IMMOBILIZED RUTHENIUM COMPLEXES BEARING N,O-BIDENTATE LIGANDS

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Immobilization of a family of arene and benzylidene N,O-bidentate ruthenium complexes by covalently anchoring the homogeneous complexes on MCM-41 is described. Successful applications of these immobilized catalytic systems in enol-ester synthesis, Kharasch addition, ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP) are illustrated. Important advantages of these heterogeneous catalyst systems in comparison with their homogeneous counterparts are also highlighted.

INTRODUCTION

Immobilization of well-defined homogeneous complexes is a beneficial strategy in catalysis that combines advantages of both heterogeneous and homogeneous systems.[1-3] This technique offers multiple advantages in organic synthesis such as simplification of the reaction procedures, better control of the process selectivity, easy separation of the catalyst from the reaction products, recyclability of expensive catalysts, possibility to design continuous flow processes at large scale, good control of morphology of polymers, high polymer bulk density.[4,5]

The currently used methodology to transform a homogeneous catalytic reaction into a heterogeneous process involves anchoring of the active catalytic site on a solid substrate having a large surface area.[6] For this purpose the structure and reactivity of the catalytic complex and the solid substrate are essential in constructing new active and efficient target architectures. Their association should not affect the initial catalytic abilities of the immobilized complex but effectively benefit of the attributes offered by both the deposited complex and the solid support.

During the last few years, the coordination and organometallic chemistry of ruthenium complexes has known an unprecedented development mainly due to the disclosure of the ever increasing potential of this class of compounds as efficient promoters in versatile catalytic processes.[7-9] The majority of these novel ruthenium complexes possess an appropriate balance between the electronic and steric properties within the ligand environment. As a result of their specific structures, these ruthenium complexes exhibit attractive catalytic abilities and particularly an enhanced activity, chemoselectivity and stability in target chemical transformations.[10-13] Immobilizing ruthenium complexes on solid supports has emerged as a highly effective improvement to enhance their potential as catalysts in chemical reactions. The best way to immobilize ruthenium complexes consists in binding the metal complex through one of its most stable ligands without altering the catalytic propensity of the initial active site.[14]

Recent studies in our group have been directed towards design, synthesis and progressive development of homogeneous N,O-bidentate ruthenium complexes bearing Schiff bases as ancillary ligands for applications in ring-closing

metathesis (RCM), Kharasch addition, ring-opening metathesis polymerization (ROMP), atom transfer radical polymerization (ATRP) and vinylation reactions.[15-18] On developing a structurally robust and effective supported catalyst, we succeeded in preparing a very efficient catalytic system in which the homogeneous ruthenium complex is attached to the carrier by a non-labile tether *via* its Schiff-base ligand, imposing little or no steric hindrance at the reactive site[19,20] (Scheme 1).
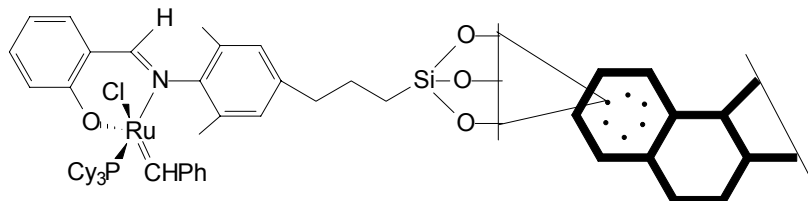
Scheme 1 – Hybrid Ru catalytic system obtained by tethering a homogeneous complex.

In our search for a suitable support, we were attracted by the inorganic mesoporous structures MCM-41 since they provide several valuable properties[21]: (i) these materials retain a rigid exposed surface area, whereas conventional polymer beads typically swell and shrink variably in different media, often resulting in unpredictable effects on the catalyst activity; (ii) because of being more robust than organic polymers, inorganic solids, and particularly those having a structured surface, have a considerably larger area and, therefore, an increased activity should in principle be achievable with such solids; (iii) anchoring the active catalytic species on a large surface area would help overcome the activity loss currently encountered when going from homogeneous to heterogeneous catalysis and that is due to an inefficient interfacial mass transfer between the liquid phase and the solid; (iv) the MCM-41 solid support consists of an ordered array of hexagonal channels with a pore diameter in the mesoporous region which permits a lower diffusion resistance (*e.g.,* nanoporous zeolite support) to reactant molecules accessing the metal active sites located within the channels.[22]

The present paper reports on the synthetic methodology used by us to immobilize homogeneous N,O-bidentate ruthenium complexes onto MCM-41[23] and applications of these hybrid heterogeneous catalysts in an array of important organic reactions such as ring-closing metathesis, Kharasch addition, enol-ester synthesis, ring-opening metathesis polymerization and atom transfer radical polymerization.[24]

