Review

Allenylidene–ruthenium complexes as versatile precatalysts for alkene metathesis reactions

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Abstract

Recent developments of ruthenium–allenylidene complexes as precatalysts for alkene metathesis reactions are described. Since the first evidence, reported in 1998 by the Dixneuf and Fürstner's groups, a variety of ionic 18-electron and neutral 16-electron ruthenium–allenylidene complexes mainly of the type $[RuCl(=C=C=CR_2)(arene)(PR_3)][X]$ and $RuCl_2(=C=C=CR_2)(L')(L'')$ have been described. The parallel formation and catalytic activity of related complexes in which the allenylidene moiety is formally transformed into an indenylidene ligand, that may take place via intramolecular rearrangement, is discussed. Applications are described for the production of both fine chemicals and polymers. Attempts for catalyst recycling in ionic liquids, or via heterogenization are also presented.
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1. Introduction

Transition metal allenylidene complexes ($M=C=C=CR_2$) have attracted interest as a new type of organometallic reagents [1–4]. The activation of three carbon atoms in the same ligand, two electrophilic centres ($C\alpha$ and $C\gamma$) and one nucleophilic site (C_B) [5,6], has made possible a remarkable development of stoichiometric reactions opening the route to a variety of new complex structures [7–10]. Metal–allenylidenes are now emerging as catalyst precursors and intermediates in catalysis [11–19]. The first ruthenium–allenylidene species involved in a catalytic cycle was proposed by Trost and Flygare [11]. Recently, Hidai and Uemura's groups have used the thiolate-bridged diruthenium complexes of the type $[Cp^*RuCl(\mu_2\text{-}SR)_2RuCp^*Cl]$ as catalyst precursors for hydroxy substitution reactions of propargyl alcohols, proposed to take place via allenylidene intermediates [12–14]. The versatility of allenylidene–metal complexes is reflected by their ability to catalyze ubiquitous reactions such as dimerization of tin hydrides [15], hydrogen transfer reactions [16], transetherification of vinyl ethers [17] or atom transfer radical polymerization [18]. However, it is in the field of alkene metathesis that allenyli-

dene complexes have found major applications for fine chemistry or polymerization.

Owing to functional group tolerance of ruthenium–alkylidene complexes of the type $L_nRu=CHR$, alkene metathesis has recently led to remarkable applications in organic synthesis as well as in polymer science [19–21]. Despite the tremendous profit brought by these catalysts, efforts still need to be made to find more accessible and active carbene-type complexes as catalyst precursors. In this context, ruthenium–vinylidene [22,23] or allenylidene derivatives [24–27], readily obtained from easy to prepare or commercially available ruthenium complexes and simple alkynes or alkynols, have been revealed as a valid alternative. Since the first catalytic application in alkene metathesis of the ionic well-defined 18-electron ruthenium–allenylidene complex $[(\eta^6\text{-}p\text{-cymene})RuCl(=C=C=CPh_2)(PCy_3)][PF_6]$ (**1a**) [24] was presented in 1998, numerous uses in catalysis have been developed by metal–allenylidene complexes in our laboratory [25–36] or by other groups [37–42]. This family of complexes has revealed their performance in ring closing metathesis (RCM) [24,26–30,36], enyne metathesis [25,26,31] or ring opening metathesis polymerization (ROMP) [33,35] either in organic solvents or in ionic liquids [32–34]. Catalytic activity of the allenylidene–ruthenium complex is modulated by the phosphine ligand, the

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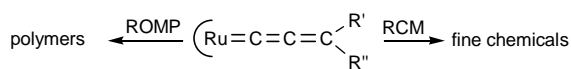
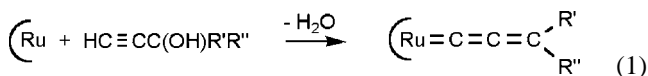Scheme 1. Application of ruthenium–allenylidene catalysts.

substituents in the phenyl groups and the escorting counterion [26,27].

