

Recent developments in design and synthesis of well-defined ruthenium metathesis catalysts – a highly successful opening for intricate organic synthesis

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Dedicated to Professor Alexandru T. Balaban on the occasion of his 75th birthday anniversary, in acknowledgement of his significant contribution to advancement in theoretical and synthetic organic chemistry

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Abstract

This paper surveys the latest and fast growing developments in the design and synthesis of homogeneous and immobilized ruthenium metathesis catalysts. These novel ruthenium carbene complexes, devised as convenient counterparts of the well-defined tungsten and molybdenum alkylidene complexes, display comparable activity and selectivity in metathesis reactions combined with good tolerance towards organic functionalities, air and moisture. Due to their valuable attributes, they have been applied successfully in a multitude of complex organic and polymer syntheses involving ring-opening and ring-closing metathesis reactions, cross-metathesis, enyne metathesis and ring-opening metathesis polymerization.

Keywords: Ruthenium metathesis catalysts, N-heterocyclic carbenes, ruthenium carbene complexes, immobilized ruthenium complexes, ring-closing metathesis, ring-opening metathesis polymerization

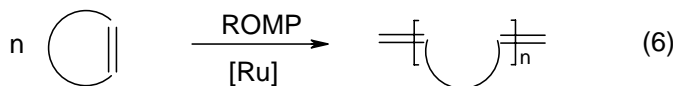
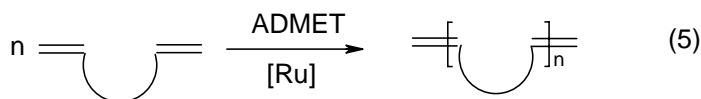
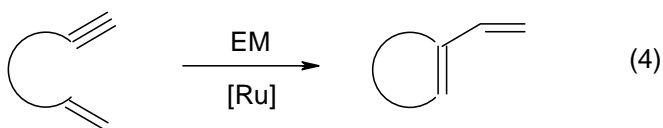
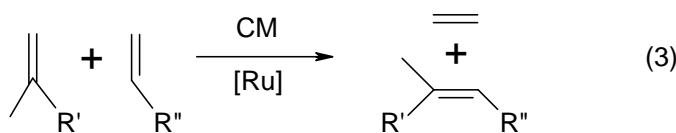
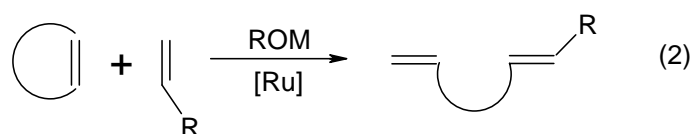
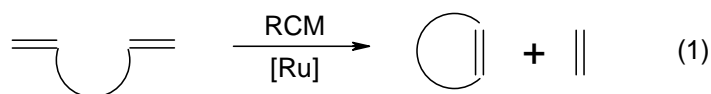
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1. Introduction

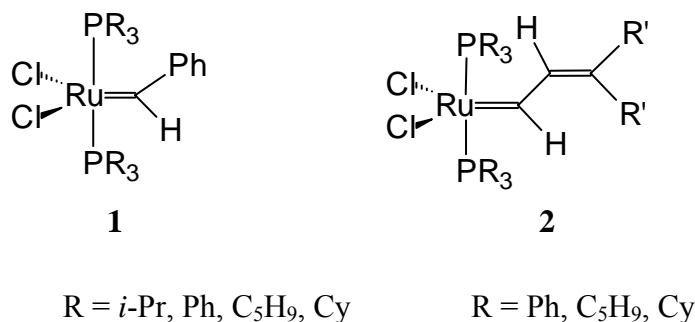
During the last decade, olefin metathesis has known a real breakthrough, becoming a powerful synthetic tool in organic and polymer chemistry.^{1,2} Along these lines, numerous ruthenium complexes, as convenient counterparts of the well-defined tungsten and molybdenum alkylidene complexes,^{3,4} have been prepared and used successfully as efficient metathesis catalyst precursors in a wide range of well-established synthetic procedures such as ring-closing metathesis (RCM) (Eq.1),⁵ ring-opening metathesis (ROM) (Eq.2),⁵ cross-metathesis (CM) (Eq.3),⁶ enyne metathesis (EM) (Eq.4),⁷ acyclic diene metathesis (ADMET) (Eq.5)⁸ and ring-opening metathesis polymerization (ROMP) (Eq.6)⁹.



Due to the ever increasing potential of these methodologies, new applications have emerged in manufacturing a diversity of natural products, biologically active organic compounds or functional polymers with special architectures.¹⁰

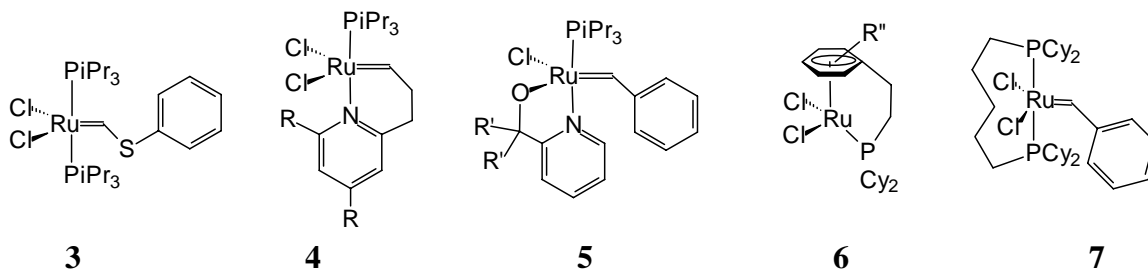
2. Ruthenium alkylidene complexes

The well-defined ruthenium-carbene complexes **1** and **2**, reported by Grubbs and coworkers,^{11,12} are the first ruthenium catalysts to show good activity and selectivity in metathesis of acyclic and cyclic olefins while exhibiting an improved tolerance towards various organic functionalities, air and moisture, opening, thus, a new era in metathesis applications in organic and polymer syntheses¹³⁻¹⁷ (Scheme 1, where R is isopropyl, phenyl, cyclopentyl or cyclohexyl (Cy) and R' is methyl or phenyl).