RESULTS AND DISCUSSION

1. Synthetic routes to immobilized N,O-bidentate ruthenium complexes

The methodology that we followed in preparing a catalyst system chemically tethered onto MCM-41 consisted in immobilizing a pre-synthesized catalyst precursor that contains an anchorable functionality. With respect to leaching, chemical tethering of organometallic compounds seems to be one of the best strategies to anchor a homogeneous catalyst to a solid support. The procedure to tether organometallic compounds onto mesoporous silica surfaces applied by us was the treatment of the inorganic support with a tris(alkoxy)silyl functionalized complex. This approach has been successfully applied to synthesize and characterize a heterogeneous arene ruthenium catalyst **2** from its homogeneous precursor **1** (Scheme 2).
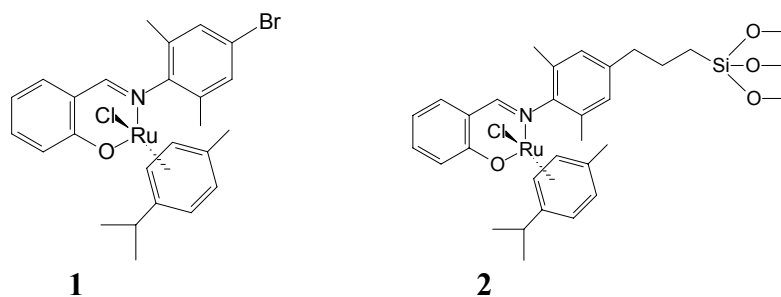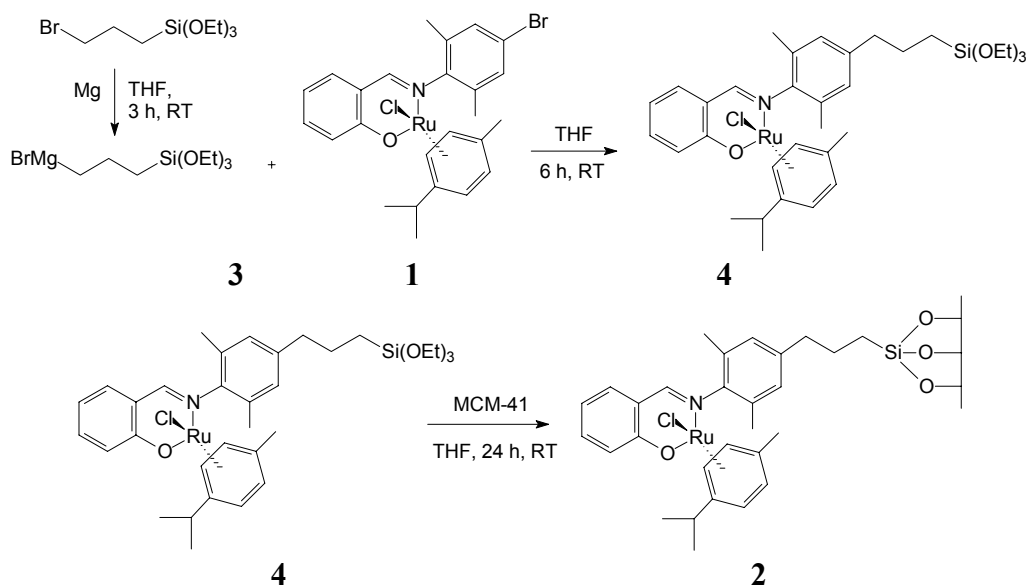

Scheme 2 – Hybrid N,O-bidentate ruthenium complex **2** and its homogeneous precursor **1**.

When employed in some representative catalytic processes, catalyst **2** exhibited excellent stability, reusability and leaching properties. Synthesis of the complex **2** occurred through two key steps from the homogeneous complex **1**, the first one involving functionalization of this complex to compound **4** with an appropriate tris(ethoxy)silyl derivative **3** (in THF, at room temperature, time 6 hours) and the second one further anchoring the tris(ethoxy)silyl complex **4** onto mesoporous MCM-41 (in THF, at room temperature, time 24 hours) (Scheme 3).

We have also fruitfully achieved the synthesis of two multifunctional Schiff base-containing ruthenium carbene complexes **5** and **6** supported on MCM-41 (Scheme 4).

