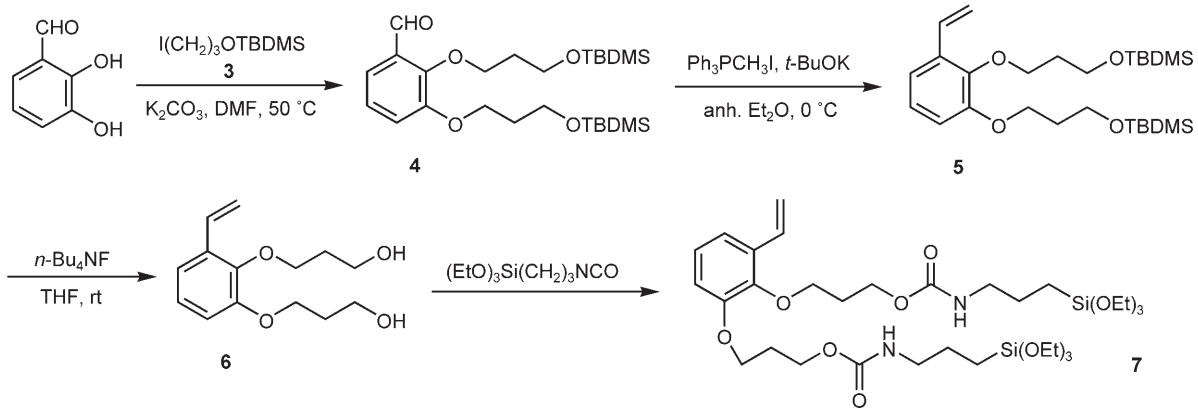
Results and Discussion

Monomer Synthesis

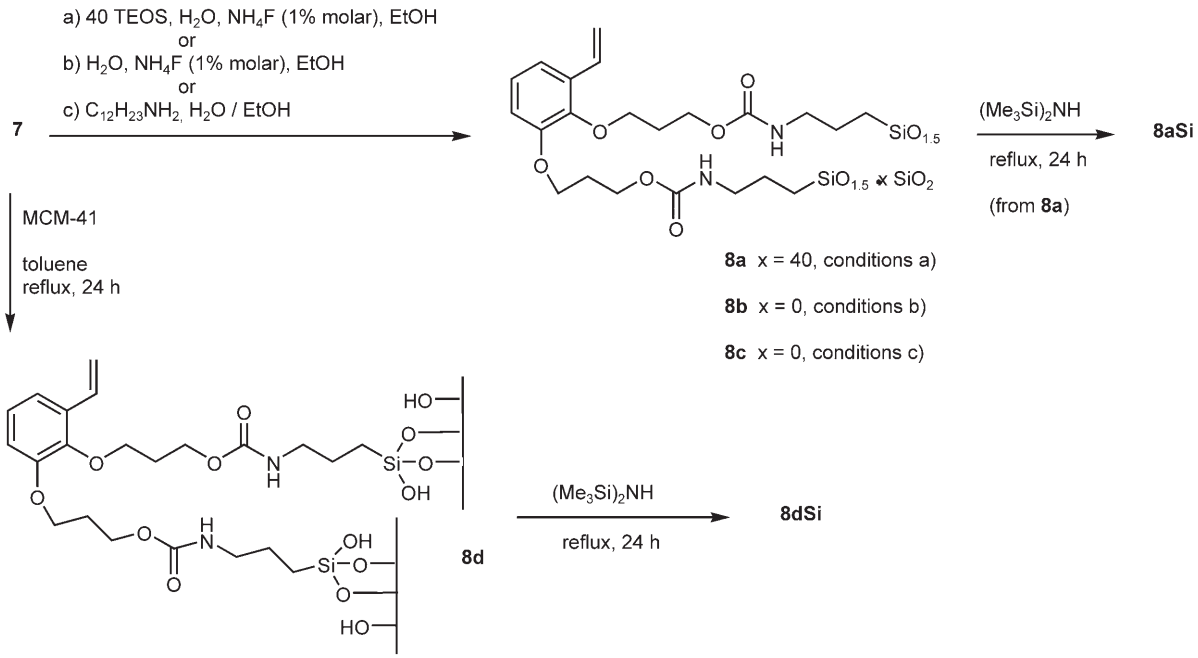
The bis-silylated monomer **7** used for the preparation of hybrid materials was synthesized as summarized in Scheme 1. Commercial 2,3-dihydroxybenzaldehyde was treated with two equivalents of iodide **3** in DMF at 50 °C in the presence of potassium carbonate to afford the protected diol **4** in 88% yield. Subsequent reaction with triphenylphosphonium methylide in anhydrous diethyl ether at 0 °C provided the styrenic compound **5** in 73% yield after column chromatography of the crude mixture. Standard deprotection of **5** with tetrabutylammonium fluoride gave the diol **6** (82% yield after trituration with petroleum ether), which was treated with two equivalents of 3-(isocyanatopropyl)triethoxysilane to afford the desired dicarbamate **7** in 92% yield.

Preparation of Hybrid Materials and Catalysts

Four different types of hybrid materials were prepared from bis-silylated compound **7** (Scheme 2). Cogelification with tetraethoxysilane (40:1 as molar ratio TEOS: **7**) in ethanol at room temperature under nucleophilic conditions (stoichiometric water, 1% molar of ammonium fluoride as catalyst) afforded **8a**, whereas hydrolytic polycondensation of monomer **7** without TEOS in the same nucleophilic conditions gave **8b**. Another sol-gel condition was tested with neat monomer **7** in order to get an organized and porous material, using dodecylamine both as basic catalyst and surfactant,[24] giving rise to material **8c**. Anchoring of **7** to mesostructured silica MCM-41 was also performed under standard conditions (refluxing toluene for 24 h), **8d** being obtained. Finally, hydrosilylation of surface hydroxy groups of materials **8a** and **8d** was achieved by refluxing with excess hexamethyldisilazane, leading to **8aSi** and **8dSi**, respec-



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



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

tively. Capping of the silanol groups was performed in order to test if improved materials could be obtained, as these silylated hybrids **8aSi** and **8dSi** are less hygroscopic than their parent **8a** and **8d**.

The materials were studied by several techniques (^{13}C and ^{29}Si solid state NMR and BET surface area measurements).

Owing to the high loading of the ligand in **8b** and **8c**, the ^{13}C solid state NMR of **8b** was performed which exhibits the chemical shifts characteristic of the organic ligand (see Figure 2a and Experimental Section). The signal at 10.8 ppm (Si–C) shows the preservation of the covalently bonded ligand to the silica network.

