Imidazolium and Imidazolinium Salts as Carbene Precursors or Solvent for Ruthenium-Catalysed Diene and Enyne Metathesis

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Abstract: This review reports the utilisation of catalytic systems prepared *in situ* from a source of ruthenium, a precursor of 1,3-diaminocarbene, and a base to perform enyne ring-closing metathesis. Silylated enynes and allyl propargyl ethers have been rearranged into cyclic derivatives bearing a conjugated diene structure in the presence of $[(p\text{-cymene})RuCl_2]_2$, an imidazolium or imidazolinium chloride, and cesium carbonate. From 1,6-dienes, the dichotomous behaviour of the catalytic system generated from imidazolinium salts makes possible the preparation of cycloisomerisation products, or metathesis compounds when the reaction is carried out in the presence of acetylene. Finally, the possibility of performing ring-closing metathesis in imidazolium salts as an ionic solvent with an ionic catalyst of the type $[(p\text{-cymene})RuCl(PCy_3)=C=C=CPh_2][X]$ is demonstrated.

Keywords: cycloisomerisation; enyne metathesis; *N*-heterocyclic carbene (NHC) ligands; homogeneous catalysis; ionic solvents; ring-closing metathesis; ruthenium

1 Introduction

Significant improvements of catalyst performance have recently been brought benefits to fine chemistry *via* simple substitution of a phosphine ligand by a nucleophilic heterocyclic diaminocarbene, such as an imidazolylidene ligand. Illustrative examples are found in various catalytic reactions with palladium catalysts in cross-coupling[1] or Heck reaction,[2] and ruthenium catalysts for the formation of furans,[3] cyclopropanation,[4] hydrogenation,[5] or dimerisation of alkynes.[6] Especially in alkene metathesis,[7] attempts to mimic the influence of bulky, electron-rich phosphines in ruthenium catalysts by the use of sterically hindered imidazolylidenes and imidazolinylidenes have revealed a dramatic activity increase.[8] Catalysts of the type RuX_2(CHPh)(N-heterocyclic carbene)(L) are now able to effect alkene metathesis reactions leading to the difficult formation of tri- and tetrasubstituted double bonds[9] as well as cross-metathesis reactions involving methyl methacrylate.[10]

The best way to coordinate a sterically hindered *N*-heterocyclic carbene to a metal centre involves the *in situ* deprotonation of an imidazolium or imidazolinium salt with a base in the presence of the host metal complex.[8] The first preparative methods of ruthenium-imidazolylidene and ruthenium-imidazolinylidene catalysts showed that their activity in alkene metathesis not only largely depended on the nature of the carbene ligand but also on the nature of the base and of the imidazolium-associated anion.[11,12] The first steps in the preparation of imidazol(in)ylidene-ruthenium complexes for alkene metathesis were dedicated, following the general trends of the 1990's, to well-defined catalyst precursors.[8] However, the catalytically active species arising from well-defined 16- or 18-electron metal complex precursors obviously result from ligand loss, generating a highly coordinatively unsaturated species. This means that similar active species for alkene and enyne metathesis could be reached more simply by direct association of a ruthenium source and a bulky electron-rich, cyclic diaminocarbene.

Preliminary studies were done using $[RuCl_2(p\text{-cymene})]_2$ as a ruthenium source, as this precursor directly gives access to a ROMP catalyst[13], $RuCl_2(=C=CHR)(PCy_3)_2$, in the presence of alkyne *via* an easy elimination of its

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Christian Bruneau graduated as Engineer in Chemistry in Rouen (1974) and obtained his Doctorate degree on Environmental Chemistry in Rennes (1979). He was hired at CNRS in 1980, and since 1986 he has been developing his research at the University of Rennes. He is now the head of a CNRS – University of Rennes research laboratory "Organometallics and Catalysis" (UMR 6509). His topics are in the field of homogeneous catalysis by transition metal complexes. His main research interests are in selective transformations of alkynes and alkenes, and enantioselective hydrogenation with metal catalysts.

David Séméril did his doctorate studies in Rennes from 1998 to 2001 on catalytic transformations of dienes and enynes *via* metathesis and cycloisomerisation reactions. He developed the *in situ* generation of active ruthenium imidazolinylidene catalysts and showed the possibility of performing olefin metathesis in ionic solvents in the presence of ionic allenylidene ruthenium catalysts.

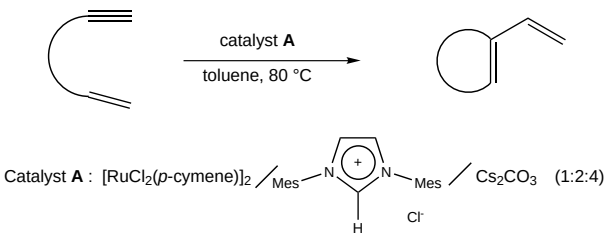
arene ligand. The treatment of $[RuCl_2(p\text{-cymene})]_2$ with an *in situ* generated imidazolylidene or imidazolinylidene from a bulky imidazolium salt and cesium carbonate led to an efficient enyne catalyst[14]. In parallel some preliminary works, in the line of *in situ* prepared ruthenium-imidazolylidene catalysts, have just been reported by Grubbs[12] and Noels.[15]

The aim of this review is to present the first results in this direction developed in the Rennes group: (i) the *in situ*, three-component preparation of enyne metathesis catalysts from a ruthenium source, an imidazolinium salt, and a base,[16] (ii) the modification of the resulting catalysts to produce alkene metathesis catalysts,[17] and (iii) the performance of catalytic alkene metathesis in imidazolium salts as ionic liquids.[18]