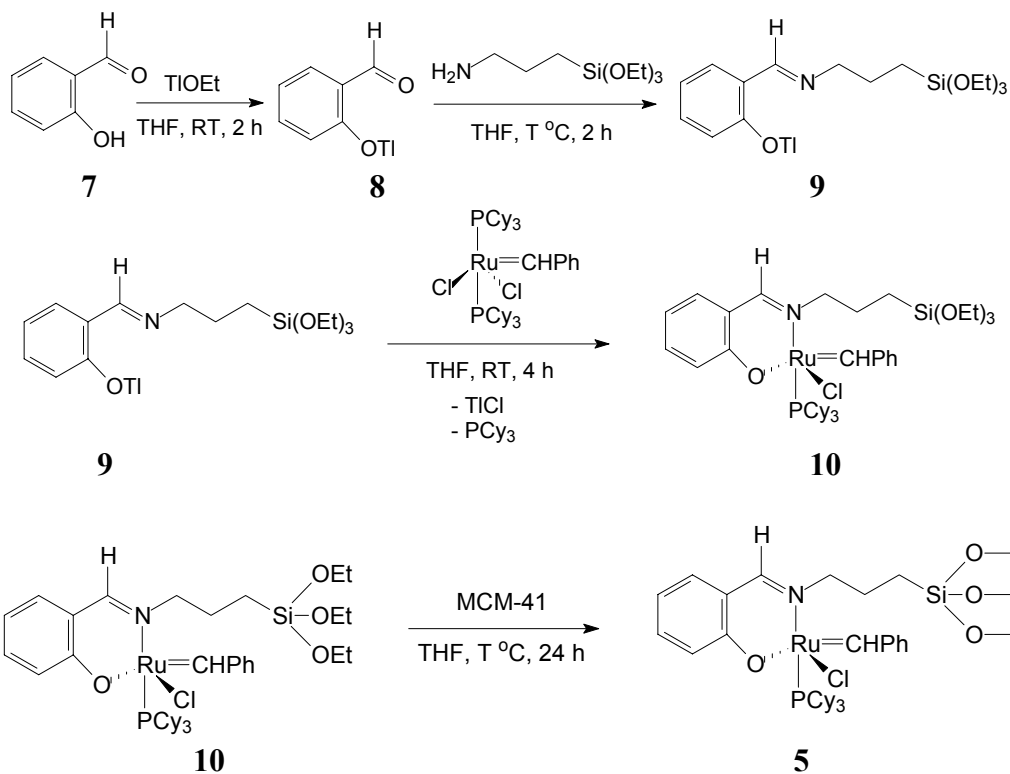Scheme 3 – Synthesis of hybrid N,O-bidentate Schiff base ruthenium complex **2**.
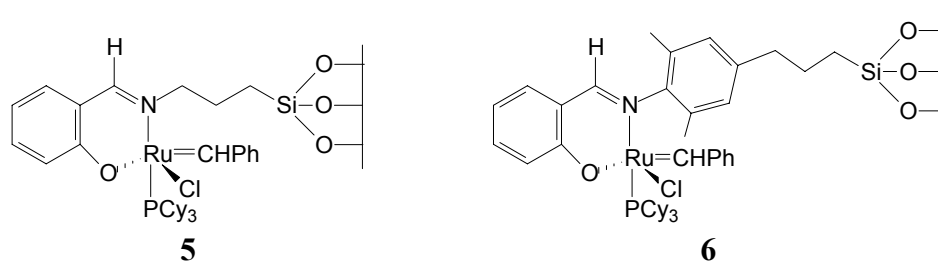
Scheme 4 – Hybrid N,O-bidentate Schiff base ruthenium complexes **5** and **6.**

In case of complex **5**, the tris(ethoxy)silyl group was incorporated in an earlier stage, i.e. during the Schiff base generation by reaction of the thalium salt of salicyl aldehyde **8** with 3-tris(ethoxy)silyl-propylamine and then the formed tris(ethoxy)silyl Schiff base **9** was reacted with the Grubbs catalyst[25] $Cl_2Ru(PCy_3)_2$=CHPh to yield the functionalized Ru complex **10**. Immobilization of the homogeneous complex **10** onto MCM-41 to complex **5** occurred effectively under the above mentioned conditions (Scheme 5).

On using a quite similar protocol, complex **6** has been obtained in high yield from the functionalized complex **15** and MCM-41.

Synthesis of complex **15** involved the intermediate formation of tris(ethoxy)silyl Schiff base **14** containing an aromatic tethering which was further reacted with the Grubbs catalyst $Cl_2Ru(PCy_3)_2$=CHPh (Scheme 6).

Structural characterization of the hybrid ruthenium complexes **2**, **5** and **6** by X-ray diffraction (XRD), N_2-adsorption analysis, Raman spectroscopy, X-ray fluorescence (XRF) and solid-state NMR showed that in all cases the anchoring of the homogeneous catalyst onto the MCM-41 took place *via* spacer molecule with two or three covalent bonds.