Substantial variations of ancillary ligands are possible, opening the way to new performances and scopes. Recently, it has been described that allenylidene ligands easily rearrange intramolecularly into indenylidenes in protic media [43]. Previously, it was shown that indenylidene complexes, obtained unexpectedly in the attempt to produce allenylidene complexes, display high activity in alkene metathesis [44–47]. The evidence that allenylidene–ruthenium complexes have become key catalytic precursors motivates that we report here a brief compilation of allenylidene–ruthenium complex developments as active precatalysts for alkene metathesis focusing on the Rennes group achievements (Scheme 1).

2. Results and discussion

An interesting feature of allenylidene ruthenium complexes is the easy formation of their Ru=C bond by simple activation of propargyl alcohols with a suitable 16-electron Ru(II) intermediate as originally shown by Selegue (Eq. (1)) [48].
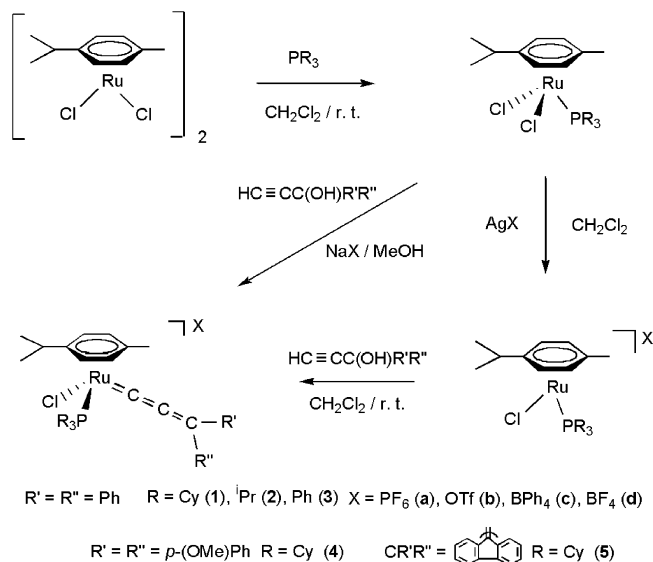
Ruthenium–allenylidene schematic synthetic pathway:

$$\left(Ru + HC \equiv CC(OH)R'R'' \xrightarrow{- H_2O} \left(Ru = C = C = C \begin{smallmatrix} R' \\ R'' \end{smallmatrix} \right. \quad (1)$$

This method is now largely used to synthesize most of allenylidene complexes described to date. Especially, cationic arene–ruthenium–allenylidene derivatives can be very easily prepared in high scale from commercially available sources [24–27] (Scheme 2). The synthesis pathways give access to a set of structurally diverse ruthenium–allenylidene complexes by modifying the arene, the phosphine, the allenylidene substituents as well as the escorting counterion.

2.1. Applications of arene–allenylidene precatalysts toward fine chemicals

The performance of cationic arene–allenylidene–ruthenium complexes in RCM using N,N-diallyltosylamide 6 (Scheme 3) arises in strong correlation with the nature of the phosphine coordinated to the metallic center (PCy$_3$ > P^{i}Pr$_3$ ≫ PPh$_3$) (Table 1). The use of sterically demanding and electron donating phosphines is required to stabilize intermediates. With 1a (2.5 mol%) as the catalyst, the diene 6 is cyclized to dihydropyrrole 7 in 95% yield after 5 h of reaction in toluene at 80 °C (entry 4) without formation of cycloisomerized product 8. The catalytic activity and

Scheme 2. Pathways for the synthesis of arene–ruthenium–allenylidene complexes.
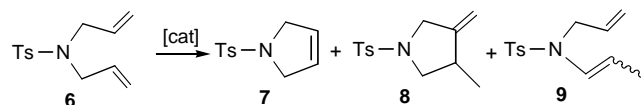
Scheme 3. Ring closing reaction or isomerization.