This was confirmed by the ^{29}Si CP-MAS solid state NMR spectrum of **8c** (Figure 2b) in which only the T units (T^1, T^2 and T^3) are observed. Due to the absence of Q units at -90 to -120 ppm, we can conclude that no Si–C cleavage occurred during the hydrolysis-condensation reactions to prepare the sol-gel materials. In the case of the materials prepared with TEOS (**8a**) or MCM type (**8d**) and also the corresponding solids treated with HMDS (**8aSi** and **8dSi**), Q units are the major peaks at about -100 (Q^3) and -110 (Q^4) which are due to the condensed TEOS part. The signal at around 13 ppm in **8aSi** and **8dSi** corresponds to the $-SiMe_3$ unit. This is illustrated by the ^{29}Si solid state NMR of **8a** (Figure 2c).

The ^{29}Si solid state NMR data, some textural properties and the ligand loading of hybrid materials **8** are summarized in Table 1.

Very low surface areas are obtained in the case of the two materials **8b** and **8c** (respectively 7.5 and <1 m^2/g). The low surface area is usual in the case of bridged silsesquioxanes bearing voluminous organic moieties and was expected for **8b**.[21,22] On the contrary, the use of dodecylamine failed to give a porous material for **8c**, most probably due to the existence of interactions between the bissilylated monomer and the long alkyl chain amine which disfavour the organization of the latter in aqueous solution. Those hybrids prepared with TEOS or anchored to the MCM-type material (**8a**, **8aSi**, **8d**, **8dSi**) are highly porous (546–766 m^2/g) as expected.

All materials (**8a–d**, **8aSi** and **8dSi**) were charged with the metal by treating them with the second generation Grubbs catalyst **1b** (0.25 or 1.1 equivs.) in refluxing anhydrous and degassed dichloromethane (Scheme 3). Ruthenium content in materials **9a–d**, **9aSi** and **9dSi** was determined by ICP (inductively coupled plasma) analysis, the results being summarized in Table 2.

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

Supported catalysts **9** have been tested in the ring-closing metathesis reaction of *N*,*N*-diallyl-4-methylbenzenesulfonamide (**10**)[25] to give 1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (**11**)[25] (Scheme 4). In all cases the reaction was performed in dichloromethane (0.05 M for **10**) at room temperature, using a 3.5% molar concentration of catalyst for the times indicated in Table 3 (the disappearance of **10** was monitored by GC). Filtration and evaporation of the solvent afforded pure **11**, together with small amounts of **10** in some cases (the molar ratio **11**/**10** was determined by ^1H NMR). Heterogeneous catalysts **9** were reused directly in the

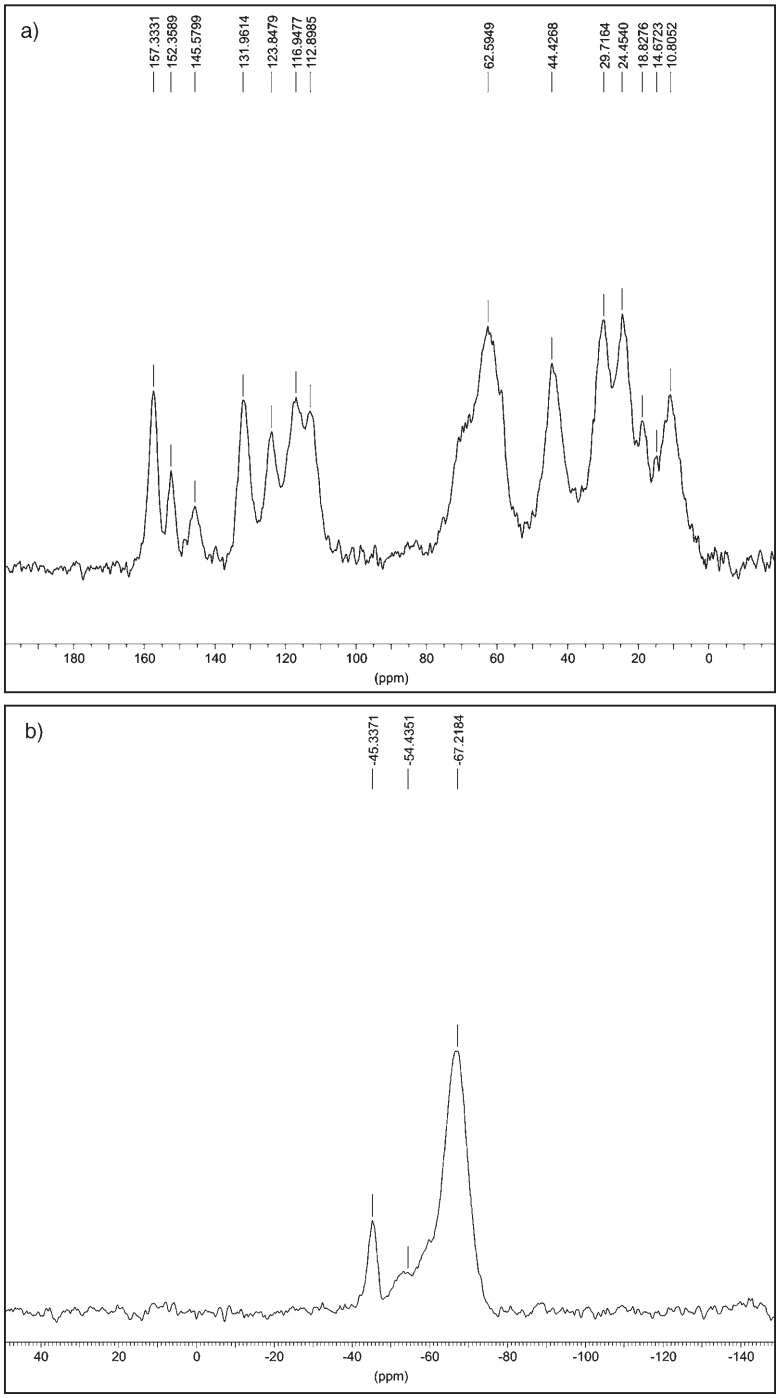


Figure 2. Solid state CP-MAS NMR spectra: (**a**) ^{13}C spectrum of **8b**, (**b**) ^{29}Si spectrum of **8c**

next run, six cycles being performed for each catalyst; until the fifth run the reaction times were maintained the same in order to follow the efficiency of the catalyst upon recycling, in the sixth run the reaction was left for 24 h.

