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Review

Ruthenium complexes bearing bidentate Schiff base ligands as efficient catalysts for organic and polymer syntheses

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Contents

Abstract

A concise overview is given on mononuclear and dinuclear, bidentate Schiff base ruthenium complexes with different additional ligands and on their applications in various chemical transformations such as Kharasch addition, enol-ester synthesis, alkyne dimerization, olefin metathesis and atom transfer radical polymerization. These new ruthenium complexes, conveniently prepared from commonly available ruthenium compounds, are very stable, exhibit a good tolerance towards organic functionalities, air and moisture and display high activity and chemoselectivity in chemical transformations. Relevant features of coordination chemistry connected with the reaction mechanism and chemoselectivity are also fully described. Since the nature of Schiff bases can be changed in a variety of ways, appealing routes for designing and preparing novel ruthenium complexes can be foreseen in the future.

Keywords: Schiff base ruthenium complex; Olefin metathesis; *N*-heterocyclic carbenes; Kharash addition; Enol-ester synthesis; Hybrid catalyst

1. Introduction

Due to their increasing potential as versatile catalysts for organic synthesis and polymer chemistry, Ru-complexes

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witnessed a spectacular development during the last decade [1–20]. Several families of ruthenium compounds have been prepared and extensively used in a variety of chemical transformations such as hydrogenation [21], hydration [22], oxidation [23], epoxidation [24], isomerization [25], decarbonylation [26], cyclopropanation [27], olefin metathesis [28], Diels–Alder reaction [29], Kharasch addition [30], enol-ester synthesis [30], atom transfer radical polymerization [31] and other related catalytic processes [32]. To achieve an appropriate balance between the electronic and steric environment around the metal and in order to control their activity, stability and chemoselectivity, many of these novel ruthenium complexes have been endowed with specific ligands (e.g. hydride, halide, hydrate, carboxylate, phosphane, amine, oxygen or nitrogen chelating groups, Schiff bases, arenes, carbenes, etc.) [33–45]. Some of the novel ruthenium complexes are chiral [46] or immobilized on solid supports [47]. As result of their particular structure, these ruthenium complexes display an enhanced activity and selectivity in a multitude of organic transformations [48]. Significantly, some of the above ligands impart to the catalyst a good tolerance towards organic functionalities, air and moisture, in this way widening the area of their application [49–51].

For several reasons, Schiff bases have been found to be among the most convenient and attractive ligands for ruthenium complexes. First, steric and electronic effects around the Ru core can be finely tuned by an appropriate selection of bulky and/or electron withdrawing or donating substituents incorporated into the Schiff bases. Secondly, the two donor atoms, N and O, of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor known to stabilize the higher oxidation state of the ruthenium atom whereas the imine nitrogen is a softer donor and, accordingly, will stabilize the lower oxidation state of the ruthenium. Thirdly, Schiff bases are currently prepared in high yield through one-step procedures via condensation of common aldehydes with amines, in practically quantitative yields [52].

Taking into account the highly desirable attributes of this type of ligands, vast families of bidentate, tridentate and tetradentate Schiff base-ligated ruthenium complexes, of wide applicability as catalysts in numerous organic reactions, have been designed and prepared. Some of them, e.g. tetradentate Ru–salen [53] and Ru–porphyrin [54–56] complexes, boast good to excellent activity and remarkably high dia- and enantioselectivity in catalyzing a variety of organic processes.

The so-called “dangling-ligands”, particularly those of salicylaldiminato-type, have been recently introduced by our group in arene, alkylidene, indenylidene, vinylidene and diene ruthenium complexes [30,57,58]. In association with other commonly used ligands like chloride, phosphane, imidazol-2-ylidene, cyclodienes, they provided a novel class of ruthenium catalysts of versatile application and utility in organic synthesis and polymer chemistry. This approach opens access to rather robust and quite stable catalysts at room temperature and highly active systems at slightly elevated temperatures that ideally promote several organic transformations such as olefin metathesis reactions (e.g. ring-closing metathesis (RCM), cross metathesis (CM), enyne metathesis and ring-opening metathesis polymerization (ROMP)), certain radical reactions (e.g. atom transfer radical addition (ATRA or Kharash addition) and atom transfer radical polymerization (ATRP)) as well as alkyne dimerization and enol-ester syntheses. Of the many types of ruthenium complexes prepared by our group, homogeneous and immobilized complexes bearing bidentate Schiff base as a specific ligand are of great current interest and will constitute the subject of this review.

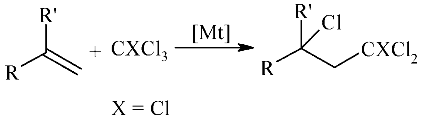
2. Homogeneous bidentate Schiff base ruthenium complexes

2.1. Arene ruthenium complexes

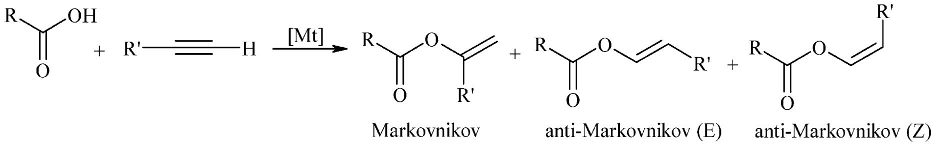
Starting from the easily accessible Ru-dimer, complex [(*p*-cymene)RuCl$_2$]$_2$ and aliphatic or aromatic salicylaldimines, three bidentate Schiff base-ligated ruthenium(II) arene complexes (**1a**–**c**) have been conveniently prepared by a two-step procedure shown in Scheme 1 [57,58].

The structure of these complexes has been determined by means of Raman, infrared, ^{1}H and ^{13}C NMR spectroscopy and corroborated with elemental analyses.

It has been demonstrated that complexes **1a**–**c** effectively catalyze the Kharash addition of halogenated alkanes to olefins to produce polyhalogenated alkanes (Eq. (1)) and reactions of carboxylic acids with alkynes leading to enol-esters by Markovnikov or anti-Markovnikov (*E* and *Z*) pathway [57] (Eq. (2)).

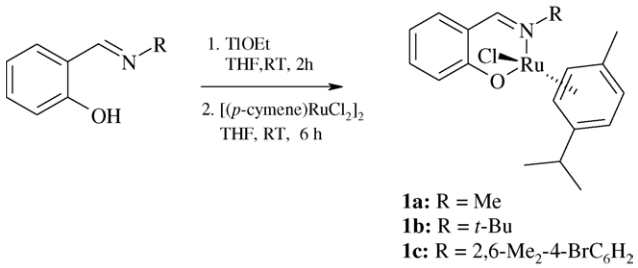


(1)



(2)

Thus, styrene and methyl methacrylate underwent a clean monoaddition of CCl$_4$ in the presence of complex **1c** yielding 88 and 73% polyhalogenated product, respectively, after 17 h at 65 °C. When performing the reaction with diethyl allylmalonate, a striking differentiation between these catalytic systems was observed. Whereas complexes **1a** and **1b**



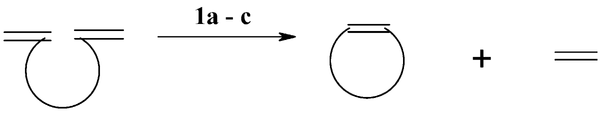
1a: R = Me
1b: R = *t*-Bu
1c: R = 2,6-Me_2-4-BrC_6H_2

Scheme 1. Synthesis of bidentate Schiff base ruthenium arene complexes.

catalyzed the addition with a conversion of ca. 40%, complex **1c**, the most active one, easily allowed a conversion of 56% to be attained. As mentioned above, Markovnikov and anti-Markovnikov pathways were clearly demonstrated in the reactions of carboxylic acids with alkynes induced by complexes **1a**–**c**. For instance, in the reaction of phenyl acetylene with either formic or acetic acid, the corresponding enolesters were produced prevailingly by a Markovnikov pathway (ca. 90%) when using complex **1b** as a catalyst, whereas complex **1c** lead to strikingly different results, depending on the substrate: for formic acid, reaction proceeded predominantly (79%) by anti-Markovnikov pathway while acetic acid yielded mainly the Markovnikov product (89%) [57].

These complexes readily induce atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate under usual conditions. For these two monomers, high yields of polymer, 93 and 84%, respectively, have been obtained upon using complex **1c** as the catalyst [58]. Herein, the role of the Schiff base ligand was assumed to be that of promoting the release of the arene ligand, creating the coordinatively unsaturated Ru-species capable of controlling the dynamic equilibrium between the propagating radicals $\sim P_n^{\bullet}$ and the dormant species in ATRP reaction (Scheme 2).

It is interesting to note that while complexes **1a**–**c** are able to readily catalyze Kharasch addition and ATRP reaction without any cocatalyst, when they are used in olefin metathesis (RCM and ROMP), they needed to be activated by trimethylsilyl diazomethane (TMSD) in order that a high conversions of the substrate to be obtained (Eq. (3) and Eq. (4)).