Scheme 1. Well-defined ruthenium benzylidene and vinylcarbene initiators.

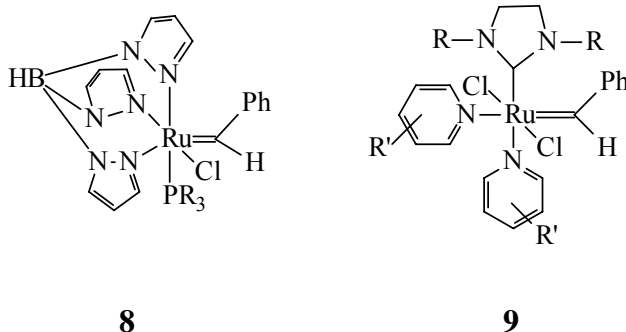
Success recorded with **1** and **2** fueled an impetus for the design and preparation of an array of ruthenium alkylidene complexes and their application, by many research teams, as a sustainable strategy for the synthesis of libraries of organic compounds and polymeric materials.¹⁸⁻²¹ An important group of catalysts, therein, consists of ruthenium alkylidene complex **3**, bearing a heteroatom-containing carbene, as well as the chelated complexes **4** and **5** developed by Ciba AG,^{18,19} complex **6** reported by Abele²⁰ and **7** reported by Mol²¹ (Scheme 2, where R is H, CH₃; R' is CH₃, C₆H₅; R'' is an alkyl group).



Scheme 2. Well-defined ruthenium alkylidene metathesis catalysts.

A practical advantage offered by these new ruthenium catalysts is that, for the first time, it became possible to use such Ru initiators in ROMP of cycloolefins (*e.g.* dicyclopentadiene) with the reaction injection molding (RIM) technique, and by immobilization on solid supports. Furthermore, their synthesis is a convenient one-step procedure starting from the ruthenium phosphane benzylidene complex **1**. For instance, reaction of two equivalents of complex **1** with one equivalent of phenyl vinyl sulphide affords the ruthenium complex **3**, with an S-containing ligand, whereas an equimolar reaction between **1** and 2-(3-butenyl)pyridine leads to the chelated ruthenium complex **4**. Likewise, bidentate phosphines with large natural bite angles (*e.g.* based on xanthene or $\text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2$, $n=3-5$) have been obtained from ruthenium complex **1** and 1, ω -bis(dicyclohexylphosphine)alkanes (*e.g.* 1,5-bis(dicyclohexylphosphine)pentane).²¹ The latter bidentate phosphine ligands could also be used to attach ruthenium alkylidene complexes to solid supports as a means of obtaining heterogenized catalysts.

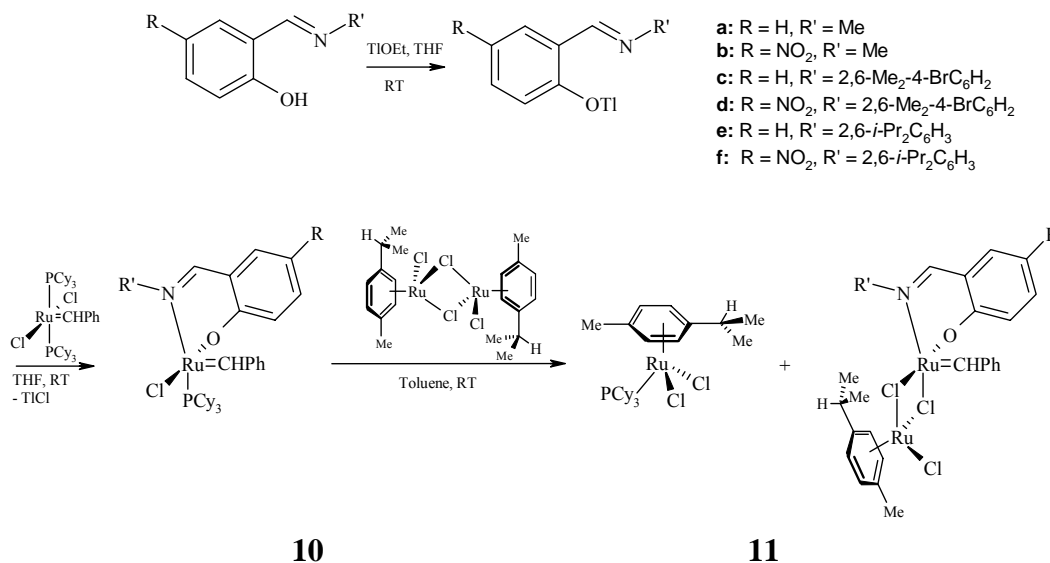
To finely tune the activity and stability of the ruthenium alkylidene complexes, further heterocyclic ligands have been incorporated into the ruthenium coordination sphere. Complexes **8** ($\text{R} = \text{Cy}$) and **9** ($\text{R} = \text{Mes}$, $\text{R}' = \text{H}$, Br , NO_2) are representative examples.^{22,23}



Scheme 3. Ruthenium benzylidene complexes with heterocyclic ligands.