2 *In situ* Prepared Imidazolylidene-Ruthenium Catalysts

Contrary to the ring-closing diene metathesis[9] and cross-metathesis reactions,[10] the enyne metathesis with the second generation of Grubbs catalysts $Ru{=}CHPh(Cl)_2(PCy_3)(L)$ [L = 1,3-bis(mesityl)imidazol-2-ylidene (MesIm) or 1,3-bis(mesityl)imidazolin-2-ylidene ($MesH_2Im$)] has been less explored. The preparation of these catalysts requires several organometallic synthetic steps and purifications under an inert atmosphere. With the aim of simplifying the metathesis catalyst preparation, a catalytic system generated *in situ* from the dimeric $[RuCl_2(p\text{-cymene})]_2$ (**1**), the 1,3-bis(mesityl)imidazolium chloride (ImMesCl), and cesium carbonate in the respective molar ratio of 1:2:4 was developed (catalytic system **A**), which represents one equivalent of imidazolium salt per ruthenium atom and an excess of base. This catalytic system **A** was able to perform enyne metathesis in toluene at 80 °C to give access to 5 and 6-membered ring derivatives with 1,3-diene unit[14] (Scheme 1).

The use of the catalytic system **A**, made from 0.5 mol % of $[RuCl_2(p\text{-cymene})]_2$ (**1**),[14] cyclised the enyne **2a** into **3a** in 93% isolated yield after 100 min at 80 °C (Table 1). This new catalytic system appeared to be more efficient than the initial ruthenium allenylidene complex $[RuCl(=C{=}C{=}CPh_2)(PCy_3)(p\text{-cymene})][PF_6]$,[20] which gave the same reaction with only 67% isolated



Scheme 1.

Table 1. Enyne metathesis with substituted double bond using the catalytic system **A**.[a]

Enyne	R^1	R^2	R^3	R^4	R^5	R^6	Z	Diene	**1** [mol %]	t [h]	Yield [%][b]
2a	Ph	Ph	H	H	H	H	O	**3a**	0.5	1.7	93
2b	Me	Ph	H	H	H	H	O	**3b**	0.5	1.7	90
2c	$-(CH_2)_5-$		H	H	H	H	O	**3c**	0.5	1.7	85
5	H	H	H	H	H	Me	Ts-N	**6**	4	0.5	89
7a	Me	Ph	H	H	H	Ph	O	**8a**	1	27	86
7b	$-(CH_2)_5-$		H	H	H	Ph	O	**8b**	1	42	65
7c	Me	Ph	H	H	H	Me	O	**8c**	1	2.5	83
9a	$-(CH_2)_5-$		Me	H	H	H	O	**10a**	0.5	0.4	86
9b	Me	Ph	Me	H	H	H	O	**10b**	0.5	1.5	75
9c	Ph	Ph	Me	H	H	H	O	**10c**	2.5	5	35
9d	Me	Ph	H	Me (H)	(Me) H	H	O	**10d**	0.5	2	61
9e	Ph	Ph	H	Me (H)	(Me) H	H	O	**10e**	1	15	52
9f	Me	Ph	H	Me	Me	H	O	**10f**	1	25	16

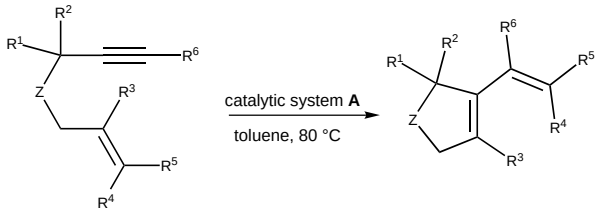
[a] $[RuCl_2(p\text{-cymene})]_2$ (**1**), (ImMes)Cl, Cs_2CO_3 in the ratio 1:2:4, toluene, 80 °C.
[b] Isolated yield.

yield after heating for 23 h. Under similar conditions, the allyl propargyl ethers **2b** and **2c** were transformed into the dienes **3b** and **3c** in 90 and 85% isolated yields, respectively.[14]

The catalytic system **A** was also more efficient than the isolated $RuCl_2$(ImMes)(*p*-cymene) complex (**4**), previously described as an active precursor for diene metathesis.[21] For example, the catalytic system **A** cyclised the mixed allyl propargyl tosylamide **5** into the diene **6** (Table 1) with full conversion and 89% isolated yield in 30 min with 4 mol % of **1**, whereas the full conversion and 71% isolated yield were reached after 1 h with 5 mol % of **4**. This difference in reactivity between the catalytic system **A** and the complex **4** indicates that the catalyst **A** differs from complex **4** and suggests that the catalytic system **A** provides a faster generation of a coordinatively unsaturated active ruthenium species *via* arene displacement, than from the isolated complex **4**. The active catalytic species is thus expected to be of the form $[RuX_2$(imidazolylidene)] surrounded by solvent or enyne.

The increased activity offered by the catalytic system **A**, compared to that of the ruthenium allenylidene, allows the transformation of enynes with substituted double and triple bonds. The introduction of one phenyl substituent on the triple bond in the enynes **7a** and **7b** did not inhibit their transformation by catalyst **A** (1 mol % of **1**) into dienes **8a** and **8b** which were produced in 86 and 65% isolated yields, respectively, although the reaction required longer reaction times (Table 1). The introduction of a methyl substituent ($R^6 = Me$) (**7c**) required less forcing conditions to produce **8c**.