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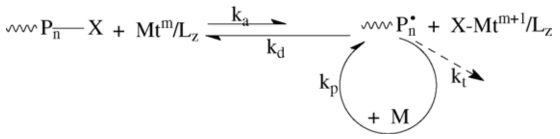
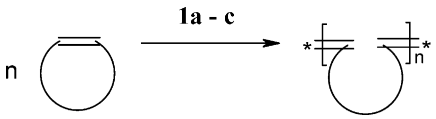


Scheme 2. Dynamic equilibrium in ATRP reaction.



(4)

In the absence of TMSD, complexes **1a**–**c** polymerize norbornene at a low monomer conversion (average yield 6%).

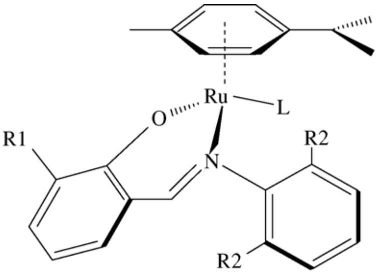
These data were rationalized by assuming that the 18-electron ruthenium complex initiates polymerization of norbornene through the loss of the *p*-cymene ligand, followed by coordination of the monomer and rearrangement of this latter coordinated ligand to form a new Ru–carbene complex which propagates further the polymerization process (Scheme 3).

Evidence for this mechanism was provided by the identification of methylene norbornene as a by-product in the norbornene polymerization with catalysts **1a**–**c**. This unprecedented finding corroborates with the amount of *p*-cymene released in the reaction medium. On the other hand, in the presence of TMSD, the Ru-complexes **1a**–**c** readily lost *p*-cymene with the formation of coordinated carbene and cycloolefin (Scheme 4).

Similar investigations dealing with olefin metathesis or related radical reactions induced by Ru–arene complexes have also shown that the release of the arene ligand is crucial for the generation of the active species in such processes [59–62].

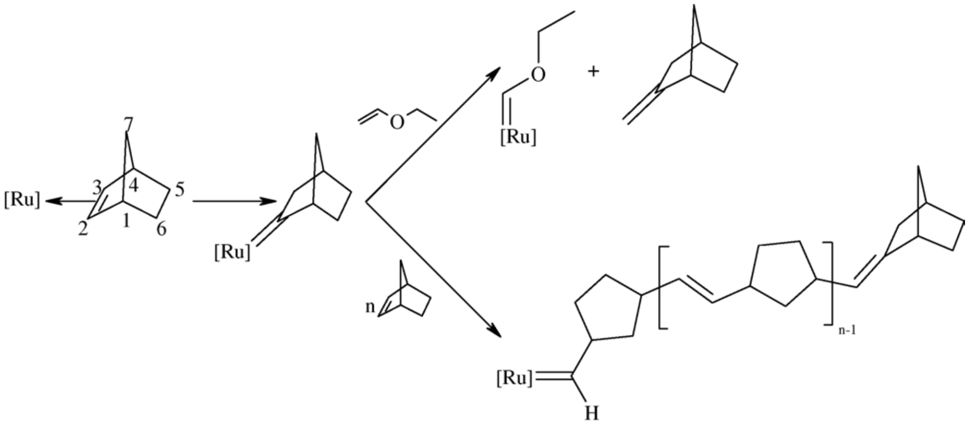
Preparation of two new Ru–arene complexes, **2** and **3**, was also successfully achieved by applying the above procedure [63]. The importance of the electronic structure of both the Schiff base ligand and the additional ligand (L) in Ru–arene complexes **2** and **3** (Fig. 1) has been clearly demonstrated in studies on ROMP and ATRP reactions.

Thus, while catalyst **2** (L = Cl) showed a moderate activity in ROMP of norbornene (yield of 35% at 85 °C) and ATRP of methyl methacrylate (yield of 33% at 85 °C) and styrene (yield of 51% at 110 °C), catalyst **3** (L = C_6F_5) displayed a high activity in both reactions (yields higher than 80%) [63]. Furthermore, though the use of cocatalysts and additives (Et_2AlCl and *n*-Bu_2NH) in the two catalytic systems improved the monomer conversion dramatically (in some cases, up to 100%), the catalyst **3** containing pentafluorophenyl group showed higher activity even in the absence of such additional compounds (e.g. yield of 86% in ROMP of norbornene at 85 °C). To rationalize the catalytic activity of these Ru–arene catalysts in ROMP of norbornene, with



2. L = Cl, R_1 = *t*-Bu,
R_2 = *i*-Pr.
3. L = C_6F_5, R_1 = *t*-Bu,
R_2 = *i*-Pr.

Fig. 1. Schiff base ruthenium arene complexes **2** and **3**.



Scheme 3. Postulated mechanism for norbornene polymerization with arene ruthenium complexes.

or without Et_2AlCl as a cocatalyst, the following possible reaction course (Scheme 5) has been proposed [63].

Herein, the formation of the initial Ru–carbene intermediate by direct coordination of the monomer to the coordinatively unsaturated Ru-species followed by 2,3-hydrogen shift has been unambiguously demonstrated by ^1H NMR studies during norbornene polymerization induced by catalysts **2** and **3** [63]. The content of the carbene proton detected in the ^1H NMR spectrum during the polymerization process was in agreement with the amount of free *p*-cymene released in solution. Alternatively, the role of the aluminum compound, added to the Ru–arene complex, was assumed to stabilize the 14-electron intermediate and facilitates the formation of the initiating metallacarbene species.

2.2. *Mononuclear and dinuclear ruthenium–alkylidene complexes*

A range of new mononuclear and dinuclear benzylidene ruthenium complexes (**4a**–**f** and **5a**–**f**), bearing Schiff bases as bidentate ligands, has been prepared, characterized and tested in RCM and ROMP reactions [30]. The synthetic routes for these two families of Ru-complexes are illustrated in Scheme 6.

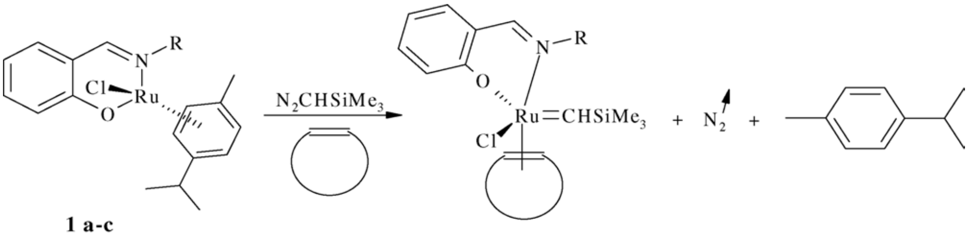
It is to be noted that the results obtained in RCM of linear dienes and ROMP of cyclooctene and norbornene revealed that the synergy of the Schiff base ligand with the existing coordinatively labile ligands around ruthenium endowed dinuclear catalytic systems with a high activity and good stability. Yields of even 100% have easily been reached in RCM of 1,6-heptadiene, 1,7-octadiene and diallyl ether as well as in ROMP of norbornene and 5-substituted norbornene. However, it is remarkable that whereas results obtained in RCM and ROMP with dinuclear complexes **5** indicated the same order of activity (**5e** > **5f** > **5c** > **5d** > **5a** > **5b**), the set of mononuclear complexes **4** behaved differently (i.e. in RCM the catalyst activities decreased generally in the order **4f** > **4e** > **4d** > **4c** > **4b** > **4a** while in ROMP the activities decreased as follows: **4b** > **4a** > **4d** > **4c** > **4f** > **4e**).

The above results for mononuclear and dinuclear ruthenium complexes in RCM and ROMP reactions can be explained by a dissociative mechanism in agreement with the ones proposed for similar complexes [64] (Scheme 7).

An interesting aspect of this mechanism is that for the mononuclear complexes of type **4** the process involves the decoordination and subsequent coordination of “one-arm” of the bidentate Schiff base ligand instead of the usual PCy_3 dissociation encountered in conventional phosphane-based complexes. Such a dissociation of the nitrogen-bonded arm of the chelated salicylaldimine ligand was supported by the following observations:

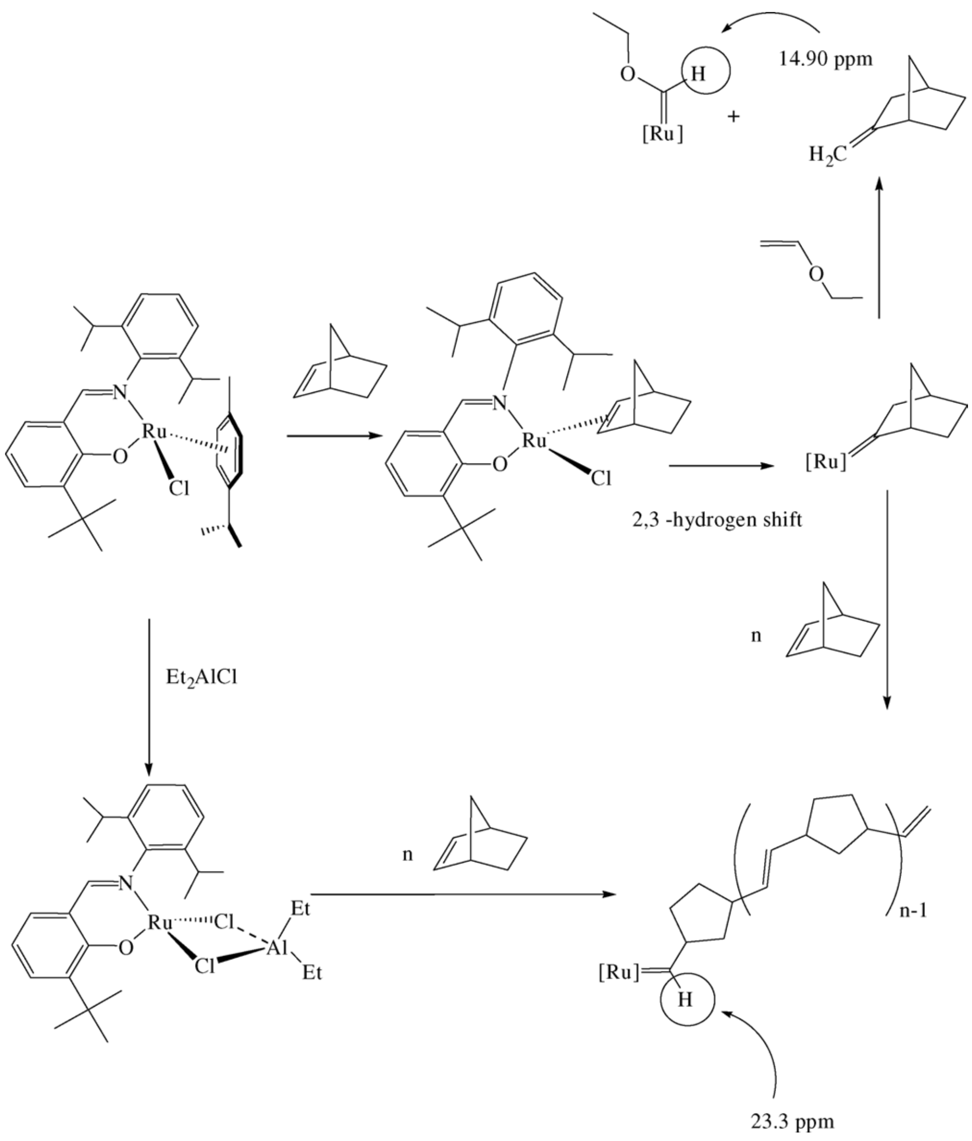
(i) Addition of CuCl, a well-known phosphane scavenger, to solutions of several catalysts of class **4**, in the presence of an olefinic substrate, did not result in a noteworthy increase of the activity in ROMP and RCM reactions.

(ii) When nitrogen donors are used as co-ligands, in combination with phosphorus counterparts as donors, the

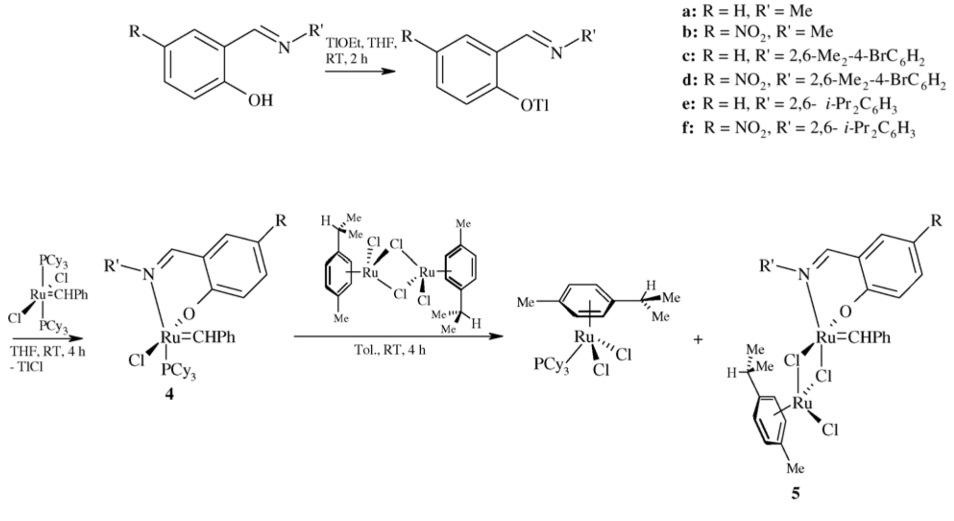


1 a-c

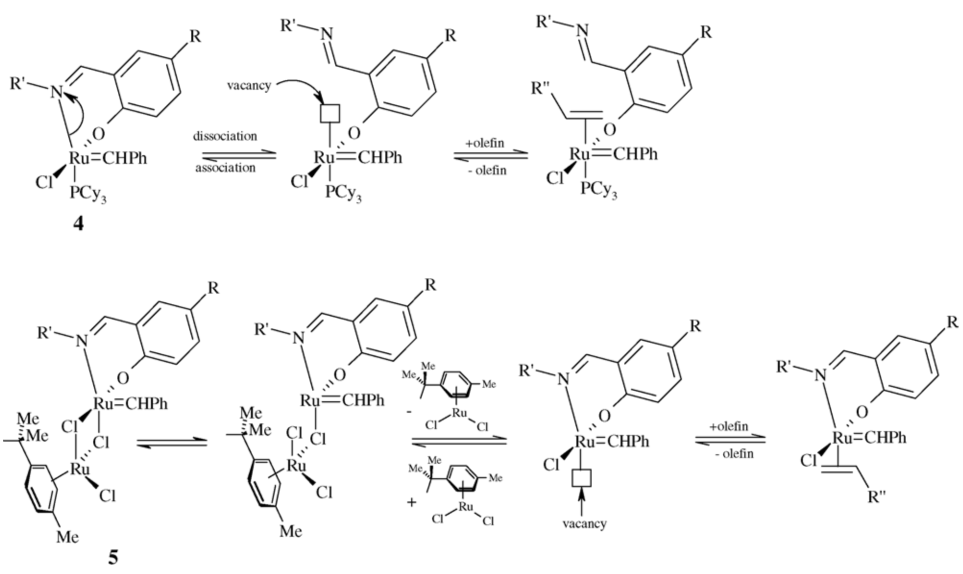
Scheme 4. Mechanism of cycloolefin coordination at the ruthenium complex.



Scheme 5. Possible reaction pathway in norbornene polymerization with ruthenium arene complexes **2** and **3**.



Scheme 6. Synthesis of mononuclear and dinuclear benzylidene ruthenium complexes.



Scheme 7. Proposed dissociative mechanism for olefin metathesis with **4** and **5**.

so-called *trans* effect [65] must be taken into account. In a given complex there may exist an inert, coordinated phosphane ligand with a kinetically labile phosphorus donor ligand trans to it. For complexes containing both nitrogen and phosphorus donor ligands in their coordination sphere, this *trans* effect will play a decisive role in the dissociation process of both ligands because of the small difference in electron donating properties of these ligands [66,67]. In this case, one should not take into account the dissociation of the oxygen-bonded arm of the salicylaldimine ligand because the oxygen atom is not in a *trans* position to the phosphorus and [Mt]–O bonds are in general much stronger than [Mt]–N bonds [68].

(iii) The "hard and soft acid-base theory" can also be considered to explain a favourable dissociation of the nitrogen donor versus the phosphorus one. The fairly soft late-transition metal ruthenium will prefer to bind with the softer phosphorus donor instead of the harder nitrogen donor [69].

(iv) Obviously, the most stable organometallic compounds are those in which all low-energy orbitals are involved in (preferably) two-electron bonding. This implies an absence of unpaired electrons on the metal centre which happens when the metal has an even number of electrons and when the complex is of the low-spin type, that is, when there is a maximum pairing of all the available metal d electrons [70]. As a matter of fact, it is well known that nitrogen donors are not as effective in producing low-spin complexes with the consequence that the species produced are less thermodynamically stable and more kinetically labile than their low-spin analogues with phosphorus donors [71].

(v) [Mt]–N bonds are mainly of the σ-type and [Mt]–P bonds of both the σ- and π-type [66,68]. However, with ligands containing sp^2-hybridized nitrogen atoms, as is the case with Schiff base ligands, π-interactions and, accordingly, π-back-bonding effects can take place. Nevertheless, while such effects doubtless intervene, the extent to which they determine the binding between a sp^2-hybridized N-ligand and the metal remains much smaller than the influence exerted on the binding properties between the P-containing ligands and metal centres [67].

(vi) The particular influence of the steric bulk of Schiff base ligands on the catalytic performance of type **4** initiators is in line with the fact that the strength of [Mt]–N bonds is considerably affected by steric factors [72].

Further evidence for a dissociative mechanism induced by catalytic systems of type **4** was provided by our group through a careful ^{31}P NMR examination of norbornene polymerization. Thus, after transferring 0.5 mmol of the catalyst solution (in C_6D_5Cl) into a vessel followed by addition of 1 equiv. of norbornene solution (in C_6D_5Cl), the reaction mixture was heated at 70 °C and NMR-samples were taken from the reaction mixture, at regular intervals, and analyzed by ^{31}P NMR spectroscopy. Monitoring the reaction course in this way, no evidence showed for the release of the PCy_3 ligands in solution.