As we see in Table 3, the activity of the catalysts to attain full conversion in the first cycle follows the sequence **9c** > **9b** > **9a** > **9d**, although the differences found are not very significant. Moreover, the decrease in conversion at the fifth cycle is greater for **9a** and **9d** than for **9b** and **9c** (where TEOS has not been used for the preparation of the material). The porosity of the material (see Table 1) does not seem to be a crucial point, as the non-porous materials **9b** and **9c** keep better their efficiency upon recycling. If we compare the material **9a**, where the organic part has been incorporated by sol-

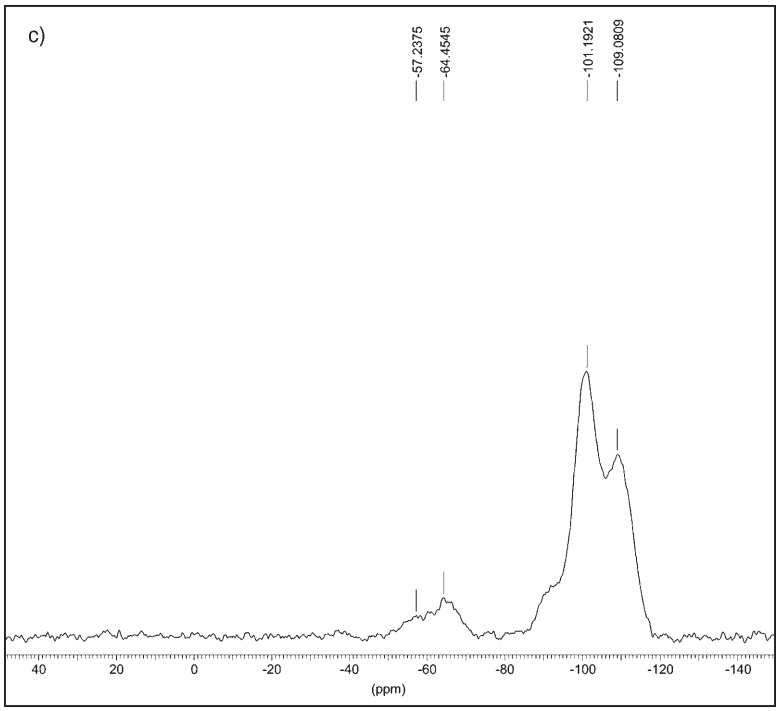


Figure 2. (**c**) ^{29}Si spectrum of **8a**.

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

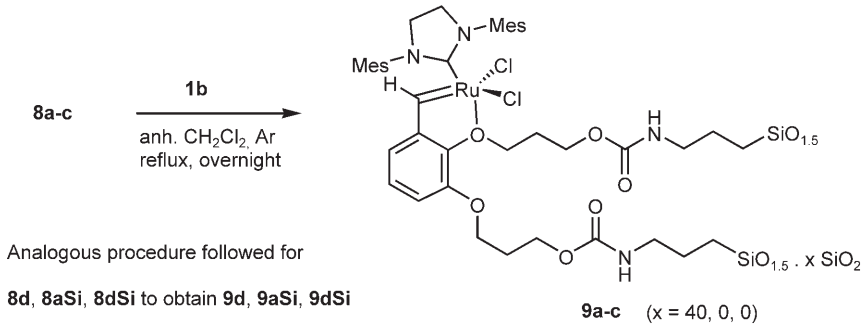
8	^{29}Si CP MAS NMR							S_{BET} [$m^2 g^{-1}$]	Pore Diam. [Å]	mmol 8/g
	R_3SiO	T^1	T^2	T^3	Q^2	Q^3	Q^4			
8a	–	–	−57.2	−64.5		−101.2	−109.2	766		0.136
8b								7.5	–	1.910
8c	–	−45.3	−54.4	−67.2				<1	–	1.806
8d	–	−51.6	−57.0	−65.0	−92.3	−100.9	−109.9	757	22–26	0.332
8aSi	13.0			−64.71		−102.0	−109.7	672	46	0.232
8dSi	13.5			−64.2		−103.0	−109.9	546	22	0.325

Table 2. Ruthenium content in hybrid materials **9**.

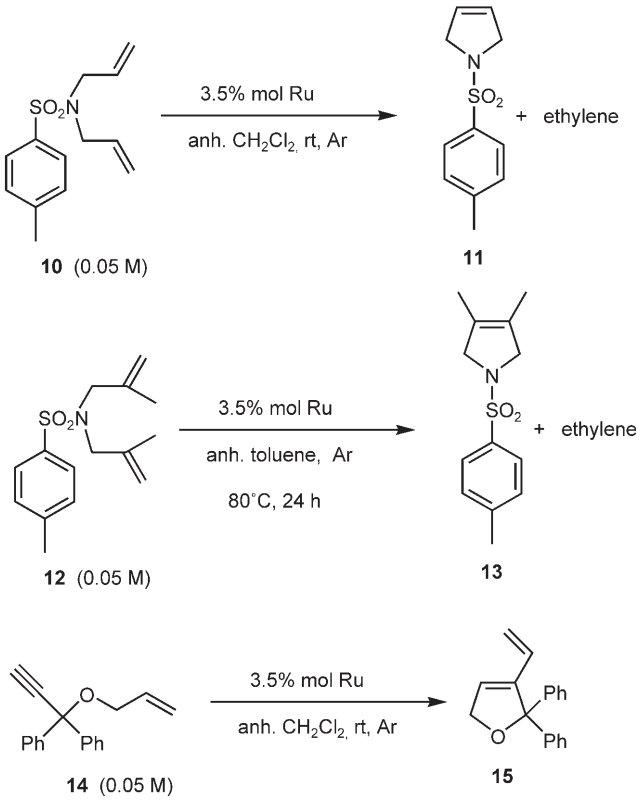
9	% Ru	mmol Ru/g
9a	1.17	0.116
9b	1.82	0.180
9c	0.7125	0.0705
9d	1.14	0.113
9aSi	0.5059	0.0500
9dSi	0.4992	0.0494

gel cogelification, with the mesostructured **9d** obtained by anchorage, the first one is slightly better (lower reaction time, higher conversion at 24 h in the sixth cycle). The silylation of residual Si–OH in **8a** and **8d** before charging with the metal (see Scheme 2 and **9aSi** and **9dSi** in Table 3) does not improve the materials. Although the reaction time in the first cycle is lowered, the efficiency upon recycling decreases very rapidly.