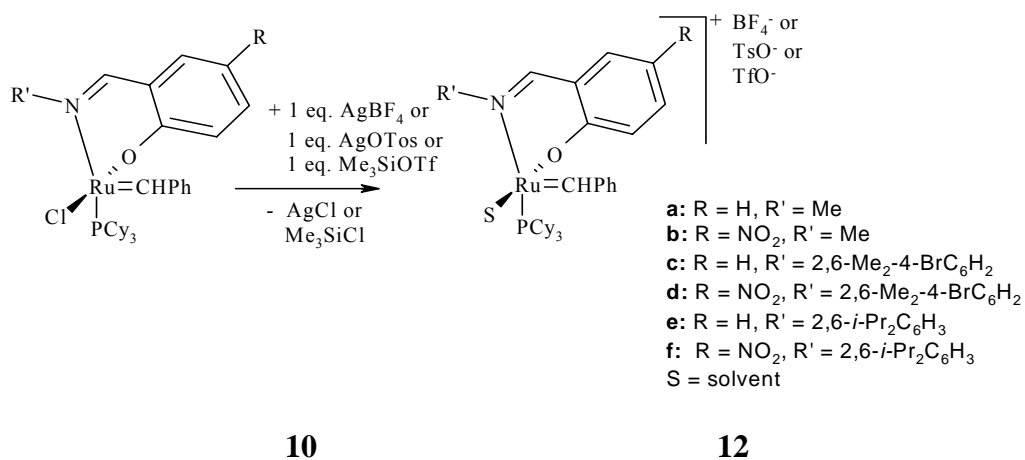
Of these two complexes, the bis-pyridine adduct **9** ($\text{R}' = \text{Br}$) is an excellent metathesis catalyst possessing a high initiation rate.

Schiff-bases proved to be another class of attractive ligands in creating new ruthenium complexes. They incorporate two donor atoms (N and O) which, on chelation, provide opposite features: the phenolate oxygen atom is a hard donor and will stabilize a higher oxidation state of the ruthenium atom whereas the imine nitrogen is a softer donor and, consequently, will rather stabilize the lower oxidation state of ruthenium. Besides, Schiff-bases are easily accessible through one-step procedures *via* almost quantitative condensation of common amines with aldehydes. To capitalize on the high potential of Schiff-bases, a wide range of efficient ruthenium catalysts, *e.g.* **10a-f** and **11a-f**, with O,N-chelated Schiff-base “dangling-ligands”, have been prepared by Verpoort and coworkers.^{24,25}



Scheme 4. Synthesis of Schiff-base ruthenium benzylidene complexes.

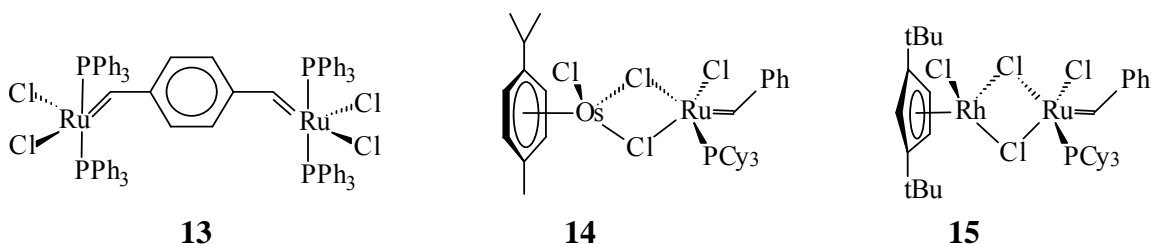
In addition, the same research group introduced cationic Ru-benzylidene complexes **12a-f** prepared *in situ* from the corresponding neutral complexes **10a-f**, by treatment with one equivalent of silver salts or trimethylsilyl salts (Scheme 5).



Scheme 5. Synthesis of cationic Schiff-base ruthenium complexes.

Schiff-base ligated ruthenium carbenes are appropriate scaffolds for manufacturing immobilized catalysts by means of spacers attached to a silylated solid support.

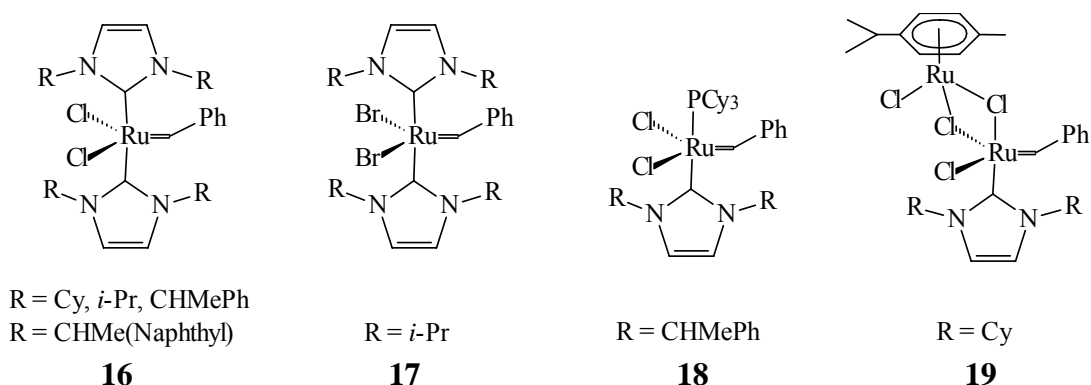
The portfolio of well-defined ruthenium alkylidene catalysts also includes dinuclear complexes such as **13**, easily obtained from RuCl₂(PPh₃)₃ and 1,4-benzene-bis(diazomethane), that provide ready access to particular polymer architectures like ABA block-copolymers by ROMP of cycloolefins²⁶ (Scheme 6).