Catalyst **A** also allows the transformation of a variety of enynes with substituted double bonds in derivatives **9** (Scheme 2).[14] The ease of cyclisation of the enynes **9a – c** with a methyl substituent at the internal position of the allylic double bond depends on the nature of the



Scheme 2.

propargylic moiety, the reaction was slower with two phenyl groups (**9c**) as compared with at least one alkyl substituents (**9a – b**) (Table 1). The substitution at the terminal position of the double bond of the enynes **9d – f** significantly decreased the reaction rates (Table 1).

3 *In situ* Prepared Imidazolinylidene-Ruthenium Catalysts

3.1 Catalytic Synthesis of Cyclic Siloxanes *via* Enyne Metathesis

It was observed that the imidazolinylidene ligand is a significantly more electron-releasing group than the related imidazolylidene group.[22] It was also observed that the catalyst precursor $RuCl_2(CHPh)(PCy_3)(L_1)$ containing the 1,3-bis(mesityl)imidazolinylidene ligand (L_1) leads to a more active catalytic species than that containing the 1,3-bis(mesityl)imidazolylidene carbene.[10,11,23] The active species is thought to result from the loss of the PCy_3 group affording the highly coordinatively unsaturated species $[RuCl_2(CHPh)(L_1)]$. It was thus likely that a catalyst system analogous to **A** but containing the electron-releasing imidazolinylidene ligand would be more active.

Table 2. Enyne metathesis with the catalytic system **B**.[a]

Diene	R^1	R^2	R^3	**1** [mol %]	T [°C]	t [h]	Isolated yield [%][b]
12a	$-(CH_2)_5-$		*n*-Bu	5	110	23	72
12b	Me	Ph	H	2.5	80	16	81
12c	$-(CH_2)_5-$		H	2.5	80	16	87
12d	Me	$CH_2CH(CH_3)_2$	H	2.5	80	15	34[d]
12e	Ph	Ph	H	2.5	80	15	70
12f	Me	Me	Ph	2.5	80	48	75
12g	$-(CH_2)_5-$		CH_2OCH_3	5	110	23	67

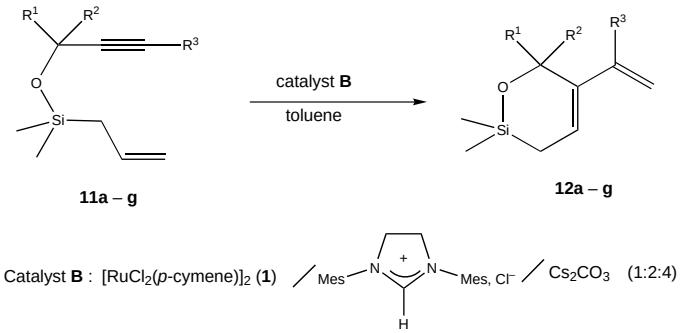
[a] Enyne **11** (1 mmol), toluene (5 mL), catalytic system **B** based on a constant molar ratio of $[RuCl_2(p\text{-cymene})]_2$ (**1**)/$MesH_2ImCl/Cs_2CO_3 = 1:2:4$.
[b] After complete conversion of enyne **11**.
[c] Degradation over silica during purification.

The catalyst **B** was prepared *in situ* by mixing three components: the ruthenium source $[RuCl_2(p\text{-cymene})]_2$ (**1**), 1,3-bis(mesityl)imidazolinium chloride (ImH_2MesCl) as the carbene ligand source, and Cs_2CO_3 in the molecular ratio of 1:2:4 in toluene.[24] Catalysts **A** and **B** based on 5 mol % of **1**, were evaluated for the transformation of the enyne **11a** into the cyclic siloxane **12a**. Catalyst **B** appeared to be more active than catalyst **A**. After 23 h in refluxing toluene the conversion was complete with catalyst **B** but reached only 60% with catalyst **A** (Scheme 3).[16]

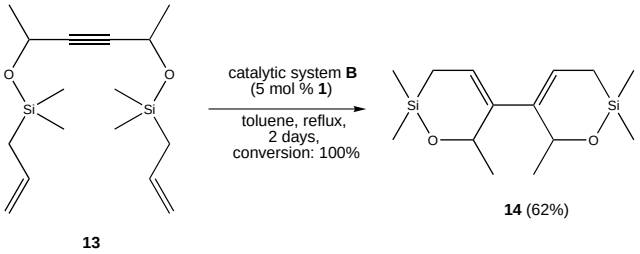
Catalyst **B** was used for the general transformation of the enynes **11** into a variety of cyclic siloxanes possessing a recreated allylsilane group and the 1,3-diene structure (Table 2).

The 6-membered ring products **12a – g** were obtained after full conversion of the enynes **11a – g** in good isolated yields (67 – 87%). For enynes with a disubstituted triple bond (**11a, f, g**), the metathesis reaction required more forcing conditions.

The catalyst **B** can be used for the rearrangement of the dienyne **13** bearing an internal triple bond. The product **14** was isolated in 62% yield as a mixture of two diastereoisomers in the ratio 62:38 (Scheme 4).



Scheme 3.



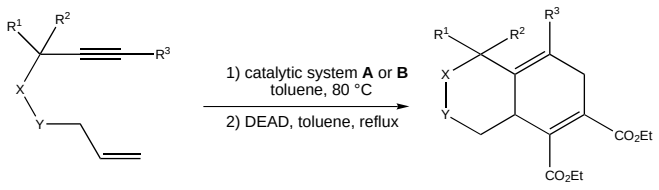
Scheme 4.