The ring-closing metathesis reaction to afford **11** has been performed in the literature with several recyclable immobilized catalyst types under different conditions.[9c, e,10a, h,j,26] Mauduit[26a] used imidazolium-tagged first and second generation Grubbs Ru complexes in ionic liquid as immobilizing solvent (2.5% molar Ru, $BMIM \cdot PF_6$, 60 °C, 45 min) obtaining full conversions up to 5 cycles. In a similar work, Yao[26b] (1% molar Ru, $BMIM \cdot PF_6$-CH_2Cl_2 1:9, 45 °C, 1 h, 0.2 M) achieved 17 cycles with conversions from >98% to 90%. Gibson[26c] reported the encapsulation of a 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[26d] performed the reaction with fluorous versions of first and second generation Grubbs–Hoveyda catalysts (5% molar Ru,



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



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

refluxing dichloromethane, 2 h) achieving 7 cycles with full conversions or 5 cycles with conversions up to 94%. Recently, Lee[26e] 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[10 h] has used a soluble polymer of a 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 very recently 4 cycles with decreasing conversions (>99% to 68%) (0.15% molar Ru, dichloromethane, room temperature, 1 h). Our conditions are milder than those used in most of the precedent works (percentage of catalyst and/or reaction temperature and/or reaction time), the recyclability being better than in most of the aforementioned solid supports and similar to (for **9a**, **9c**, **9d**) or better (for **9b**) than in the recent work of Blechert.[10j] Although some recycling strategies involving the reaction performed under homogeneous conditions[10h,26a, b,d, e] remain superior, the advantage of simplicity in the separation procedure must be taken into account.

Then, we also wanted to test the formation of a tetrasubstituted olefin. In our hands, treatment of *N*,*N*-bis(2-methylallyl)-4-methylbenzenesulfonamide (**12**) with second generation Grubbs catalyst **1b** (3.5% molar) under homogeneous conditions (toluene, 80 °C, 7 h) gave 90% conversion to 3,4-dimethyl-1-[(4-methylphenyl)-sulfonyl]-2,5-dihydro-1*H*-pyrrole (**13**). When our material **9a** was used as catalyst under analogous conditions (3.5% molar of Ru, toluene, 80 °C) a 77% conversion (^{1}H NMR) was found after 24 h (Scheme 4). The conversion decreased to 3% after the same reaction time in the second cycle. The catalytic material **9d** provided poorer results, giving only 26% conversion after 24 h of reaction under analogous conditions, no recycling being attempted. We should mention that very few reports appear in the literature about this challenging ring-closing metathesis reaction. K. Grela[10e] found a 45% conversion in a homogeneous process with a modified Hoveyda–Grubbs second generation catalyst (5% molar Ru, re-

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

Run	**9a**		**9b**		**9c**		**9d**		**9aSi**[a]		**9dSi**[a]	
	t [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]	*t* [h]	Conv. [%]
1	2	>98	1.5	>98	1.3	>98	2.5	>98	1.5	>98	1.15	>98
2	2	>98	1.5	>98	1.0	98	2.5	>98	1	63	1.15	69
3	2	92	1.5	94	1.0	94	2.5	91	1.5	20	1.15	29
4	2	68	1.5	81	1.0	68	2.5	60	1.5	10	1.15	13
5	2	31	1.5	66	1.0	53	2.5	32	1.5	4	1.15	3
6	24	57	24	94	24	93	24	38	24	18	24	23

[a] A 2% molar Ru was used.

fluxing dichloromethane, 16 h), describing also the first reported attempt to obtain **13** with a supported catalyst (0% conversion, 5% molar Ru, refluxing dichloromethane, 16 h). Very recently, Mauduit[26a] describes this reaction using imidazolium-tagged ruthenium complexes in room temperature ionic liquids (5% molar Ru, BMI·PF_6/toluene, 60 °C, 7 h, 65% conversion in the first cycle, 0% conversion in the second cycle). Thus, although our results with tetrasubstituted olefin **13** could appear as modest, they constitute the first successful report for the preparation of **13** with a polymer-supported catalyst. 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,26b] 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[26b] 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%).

Table 4. Results for the RCM of **14** to **15** with supported catalysts **9**.

Run	**9a**		**9d**	
	t [h]	Conv. [%]	*t* [h]	Conv. [%]
1	1.1	>98	1.5	96
2	1.1	97	1.5	88
3	1.1	95	1.25	72
4	1.1	89	1.5	55
5	1.3	88	1.5	43

On the other hand, the ring-closing enyne metathesis was successfully performed on 1-allyloxy-1,1-diphenyl-2-propyne (**14**) to give 2,2-diphenyl-3-vinyl-2,5-dihydrofuran (**15**) with our heterogeneous catalysts **9a** and **9d** (Scheme 4 and Table 4). Good conversions (*ca.* 100%) were obtained in very short reaction times (1 to 1.5 h) with 3.5% molar of catalyst in anhydrous dichloromethane at room temperature. If we compare the recyclability properties of both catalysts in Table 4, material **9a**, obtained from sol-gel cogelification, was clearly superior to **9d**, prepared by anchoring the bis-silylated monomer **8d** to mesoporous MCM-41. The efficiency of the catalyst **9d** was significantly decreased after the third cycle. This enyne ring-closing metathesis process has been described in the literature[27,28] using several catalysts and homogeneous conditions, but there is no report about recycling and about using polymer-supported catalysts for the preparation of **15**. Our results under heterogeneous conditions are even better than some homogeneous reports (milder conditions, lower reaction times).

Our catalyst does not bear the classical isopropyl group present in most of the recyclable Hoveyda-type ligands. Lamaty[10c] has also described a soluble-polymer bound Ru carbene with the chelating oxygen of the Hoveyda ligand directly linked to a polyethylene glycol chain. From the original work of Hoveyda[4a] it appears that an isopropoxy is better than a methoxy chelating group for the stability and catalytic activity of derived Ru catalysts, due to the larger steric bulkiness of the former, which may facilitate dissociation of the oxygen atom from Ru during initiation. In our case the isopropyl group is substituted by an alkylidene chain, which is undoubtedly bulkier than a methyl group. Nevertheless, as classical chelating isopropoxy group could remain the best choice, further studies are being developed in our group with supported catalysts derived from a sol-gel bearing this isopropoxy group that will be published in the near future. Another structural feature of our catalyst deserves also some comment. Blechert has shown[29] that the presence of a steric bulky group adjacent to the chelating isopropoxy moiety improves the activity of the

Hoveyda-type Ru catalysts. Our catalysts **9** present an additional group on this position, which should contribute to enhance their activity.

Conclusion

In summary, we have described the synthesis of a bis-silylated Hoveyda-type monomer, the preparation of several hybrid organic-inorganic materials by sol-gel methodologies (with and without TEOS) and by anchorage to mesoporous MCM-41, then the preparation of the corresponding second-generation Grubbs–Hoveyda-type ruthenium complexes and their evaluation as recyclable catalysts in the ring-closing metathesis reactions of dienes and enynes. The RCM on *N,N*-diallyl-4-methylbenzenesulfonamide offers milder conditions and better results than previous works based on catalysts anchored to insoluble solid supports. The RCM on a more challenging substrate, *N,N*-bis(2-methylallyl)-4-methylbenzenesulfonamide, gives rise to a tetrasubstituted alkene. Although recyclability has not been achieved in this case, there is no successful precedent in the literature about recycling for this substrate. Our materials are good recyclable catalysts for the ring-closing enyne metathesis performed on 1-allyloxy-1,1-diphenyl-2-propyne. This is the first case described in the literature about recycling in a ring-closing enyne metathesis reaction. In all cases, materials prepared from the sol-gel are superior to those coming from anchorage to mesostructured silica. Further investigations are underway with other structurally modified ligands in order to get better activity and also to achieve high surface area and highly porous materials using appropriate structuring templates with a view to improve the efficiency of these catalysts. Bridged silsesquioxanes appear to be good alternatives for the immobilization of the Hoveyda-type catalyst.