Scheme 6. Dinuclear ruthenium alkylidene complexes.

Heterobimetallic ruthenium catalysts are also to be mentioned, *e.g.* compounds **14** and **15**, containing both ruthenium and osmium or rhodium, conveniently resulting from reaction of complex **1** with the corresponding diosmium or dirhodium derivatives. Such heterobimetallic complexes were reported to possess significantly enhanced activity in ROMP of 1,5-cyclooctadiene and 2,2-bis(trifluoromethyl)norbornene.²⁷

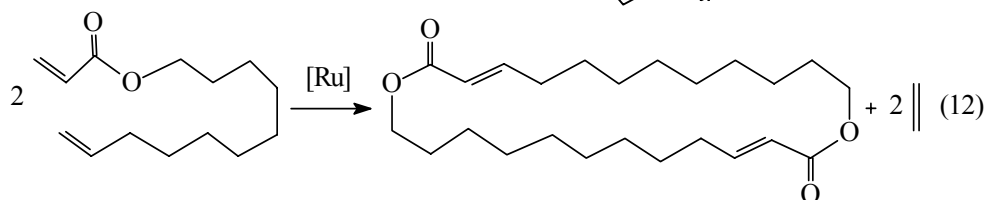
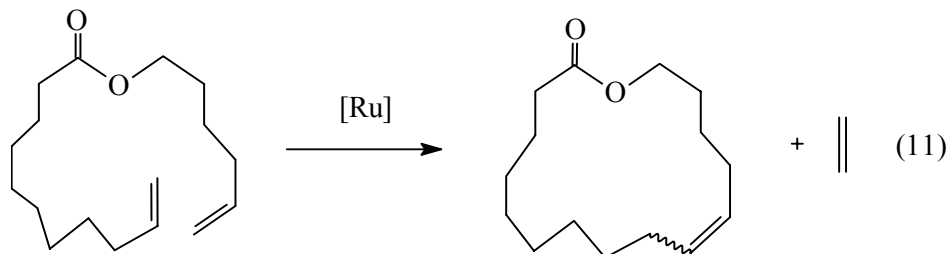
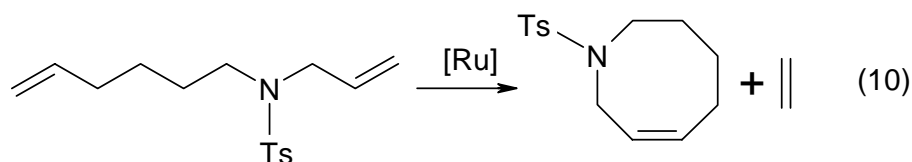
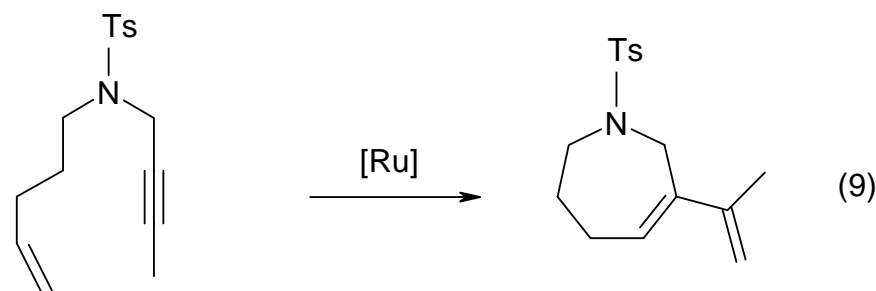
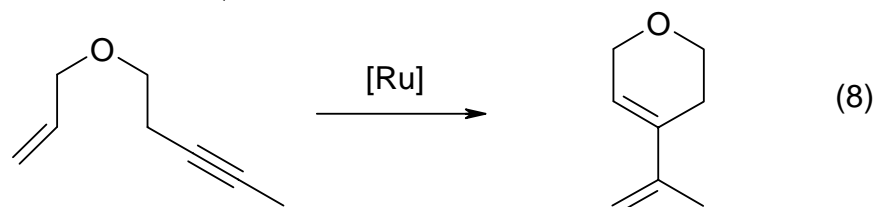
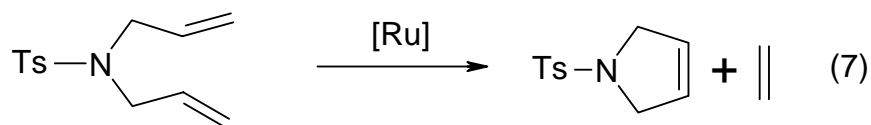
Striking progress in the chemistry of ruthenium carbene complexes was achieved through the synthesis by Herrmann *et al.* of a novel class, the ruthenium benzylidene complexes **16-19**,^{28,29} obtained *via* derivatization of the phosphane complex **1**. To this end, one or both PCy₃ ligands in **1** have been replaced by the sterically demanding imidazolin-2-ylidenes, easily accessible and known to be more Lewis-basic than PCy₃. In contrast to phosphane, these non-labile ligands possess strong σ -donor and weak π -acceptor properties stabilizing both the 16-electron precatalysts and the highly electron deficient metathesis intermediates. The approach also allowed control of the reactivity by systematic variation of the R groups in the imidazolin-2-ylidene moiety (Scheme 7).



Scheme 7. N-Heterocyclic carbene (NHC) ruthenium complexes.