One advantage of 1,3-dienes **12**, produced by catalysts **A** or **B**, consists in their inertness toward further metathesis and polymerisation, and they can be used for Diels–Alder reactions[14,16,25,26] to give access to heterobicyclic products such as **15a – c**. Catalysts **A** and **B** do not inhibit the Diels–Alder reaction. Both metathesis and Diels–Alder reactions can be successively performed without intermediate isolation (Scheme 5).[14,16]

The enynes were first transformed into 1,3-dienes with the catalytic systems **A** or **B**, at 80 °C in toluene, then 2 equivalents of diethyl acetylenedicarboxylate (DEAD) were added to the reaction mixture.[27] The Diels–Alder product **15a** was isolated in an overall yield of 63% using the catalytic system **A**. The bicyclic products **15b** (78%) and **15c** (61%) were obtained, with the use of the catalytic system **B**, as a mixture of two diastereoisomers.

The Diels–Alder products could be further oxidised to give access to aromatic heterobicyclic derivatives. This oxidation by 2,3-dichloro-5,6-dicyanoquinone (DDQ)[28] could be done directly from the crude product. The three-step, one-pot transformation of enyne **2a** gave the aromatic derivative **16** in 76% overall yield (Scheme 6).

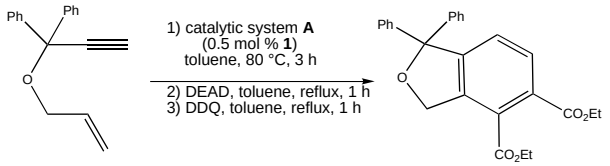
The 6-membered ring metathesis products **12** offer the possibility of selective desilylation. The allylsilane **12b** led to the allylic diol **17** in 77% isolated yield[16] upon oxidation with hydrogen peroxide[25,29] (Scheme 7).



15a – c

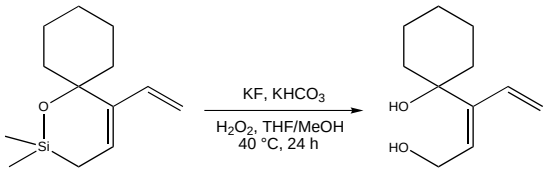
R^1	R^2	R^3	X	Y	Product	Yield [%]
H	H	Me	CH_2	O	**15a**	63
Me	Ph	H	O	$SiMe_2$	**15b**	78
Me	CH_2CHMe_2	H	O	$SiMe_2$	**15c**	61

Scheme 5.



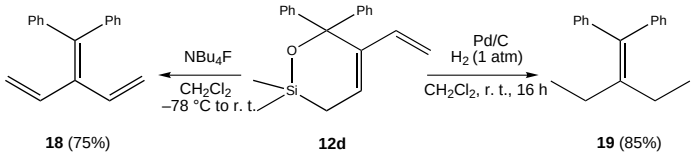
2a **16** (overall yield 76%)

Scheme 6.



12b **17** (77%)

Scheme 7.



18 (75%) **12d** **19** (85%)

Scheme 8.

Whereas the product **12d** reacted with tetrabutylammonium fluoride[30] to give the triene **18** (Scheme 8), the reduction in the presence of H_2 over palladium/charcoal at room temperature provided the tetrasubstituted olefin **19**.

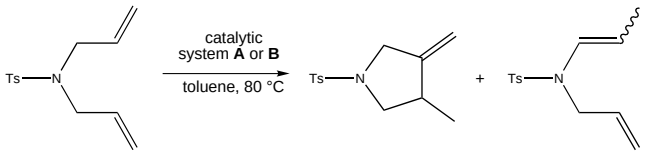
3.2 Selective Transformation of Dienes into Cycloisomerisation versus Metathesis Derivatives

The complex $RuCl_2$(ImMes)(*p*-cymene) (**4**) itself showed some activity for RCM of dienes, especially with diallyl malonate.[21] The scope of the *in situ* generated catalytic system **B** toward the RCM reaction of dienes was evaluated.

Contrary to complex **4**, *in situ* generated catalytic systems **A** and **B** led to complete transformation of 1,6-dienes but did not give the metathesis product. With diallyltosylamide **20**, the catalytic system **A** (2.5 mol % of **1**), gave a mixture of the cycloisomerisation product **21** and isomerisation product **22** in the ratio 74:26 after 16 h at 80 °C (Scheme 9). When the catalytic system **B** was prepared with 2.5 mol % of **1**, the reaction selectively gave the cycloisomerisation product **21** after 1 h at 80 °C. Thus, the reactivity and selectivity strongly depend on the nature of the heterocyclic carbene ligand, the more electron-releasing the carbene, the faster and the more selective is the cycloisomerisation reaction.

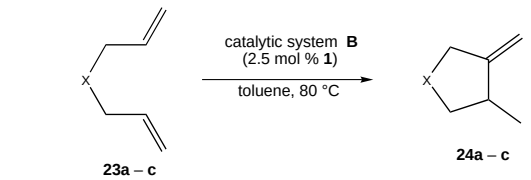
The catalytic system **B** was able to perform 1,6-diene cycloisomerisations with a variety of dienes (**23a – c**) when made from 2.5 mol % of **1** (Scheme 10).[17] The ketal **24a** was obtained in 64% isolated yield after heating in toluene at 80 °C during 8 h. The methylenecyclopentanes **24b** and **24c** were isolated after 8 and 5.5 h in 85 and 78% yields, respectively, as mixtures of diastereoisomers in the ratios 57:43 and 55:45 (Scheme 10).