selectivity is also modulated by the counterion nature [26]. The best results are achieved with triflate complex (entry 5) allowing the RCM reaction to proceed at room temperature. By contrast, complex 1d with BF$_4$$^-$ as counterion is less selective, favoring the cycloisomerization product 8 (entry 7). A significantly enhanced activity was found by addition of 20 eq. of HBF$_4$·Et$_2$O to the catalyst precursor 1a (entry 8), although at the expense of a much shorter lifetime of catalyst [27]. Although it was not understood at that time, this experiment revealed for the first time the drastic influence of

Table 1
Screening of the catalytic activity of arene–allenylidene complexes[a]

Entry	Catalyst	Counterion	Time (h)	Product distribution		
				7	8	9
1	1a	PF$_6$$^-$	3	79	–	–
2	2a	PF$_6$$^-$	3	66	–	–
3	3a	PF$_6$$^-$	3	2	–	–
4	1a	PF$_6$$^-$	5	95	–	–
5	1b	OTf$^-$	19[b]	90	–	–
6	1c	BPh$_4$$^-$	5	91	–	–
7	1d	BF$_4$$^-$	5	31	43	16
8	1a + HBF$_4$ (20 eq.)	BF$_4$$^-$	1[b]	79	–	–
9	4d	BF$_4$$^-$	5	90	7	–
10	5d	BF$_4$$^-$	5	56	29	Traces

[a] 2.5 mol% of catalyst in toluene at 80 °C.
[b] 2.5 mol% of catalyst in toluene at 20 °C.
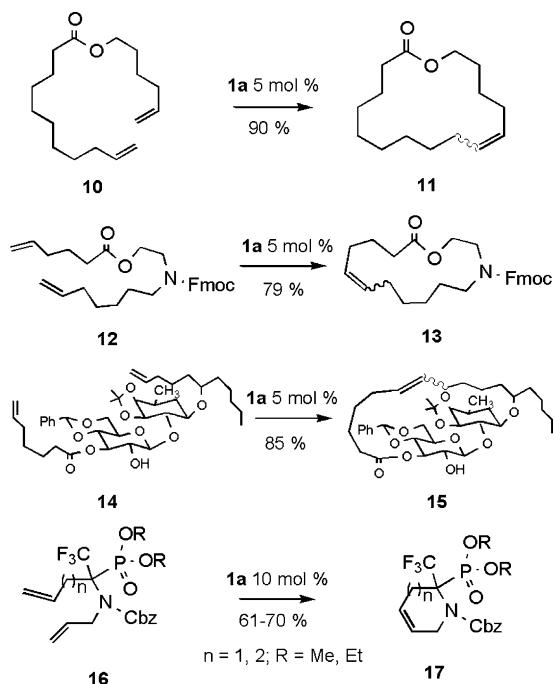
Fig. 1. Some examples of RCM using ruthenium–allenylidene precatalysts.

Scheme 4. Fluorinated dehydroproline analogs synthesis by enyne metathesis.

strong acids on the catalytic activity of metal–allenylidenes, that has now found explanation [43]. Other phenyl substituted allenylidene complexes were found to be active but with lower activity than diphenyl derivatives (entries 9–10).

Complex **1a** has been extensively used to produce by RCM reaction macrocycles of high added value showing an activity in the range of that of $RuCl_2(=CHPh)(PCy_3)_2$ [49] and a very good tolerance to heteroatoms and polar functionalities (Fig. 1). It promotes smooth cyclization of dienes **10**, **12**, and **14** to yield respectively, **11,** a precursor of Exaltolide® a valuable perfume ingredient, **13** which under deprotection affords a potent insect repellent and **15**, an advanced intermediate to the carcinostatic resin triclorin A [27]. Fluorinated α-aminophosphonates **16**, which exhibit high potential as antibacterial agents, are also cyclized in **17** in good yields [29].