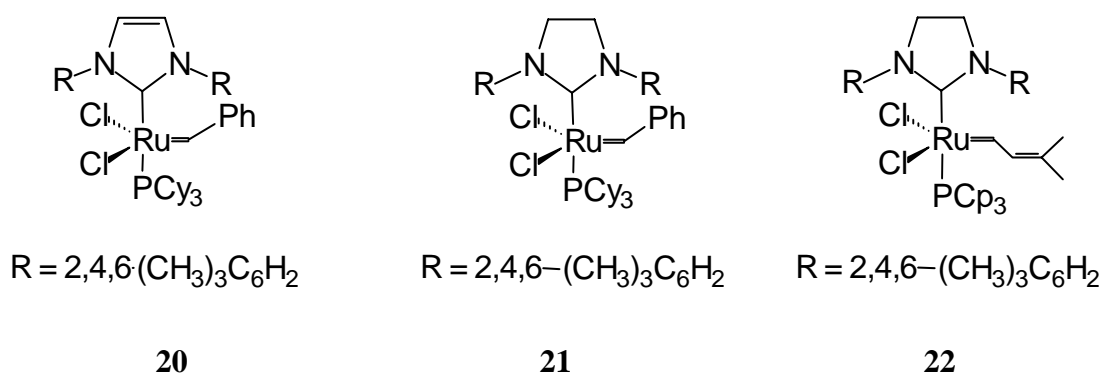
In spite of significant differences observed in the reactivity of **16-19**, these ruthenium benzylidene complexes bearing N-heterocyclic carbenes (NHC) as ancillary ligands were found to promote conversion of a wide panel of dienes or enynes into the corresponding cyclic compounds by ring closing metathesis (RCM) or enyne metathesis (EM).³⁰ Applications include synthesis of five-, six-, seven-, eight- and higher-membered ring system compounds, of N- and

O-heterocyclic compounds (Eq. 7-12), as well as of macrocyclic products such as the commercially important perfume ingredient Exaltolid[®]. Significantly, compatibility between these ruthenium benzylidene complexes and functional groups in different organic compounds seems to practically match that of the complex **1**. An unexpected supplemental advantage of this class of catalysts is their excellent performance in the formation of tri- and even tetra-substituted cycloalkene products by RCM.



At the same time, on applying a similar procedure for ligand exchange in ruthenium carbene complexes, Grubbs and coworkers³¹ prepared another series of ruthenium catalysts (**20-22**)

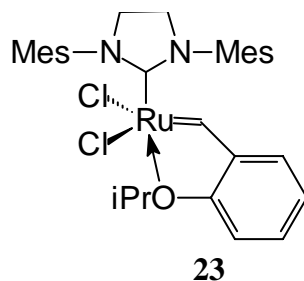
within the imidazolin-2-ylidene class, using different members of the Arduengo imidazolin-2-ylidene ligands³² (Scheme 8).



Scheme 8. N-Heterocyclic carbene (NHC) ruthenium complexes of the Grubbs type.

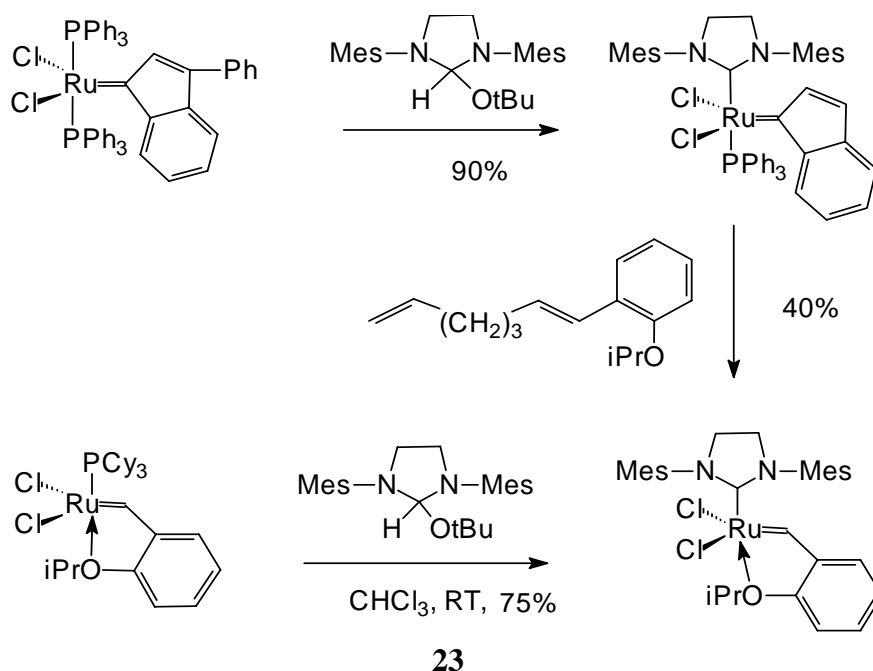
Synthesis occurs readily by a two-step sequence. In the first step, the imidazolin-2-ylidene carbene ligand is conveniently synthesized from the corresponding salt with sodium hydride in liquid ammonia/THF, and used without purification in the subsequent step involving a ligand exchange reaction in the ruthenium complex **1**; the latter reaction is rapid at room temperature, in toluene. The final product was isolated as a pinkish-brown microcrystalline solid that could be purified by recrystallization from pentane at -78°C . Of the numerous 1,3-diaryl-imidazolin-2-ylidenes tried by Grubbs, only the 2,6-disubstituted aryls (including the 1,3-dimesitylimidazolin-2-ylidene), which are sufficiently bulky to prevent substitution of the second phosphane ligand, gave clean reaction products. Synthesis and characterization of NHC ruthenium alkylidene complexes were reported simultaneously by the Nolan group as well.³³

Very stable and highly selective for cross-metathesis (CM) and ring-closing metathesis (RCM) proved to be the O-chelated NHC ruthenium isopropoxy-benzylidene complex **23**, incorporating a 1,3-dimesitylimidazolidin-2-ylidene ligand, prepared by Hoveyda et al.³⁴ (Scheme 9).