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, 2,3-dihydroxybenzaldehyde and tetrabutylammonium fluoride were purchased from Acros. The second-generation Grubbs catalyst has been purchased from Aldrich and also from Acros. Spectral data were obtained in the following spectrophotometers: IR Bruker Tensor 27 with ATR Golden Gate; solution NMR 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 time of 5 milliseconds. The CP MAS ^{13}C solid state NMR spectra were recorded on a Bruker FT-AM 400. Surface areas were determined by the 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 analyses 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) analysis.

1-(*tert*-Butyldimethylsiloxy)-3-iodopropane (**3**)[30] was prepared in two steps from 3-chloro-1-propanol as reported.[31] Mesostructured silica MCM-41 was prepared following the standard procedure.[23] Methyltriphenylphosphonium iodide was synthesized from methyl iodide and triphenylphosphine. The diene **12**[10e,27] and enyne **14**[27,28] have been mentioned in the literature but no spectroscopic data were described.

Synthesis of 2,3-Bis(3-*tert*-butyldimethylsiloxypropoxy)benzaldehyde (4)

Potassium carbonate (14.38 g, 100 mmol) and iodide **3** (12.02 g, 40.0 mmol) were added to a stirred solution of 2,3-dihydroxybenzaldehyde (2.85 g, 20.0 mmol) in DMF (150 mL). The mixture was stirred overnight at 50 °C under argon. Upon cooling at room temperature water was added (150 mL) and the solution was extracted with petroleum ether (3 × 100 mL). The combined organic layers were washed with water (100 mL) and with saturated aqueous NaCl (75 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum to afford **4** as a brown oil pure enough to carry out the next step; yield: 8.50 g (88%). Further purification can be accomplished by column chromatography through silica gel (hexane and hexane/AcOEt, 20:1 as eluents).

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

Potassium *tert*-butoxide (3.8 g, 33.2 mmol) was added to a suspension of methyltriphenylphosphonium iodide (13.7 g, 33.9 mmol) in anhydrous diethyl ether (120 mL) and the mixture was stirred at 0 °C under argon for 15 min. A solution of aldehyde **4** (8.0 g, 16.6 mmol) in anhydrous diethyl ether (50 mL) was added and the mixture was allowed to stir at 0 °C under argon for one hour and then at room temperature for 3 h. Water (200 mL) was added and the organic layer was separated. The aqueous phase was extracted with diethyl ether (2 × 100 mL), the combined organic layers were washed with water (100 mL) and saturated aqueous NaCl (50 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was chromatographed through silica gel (hexane/AcOEt 30:1 as eluent) to afford **5** as a pale yellow oil; yield: 5.8 g (73%).

Synthesis of 2,3-Bis(3-hydroxypropoxy)styrene (6)

A solution of tetrabutylammonium fluoride (10.42 g, 32 mmol) in anhydrous THF (25 mL) was added under argon to a stirred solution of **5** (4.013 g, 8.35 mmol) in anhydrous THF (25 mL) at 0 °C. The mixture was allowed to stir overnight at room temperature under argon. Water was added (100 mL) and extractions with distilled diethyl ether (3 × 60 mL) were performed. The combined organic layers were washed with water (2 × 50 mL) and saturated aqueous NaCl (50 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The oily residue was washed three times by trituration with petroleum ether at room temperature for 1 h. After removing of the supernatant the residual oil was dried under vacuum to afford **6**; yield: 1.72 g (82%).

Synthesis of *O*-{3-[2-(3-triethoxysilylpropylcarbamoyloxypropoxy)-6-vinylphenoxy]propyl} *N*-(3-Triethoxysilylpropyl)carbamate (7)

Freshly distilled 3-(triethoxysilyl)propyl isocyanate (2.4 mL, 0.99 g/mL, 9.6 mmol) was added dropwise *via* syringe under argon to compound **6** (0.88 g, 3.49 mmol). The homogeneous mixture was stirred under argon at room temperature for 4 days, then at 50 °C overnight (^{1}H NMR monitoring). Anhydrous diethyl ether was added and the solution was filtered under nitrogen atmosphere. The solvent was removed under vacuum and excess isocyanate was distilled off (100 °C, 1.7 mbar). Anhydrous diethyl ether (10 mL) was added to the residue, the solution was filtered under nitrogen atmosphere and the solvent was evaporated, to give **7** as an oil; yield: 2.40 g (92%).

Preparation of Hybrid Material 8a

A solution of ammonium fluoride (82 μL of a 1 M solution, 0.082 mmol of fluoride, 4.56 mmol of water) and distilled and deionized water (0.45 mL, 25 mmol) in anhydrous ethanol (4 mL) was added to a solution of **7** (0.147 g, 0.20 mmol) and TEOS (1.693 g, 8.14 mmol) in anhydrous ethanol. The mixture was stirred manually for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation occurred after a 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 mm Hg, room temperature, 15 h), affording **8a** as a white powder; yield: 0.609 g.

Preparation of Hybrid Material 8b

A solution of ammonium fluoride (50 μL of a 0.1 M solution, 0.005 mmol of fluoride, 2.8 mmol of water) and distilled and deionized water (10 μL, 0.56 mmol) in anhydrous ethanol (0.25 mL) was added to a solution of **7** (0.372 g, 0.5 mmol) in anhydrous ethanol (0.25 mL). The mixture was stirred manually for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation occurred after one night and the gel was allowed to age for 6 days, after which it was powdered and washed successively with water (twice) and ethanol (5 times). The solid was dried under vacuum (1 mmHg, room temperature, 15 h), furnishing **8b** as a white powder; yield: 0.231 g.

Preparation of Hybrid Material 8c

A solution of dodecylamine (0.041 g, 0.22 mmol) in ethanol (0.3 mL) was added to distilled and deionized water (3 mL) and stirred for 30 minutes. A solution of **7** (0.373 g, 0.5 mmol) in anhydrous ethanol (0.2 mL) was added and then more water (2 mL). 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 **8c** as a white powder; yield: 0.197 g.

Preparation of Hybrid Material 8d

Mesostructured MCM-41 (0.480 g, 8 mmol SiO_2) was added to a solution of **7** (0.148 g, 0.198 mmol) in toluene (10 mL). The mixture was refluxed for 24 h with a Dean–Stark apparatus. The solid was filtered and washed successively with toluene (twice), ethanol (3 times) and acetone (twice), then it was dried at 70 °C at atmospheric pressure, affording **8d** as a white powder; yield: 0.547 g.