The cycloisomerisation reaction is expected to take place with metal-hydride catalysts as with a palladium/acid system[31] or with an electron-rich metal moiety capable of promoting an oxidative coupling of the two C=C bonds of the diene. In this respect, it is noteworthy that other ruthenium systems based on $[Ru(cod)Cl_2]_n$ and Cp*Ru(cod)Cl in a protic solvent such as an alcohol have recently been found as excellent catalysts for the cycloisomerisation of 1,6-heptadiene derivatives.[32] The catalytic behaviour of the system **B** could be explained with the mechanism shown in Scheme 11. The catalytic

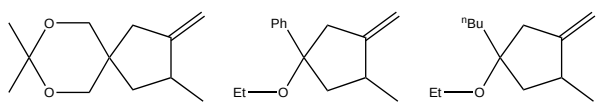


20 **21** **22**

Scheme 9.

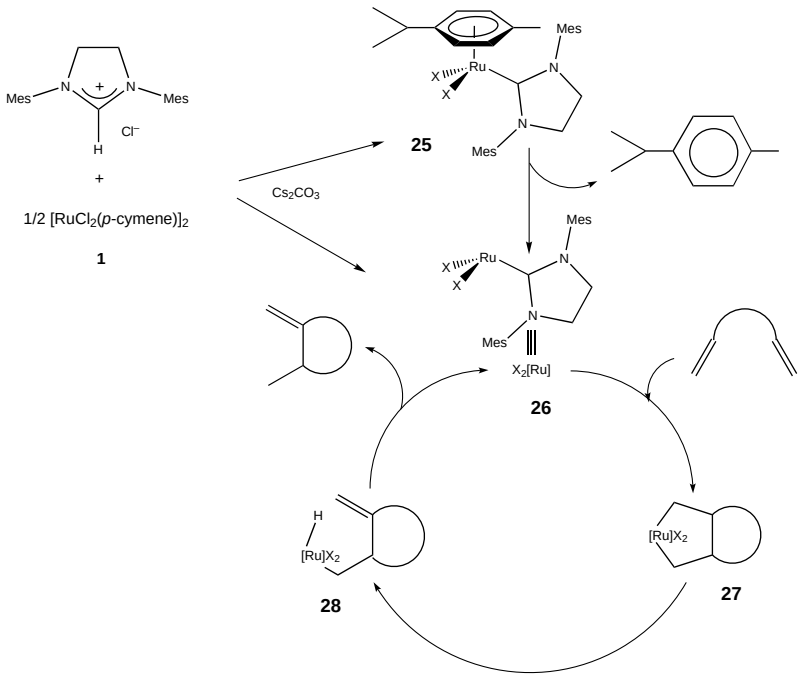


23a – c **24a – c**



24a (64%) **24b** (85%) **24c** (78%)

Scheme 10.

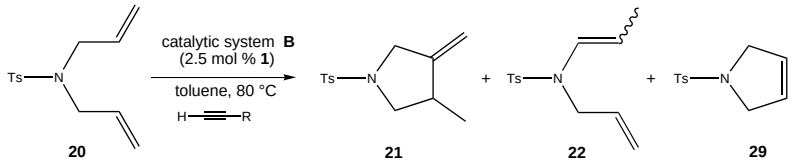


Scheme 11.

species is expected to be of the type $[RuX_2(carbene)]$ **26** resulting from the interaction of the imidazolinylidene carbene, generated upon deprotonation of the 1,3-bis(mesityl)imidazolinium chloride, with the ruthenium source **1** and elimination of the arene ligand. The formation of **26** may arise from the $RuCl_2$(imidazolinylidene)(*p*-cymene) complex (**25**). Due to the electron-releasing ability of the carbene ligand on addition of the diene to **26**, the oxidative coupling to give the ruthenacyclopentane **27** should be favoured. Then β-elimination to form the ruthenium(IV) hydride **28** and reductive elimination to give the cycloisomerisation product together with the regeneration of the catalytic species should take place.

In order to rather promote the ring-closing metathesis of dienes, the catalyst **B** had to be modified by formation of a carbene intermediate as in the Grubbs catalyst $RuCl_2(CHPh)L_2$. It is well known that ruthenium(II) complexes readily activate terminal alkynes into ruthenium vinylidene Ru=C=CHR, which has an Ru=CHR carbene character.[13,33] Such a vinylidene species/ruthenium moiety arising from the enyne triple bond may initiate the above enyne metathesis. Ozawa[13] prepared the complex $RuCl_2(=C=CHPh)(PCy_3)_2$ which promoted the ROMP polymerisation of norbornene derivatives. Kurosawa[34] has shown that the addition of phenylacetylene to chelating arene ruthenium(II) complexes led to efficient catalyst precursors for diene RCM reaction. In parallel, Grubbs has generated another *in situ* catalytic system,[12] starting from ImMesCl, $[RuCl_2(p\text{-cymene})]_2$, NaOBu-*t* and *tert*-butylacetylene possibly leading to the $[RuCl_2(=C=CHBu\text{-}t)$(imidazolinylidene)] species that catalyses cross-coupling metathesis. The catalytic system **B** was thus reacted with a terminal alkyne and then with a large excess of diallyltosylamide (**20**) at 80 °C and the ring-closing metathesis reaction leading to **29** took place under these conditions (Scheme 12).[17]