In the case of the dinuclear initiators **5** the above dissociative mechanism is in total agreement with the findings of Herrmann and co-workers [64a] with similar dinuclear ruthenium complexes. A two-step dissociation mechanism involving a sequential heterolytic cleavage of the two chloro bridges in the complex **5** and liberation of the coordinatively labile ligand {(*p*-cymene)RuCl$_2$} as the key step in the olefin metathesis is highly probable. The *trans* effect exerted by the chloro-metal bond on the stability of the [Mt]–N bond should not be considered here because it is well known that chloride ligands exhibit very weak *trans* labilizing effects [66]. Thus, taking into account (i) the absence of a ligand with a strong labilizing effect *trans* to the [Mt]–N bond, (ii) the lability of the $\{(p\text{-cymene})RuCl_2\}$ fragment and (iii) the possibility that the dissociation of the $\{(p\text{-cymene})RuCl_2\}$ fragment can be assisted by the exothermic dimerization reaction yielding $[(p\text{-cymene})RuCl_2]_2$ [64a], it is quite reasonable to believe that the dinuclear catalysts **5** are able to populate the dissociative pathway.

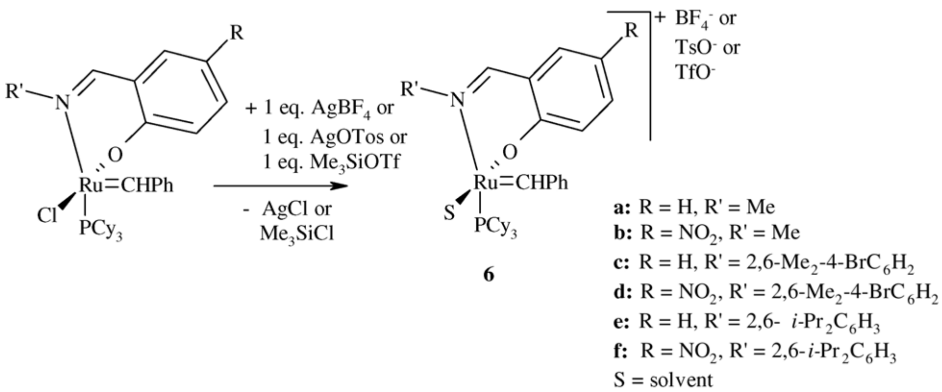
The observed activities of the catalytic systems **4** and **5** in ROMP and RCM reactions have been explained according to the mechanism illustrated in Scheme 5. In the case of dinuclear complexes, the high activity in ROMP and RCM due to increased bulkiness of the Schiff base ligand and the electron-withdrawing effect of the nitro substituent make perfect sense because according to the proposed mechanism, the active intermediate (having a vacancy for olefin coordination) is stabilized; when the steric and electronic parameters are altered through different substitution the active intermediate will be either stabilized or destabilized. Furthermore, for mononuclear complexes, the influence of the electron-withdrawing nitro substituent from the Schiff base on the catalytic activity in RCM and ROMP reactions is in excellent agreement with the proposed scheme. Indeed, by diminishing the electron density on the nitrogen atom, the "one-arm" decoordination of the chelated salicylaldimine ligand is stimulated. The opposite influence of the steric bulk on the RCM and ROMP performances with this type of initiators can be understood when keeping in mind that during the ROMP process the growing polymer chain remains attached at the metal centre. Only after a certain degree of polymerization the incoming new monomer will be severely hindered by this "polymer-tail" when the Schiff base is too bulky.

Interesting results were obtained in ATRP reactions of vinyl monomers mediated by cationic Ru–benzylidene catalysts **6a–f**, prepared in situ from the corresponding neutral complexes (Scheme 8) [73].

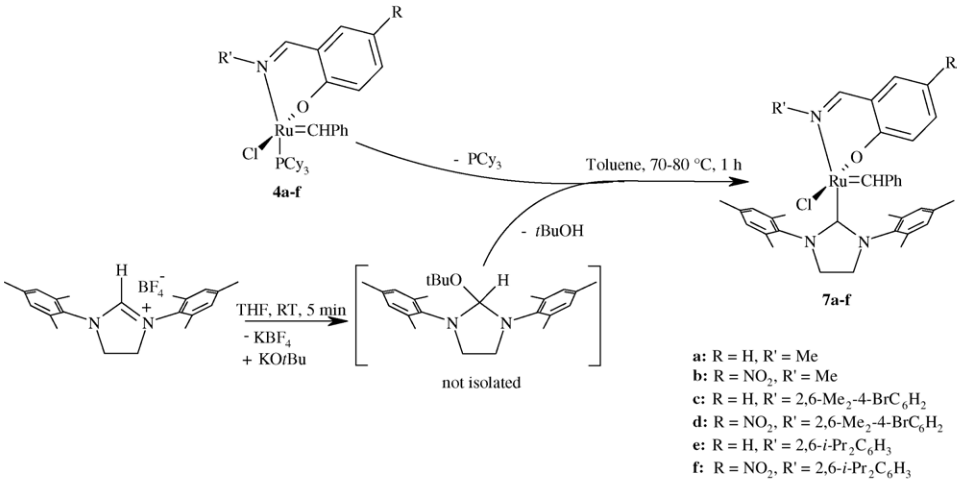
For instance, the best member in this panel of complexes, **6d**, having BF_4^- as counterion, catalyzed polymerization of styrene, methyl acrylate and methyl methacrylate, in toluene, giving 98, 81 and 77% yields, respectively, whereas in a water/toluene mixture the yield reached 91, 68 and 67%, respectively. In both reaction media, in water/toluene mixture and in toluene, the monomer conversion depends dramatically upon the counterion, decreasing in the order $BF_4^- > TsO^- > TfO^-$. With BF_4^- as the counterion and water/toluene mixture as the solvent, the polydispersities were 1.48, 1.37 and 1.34 and the initiation efficiencies 0.88, 0.81 and 0.89, for polystyrene, poly(methyl acrylate) and poly(methyl methacrylate), respectively, whereas in toluene solution the polydispersities increased to 1.71, 1.66 and 1.46 while the initiation efficiency decreased to 0.73, 0,66 and 0.67, respectively. In conclusion, our data revealed that both the counterion of the cationic complex and the solvent used for polymerization exert a considerable effect on the activity of these catalytic systems and on their ability to control the polymerization process. These cationic ruthenium benzylidene complexes are the first Ru–alkylidene complexes reported so far to perform the controlled radical suspension polymerization of styrene, methyl acrylate and methyl methacrylate in water, with good to excellent yields. Furthermore, the fact that these catalysts also exhibit promising activities in ROMP reactions allowed us to combine the ATRP and ROMP methodologies to make block copolymers with valuable properties by using new monomer formulations [73].

2.3. N-heterocyclic carbene (NHC) ruthenium–alkylidene complexes

A substantial advancement in the chemistry of Ru–carbene complexes has taken place with the development of Ru–benzylidene complexes containing *N*-heterocyclic carbene (NHC) ligands [74–76]. NHC ligands are excellent σ-donors and form quite strong metal carbon bonds; and therefore, catalysts bearing NHC ligands generally have better air and thermal stability than the corresponding phosphane complexes. In addition, their high dissociation energy makes them promising candidates for chiral modification and catalyst immobilization. As our previous studies pointed out, the



Scheme 8. Synthesis of cationic Ru–benzylidene catalysts **6a–f**.



Scheme 9. Synthesis of NHC ruthenium Schiff base complexes (**7a**–**f**).

electron density at the metal centre is crucial for good catalyst performances of the ruthenium Schiff base complexes. The properties mentioned above, of the NHC ligands, could translate into catalysts with improved reactivity and stability. To this end, we have synthesized and characterized a new class of bidentate Schiff base ruthenium complexes (**7a**–**f**) containing 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene ligands (Scheme 9) [77].

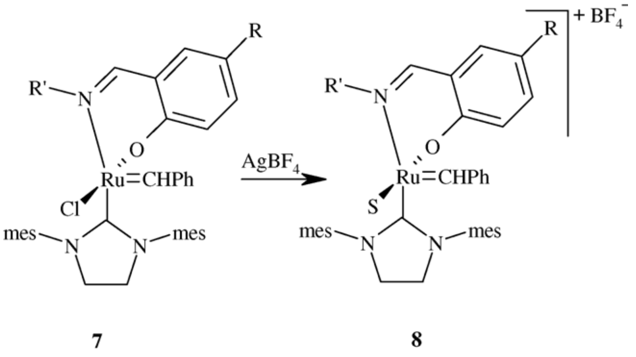
Extensive studies on RCM, ROMP, Kharasch addition, enol-ester and enyne syntheses induced by catalysts of type **7** indicated constantly higher activity and improved stability of the NHC Ru-catalysts as compared to the phosphane congeners [77,78]. Yields of 100% have easily been attained in RCM of 1,6-heptadiene, 1,7-octadiene or diallyl ether with catalysts **7a**–**f** under very mild conditions. ROMP of a wide range of 5-substituted norbornenes occurred with conversions ranging currently from ca. 50 to 100%, depending essentially on the catalyst and substituent. Best results have been obtained when complexes **7a** and **7b** have been employed with 5-ethyl-, 5-butyl-, 5-chloromethyl- and 5-triethoxysilylnorbornene as substrate [77]. Interestingly, appreciable conversions (70–96%) have been recorded in Kharash addition of carbon tetrachloride to methyl methacrylate, isobutyl methacrylate, diethyl allylmalonate and styrene induced by complex **7d**, working either under normal conditions or upon heating [78].