Preparation of Hybrid Material 8aSi

A suspension of **8a** (0.157 g) in *N*,*N*-bis(trimethylsilyl)amine (10 mL) was refluxed under argon 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 mmHg, 60 °C, 15 h), affording **8aSi** as a white powder; yield: 0.155 g.

Preparation of Hybrid Material 8dSi

A suspension of **8d** (0.170 g) in *N*,*N*-bis(trimethylsilyl)amine (10 mL) was refluxed under argon 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 mmHg, 60 °C, 15 h), affording **8dSi** as a white powder; yield: 0.168 g.

Preparation of Hybrid Catalyst 9a

Anhydrous and degassed dichloromethane (6 mL) was added under argon to a stirred mixture of **8a** (0.375 g, 0.272 mmol N/g, 0.051 mmol) and **1b** (0.0476 g, 0.0561 mmol, 1.1 equivs.) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with 5 mL portions of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mm Hg, room temperature, 15 h) to obtain **9a** as a pale brown powder; yield: 0.321 g; elemental analysis found: N 1.15, Ru (ICP) 1.17.

Preparation of Hybrid Catalyst 9b

Anhydrous and degassed dichloromethane (5 mL) was added under argon to a stirred mixture of **8b** (0.0995 g, 3.82 mmol N/g, 0.190 mmol) and **1b** (0.0409 g, 0.0482 mmol, 0.25 equivs.) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with 5 mL portions of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, room temperature, 15 h) to obtain **9b** as a green powder; yield: 0.0879 g; Ru 1.82% (ICP).

Preparation of Hybrid Catalyst 9c

Anhydrous and degassed dichloromethane (4 mL) was added under argon to a stirred mixture of **8c** (0.0848 g, 3.614 mmol N/g, 0.153 mmol) and **1b** (0.0321 g, 0.0378 mmol, 0.25 equivs.) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with 5 mL portions of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, room temperature, 15 h) to obtain **9c** as a pale green powder; yield: 0.0677 g; elemental analysis found: N 4.365, Ru (ICP) 0.7125.

Preparation of Hybrid Catalyst 9d

Anhydrous and degassed dichloromethane (10 mL) was added under argon to a stirred mixture of **8d** (0.2997 g, 0.664 mmol N/g, 0.0995 mmol) and **1b** (0.0875 g, 0.103 mmol, 1.04 equivs.) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with 5 mL portions of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, room temperature, 15 h) to obtain **9d** as a pale brown powder; yield: 0.3011 g; elemental analysis found: C 15.60, H 2.46, N 1.25, Ru (ICP) 1.14.

Preparation of Hybrid Catalyst 9aSi

Anhydrous and degassed dichloromethane (2.2 mL) was added under argon to a stirred mixture of **8aSi** (0.0842 g, 0.464 mmol N/g, 0.0195 mmol) and **1b** (0.017 g, 0.020 mmol, 1.02 equivs.) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 2.5 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, room temperature, 15 h) to obtain **9aSi** as a pale brown powder; yield: 0.0722 g; elemental analysis found: N 1.18, Ru (ICP) 0.506.

Preparation of Hybrid Catalyst 9dSi

Anhydrous and degassed dichloromethane (3.5 mL) was added under argon to a stirred mixture of **8dSi** (0.0900 g, 0.650 mmol N/g, 0.0292 mmol) and **1b** (0.0252 g, 0.0297 mmol, 1.01 equivs.) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with 4 mL portions of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, room temperature, 15 h) to obtain **9dSi** as a pale brown powder; yield: 0.0797 g; elemental analysis found: N 1.40, Ru (ICP) 0.50.

Synthesis of *N*,*N*-Diallyl-4-methylbenzenesulfonamide (10)

A stirred mixture of 4-methylbenzenesulfonamide (3.17 g, 18.2 mmol), allyl bromide (6 mL, 1.398 g/mL, 68.6 mmol) and potassium carbonate (11.9 g, 85.4 mmol) in acetonitrile (100 mL) was heated under pressure at 100 °C for 24 h in a closed reactor. The mixture was filtered and the solvent from filtrate was evaporated to give **10**[25] as an oil; yield: 4.47 g (98%).

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

A solution of **10** (0.1004 g, 0.399 mmol) in anhydrous and degassed dichloromethane (8 mL) was added under nitrogen to **9a** (0.1204 g, 0.116 mmol Ru/g, 0.0140 mmol Ru) and the mixture was stirred under argon at room temperature for 2 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 afford **11**;[25] yield: 0.096 g (the molar ratio **11/10** by ^{1}H NMR was 53/1, 98% conversion). The solid catalyst **9a** was dried and reused in the next run.

The same conditions were adopted for the other catalysts **9b**–**d**, **9aSi**, **9dSi** except for the reaction times that are summarized in Table 3 together with the attained conversions.

Synthesis of *N*,*N*-Bis(2-methylallyl)-4-methylbenzenesulfonamide (12)

A stirred mixture of 4-methylbenzenesulfonamide (1.58 g, 9.04 mmol), 3-bromo-2-methylpropene (2.6 mL, 1.339 g/mL, 25.01 mmol) and potassium carbonate (4.75 g, 34 mmol) in acetonitrile (50 mL) was heated under pressure at 110 °C for 48 h in a closed reactor. The cooled mixture was filtered and the solvent from filtrate was evaporated to give **12** as a pale yellow oil; yield: 2.45 g (97%).

Ring-Closing Metathesis Reaction on *N*,*N*-Bis(2-methylallyl)-4-methylbenzenesulfonamide (12) with Supported Catalysts 9. Synthesis of 3,4-Dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (13). Typical Experimental Procedure

A solution of **12** (0.0744 g, 0.266 mmol) in anhydrous and degassed toluene (5.5 mL) was added under nitrogen to **9a** (0.0805 g, 0.116 mmol Ru/g, 0.00934 mmol Ru) and the mixture was stirred under argon at 80 °C for 24 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed 4 times with 5.5 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to afford **13**; yield: 0.073 g (the molar ratio **13/12** by ^{1}H NMR was 3.4/1, 77% conversion). ^{1}H and ^{13}C NMR data of **13** were coincident with those described for this com-

pound in the literature.[32] The solid catalyst **9a** was dried and reused in the next run.