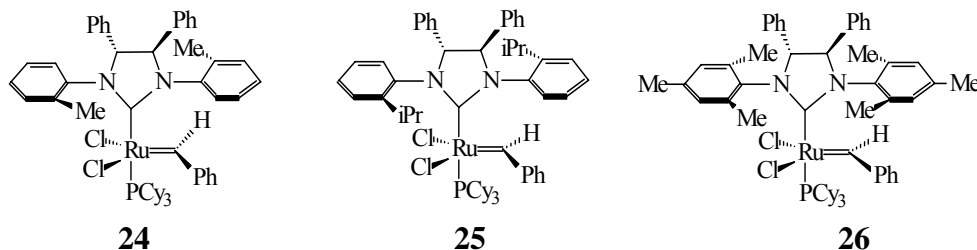
Scheme 9. O-Chelated, NHC ruthenium complexes of Hoveyda type.

Two alternative synthetic pathways for the ruthenium benzylidene complex **23**, employing as precursors different ruthenium alkylidene complexes, have been reported by Blechert *et al.*³⁵ (Scheme 10).



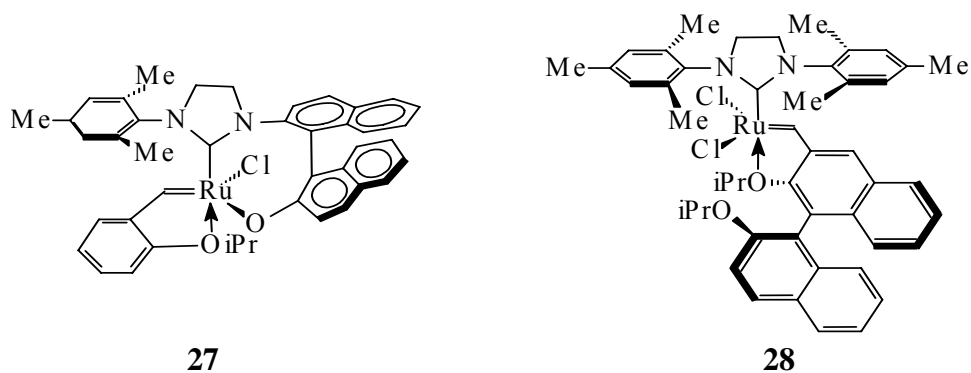
Scheme 10. Convenient synthesis of ruthenium complexes of the Hoveyda type.

Of great interest for asymmetric metathesis chemistry is the family of chiral ruthenium alkylidene complexes. In this juncture, the ruthenium benzylidene complexes **24-26**, which use backbone stereogenicity to induce atropisomeric chirality in the unsymmetrical N-aryl substituents, have been synthesized and applied in metathesis reactions.^{36,37} Among these complexes, compound **26** exhibited considerable metathesis activity and a particularly enhanced stereoselectivity.³⁷



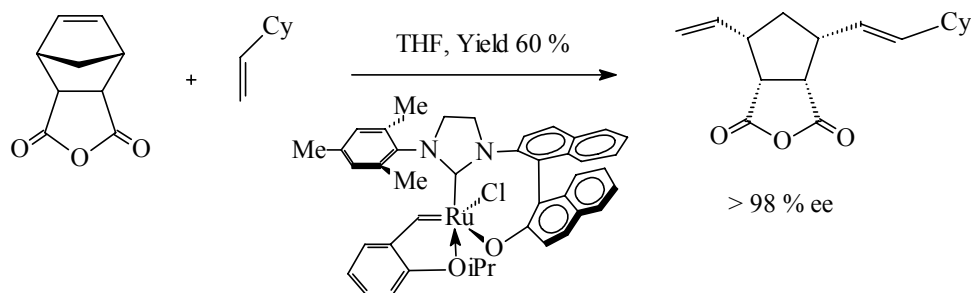
Scheme 11. Chiral ruthenium benzylidene complexes.

Other new chiral ruthenium complexes, **27** and **28**, bearing different alkylidene moieties, also have been synthesized and used in enantioselective metathesis reactions.³⁸



Scheme 12. Chiral O-chelated ruthenium benzylidene complexes.

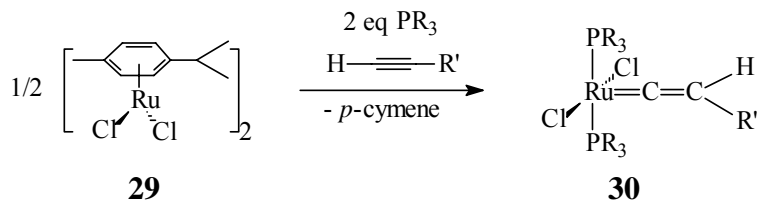
Remarkably, over 98% enantioselectivity has been reported when applying complex **27** in ring-opening metathesis of a norbornene derivative and a substituted olefin^{38a} (Scheme 13).



Scheme 13. Enantioselective ring-opening metathesis with chiral ruthenium complexes.