Furthermore, the corresponding cationic Ru–benzylidene complexes **8** have been prepared and their catalytic properties in ATRP of vinyl monomers have been investigated (Scheme 10) [79].

Comparative studies on radical polymerization of hydrophobic monomers such as methyl methacrylate, methyl acrylate and styrene, using both toluene and water/toluene mixtures as the solvent, demonstrated that with these cationic systems the solvent is crucial for the activity and controllability of the process. Moreover, our results showed that in aqueous/organic biphase conditions, these ruthenium cationic complexes are highly active in radical polymerization of hydrophobic monomers leading to polymers with controlled molecular weights and narrow molecular weight distributions [79].

It is interesting to note that the Fischer-type Ru–alkylidene complexes **8a** and **8b** have been generated in situ from the corresponding indenylidene counterparts (vide infra) by metathesis with vinyl ether derivatives [30] (Fig. 2).

When tested for ATRP of methyl methacrylate, catalyst **8b** manifested itself as one of the most active Ru–carbene systems known to date, leading to almost quantitative conversion of the monomer. Significantly, this catalyst gave a polymer with a polydispersity index of 1.30 and an initiation efficiency of 0.97. On top of that, the cationic congeners were very active (100% conversion) in pure toluene and water/toluene mixtures and in both cases the observed molecular weight distribution remained relatively narrow ($M_w/M_n = 1.28$ and 1.40). The exact mode of action of the carbene entity is not clear yet and needs further investigations. We assume that the active ATRP species derive from the carbene fragment. This assumption is strongly supported by the fact that the phosphane containing system, **8c**, is not active in ATRP reactions. Remarkably, the results obtained with the high performing system **8b** can compete with the well-known copper systems for ATRP polymerization of methyl methacrylate [80].



Scheme 10. Synthesis cationic NHC Ru–benzylidene catalysts **8**.

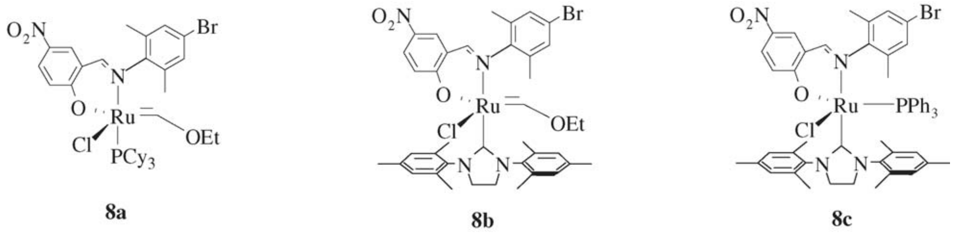


Fig. 2. Fischer-type Ru–alkylidene complexes **8a** and **8b** and phosphane containing analogue **8c**.

2.4. Ruthenium–indenylidene complexes

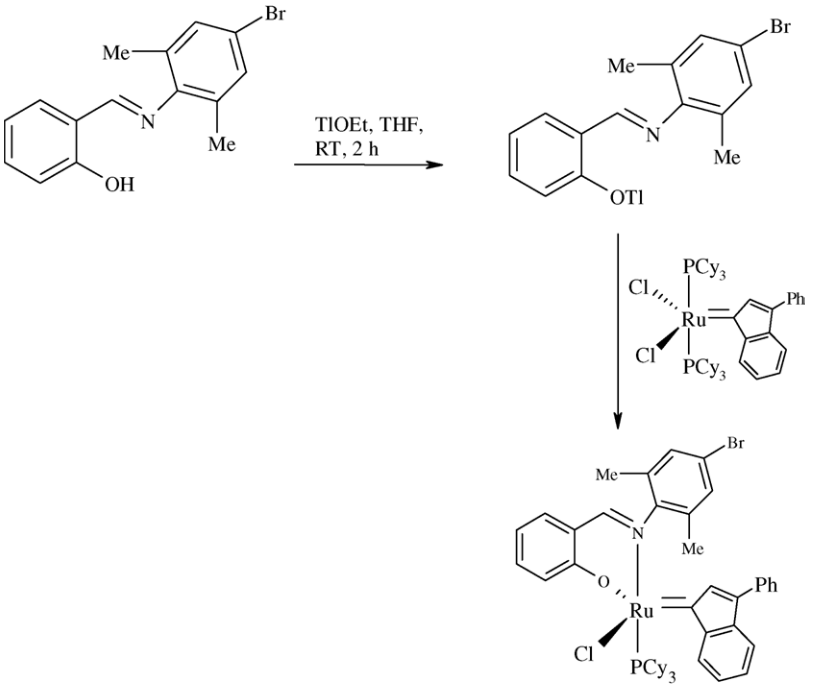
Ru–indenylidene complexes bearing diphosphane ligands have been readily prepared by several groups [81–83] through treatment of $RuCl_2(PPh_3)_3$ with 1,1-diphenylprop-2-yn-1-ol, in refluxing tetrahydrofuran, followed by exchange of PPh_3 for PCy_3, in CH_2Cl_2 at room temperature. Even though initially the catalyst structure was not unambiguously clear, the expected catalytic activity in RCM was rapidly recognized [84,85]. Starting from such a diphosphane Ru–indenylidene complex and aromatic salicylaldimine, we prepared the Ru–indenylidene complex **9**, containing Schiff base as a bidentate ligand (Scheme 11) [86].

Complex **9** was characterized by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and elemental analysis and successfully applied in enol-ester synthesis through nucleophilic addition of carboxylic acids to terminal alkynes.

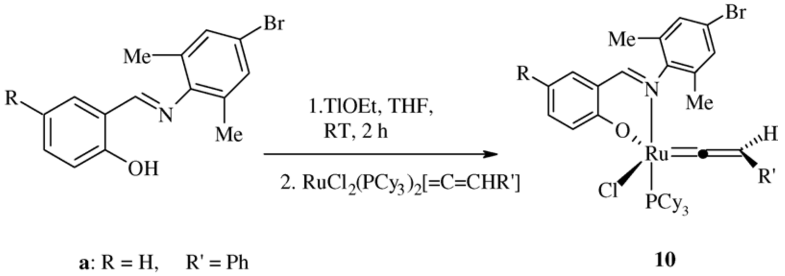
On using this complex, high yields (95–98%) have been obtained in addition reactions of aromatic acids (e.g. benzoic acid) with phenylacetylene and moderate yields (60–77%) in the similar reaction of aliphatic acids (e.g. formic, acetic, isovaleric acids). Rather satisfactory results were recorded in ATRA of carbon tetrachloride with methyl methacrylate, methyl acrylate, *n*-butyl acrylate, acrylonitrile and styrene as well as in ATRP of methyl methacrylate and styrene [87]. Further improvements in the catalyst activity and stability have been achieved by substitution of the phosphane ligand with 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene group [1a]. Interestingly, some results obtained with catalyst **9** are comparable with the data for the best Ru-catalysts in this type of reactions [88].

2.5. Ruthenium–vinylidene complexes

Taking advantage of our methodology applied in the synthesis of Schiff base Ru-complexes, we prepared and characterized a new class of Ru–vinylidene complexes **10** from



Scheme 11. Synthesis of bidentate Schiff base Ru–indenylidene complex **9**.



a: R = H, R' = Ph
b: R = NO$_2$, R' = Ph
c: R = H, R' = *t*-Bu
d: R = NO$_2$, R' = *t*-Bu
e: R = H, R' = SiMe$_3$
f: R = NO$_2$, R' = SiMe$_3$

Scheme 12. Synthesis of Schiff base Ru–vinylidene complexes **10a**–**f**.

the Ru–vinylidene complex $RuCl_2(PCy_3)_2[=C=CHR']$ and aromatic salicylaldimines [87] (Scheme 12).

Remarkably, on using **10** as catalysts in enol-ester synthesis via nucleophilic addition of carboxylic acids (formic, acetic, isovaleric and benzoic acid) to terminal alkynes (phenylacetylene, *t*-butylacetylene, 1,7-octadiyne), enhanced activities have been observed, compared to the ones obtained with Ru–indenylidene catalysts [89]. To explain these unexpected results a reaction mechanism similar to that proposed earlier for olefin metathesis with Ru-catalysts **4** and **5** has been proposed. According to this proposal, the vacant site is also generated via "one-arm" decoordination from the bidentate chelated salicylaldimine ligand when an alkyne is used as a substrate (Scheme 13).

The equilibrium between compounds **I** and **II** in Scheme 13 has already been discussed in the literature [90]. It is obvious that when weak acids (acetic acid, isovaleric acid) are used, the dimerization reaction is favoured (lower cycle). Yet, with stronger acids (benzoic acid, formic acid) these compounds bind preferentially at the ruthenium center and attack the C_1 or C_2 atoms of the coordinating alkyne. The attack of the acid on C_1 or C_2 sites of the alkyne is strongly governed by the steric environment. The coordination of an alkyne on **V** has also been postulated by several groups [91–93]. Since the active species involved in both enol ester synthesis and alkyne dimerization are of vinylidene type, it is not surprising that the catalysts **10** showed the highest activity in comparison with the indenylidene complexes [94].