The selectivity of the reaction depends of the nature of the alkyne. The addition of 4.8 equivalents of phenylacetylene to the catalytic system **B** reoriented the transformation of the diene **20** into 90% of the metathesis product **29** and 10% of the cycloisomerisation product **21**. Trimethylsilylacetylene or *tert*-butylacetylene did not give better selectivities (Table 3). The use of 1-hexyne led to complete conversion into the metathesis

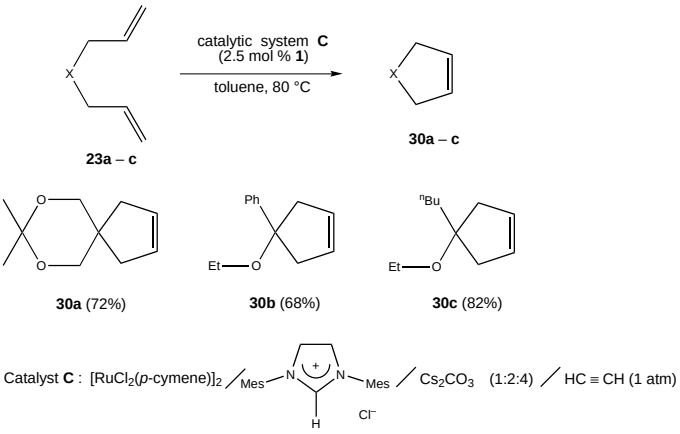


Scheme 12.

Table 3. Transformation of diene **20** after addition of a terminal alkyne to the catalytic system **B**.[a]

HC≡CR	Conversion (%)	Product distribution		
		21	**22**	**29**
HC≡CPh	100	10	/	90
HC≡CSiMe$_3$	100	60	26	14
HC≡CBu-*t*	51	41	10	traces
HC≡CBu-*n*	100	traces	/	99
HC≡CH[b]	100	/	/	100

[a] Diene (0.5 mmol), catalytic system **B** based on 2.5 mol % of **1**, alkyne 4.8 equivalents based on ruthenium, toluene (2.5 mL), 80 °C.
[b] 1 atmosphere.



Scheme 13.

product **29** with only traces of the cycloisomerisation product **21**. The sole formation of the metathesis product **29** was obtained when the catalytic reaction was carried out under an atmosphere of acetylene for 2.5 h. It is noteworthy that acetylene rapidly transformed the catalyst **B** as the new catalytic species selectively performed the metathesis reaction and completely inhibited the cycloisomerisation reaction which is actually faster.

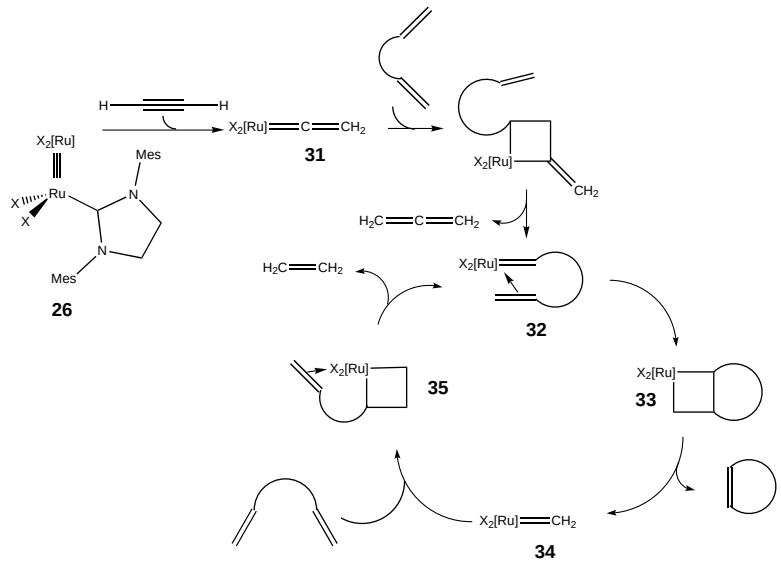
The new *in situ* prepared four component catalytic system **B**/acetylene[35] (catalyst **C**) was able to selectively perform the ring-closing metathesis reaction from the 1,6-dienes **23a – c** (Scheme 13). The ketal **30a** was isolated after 8 h in 76% yield. For the formation of products **30b** and **30c**, the metathesis reactions were slower. They were isolated after heating during 16 h in 68 and 82% yields, respectively.

To explain the drastic change of reactivity introduced by addition of acetylene on the catalytic system **B**, the mechanism shown in Scheme 14 can be proposed.

The ruthenium(II) species **26** is expected to form the ruthenium vinylidene **31** upon reaction with acetylene. Then, upon interaction with one double bond of the diene and elimination of allene, the ruthenium carbene **32** can be obtained, and leads to the formation of the ruthenacyclobutane **33** and liberation of the metathesis product with formation of the more active species **34**. The reaction of **34** with a diene regenerates the ruthenium carbene **32** *via* complex **35** and elimination of ethene.

4 Alkene Metathesis in Ionic Liquids

One important aspect of metal-catalysed metathesis is that, whereas it opens the route to a variety of useful functional organic compounds, macrocycles and polymers, the activity requires 1 – 5 mol % of catalyst.



Scheme 14.

Industrial applications require that the catalyst should be recovered or the metal residue easily removed to lower the costs and increase the purity.