Synthesis of 1-Allyloxy-1,1-diphenyl-2-propyne (14)

To a suspension of NaH 60% (0.198 g, 4.95 mmol, 1.04 equivs.) in DMF (100 mL) at 0 °C were added successively 1,1-diphenyl-2-propyn-1-ol (0.999 g, 4.75 mmol) and allyl bromide (1.6 ml, 1.398 g/ml, 18.3 mmol). The mixture was allowed to stir at room temperature under Ar overnight. Water was added (150 mL) and extractions with distilled diethyl ether (3 × 100 mL) were performed. The combined organic layers were washed with water (50 mL) and saturated aqueous NaCl (50 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was chromatographed through silica gel (hexane/AcOEt, 19:1 as eluent) to afford **14** as a pale yellow oil; yield: 0.992 g (84%).

Ring-Closing Metathesis Reaction on 1-Allyloxy-1,1-diphenyl-2-propyne (14) with Supported Catalysts 9. Synthesis of 2,2-Diphenyl-3-vinyl-2,5-dihydrofuran (15). Typical Experimental Procedure

A solution of **14** (0.0631 g, 0.254 mmol) in anhydrous and degassed dichloromethane (5 mL) was added under nitrogen to **9a** (0.0766 g, 0.116 mmol Ru/g, 0.00889 mmol Ru) and the mixture was stirred under argon at room temperature for 65 minutes (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed 4 times with 5 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **15** whose spectroscopic data were coincident with that reported in the literature;[27] yield: 0.066 g (100% conversion by ^{1}H NMR). The solid catalyst **9a** was dried and reused in the next run.

The same conditions were adopted for the other catalyst **9d** except the reaction time (1.5 h). The results are summarized in Table 4.

See Supporting Information for characterization data of compounds **4**–**8**, **12** and **14**.

Acknowledgements

Financial support from the Ministry of Science and Technology of Spain, Generalitat de Catalunya and Universitat Autònoma de Barcelona (Projects BQU2002-04002, SGR2001-00181, PNL2005-10), from the French Ministry of Research and Technology and from the CNRS is gratefully acknowledged.

References and Notes

[1] Selected reviews: a) R. H. Grubbs, S. J. Miller, G. C. Fu, *Acc. Chem. Res.* **1995**, *28*, 446; b) H. G. Schmalz, *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 1833; c) M. Schuster, S. Blechert, *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2037; d) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413; e) S. K. Armstrong, *J. Chem. Soc. Perkin Trans. 1* **1998**, 371; f) M. L. Randall, M. L. Snapper, *J. Mol. Catal. A* **1998**, *133*, 29; g) K. J. Ivin, *J. Mol. Catal. A* **1998**, *133*, 1; h) Ch. Pariya, K. N. Jayaprakash, A. Sarkar, *Coord. Chem. Rev.* **1998**, *168*, 1; i) M. E. Maier, *Angew. Chem. Int. Ed*. **2000**, *39*, 2073; j) A. Fürstner, *Angew. Chem. Int. Ed*. **2000**, *39*, 3012; k) R. Roy, S. K. Das, *Chem. Commun*. **2000**, 519; l) M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565; m) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18; n) A. H. Hoveyda, R. R. Schrock, *Chem. Eur. J.* **2001**, *7*, 945; o) F. X. Felpin, J. Lebreton, *Eur. J. Org. Chem*. **2003**, 3693; p) M. D. McReynolds, J. M. Dougherty, P. R. Hanson, *Chem. Rev.* **2004**, *104*, 2239; q) A. Deiters, S. F. Martin, *Chem. Rev.* **2004**, *104*, 2199; r) R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117; s) H. Katayama, F. Ozawa, *Coord. Chem. Rev.* **2004**, *248*, 1703; t) D. Astruc, *New. J. Chem*. **2005**, *29*, 42.

[2] For reviews on enyne metathesis and its use in organic synthesis: a) M. Mori, *Top. Organomet. Chem*. **1998**, *1*, 133; b) C. S. Poulsen, R. Madsen, *Synthesis* **2003**, 1; c) S. T. Diver, A. J. Giessert, *Chem. Rev.* **2004**, *104*, 1317; d) M. Mori, *J. Mol. Cat. A: Chem*. **2004**, *213*, 73; for a one-pot enyne metathesis-Diels–Alder process described by some of us: e) M. Moreno-Mañas, R. Pleixats, A. Santamaria, *Synlett* **2001**, 1784.

[3] a) M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953; b) A. K. Chatterjee, R. H. Grubbs, *Org. Lett*. **1999**, *1*, 1751; c) L. Ackermann, A. Fürstner, T. Weskamp, F. J. Khol, W. A. Herrmann, *Tetrahedron Lett.* **1999**, *40*, 4787; d) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett*. **1999**, *40*, 2247; e) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674.

[4] a) J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus Jr, A. H. Hoveyda, *J. Am. Chem. Soc*. **1999**, *121*, 791; b) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168.

[5] See the review article and references cited therein: M. R. Buchmeiser, *New. J. Chem*. **2004**, *28*, 549.

[6] a) S. T. Nguyen, R. H. Grubbs; *J. Organomet. Chem*. **1995**, *497*, 195; b) F. Verpoort, P. Jacobs, D. De Vos, K. Melis, *J. Mol. Cat. A* **2001**, *169*, 47.

[7] a) S. C. Schürer, S. Gessler, N. Buschmann, S. Blechert, *Angew. Chem. Int. Ed.* **2000**, *39*, 3898; b) S. Randl, N. Buschmann, S. J. Connon, S. Blechert, *Synlett* **2001**, 1547, c) M. Mayr, B. Mayr, M. R. Buchmeiser, *Angew. Chem. Int. Ed.* **2001**, *40*, 3839; d) M. Mayr, M. R. Buchmeiser, K. Wurst, *Adv. Synth. Catal*. **2002**, *344*, 712; e) S. Prühs, C. W. Lehmann, A. Fürstner, *Organometallics* **2004**, *23*, 280.

[8] a) P. Nieczypor, W. Buchowicz, W. J. N. Meester, F. P. J. T. Rutjes, J. C. Mol, *Tetrahedron Lett.* **2001**, *42*, 7103; b) J. O. Krause, S. H. Lubbad, O. Nuyken, M. R. Buchmeiser, *Adv. Synth. Catal*. **2003**, *345*, 996; c) J. O. Krause, K. Wurst, O. Nuyken, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 778; d) J. O. Krause, S. H. Lubbad, O. Nuyken, M. R. Buchmeiser, *Macromol. Rapid Commun*. **2003**, *24*, 875.

[9] a) M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Lett*. **1999**, *40*, 8657; b) A. G. M. Barrett, S. M. Cramp, R. S. Roberts,

Org. Lett. **1999**, *1*, 1083; c) M. Ahmed, T. Arnauld, A. G. M. Barrett, D. C. Braddock, P. A. Procopiou, *Synlett* **2000**, 1007; d) L. Jafarpour, S. P. Nolan, *Org. Lett*. **2000**, *2*, 4075; e) L. Jafarpour, M. P. Heck, C. Baylon, H. Man Lee, C. Mioskowski, S. P. Nolan, *Organometallics* **2002**, *21*, 671.