2.6. *Ruthenium–cyclodiene complexes*

To further explore the scope and limitations of bidentate Schiff base complexes, we prepared two new dinuclear Ru-complexes, **11** and **12**, having as additional ligand norbornadiene (NBD) and 1,5-cyclooctadiene (COD), respectively [63]. Their syntheses were carried out by reaction of the Tl-salt of salicylaldimine with the corresponding ruthenium precursors, $[RuCl_2(NBD)]_n$ or $[RuCl_2(COD)]_x$, in dichloromethane, at room temperature (Scheme 14).

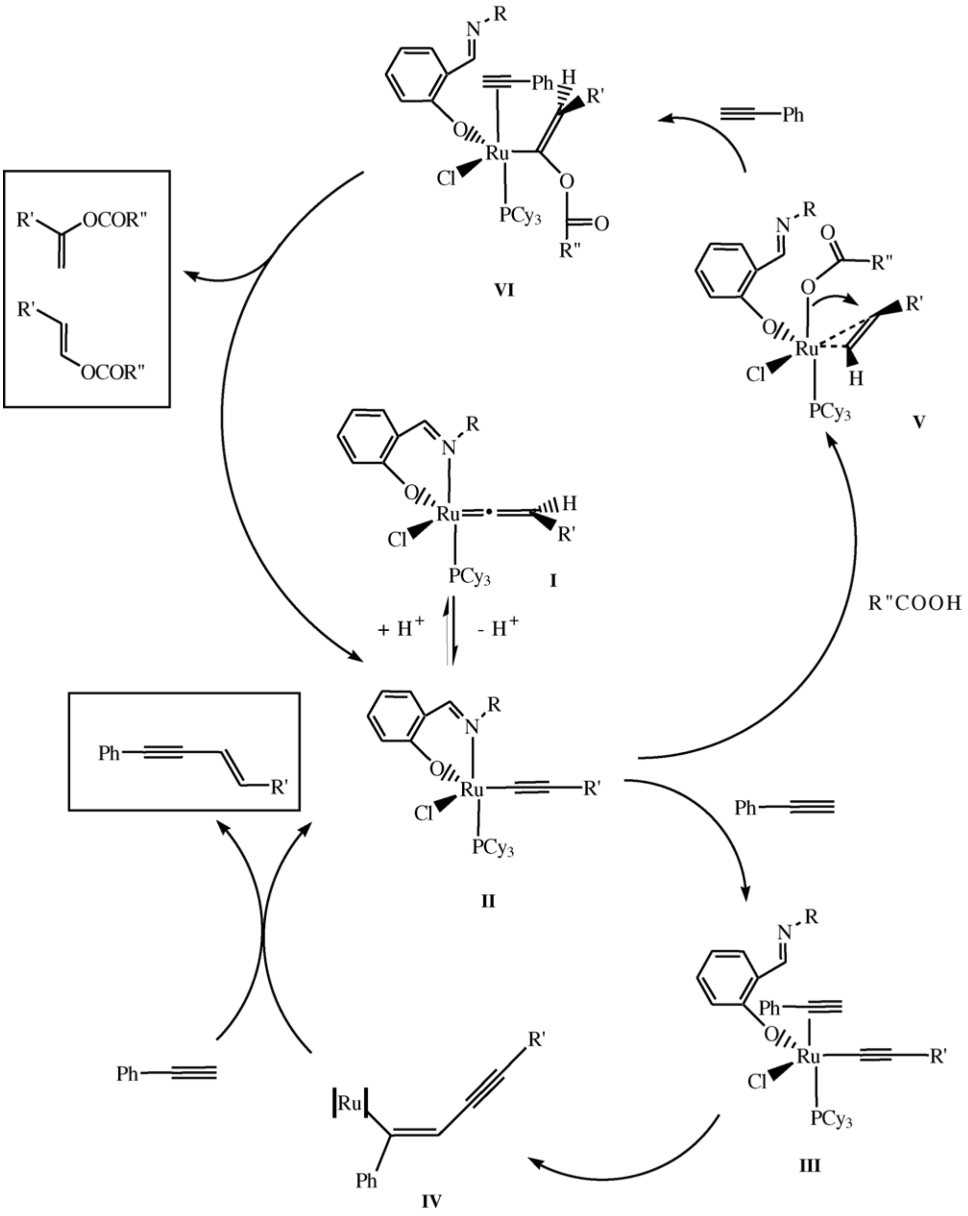
Appraisal of the catalytic behaviour of **11** and **12** has been effected through ROMP of norbornene and ATRP of methyl methacrylate and styrene. Working under various reaction conditions, in the presence or absence of cocatalysts or additives, a wide range of activities was recorded in both reaction series. Thus, when the reaction temperature was raised from 25 to 85 °C, norbornene conversion increased substantially, from 5 to 50% and 69%, for catalysts **11** and **12**, respectively. However, on using Et_2AlCl as a cocatalyst associated with Ru-complexes **11** and **12**, yields of 87 and 88% have readily been attained for the two catalysts, respectively.

Based on ^1H NMR studies carried out on norbornene polymerization with related Ru–arene complexes, a dissociative mechanism with direct formation of a Ru–carbene species from the mononuclear 14-electron coordination compound, has been suggested (Scheme 15). The role of the aluminum compound is not unambiguously clear but, beside its contribution as an alkylating agent with subsequent formation of a Ru–carbene species, we assumed that it might stabilize the 14-electron intermediate and facilitate the formation of the metallacarbene intermediate. In the atom transfer radical polymerization of methyl methacrylate and styrene, addition of $Al(O\text{-}i\text{-}Pr)_3$ and $n\text{-}Bu_2NH$ to the Ru-complex increased considerably the polymer yield. This result was attributed to assistance of these additional compounds for the in situ dissociation of the dinuclear precursor species to coordinatively unsaturated mononuclear ones.

3. Immobilized bidentate Schiff base ruthenium complexes

3.1. *Synthesis of immobilized ruthenium complexes*

There is at present considerable theoretical and practical interest in the immobilization of well-defined homogeneous catalysts [95–104]. The ultimate goal of this technique is to benefit from the combined advantages of heterogeneous and homogeneous catalysts. From economical and environmental points of view, use of heterogeneous catalysts offers several

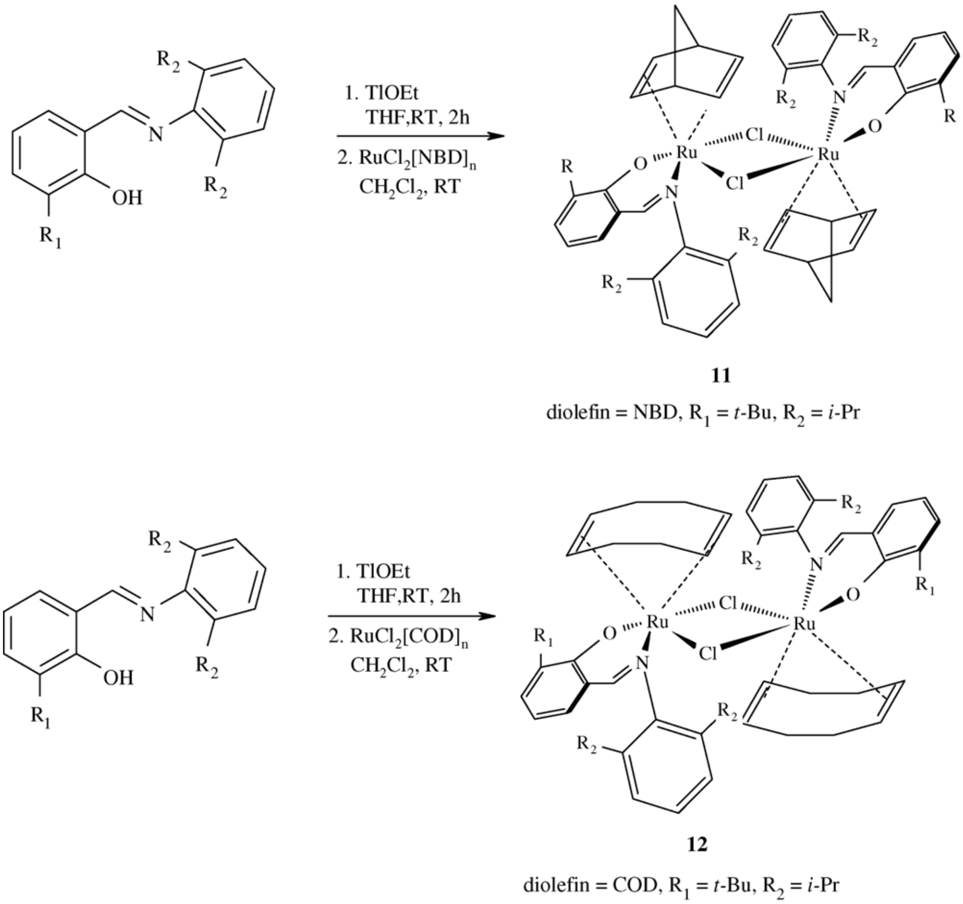


Scheme 13. Proposed mechanism for enol-ester synthesis with Ru-complexes **10**.

advantages in organic synthesis such as simplification of the reaction procedures, easy separation of products, recyclability of expensive catalysts, possibility to design continuous flow processes, good control of morphology of polymers and high polymer bulk density [100,101].