3. Ruthenium vinylidene complexes

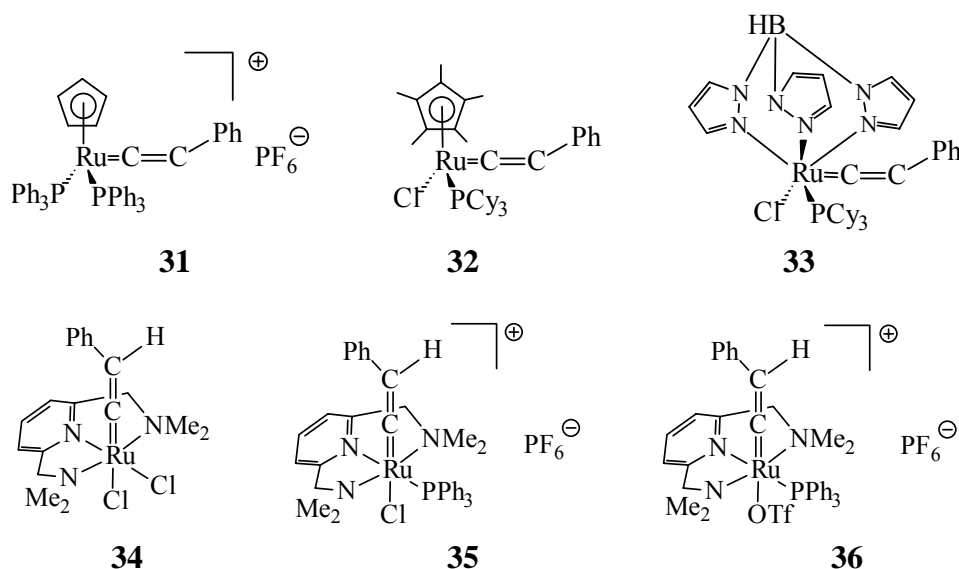
Ruthenium vinylidene complexes also are having a considerable impact on metathesis related chemistry.^{39a,b} Originally, the neutral 16-electron ruthenium vinylidene complexes **30** (R = *i*-Pr, Cy; R' = Ph, *t*-Bu, Fc, *p*-MeO₂CC₆H₄, *p*-MeOC₆H₄) were prepared by Katayama and Osawa^{39c,d} from commercially available starting materials, namely terminal alkynes and the arene ruthenium dimer **29**.



Scheme 14. Bisphosphane ruthenium vinylidene complexes.

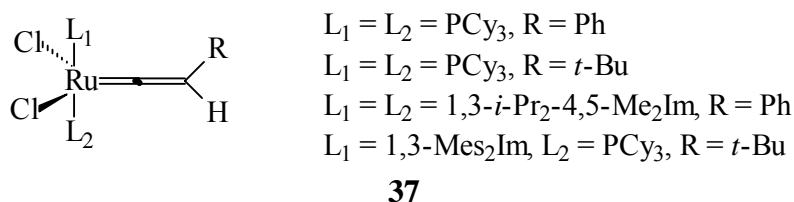
However, these complexes showed only moderate metathesis activity in RCM of unsubstituted α,ω -dienes and ROMP of highly strained norbornenes.⁴⁰

Other interesting cationic and neutral 18-electron ruthenium vinylidene complexes were obtained by Bruce^{41a}, Osawa^{41b} (**31-33**) and van Koten⁴² (**34-36**) and were screened for their metathesis activity, but their applicability remains limited to a small range of olefinic substrates.



Scheme 15. Cationic and neutral ruthenium vinylidene complexes.

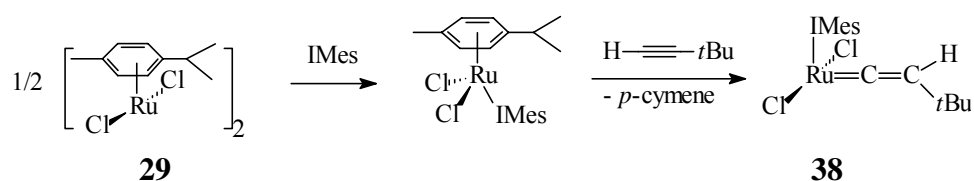
A substantial improvement was accomplished by Louie and Grubbs through synthesis of ruthenium vinylidene complexes coordinating an imidazolin-2-ylidene ligand.⁴³ Complexes **37** resulted from the bisphosphane ruthenium complex **1** (R = Cy) and free imidazoline carbenes or their salts (Scheme 16).



Scheme 16. Ruthenium complexes bearing various ancillary ligands.

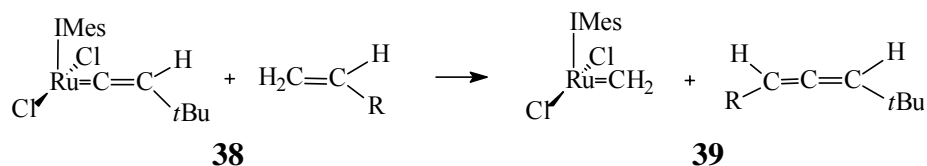
In this class, complexes possessing both the phosphane and imidazolin-2-ylidene ligands, displayed substantial metathesis activity in RCM of diethyl diallylmalonate yielding substituted cycloolefin, but the reaction rate was slower than that with the corresponding bisimidazolin-2-ylidene ruthenium vinylidene complex. As detailed mechanistic investigations on the metathesis reaction by Grubbs and coworkers⁴³ cogently displayed that increased ligand dissociation (*i.e.* of

phosphane) is necessary to accelerate the initiation step and thereby enhance the catalytic activity, a coordinatively unsaturated, phosphane-free ruthenium vinylidene complex **38** might be formed directly *in situ* from the ruthenium dimer **29**, in the presence of a terminal alkyne and the N-heterocyclic carbene (IMes), as such or as its salts.