Scheme 5 – Synthesis of hybrid N,O-bidentate Schiff base ruthenium complex **5.**
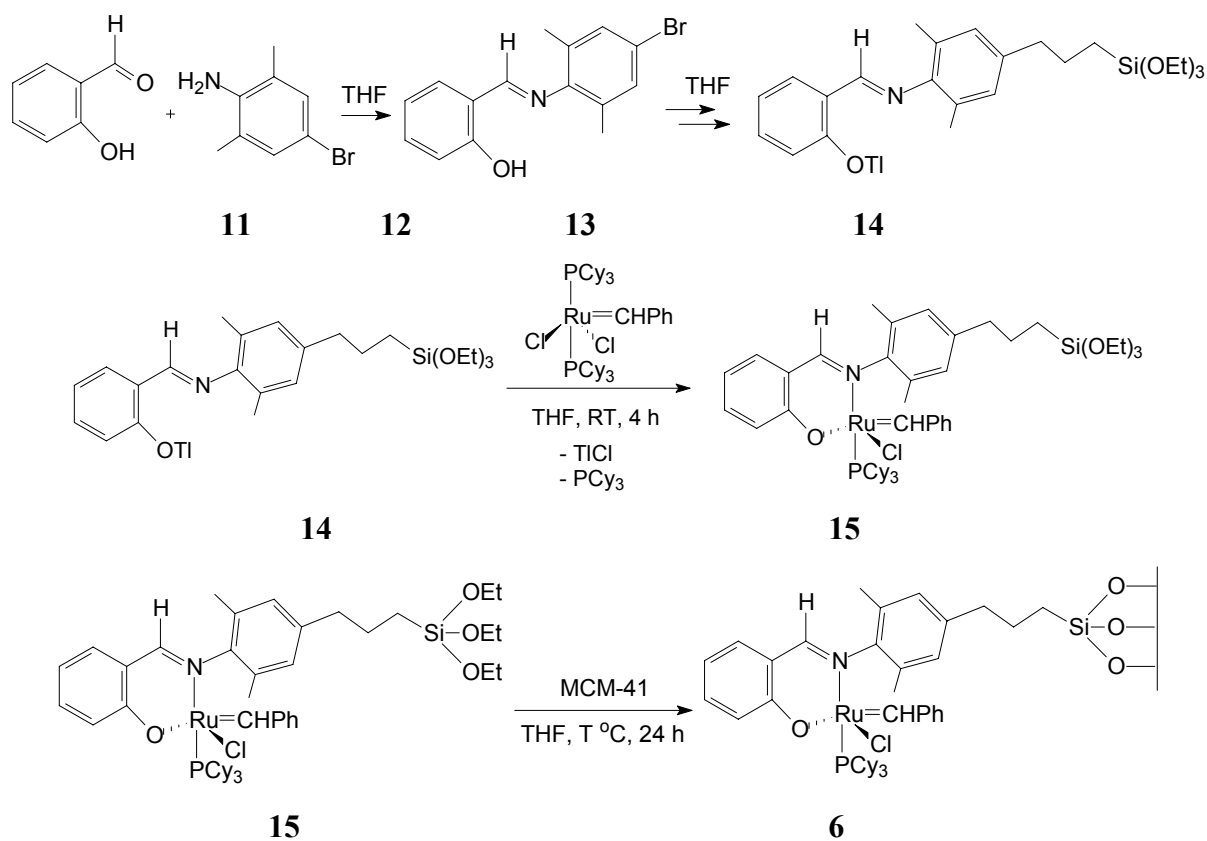
Scheme 6 – Synthesis of hybrid N,O-bidentate ruthenium complex **6.**

XRD measurements for supported complexes **2**, **5** and **6** indicated d_{100} spacing values of 3.692, 3.611 and 3.714 nm and a_0 values ($a_0 = 2d_{100}/\sqrt{3}$) of 4.260, 4.170 and 4.289 nm, respectively. The pore size distributions of the support and heterogeneous catalysts were calculated using the desorption branches of the N_2 adsorption isotherms and the Barrett-Joyner-Halenda (BJH) algorithm.[26] The specific surface areas were determined using Brunauer-Emmett-Teller (BET) equation.[27] The data obtained from N_2 adsorption analyses and XRD measurements for catalysts **2**, **5** and **6** as compared with that of the MCM-41 support are summarized in Table 1.

Table 1

Characteristics of the MCM-41 support and the heterogeneous catalysts **2**, **5** and **6** determined from XRD measurements and N_2 adsorption analyses

Catalyst	d_{100} nm	a_0 nm	S_{BET} m^2/g	V_P cm^3/g	APD nm	Wall thickness
MCM-41	3.733	4.310	1303	1.0213	2.53	1.76
2	3.692	4.260	625	0.6216	2.43	1.83
5	3.611	4.170	592	0.6054	2.40	1.77
6	3.714	4.289	602	0.6108	2.42	1.79

Note: d_{100} = determined from XRD spectrum; $a_0 = 2d_{100}//3$; S_{BET} = specific surface area determined from N_2 adsorption isotherms using Brunauer-Emmett-Teller (BET) equation[27]; V_P = pore volume determined by Barrett-Joyner-Halenda (BJH) algorithm[26]; APD = average pore diameter obtained from pore size distribution curve; Wall thickness = a_0 – APD.

As the XRD pattern for supported catalysts is practically the same as for the solid support sample (d_{100} = 3.733 nm and a_0 = 4.310 nm), we concluded that the anchoring of the complex *via* a spacer molecule did not affect the hexagonal long-range ordered structure of the mesoporous MCM-41. However, the N_2 adsorption analysis clearly indicated that the specific surface area, pore size and volume of the solid support were diminished by incorporation of the Ru complexes. These results revealed that all the parameters of the internal pores from the MCM-41 have been altered by the catalytic complex but the accessibility of the mesoporous structure is further maintained after the modification.