The metathesis of enynes is a powerful method for generating conjugated alkenyl cycloolefins with atom economy. It has been demonstrated that $(\eta^6\text{-}p\text{-cymene})RuCl_2(PCy_3)$ can be converted into an efficient alkene metathesis catalyst for ROMP upon photochemical irradiation [50]. It is expected to favor decomplexation of *p*-cymene of saturated complex **1** generating vacant sites. The straightforward synthesis of 3-vinyl-2,5-dihydrofurans can be achieved by preliminary UV activation of complex **1a** under mild conditions [25]. An interesting feature of the enyne metathesis products is the generation of conjugated dienes and their use as enophile in a Diels–Alder reaction. This possibility has been used to synthesize a new fluorinated dehydroproline **21** and analogs by succesive reactions performed in the same flask (Scheme 4) [31].
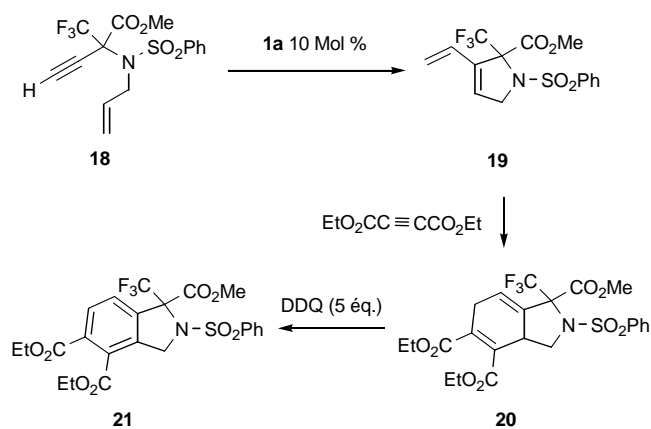
2.2. In the search of new environments of ruthenium–allenylidene complexes

In order to improve catalytic performance of arene–allenylidene–ruthenium complexes, variations on complex structure and ligands have been carried out. Catalytic activity of previously described pentacoordinated 16 electron ruthenium diphosphine dichloro alkylidene $RuCl_2(=CHPh)$ $(PCy_3)_2$ [49] or vinylidene $RuCl_2(=C=CHPh)(PCy_3)_2$ [22] complexes prompted to synthesize their related neutral 16-electron allenylidene compounds. The complex $RuCl_2(=C=C=CPh_2)(PCy_3)_2$ (**22**) was obtained from $[(\eta^6\text{-}p\text{-cymene})$ $RuCl_2]_2$, tricyclohexylphosphine, and 3,3-diphenylpropyn-3-ol [38] (Fig. 2). It was the first coordinatively unsaturated 16-electron ruthenium–allenylidene complex [51][1] but its catalytic activity was found to be moderate.

Herrmann and coworkers [52], and Grubbs and Bielawski [53] showed that the replacement of a phosphine in the ruthenium–alkylidene Grubbs catalyst by a more electron-donating and bulky *N*-heterocyclic carbene ligand tremendously increases the catalytic activity. Thus, Nolan and coworkers [38] presented the synthesis of neutral and cationic complexes $RuCl_2(=C=C=CPh_2)\{=\overline{CN(Mes)CHCHN}(Mes)\}$ $(PCy)_3$ (Mes = 2,4,6-trimethylphenyl) (**23**) and $[(\eta^6\text{-}p\text{-cym-}$ ene)$RuCl(=C=C=CPh_2)\{=\overline{CN(Mes)CHCHN}(Mes)\}][PF_6]$ (**24**) [37] by formal replacement of the phosphine by the *N*-heterocyclic carbene in complexes **22** and **1a**, respectively. The catalytic activity of **23** is higher than that of **22,** but remains moderate.