The conventional way 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. In search of an appropriate support, we were attracted by inorganic MCM-41 solid supports since they provide several advantages: (i) these porous 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 diffusional resistance (e.g. nanoporous zeolite support) to reactant molecules accessing the metal active sites located within the channels.

To design a structurally robust and effective supported catalyst, we attempted to prepare a catalytic system in which



11

diolefin = NBD, R_1 = *t*-Bu, R_2 = *i*-Pr

12

diolefin = COD, R_1 = *t*-Bu, R_2 = *i*-Pr

Scheme 14. Synthesis of ruthenium–cyclodiene complexes **11** and **12**.

the homogeneous catalyst is attached to the carrier by a non-labile tether imposing little or no steric burden at the reactive Ru center [105,106] (Fig. 3). 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.

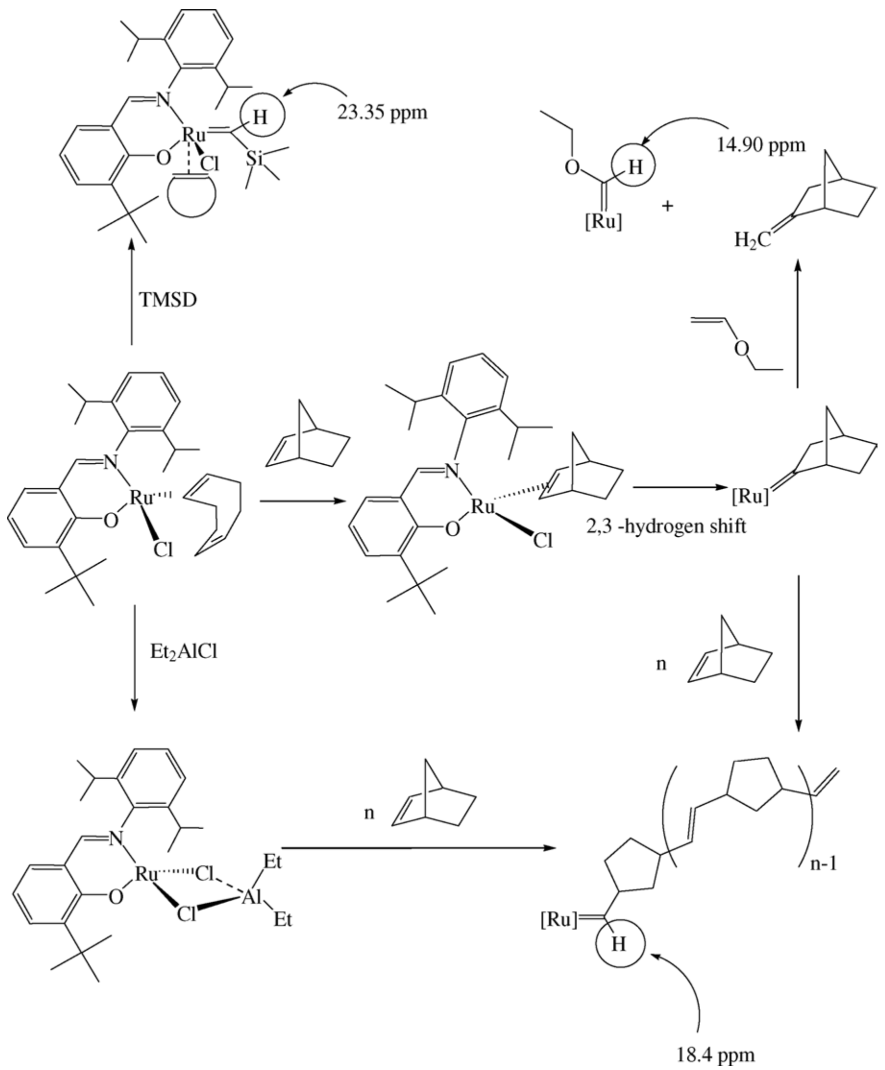
Recent efforts in our group have been directed toward design, synthesis and further development of hybrid bidentate Schiff base ruthenium complexes for applications in ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), Kharasch addition, atom transfer radical polymerization (ATRP) and vinylation reactions [106–109]. To boost the commercial potential of these chemical processes, we have recently achieved the synthesis of two multifunctional Schiff base ruthenium carbene complexes supported on MCM-41 (**13** and **14**), able to provide recyclable and efficient solid catalysts [110] (Fig. 4).

The methodology that we followed in preparing a catalyst system chemically tethered onto MCM-41 consisted of immobilizing a pre-synthesized catalyst precursor that contain an anchorable functionality. The commonly applied procedure to tether organometallic compounds on to mesoporous silica surfaces was by treating the inorganic support with tris(alkoxy)silyl functionalized complexes. The two different routes used for solid supported catalysts **13** and **14** are illustrated in Scheme 16.

Structural examination by Raman spectroscopy, X-ray diffraction, X-ray fluorescence, solid-state NMR and N_2-adsorption analysis showed that in all the cases the anchoring of the homogeneous catalyst onto the MCM-41 via spacer molecule took place with two or three covalent bonds. A similar approach has been employed to synthesize and characterize another new heterogeneous ruthenium catalyst, **15**, that exhibited excellent stability, reusability and leaching properties [109] (Scheme 17).

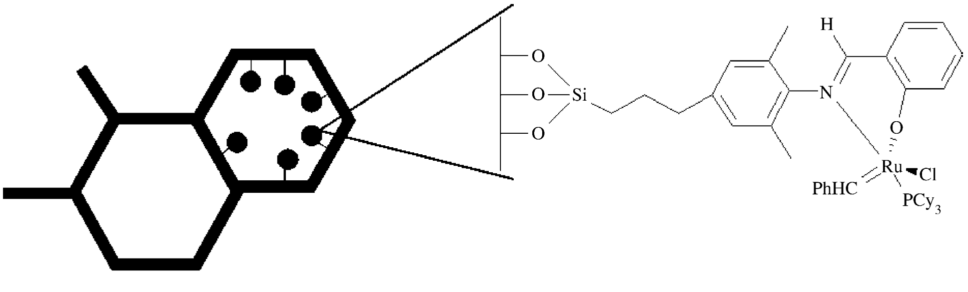
3.2. Synthetic applications of immobilized ruthenium complexes

Immobilized complexes **13**, **14** and **15** generally showed comparable or, in some cases, even slightly lower catalytic activity than their homogeneous counterparts, yet results obtained in our group on enol-ester synthesis, Kharasch addition, RCM and ROMP reactions combined with the very easy separation of reaction products and efficient recovery of the catalyst certainly advocate use of these hybrid heterogeneous systems in such important catalytic processes [108].



Scheme 15. Proposed dissociative mechanism for norbornene polymerization with ruthenium–cyclodiene complexes.

Enol-ester synthesis by vinylation of carboxylic acids with substituted acetylenes in the presence of catalysts **13** and **14** 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 prevailing Markovnikov pathway (45–82%) whereas the reaction of the same carboxylic acids with octadiyne gave mainly anti-Markovnikov products (76–82%) in 63–86% yields. In all cases, the catalyst **14** displayed a higher activity as compared to the catalyst **13**. 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



14

Fig. 3. Graphical representation of the hybrid catalytic system **14**.