To further demonstrate that the homogeneous complexes formed a covalent bond with MCM-41 through immobilization, we underwent a detailed Raman spectroscopic study of the heterogeneous complexes **2**, **5** and **6** in comparison with the homogeneous counterparts. Taking advantage of the low intensity scattered by the mesoporous support, Raman spectroscopy showed in our case to be an ideal technique to examine the grafting of the homogeneous complex. By comparing the Raman spectra of MCM-41 with those of the spacer modified supports the superposition of the spacer vibrations on the MCM-41 baseline has been observed. Furthermore, comparison of the Raman spectrum of spacer modified homogeneous complexes with that of hybrid catalyst were performed to eliminate any doubt concerning the chemical attachment of the homogeneous complex on the support. We clearly observed that every peak in the spectrum of the homogeneous complex was also present in the spectrum of the heterogeneous catalyst. However, the small shifts of several of the original peaks indicated the change in chemical environment of the different functional groups stemming from the chemical attachment of the catalyst to the carrier. Based on these results, we may conclude that the covalent anchoring of the spacer modified homogeneous catalyst precursors occurred successfully on the mesoporous MCM-41 support. Additionally, X-ray fluorescence (XRF) and inductive coupled plasma/mass spectrometry (ICP/MS) revealed loadings of 0.088, 0.1069 and 0.054 mmol Ru complex/g heterogeneous catalyst **2**, **5** and **6**, respectively.

The structures of **2**, **5** and **6** have also been studied by solid state NMR spectroscopy. For the MCM-41 support the proton spectrum reveals only the presence of silanol groups and water. In the ^{29}Si CP MAS NMR spectrum of MCM-41 three different peaks were observed assigned to $Si(OH)_2(OSi)_2$, $Si(OH)(OSi)_3$ and $Si(OSi)_4$, respectively. The proton NMR spectra of the heterogeneous catalysts **2**, **5** and **6** reveal the presence of aromatic and aliphatic protons as broad unresolved peaks. The ^{13}C CP MAS NMR spectra revealed the carbon of the C=N bond in addition to the aromatic and aliphatic carbon atoms. The ^{29}Si CP MAS NMR spectra indicated the presence of $(SiO)_3Si^*C-$, $(SiO)_2(OEt)Si^*C-$, $(SiO)_2(OH)Si^*C-$

species while the ^{31}P CP MAS NMR spectra revealed the presence of PCy$_3$. All these data indicated that the anchoring of the homogeneous complex *via* the spacer molecule onto the MCM-41 support took place through two and three covalent bonds. Moreover, these results definitely showed that the homogeneous complexes **2**, **5** and **6** were linked covalently with the mesoporous MCM-41 carrier.

2. Selective applications of immobilized ruthenium complexes

The immobilized ruthenium complexes **2**, **5** and **6** generally displayed a comparable or higher selectivity than their homogeneous counterparts. Results obtained in our group on enol-ester synthesis (Eq. 1), Kharasch addition (Eq. 2), RCM (Eq. 3), ROMP (Eq. 4) and ATRP (Eq. 5) reactions, using the above immobilized Ru complexes [Mt] combined with the very easy separation of reaction products and efficient recovery of the catalyst, certainly strongly recommend the application of the hybrid heterogeneous systems in these catalytic processes.

Enol-ester synthesis by vinylation of carboxylic acids with substituted acetylenes in the presence of catalysts 2, **5** and **6** showed to be an efficient process, with a high synthetic value. Reaction of formic and acetic acids with phenylacetylene occurred in 90-99% yields by a prevailingly Markovnikov (M) pathway (up to 82%) whereas the reaction of the same carboxylic acids with 1,7-octadiyne gave mainly *anti*-Markovnikov products (up to 79%) in 63-86% yields. Catalysts **2** and **6** displayed a higher activity as compared to the catalyst **5** (Table 2). The total yield, however, was essentially dependent on the carboxylic acid used and other reaction parameters (temperature, molar ratios). It should be pointed out that dimerization of acetylenes to enynes was not observed in this process, in contrast to related ruthenium (II) complexes containing N,N-bidentate ligands.[28,29]