Surprisingly, performance of **24** does not attain that of **1**. In this particular case, the higher electron-releasing power of the *N*-heterocyclic carbene could retard the rearrangement of the allenylidene moiety to indenylidene species [43], which

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[1] The analogous 16-electron ruthenuim allenylidene complex containing PPh₃ was reported to arise from $RuCl_2(PPh_3)_3$ and 3,3-diphenyl-propyne [51] but was later shown to be an indenylidene derivative, see ref. [45].
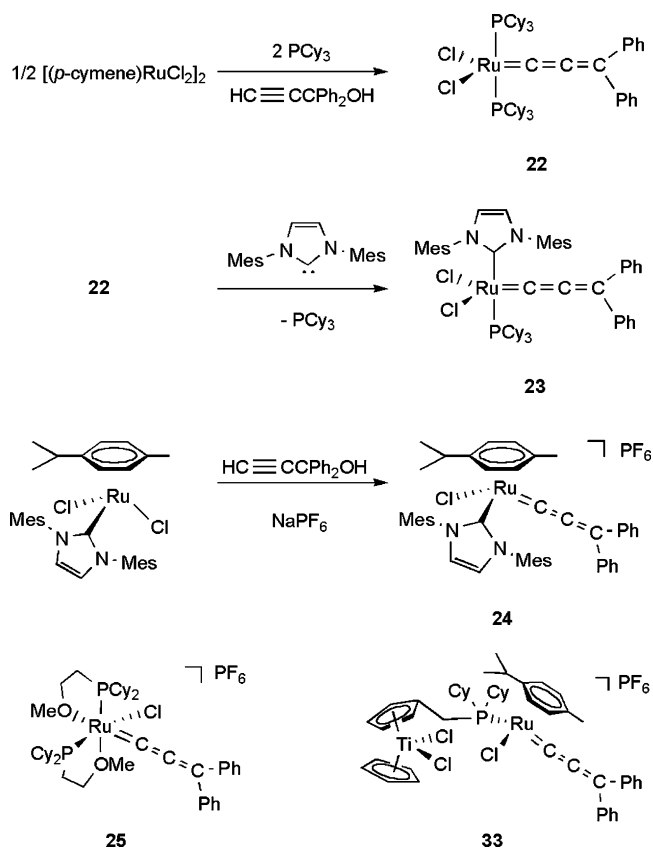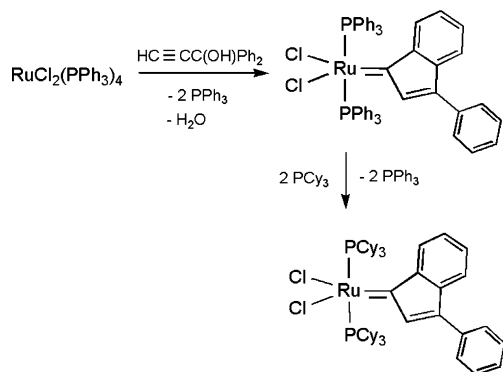
Fig. 2. Ruthenium–allenylidene complexes.

is favored by the lack of electron density. Actually, when the synthesis of the allenylidene complex analogous to **22**, but containing the PPh$_3$ ligands was attempted, the indenylidene complex RuCl$_2$(PPh$_3$)$_2$=$\overline{\text{CCH}=\text{C(Ph)C}}_6H_4$ was obtained (Scheme 5) [45]. Although it was thought that its formation corresponds to an intramolecular rearrangement of the allenylidene ligand, such a rearrangement was not directly observed [38,45]. It was only recently observed to take place via an alkenylcarbyne intermediate [43]. However, the resulting indenylidene–ruthenium complex containing PCy$_3$ ligands was proved by Fürstner et al. to be a highly active

alkene metathesis catalyst for a large variety of substrates [44–47]. The above observations and rate studies [54], also suggest that the allenylidene–ruthenium precatalyst **1** could rearrange into the corresponding indenylidene to give, after loss of its arene ligand, the active species for RCM. However, other mechanisms of activation are necessary to explain the catalytic activity of fluorene–allenylidene complex **5**, which cannot rearrange into the related indenylidene derivative (Scheme 2).