[10] a) Q. Yao, *Angew. Chem. Int. Ed*. **2000**, *39*, 3896; b) Q. Yao, A. Rodriguez Motta, *Tetrahedron Lett.* **2004**, *45*, 2447; c) S. Varray, R. Lazaro, J. Martinez, F. Lamaty, *Organometallics* **2003**, *22*, 2426; d) J. Dowden, J. Savovic, *Chem. Commun*. **2001**, 37; e) K. Grela, M. Tryznowski, M. Bieniek, *Tetrahedron Lett*. **2002**, *43*, 9055; f) J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas, A. H. Hoveyda, *Angew. Chem. Int. Ed*. **2001**, *40*, 4251; g) A. H. Hoveyda, D. G. Gillingham, J. J. Van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury, J. P. A. Harrity, *Org. Biomol. Chem*. **2004**, *2*, 8; h) S. J. Connon, A. M. Dunne, S. Blechert, *Angew. Chem. Int. Ed*. **2002**, *41*, 3835; i) S. J. Connon, S. Blechert, *Biorg. Med. Chem*. *Lett*. **2002**, *12*, 1873; j) D. Fischer, S. Blechert, *Adv. Synth. Catal*. **2005**, *347*, 1329.

[11] C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic Press, London, **1990**.

[12] a) R. M. Laine, C. Sanchez, C. J. Brinker, E. Giannelis (Eds.), *Organic/inorganic Hybrid Materials,* MRS Symp. Vol. 628, **2000**; b) R. M. Laine, C. Sanchez, C. J. Brinker, E. Giannelis (Eds.), *Organic/inorganic Hybrid Materials,* MRS Symp. Vol. 726, **2002**.

[13] D. Avnir, *Acc. Chem. Res.* **1995**, *28*, 328.

[14] K. J. Shea, J. J. E. Moreau, D. Loy, R. J. P. Corriu, B. Boury, in: *Functional Hybrid Materials*, (Eds.: P. Gomez-Romero, C. Sanchez), Wiley-VCH, Weinheim, **2004**, 50.

[15] a) J. J. E. Moreau, M. Wong Chi Man, *Coord. Rev.* **1998**, *178–180*, 1073; b) J.-C Broudic, O. Conocar, J. J. E. Moreau, D. Meyer, M. Wong Chi Man, *J. Mater. Chem.* **1999**, *9*, 2283; c) S. Bourg, J.-C. Broudic, O. Conocar, J. J. E. Moreau, D. Meyer, M. Wong Chi Man, *Chem. Mater.* **2001**, *13*, 491; d) O. Dautel, J.-P. Lère-Porte, J. J. E. Moreau, M. Wong Chi Man, *Chem. Commun.* **2003**, 2662.

[16] H. W. Oviatt, K. Shea, S. Kalluri, Y. Shi, W. H. Steier, L. R. Dalton, *Chem. Mater.* **1995**, *7*, 493.

[17] a) R. Abu-Reziq, D. Avnir, J. Blum, *Angew. Chem. Int. Ed.* **2002**, *41*, 4132; b) R. Abu-Reziq, D. Avnir, J. Blum, *J. Mol. Catal. A: Chem.* **2002**, *187*, 277.

[18] a) U. Schubert, *New J. Chem.* **1994**, *18*, 1049; b) U. Schubert, N. Hüsing, A. Lorenz, *Chem. Mater.* **1995**, *7*, 2010.

[19] a) E. Lindner, T. Schneller, F. Auer, H. A. Mayer, *Angew. Chem. Int. Ed.* **1999**, *38*, 2154; b) Z.-I. Lu, E. Lindner, H. A. Mayer, *Chem. Rev.* **2002**, *102*, 3543.

[20] a) K. J. Shea, D. A. Loy, O. Webster, *Chem. Mater.* **1989**, *1*, 512, b) K. J. Shea, D. A. Loy, O. Webster, *J. Am. Chem. Soc.* **1992**, *114*, 6700–6710.

[21] R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. Wong Chi Man, *Chem. Mater*. **1992**, *4*, 1217.

[22] a) A. Adima, J. J. E. Moreau, M. Wong Chi Man, *J. Mater. Chem.* **1997**, *7*, 2331; b) A. Adima, J. J. E. Moreau, M. Wong Chi Man, *Chirality* **2000**, *12*, 411; c) A. Brethon, J. J. E. Moreau, M. Wong Chi Man, *Tetrahedron: Asymmetry* **2004**, *15*, 495.

[23] T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartulli, J. S. Beck, *Nature* **1992**, *359*, 710.

[24] L. Mercier, T. J. Pinnavaia, *Chem. Mater*. **2000**, *12*, 188.

[25] S. Cerezo, J. Cortés, M. Moreno-Mañas, R. Pleixats, A. Roglans, *Tetrahedron* **1998**, *54*, 14869.

[26] a) H. Clavier, N. Audic, J-C. Guillemin, M. Mauduit, *J. Organometallic Chem*. **2005**, *690*, 3585; b) Q. Yao, M. Shetts, *J. Organometallic Chem*. **2005**, *690*, 3577; c) S. E. Gibson, V. M. Swamy, *Adv. Synth. Catal*. **2002**, *344*, 619; d) M. Matsugi, D. P. Curran, *J. Org. Chem*. **2005**, *70*, 1636; e) B. S. Lee, S. K. Namgoong, S. Lee, *Tetrahedron Lett.* **2005**, *46*, 4501.

[27] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236.

[28] a) M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun*. **1998**, 2249; b) K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem. Int. Ed*. **2002**, *41*, 4038; c) A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, *J. Am. Chem. Soc*. **2004**, *126*, 9318; d) J. C. Conrad, H. H. Pamas, J. L. Snelgrove, D. E. Fogg, *J. Am. Chem. Soc*. **2005**, *127*, 11882; e) R. Castarlenas, M. Eckert, P. H. Dixneuf, *Angew. Chem. Int. Ed*. **2005**, *44*, 2576.

[29] H. Wakamatsu, S. Blechert, *Angew. Chem. Int. Ed.* **2002**, *41*, 2403.

[30] H. Poleschner, M. Heydenreich, D. Martin, *Synthesis* **1991**, 1231.

[31] a) S. T. Hill, M. Mokotoff, *J. Org. Chem*. **1984**, *49*, 1441; b) C. A. Willoughby, S. L. Buchwald, *J. Am. Chem. Soc*. **1994**, *116*, 8952.

[32] Y. Terada, M. Arisawa, A. Nishida, *Angew. Chem. Int. Ed.* **2004**, *43*, 4063.