Kharasch addtion of CCl$_4$ to olefinic substrates (styrene, diethyl allylmalonate, methyl methacrylate, isobutyl methacrylate, methyl acrylate and butyl acrylate) occurred effectively with the immobilized catalysts **2**, **5** and **6,** under standard conditions (Table 3).
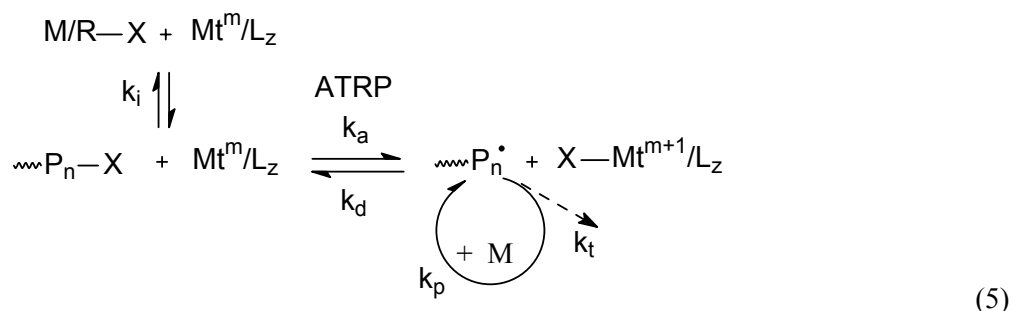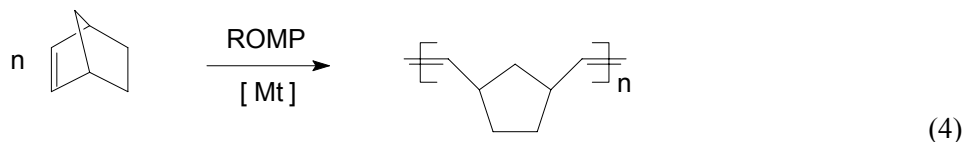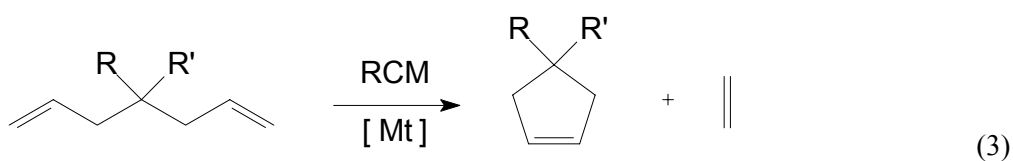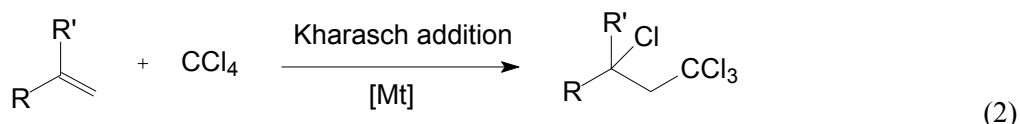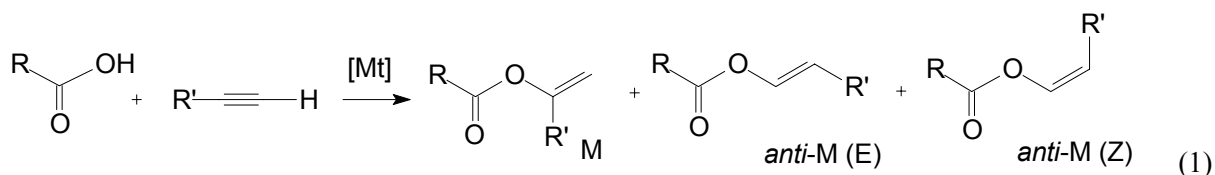

(1)

(2)

(3)

(4)

(5)

Table 2

Enol-ester synthesis from substituted acetylenes and carboxylic acids using immobilized Ru complexes **2**, **5** and **6**

Substituted acetylene	Carboxylic acid	Yield (%)			Markovnikov (M) (%)			*anti*-Markovnikov (Z)(%)			*anti*-Markovnikov (E)(%)		
Catalyst		**2**	**5**	**6**	**2**	**5**	**6**	**2**	**5**	**6**	**2**	**5**	**6**
Phenylacetylene	Formic acid	99	90	96	2	71	82	-	9	5	8	20	13
	Acetic acid	93	93	99	-	45	74	-	22	9	6	33	17
	Formic acid	70	75	63	16	8	6	6	5	4	74	76	72
1,7-Octadiyne	Acetic acid	82	86	75	14	11	15	3	3	-	78	79	78

Table 3

Yields (%) in Kharasch addition of CCl_4 to olefinic substrates with immobilized Ru catalytic systems

Olefinic substrate	Catalyst **2**	Catalyst **5**	Catalyst **6**
Methyl methacrylate	78	16	43
Isobutyl methacrylate	50	9	25
Methyl acrylate	29	19	37
n-Butyl acrylate	15	13	22
Styrene	85	67	91
Diethyl allylmalonate	-	74	85