Complex **1** possesses an 18-electron configuration and, as free *p*-cymene was observed in stoichiometric and catalytic reactions, it is assumed that the weakly bound arene group decoordinates in order to generate vacant sites for coordination of alkenes. Why do not use other allenylidene-saturated complexes bearing labile or hemilabile ligands as catalyst in olefin metathesis? Werner and co-workers answered the question by synthesizing the 18-electron derivative [RuCl(=C=C=CPh$_2$)(κ^2-*P,O*-Cy$_2$PCH$_2$CH$_2$OCH$_3$)$_2$][PF$_6$] (**25**) (Fig. 2) [40] which became unsaturated by breaking one or both Ru–O bonds. Unfortunately complex **25** is less active than **1** probably due to the fact that the olefin coordination cannot compete with that of –OMe groups. Other class of arene free ruthenium–allenylidene complexes, such as RuCl$_2$(=C=C=CPh$_2$)(PCy$_3$)$_2$(DMSO) (**26**) and [RuCl(=C=C=CPh$_2$)(PCy$_3$)$_n$(DMSO)$_2$][OTf] (*n* = 1, **27**; *n* = 2, **28**) bearing dimethylsulfoxide ligands, has been synthesized and tested in ROMP (Scheme 6) [33].

Complex **1** is not stable for a long time at high temperatures. A way to increase the stability of ruthenium–allenylidene complexes was investigated by the use of a chelating ligand. Due to the lability of *p*-cymene ligand, a phosphine with an arene pendent chain can displace it to form the chelating complex **29** (Scheme 7) [27]. Subsequent treatment with NaPF$_6$ and 3,3-diphenylpropynol in methanol yielded **30**. The precatalyst give satisfactory results in RCM with a representative set of substrates but rates are lower than those of the non-chelated analogue. Related complexes **32** were prepared with chelating mixed η^8-*N*-heterocarbene arene ligands but their stability was poor (Scheme 7). The catalytic pattern of RCM reactions with the latter complexes is rather complex showing that both the diene and solvent nature dramatically influences both activity and selectivity [36].

Scheme 5. Synthesis of ruthenium–indenylidene complexes.
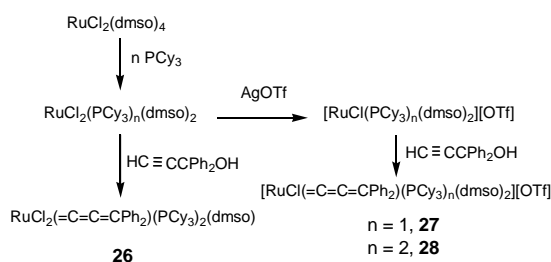
Scheme 6. Synthesis of ruthenium–allenylidene derivatives bearing DMSO ligands.
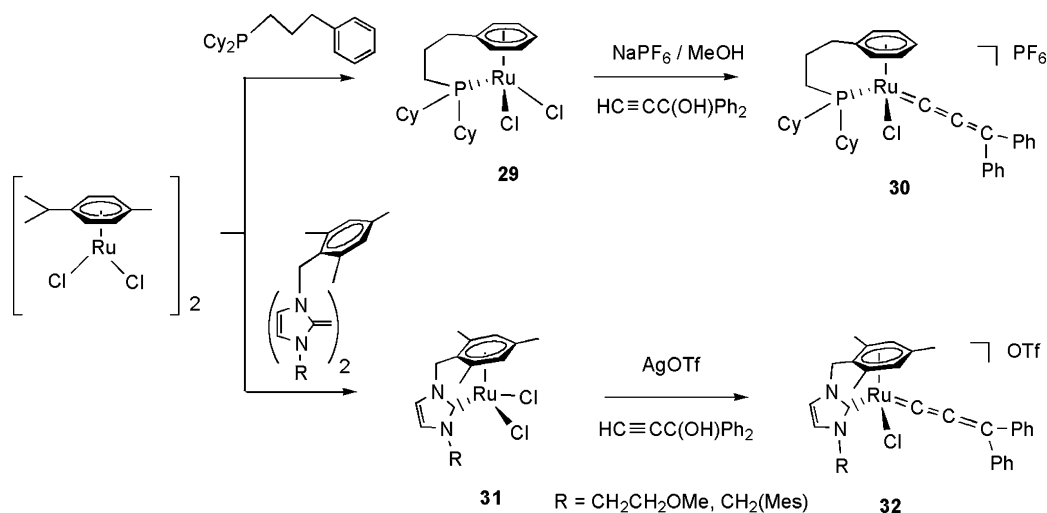
Scheme 7. Synthesis of chelating allenylidene complexes.