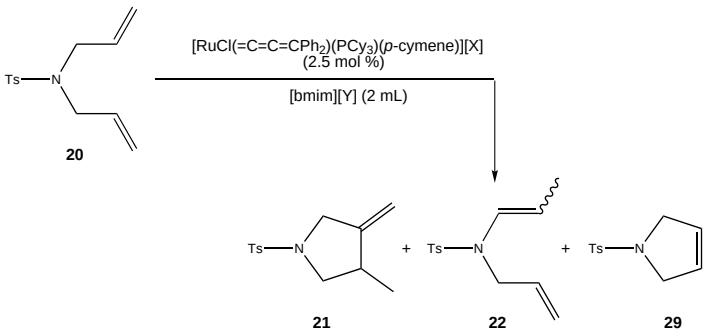
One possible approach to recover a metal catalyst is based on catalysis performed in ionic liquids.[36] Imidazolium salts constitute now a classical class of ionic liquids.[37] These salts offer the possibility to dissolve ionic catalysts and allow the catalytic transformation of an organic substrate dissolved in an organic solvent, thus in a separate phase in contact with the ionic liquid phase.

We have presented above the use of *in situ* prepared catalysts by the combination of a ruthenium source and a bulky imidazolium salt leading to an electron-rich carbene ligand in the presence of a base (Cs_2CO_3). These results revealed that (i) the presence of an imidazolium salt does not inhibit alkene metathesis, (ii) this *in situ* formation of catalyst is not appropriate in an imidazolium salt as it may lead to a carbene exchange, arising from the two types of imidazolium salts, (iii) the use of imidazolium salts avoids the use of a base to generate the catalyst, and (iv) the *in situ* prepared catalysts are neutral and thus the dissolution in ionic liquids should not be favoured.

We have thus considered the use of the first well-defined ionic alkene metathesis catalyst precursors, the ruthenium allenylidene salts [RuCl(=C=C=CPh$_2$)(PCy$_3$)(*p*-cymene)][X][38] in [1-butyl-3-methylimidazolium][Y] ([bmim][Y]) salts as ionic liquids, being aware that the catalyst activity and chemoselectivity dramatically depends on the nature of the escorting anions X^- and Y^-.[38,39]

During this work,[18,40] the first two examples of metathesis catalysis in ionic liquids were reported. The first one by Bayer[41] used methyl ethylimidazolium chloroaluminate salts and Grubbs complex modified with a Schiff base ligand. The second example was reported by Buijsman[42] using this time the Grubbs catalyst in imidazolium salts.

To study the different parameters of the ring-closing metathesis reaction catalysed by ruthenium allenylidene salts in ionic liquids, the diallyltosylamide (**20**) was used, which can give, depending on the catalytic conditions, the metathesis product **29** but also, when it is not selective the cycloisomerisation **21** or isomerisation **22** by-products (Scheme 15).



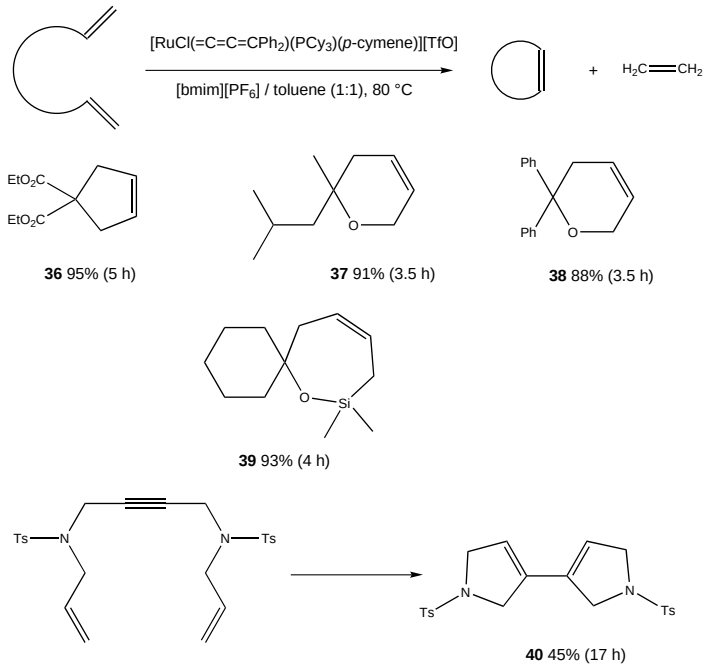
Scheme 15.

As previously reported for the reaction in toluene,[39] we observed a dramatic influence of the associated anion X^- of the cationic allenylidene complexes and of the ionic liquids (Y^-) (Table 4). Indeed, the use of 2.5 mol % of the complex [RuCl(=C=C=CPh$_2$)(PCy$_3$)(*p*-cymene)][BF$_4$] in the ionic liquid [bmim][BF$_4$] led to 75% of conversion after 6 h at 80 °C. The reaction was not as selective as in toluene,[39] and the products **21**, **22**, and **29** were obtained in the respective ratio of 30:8:37. The combination between the ruthenium allenylidene with PF_6^- as counteranion and [bmim][PF$_6$] (Entry 2) gave a moderate conversion and mainly the metathesis product **29** (58%). The use of a ruthenium precursor with triflate in [bmim][OTf] (Entry 3) rapidly and selectively gave the metathesis product **29** (97%) and only 3% of cycloisomerisation product **21** was observed. Another way to selectively obtain the metathesis product **29** was to use the ionic liquid [bmim][PF$_6$] with [RuCl(=C=C=CPh$_2$)(PCy$_3$)(*p*-cymene)][OTf] (Entry 7). Under these conditions, the reaction was slower, 85% of conversion in 5 h, but led to a good selectivity in **29** (83%). When different escorting anions were present in the complex and in the ionic liquid, a rapid exchange of counteranions gave poor reactivity and chemoselectivity (Entries 5 and 6).