The outcome of the reaction depended very much on the catalytic system, the olefinic substrate and the reaction temperature. For all substrates the activity of the catalyst **5** was considerable lower than that of **6** and this substantial difference was also maintained at high reaction temperatures. For instance, catalyst **6** converted styrene in 63 and 91% yield at 65 and 85°C, respectively, whereas catalyst **5** only reached 45 and 67% conversion at the respective temperatures. Styrene and diethyl allylmalonate were clearly the two substrates that allowed the highest turnover, irrespective of the catalytic system employed. A comparison of the results obtained for methyl acrylate and butyl acrylate, on one hand, and methyl methacrylate and isobutyl methacrylate, on the other, revealed that the conversion decreased substantially when the substrate became too bulky and this happened for both catalysts. To illustrate this fact, the best performing catalyst **6** gives halogenated product from methyl acrylate and methyl methacrylate in 37 and 43% yield, respectively, at 85°C, whereas the more bulky counterparts, butyl acrylate and isobutyl methacrylate, were converted in only 22 and 25% yield, respectively, at the same reaction temperature. Another striking feature of this process was the spectacular increase of conversion with temperature in case of the most performant system **6**. Thus, nearly quantitative conversions were obtained for styrene and diethyl diallylmalonate in Kharasch addition with CCl_4 when reaction temperature was increased from 65 to 85°C, a result that has a considerable practical significance.

Ring-closing metathesis (RCM) reactions of various dienic substrates induced by catalysts **5** and **6** allowed cyclization to five-, six- and larger rings, in moderate to high yields, depending mainly on the dienic substrate, catalyst and reaction temperature (Table 4). Again catalyst **6** proved to be more active, but both catalysts led easily to quantitative conversions of 1,7-octadiene, diethyl diallylmalonate and diallyl ether to give the corresponding cyclic products, when working at 85°C. In the case of tri- and tetrasubstituted diallylmalonate, where currently lower conversions

(in the range 20-40%) have been obtained, harsh reaction conditions (temperature and time) had to be applied in order to reach satisfactory yields. Importantly, work-up of the RCM reaction simply consisted of the removal of the catalyst through filtration and evaporation of the solvent under vacuum.

Table 4

Isolated yields (%) in ring-closing metathesis of α,ω-dienes using immobilized Ru precatalysts **2, 5** and **6** *vs* homogeneous complex **1**[a]

α,ω-Diene	Product	1	2	5	6
		100	100	100	100
		71	73	41	58
		23	21	28	37
		100	100	100	100
		100	100	100	100
		94	89	69	82
		76	78	51	73

[a]Reaction conditions: catalyst loading = 5 mol%, temperature = 85°C, time = 17 h, solvent = toluene.

It is noteworthy that both strained and low-strained cycloolefins (e.g. norbornene or norbornene derivatives and cyclooctene) displayed a high reactivity in ring-opening metathesis polymerization (ROMP) on using both catalytic systems **5** and **6**, under normal reaction conditions. Thus, a large range of 5-substituted norbornenes as well as cyclooctene underwent ROMP in high yields (90-100%), in toluene or dichloromethane (Table 5). Notwithstanding, for some norbornene derivatives (*e.g.* 5-ethylidene-, 5-cyano- and 5-hydroxymethylnorbornene) only more severe conditions afforded high polymer yields. Although the solvent was not always relevant for results obtained in polymerization, there was a marked increase of the catalyst performance when working in dichloromethane, irrespective of the monomer employed. This effect was observed for catalyst **5**, even with less reactive monomers like 5-cyanonorbornene and 5-hydroxymethylnorbornene, when polymer yields increased from 17 to 68% and from 21 to 74%, respectively, upon changing the solvent from toluene to dichloromethane. Interestingly, in all ROMP reactions, the catalyst **5** proved to be more active than catalyst **6**; this result is in sharp contrast to that obtained in vinylation, Kharasch addition and RCM reactions with the same catalytic systems. On the other side, in perfect agreement with the general trend in the stereochemistry of ROMP, the polymers formed were mainly *trans*. Significantly, the *cis/trans* ratios were not considerably affected by the polymerization solvent.

From our data, it is obvious that heterogeneous catalytic systems **5** and **6** can be employed in

ROMP of a broad range of monomers including various norbornene derivatives and less strained cycloolefins. Moreover, in contrast to ROMP polymers obtained with related homogeneous ruthenium catalytic systems where after work-up the products have a pronounced discoloration due to ruthenium traces, the heterogeneous catalysts **5** and **6** provide colorless polymers of higher purity. Considering the behaviour of this class of immobilized catalysts in ROMP reactions, it is reasonable to state that they hold great promise for a full exploitation in separation techniques with high commercial potential. Their performance compares well with the recently developed separation techniques *via* ROMP or the ROMP based synthesis of heterogeneous catalytic supports.[30]

Table 5

Isolated yields (%) in polymer synthesis by ring-opening metathesis polymerization of 5-substituted norbornene and cyclooctene using immobilized Ru precatalysts **5** and **6**[a]

5-Substituted Norbornene(X) /Catalyst	**5**[b]	**6**[b]	**5**[c]	**6**[c]
X = Hydrogen	78	65	86	76
Ethyl	100	100	100	100
Butyl	100	100	100	100
Hexyl	83	76	89	79
Decyl	81	71	84	72
Ethylidene	34	28	45	32
Phenyl	70	61	77	64
Cyclohexyl	100	87	100	94
Cyano	17	5	68	53
Hydroxymethyl	21	8	74	66
Chloromethyl	79	74	98	91
Triethoxysilyl	100	86	100	90
Cyclooctene	98	90	100	100

a) Reaction conditions:catalyst = 0.005 mmol in toluene, norbornene = 2000 equiv., substituted norbornene = 800 equiv., cyclooctene = 200 equiv., temperature = 35°C, time = 6 h; b) Solvent = toluene; c) Solvent = dichloromethane