The presence in the same molecule of two early and late metal centres was investigated for the evidence of enhanced cooperative effect. Complex **33** was synthesized in good yields by reaction of a titanocene phosphine and [(*p*-cymene)RuCl$_2$]$_2$, followed by abstraction with AgOTf of one chloride of the resulting saturated complex and treatment with 3,3-diphenyl-propynol [41]. (Fig. 2). The catalytic activity of this complex **33** is similar to that of complex **1**.
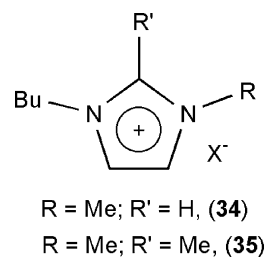
2.3. Ruthenium–allenylidenes in polymerization of cyclic olefins

The ring opening metathesis polymerization (ROMP) of cyclic olefins constitutes an excellent method to synthesize linear polymers with regularly disposed CH=CH double bonds that can be further functionalized or hydrogenated [55,56]. It has been revealed that complex **1b** promotes the polymerization of norbornene at room temperature whereas that of cyclooctene takes place at 80 °C (Table 2) [35]. Previous activation of catalyst, either thermally or by UV irradiation, was necessary to polymerize the less unstrained cyclooctene at room temperature. Both polymers present rather low polydispersity. Neutral and cationic arene-free complexes **26–28** polymerize either norbornene or cyclooctene but with lower efficiency.

R = Me; R' = H, (**34**)
R = Me; R' = Me, (**35**)

Fig. 3. Imidazolium salts.

2.4. Green catalysis of ruthenium–allenylidene derivatives

2.4.1. Catalysis in ionic liquids

One major challenge of homogeneous catalytic reactions deals with the recovery and recycling of the catalyst for both cost and environmental issues. An elegant solution is the use of ionic liquids, which are known to be non-volatile, reusable, and compatible with many organic and catalytic reactions [57,58]. The ionic nature of arene–allenylidene derivatives **1** was expected to favor their solubility in this media. One first attempt revealed good RCM activity of these precatalysts in imidazolium-based ionic liquids **34** at 80 °C (Fig. 3) [32]. Due to low miscibility between these

Table 2
Polymerization of cyclic olefins with allenylidene catalysts

Catalyst	Monomer	Ratio	Conditions	Yield (%)	M_n ($\times 10^{-3}$)	PDI	*Cis* (%)
1b	Norbornene	1000	5 min at RT	90	198	1.8	25
1b	Cyclooctene	1000	5 min at 80 °C	90	267	1.4	22
1b	Cyclooctene	150	UV 2 h at RT	99	143	1.8	–
26	Norbornene	300	4 h at 60 °C	56	16	4.1	–
27	Norbornene	300	4 h at 60 °C	70	37	3.9	15
28	Norbornene	300	4 h at 60 °C	22	17	3.8	–
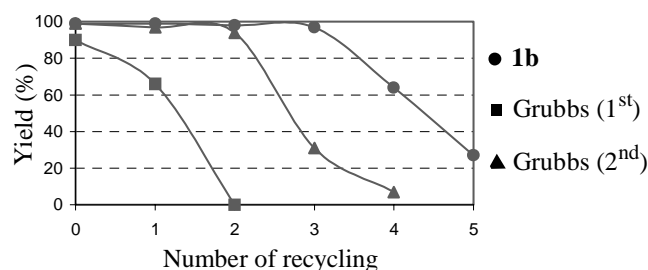
Fig. 4. Recycling comparision of the norbornene polymerization.