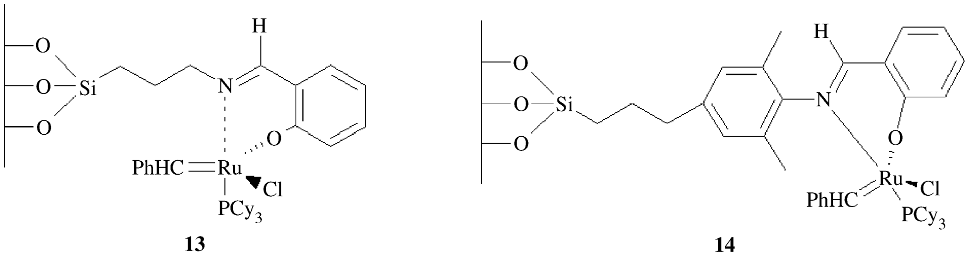
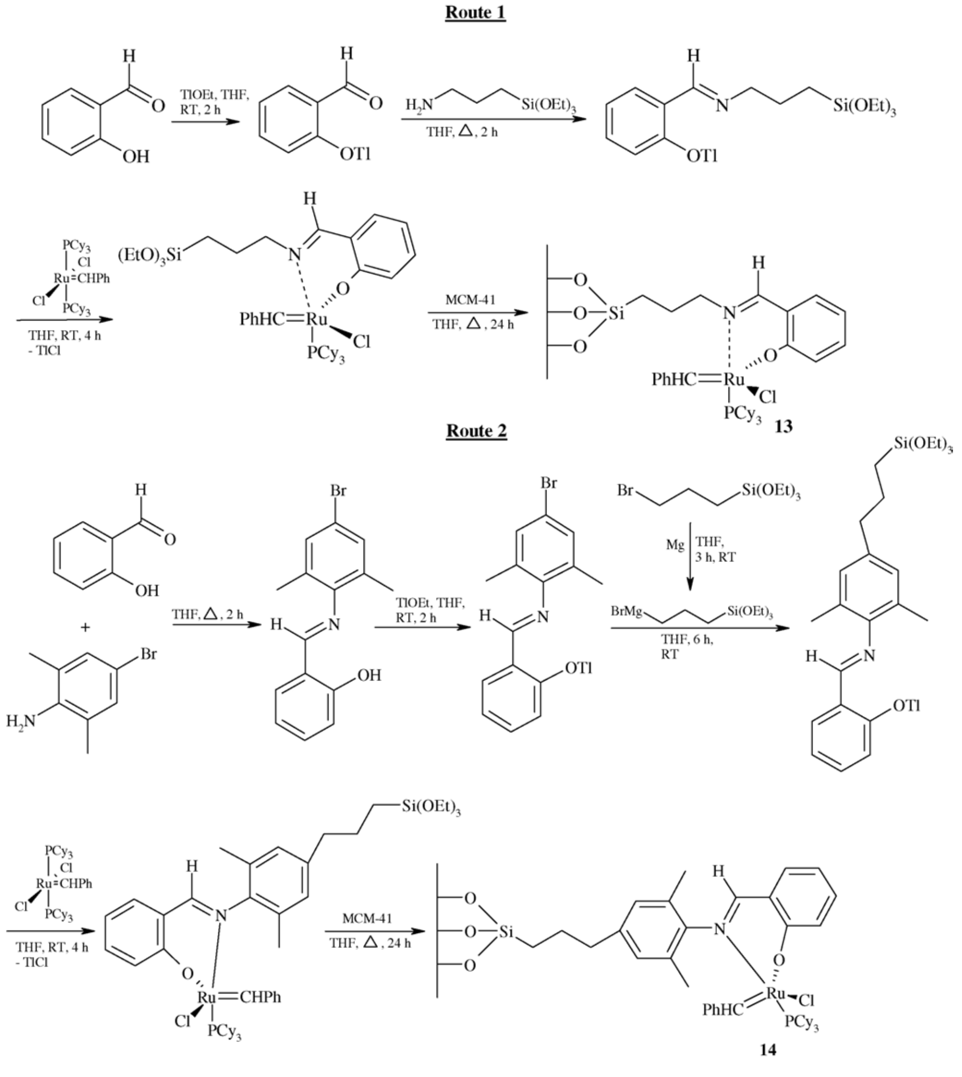


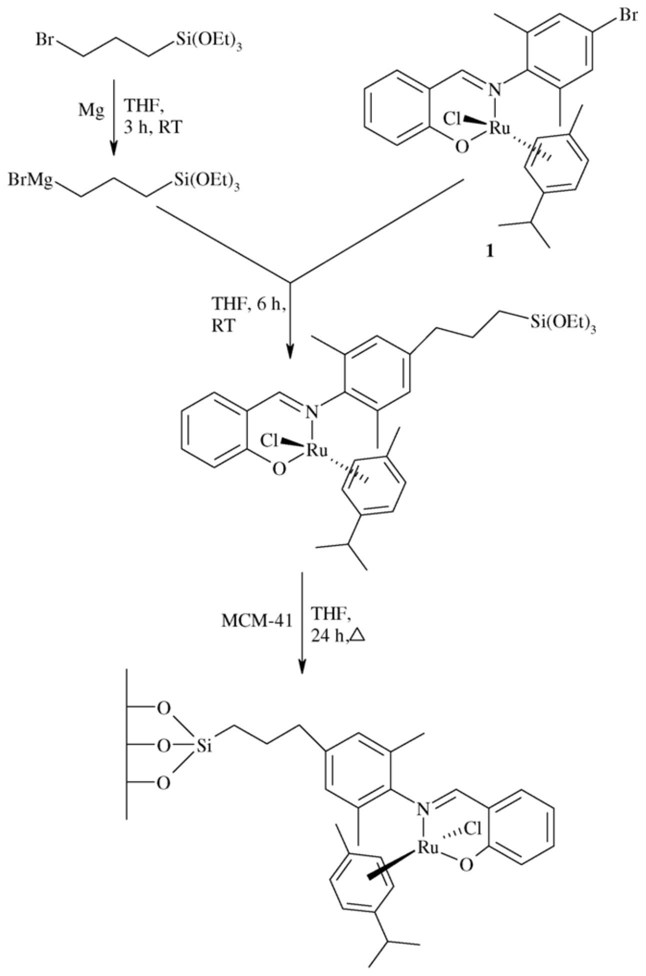
Fig. 4. Hybrid bidentate Schiff base ruthenium complexes **13** and **14**.

ruthenium (II) complexes containing bidentate nitrogen ligands [16c,111].

Kharash addition of CCl_4 on six olefinic substrates (styrene, diethyl allylmalonate, methyl methacrylate, isobutyl methacrylate, methyl acrylate and butyl acrylate) occurred effectively with the catalysts **13** and **14**, under standard conditions [110]. 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 **13** was considerable lower than that of **14** and this substantial difference was also maintained at high reaction temperatures. For instance, catalyst **14** converted styrene in 63 and 91% yield at 65 and 85 °C, respectively, whereas catalyst **13** only reached 45 and 67% conversion at the respective temperatures. Styrene and diethyl allylmalonate were clearly the two substrates that allowed the highest turnover,



Scheme 16. Synthesis routes for the manufacture of immobilized catalysts **13** and **14**.



15

Scheme 17. Synthesis of supported arene ruthenium complex **15**.

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, the best performing catalyst **14** 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 in this process was the spectacular increase of conversion with temperature in the case of the most performant system **14**. 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 reactions of various dienic substrates induced by catalysts **13** and **14** allowed cyclization to five-, six- and larger rings, in moderate to high yields, depending mainly on the dienic substrate, catalyst and reaction temperature [110]. Again catalyst **14** 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.

Both strained and low-strained cycloolefins (e.g. norbornene derivatives and cyclooctene) displayed a high reactivity on using both catalytic systems **13** and **14**, under normal reaction conditions [110]. Thus, a large range of 5-substituted norbonenes as well as cyclooctene underwent ROMP in high yields (90–100%), in toluene or dichloromethane. 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 **13**, 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 **13** proved to be more active than catalyst **14**; this result is in sharp contrast to that obtained in vinylation, Kharash 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 **13** and **14** 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 **13** and **14** provide colorless polymers of higher purity. Considering the characteristics of this class of immobilized catalysts in ROMP reactions, it is reasonable to state that they hold great promise for a full exploitation of 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 [112].

Catalysts **13** and **14** displayed two different levels of activity in atom transfer radical polymerization (ATRP) of styrene; the latter was more active, yielding 73% polymer, while the former produced only 11% polymer, under the same reaction conditions. 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 this type of heterogeneous catalysts proceeds in a controlled fashion, allowing synthesis of polymers with predetermined molecular weights and narrow polydispersities [110].

Comparative studies on the activity and selectivity of the immobilized ruthenium complex **15** in Kharash addition, enol-ester synthesis, RCM, ROMP and ATRP reactions led to the conclusion that the same general trends are manifested as for the related catalytic systems **13** and **14** [108]. A variable range of activities has been demonstrated in Kharash addition to a number of olefinic substrates, ROMP of cycloolefins and ATRP of styrene, but that is generally lower than in the case of the homogeneous congener. However, a remarkably high activity has been observed for the catalyst **15** in RCM of dienic substrates as well as in enol-ester synthesis starting from carboxylic acids and substituted acetylenes. In the latter process, catalyst **15** showed to be the most active and selective heterogeneous ruthenium catalyst reported so far for the production of (*E*)-alk-1-enyl esters via reaction of alkadiynes with saturated carboxylic acids and for the dimerization of monoalkynes into the corresponding (*E*)-enynes.

4. Conclusions and future outlook

Schiff bases of salicylaldiminato-type used in our work showed to be very attractive and quite convenient bidentate ligands for Ru-complexes. Taking advantage of their easy accessibility and particular electronic and steric configuration, we have designed, prepared and characterized a wide range of novel homogeneous Ru-catalysts. To this end, an array of Schiff bases have been associated with common ligands of Ru-complexes such as chloride, phosphane, arene, alkylidene, *N*-heterocyclic carbenes, vinylidene and cyclodienes.

The newly synthesized ruthenium complexes have been applied successfully in a range of organic reactions such as olefin metathesis (RCM), Kharasch addition, alkyne dimerization, enol-ester synthesis as well as in polymer chemistry for ring-opening metathesis polymerization (ROMP) of cycloolefins and atom transfer radical polymerization (ATRP) of vinyl monomers. It is noteworthy that by varying the steric and electronic configuration of the Schiff base, the catalytic activity and stability of the ruthenium complexes have been finely tuned resulting in quite robust and active catalysts. By a proper choice of ligands, the Ru-complexes have been induced to display a good tolerance towards organic functionalities, air and moisture. Due to the wide potentiality for changing the structure of the Schiff base, further convenient routes to design and synthesize novel complexes can be foreseen in the near future.

At the same time, heterogeneous hybrid ruthenium catalysts in which the bidentate Schiff base ruthenium complexes were anchored on the solid support MCM-41 have been prepared and adequately characterized by our group. Their application in organic synthesis and polymer chemistry has a lot of scope for future years as it brings important benefits such as easy isolation of the reaction products, reusability of the catalysts and high potentiality for designing continuous processes.

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