Atom transfer radical polymerization (ATRP) of styrene with both homogeneous and heterogeneous catalysts **1** and **2** showed clearly a marked decrease in activity when the heterogeneous system is employed. Furthermore, the decrease in initiation efficiency and the increasing polydispersity indicated a loss of control over polymerization with the heterogeneous system. Catalysts **5** and **6** displayed two different levels of activity in ATRP of styrene; the latter was more active, yielding 73% polymer, while the former produced only 11% polymer, under the same reaction conditions (Table 6).

For both catalysts the dependence of molecular weight (M_n) and polydispersity (PDI) on the monomer conversion indicated a "living" character, the termination reactions being almost completely excluded. These results demonstrate that ATRP with these two heterogeneous catalysts proceeds in a controlled fashion, allowing synthesis of polymers with predetermined molecular weights and narrow polydispersities.

Table 6

Atom transfer radical polymerization of styrene using homogeneous (**1**) and immobilized catalysts (**2**, **5** and **6**)

Catalyst	Polymer yield (%)	M_n (x 10^3)	PDI	Initiation efficiency[a] f_i
1	95	54	1.81	0.70
2	86	63	2.15	0.57
5	11	5.6	1.64	0.82
6	73	39	1.62	0.79

[a] Initiation efficiency, $f_i = M_{n\ theor}/M_{n\ exp}$

EXPERIMENTAL

All reactions and manipulations were performed under argon atmosphere by using conventional Schlenk-tube technique. Argon gas was dried over P_2O_5 (Aldrich, 97%). Commercial grade solvents were purified for 24 h over appropriate drying agents under nitrogen atmosphere. Cyclooctene and norbornene were purchased from Aldrich and distilled over CaH_2. All other compounds were purchased from Aldrich and used as such. The homogeneous catalysts were synthesized as previously described.[31] MCM-41 support was prepared according to literature.[32] Elemental analyses, N_2-adsorption analyses, GC analyses, X-ray diffraction (XRD) spectra, Raman spectra, X-ray fluorescence (XRF) and solid-state NMR spectra were recorded using the instruments and equipment associated with the laboratory of Inorganic and Physical Chemistry of Ghent University. Elemental analyses were performed with Carlo Erba EA 1110 equipment. The BET analyses were carried out on a Gemini Micromeritics 2360 surface area analyzer with Flow prep 060 degasser. XRD spectra were recorded on a Siemens diffractometer D5000. ^{1}H-NMR spectra (500 MHz) were recorded on a Bruker AM spectrometer. The chemical shifts were reported in ppm (TMS as reference standard). Solid NMR spectra were performed on a Bruker DSX-300 spectrometer operating at 300.18 MHz for ^{1}H-NMR, 75.49 MHz for ^{13}C-NMR, 121.51 MHz for ^{31}P-NMR and 59.595 MHz for ^{29}Si-NMR. The spectra were recorded under MAS conditions with a classical probe head allowing spinning frequencies up to 12 kHz. Raman spectra were recorded on a Bruker Equinox 55 spectrometer equipped with a FRA 106 module. The loadings of the heterogeneous catalysts were determined using a Varian Liberty ICP/MS spectrometer and an ARL 9400 Sequential XRF spectrometer. GC analyses were performed using a SPB-5 column, 30m x 0.25 mm x 0.25 μm film thickness, carrier gas He, 100 kPa, detector FID, gas chromatograph Varian 4600, MS Finnigan MAT ITD. The number- and weight-average molecular weights (M_n and M_w) and polydispersity index, (M_w/M_n) of the polymers were determined on a Waters Maxima 820 GPC instrument ($CHCl_3$, 25°C) equipped with PL gel column, using polystyrene (for styrene) and polymethylmethacrylate (for acrylates) standards.

CONCLUSIONS

The approach to immobilize Schiff base containing Ru complexes onto mesoporous silica surfaces MCM-41 applied by us essentially consisted of the treatment of the inorganic support with the tris(alkoxy)silyl functionalized Ru complex. This methodology has been successfully applied to synthesize and characterize heterogeneous arene and benzylidene ruthenium complexes **2**, **5** and **6**. Comparative studies on the activity and selectivity of the immobilized ruthenium complexes in enol-ester synthesis, Kharasch addition, ROMP and ATRP reactions led to the conclusion that the same general trend is manifested for complex **2** as for the related systems **5** and **6**. However, it should be outlined that under certain conditions a higher

activity has been observed for the catalyst **2** in RCM of dienic substrates as well as in enol-ester synthesis from the carboxylic acids and substituted acetylenes.

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