Olefin metathesis in water:

$$ (2) $$

ionic liquids and apolar organic solvents, easy recovery of the products arising from catalytic reactions was possible by simple extractions with an organic solvent such as toluene. The ionic liquid-phase was deeply red, whereas no color was observed in the organic phase indicating that the ruthenium catalyst remains in the ionic liquid-phase. Recycling attempts have been performed at room temperature. Two consecutive runs have been possible with good yields but the long reaction time required (18 h) resulted in a rapid decreasing of the catalytic activity after the second run.

The same principle has been applied to carry out ROMP of norbornene [34]. In this case a C_1 methylated imidazolium salt **35** was used in order to prevent side reactions with the catalyst. Good catalytic activity was observed within the four initial cycles. Moreover, complex **1b** showed better recycling ability within this system than neutral standard Grubbs first and second generation catalysts $RuCl_2(=CHPh)(PCy_3)_2$ and $RuCl_2(=CHPh)(PCy_3)(NCH)$ respectively, probably because of its ionic nature (Fig. 4).

2.4.2. Heterogenized allenylidene catalysts

A method to heterogenize the allenylidene catalyst was recently described by Kobayashi and Akiyama [42]. They immobilize the ruthenium catalyst using benzene rings of polystyrene to generate $(arene)RuCl_2(PR_3)$ groups that can be further transformed into allenylidene complexes analogous to **1**. Although catalytic conditions of in situ generated allenylidene species are rather drastic (20 mol% of catalyst, 12 h under ^iPrOH:hexane reflux) good activity was observed after the third recycling.

2.4.3. Catalysis in water

From economical and environmental friendly point of view, catalysis in water attracts great deal of attention. A water-soluble allenylidene–ruthenium complex [{RuCl-(μ-Cl)(=C=C=CPh$_2$)(TPPMS)$_2$}$_2$]Na$_4$ **36** bearing the sulfonate-derived phosphine TPPMS $(Ph_2P(C_6H_4SO_3)^-Na^+)$ has been presented by Peruzzini and co-workers [39]. Complex **36** promotes cross-olefin metathesis of cyclopentene with methyl acrylate in water to give polyunsaturated esters (Eq. (2)).
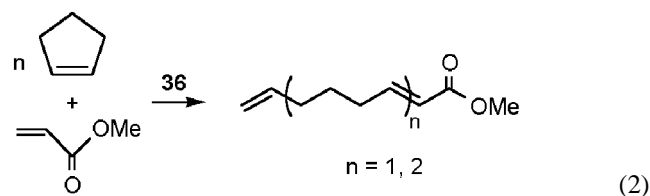
3. Concluding remarks

The first evidence reported in 1998 that ionic, 18-electron ruthenium–allenylidene complexes are catalyst precursors for alkene metathesis for the production of both fine chemicals and polymers has actually led in 5 years to a variety of developments. Several catalytic applications have led to functional macrocycles, fluorinated derivatives, and conjugated alkenylcycloalkenes, but also to polymers via ROMP process. Ruthenium allenylidenes tolerate ionic liquids and water as media and can be heterogenized thus favoring recycling. The first involvement of ruthenium–allenylidene in alkene metathesis has motivated the search for a variety of new ruthenium–allenylidene complexes with structural variations and has led to observe that indenylidene–ruthenium complexes, resulting from intramolecular rearrangement, are often more active alkene metathesis catalysts. The latter are suggested to arise from intramolecular rearrangement of allenylidene ligand. A crucial aspect of the ruthenium–allenylidene precatalysts, like all alkylidene–ruthenium alkene metathesis catalyst, remains the stability of the catalytic species and its recycling properties. These observations motivate efforts to reach more active catalysts for the decreasing of both metal traces in products and process cost.

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