Table 4. Metathesis reaction of diallyltosylamide (**20**) with ruthenium allenylidene in [bmim][Y].[a]

Entry	[Ru][X]	Solvent	Time [h]	conversion [%]	**21** [%]	**22** [%]	**29** [%]
1	[Ru][BF$_4$]	[bmim][BF$_4$]	6	75	30	8	37
2	[Ru][PF$_6$]	[bmim][PF$_6$]	5	65	5	2	58
3	[Ru][OTf]	[bmim][OTf]	2.5	100	3	/	97
4	[Ru][OTf][b]	[bmim][OTf]	18	100	/	/	100
5	[Ru][OTf]	[bmim][BF$_4$]	5	60	31	6	23
6	[Ru][OTf]	[bmim][(CF$_3$SO$_3$)$_2$N]	5	53	18	4	31
7	[Ru][OTf]	[bmim][PF$_6$]	5	85	2	/	83

[a] Diene **20** (0.5 mmol), [RuCl(=C=C=CPh$_2$)(PCy$_3$)(*p*-cymene)][X] (2.5 mol %), [bmim][Y] (2 mL), 80 °C, then the products were extracted with 3 × 5 mL of toluene.
[b] Performed at room temperature.



36 95% (5 h) **37** 91% (3.5 h) **38** 88% (3.5 h)

39 93% (4 h)

40 45% (17 h)

Scheme 16.

It is noteworthy that, when the catalytic reaction was performed at room temperature (Entry 4) with triflate as the common anion, the reaction was slower but became selective in the formation of the metathesis product **29**.

With the aim of increasing the catalyst reactivity in ionic liquids and facilitating the product separation and catalyst recovery, an organic co-solvent was added to the reaction mixture, which led to a biphasic mixture. Addition of 2.5 mL of toluene to 2 mL of [bmim][BF_4] increased the reaction rate in the presence of [RuCl(=C=C=C(*p*-$C_6H_4Cl)_2$)(PCy_3)(*p*-cymene)][BF_4]. In this case, the conversion was 96% after 5.25 h at 80 °C with respect to 40% conversion after 5.5 h without toluene. In this biphasic system the catalyst was located in the ionic liquid as the initial violet colour of the catalyst was completely transferred into the ionic liquid phase while the organic phase remained colourless.

An easy procedure was performed to facilitate the extension of the metathesis reaction in ionic liquids to different dienes, the catalyst [RuCl(=C=C=CPh_2)(PCy_3)(*p*-cymene)][OTf] was generated *in situ* from [RuCl(PCy_3)(*p*-cymene)][OTf] and HC≡$CCPh_2OH$ in toluene before addition of [bmim][PF_6] (Scheme 16). After reaction, the products were extracted from the reaction mixture with toluene. With this catalytic system[43] operating at 80 °C, it was possible to obtain the 5-membered ring derivative **36** (95%). The formation of the 6-membered ring products **37** (91%) and **38** (88%) was faster. The cyclic 7-membered ring allylsilane **39** was isolated in 93% after 4 h and the bicyclic derivative **40** was obtained (45%) by dienyne metathesis in trifluorotoluene.

The recycling of the catalyst was studied in the RCM of diallyltosylamide (**20**). The complex [RuCl(=C=C=CPh_2)(PCy_3)(*p*-cymene)][OTf] (2.5 mol %) was dissolved in 2 mL of [bmim][OTf] and to obtain the best selectivity, the reaction was carried out at room temperature. The first metathesis run gave after 18 h a full conversion in the metathesis product **29**. The second loading of diene **20** gave, after 18 h, the metathesis product **29** in 86% conversion, and the third loading of **20** was converted in only 33% to the product **29** after 23 h. These results show that the catalyst is able to perform in good conversion for the first two consecutive runs and that the catalyst remains active for an overall time of more than 40 h.

However, the ionic liquid itself could be reused several times if the organometallic residues were eliminated between two successive runs by a treatment with black carbon at 80 °C in 1,2-dichloroethane. On adding a new loading of catalyst to this purified ionic liquid for each reaction, no lost of reactivity and selectivity was observed.

5 Conclusion

The utilisation of the efficient catalytic system *in situ* generated from an air-stable and commercially available ruthenium source [$RuCl_2$(*p*-cymene)]$_2$ (**1**), 1,3-bis(mesityl)imidazolinium salt, ImH_2MesCl as carbene precursor, and Cs_2CO_3, may represent an important development for metathesis reactions.

For enyne metathesis, the reactivity largely depends on the nature of the carbene precursor. The more electron-rich the carbene ligand, the more efficient is the resulting catalyst. With 1,6-dienes, the catalytic system **B** presents a dichotomous behaviour: in toluene under an atmosphere of argon or nitrogen, the cycloisomerisation products were selectively obtained, but under an atmosphere of acetylene a complete change of reactivity was observed and only the metathesis products were isolated.

1-Alkyl-3-methylimidazolium salts were also shown to be host ionic solvents for ionic ruthenium allenylidene precursors. This study revealed a dramatic influence of the counteranion from both the catalyst and the ionic liquid. The most efficient catalyst/solvent combinations are based on the ruthenium allenylidene with triflate and ionic liquid with triflate or hexafluorophosphate as counteranion.

This concept for making catalysts *in situ* opens the way for the discovery of many new catalysts *via* the interaction of commercially available metal complexes and suitable, sterically hindered, electron-releasing ligands.

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