Scheme 17. Synthesis of imidazol-2-ylidene ruthenium vinylidene complex **38**.

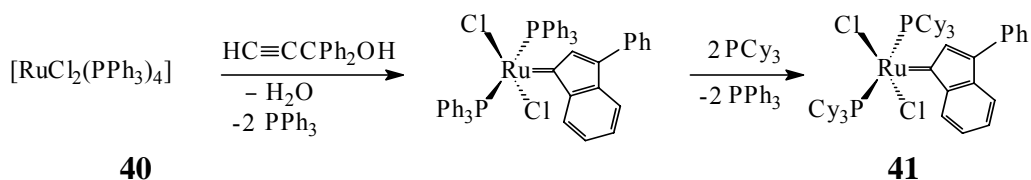
Indeed, the catalytic activity of **38** proved to be even higher than that of the complex **35**, evidencing a higher unsaturation degree in the coordination metal sphere. The pathway for generation of the real catalytically active species, **39**, from **38** and the olefin substrate can be seen in Scheme 18.



Scheme 18. Generation of the active species from catalyst **38**.

4. Ruthenium indenylidene complexes

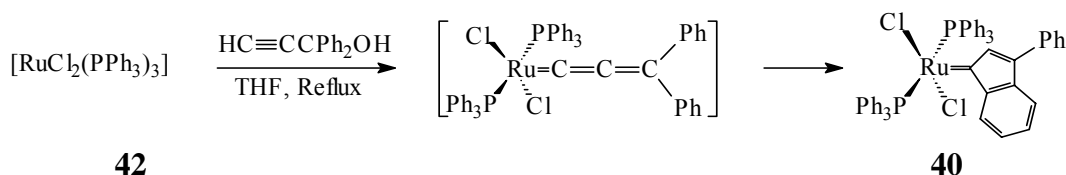
First, 3-phenyl indenylidene complex **40** was prepared from commercial $[\text{RuCl}_2(\text{PPh}_3)_4]$ and 3,3-diphenylpropyn-3-ol as the carbene source. Then, the PPh_3 ligands in complex **40** were readily substituted by the better donating PCy_3 affording the parent indenylidene complex **41**.^{44,45}



Scheme 19. Synthesis of ruthenium indenylidene complexes **40** and **41**.

The methodology can also use the trisphosphane complex $[\text{RuCl}_2(\text{PPh}_3)_3]$ for synthesis of indenylidene complex **40**. It has been proved unequivocally that the initially formed allenylidene

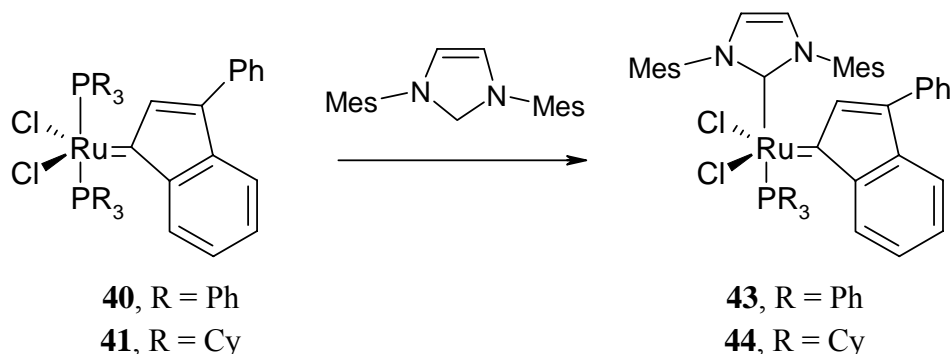
complex **42** leads by intramolecular rearrangement to the more stable indenylidene complex **40**.⁴⁶



Scheme 20. Reaction pathway for synthesis of ruthenium indenylidene complex **40**.

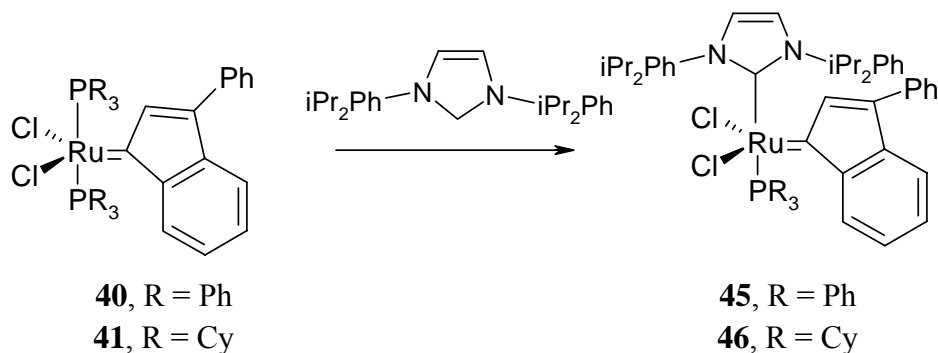
These ruthenium indenylidene complexes have higher thermal stability as compared to the related alkylidene complexes **1** and **2** and also perform well in various ring-closing metathesis reactions.

Substitution of phosphane ligands in complexes **40** and **41** by imidazolin-2-ylidene ligands enabled synthesis of new 16-electron ruthenium indenylidene complexes of even higher activity and stability. Thus, addition of 1,3-dimesitylimidazolin-2-ylidene to the 3-phenylindenylidene complexes **40** and **41**, in toluene at room temperature, leads to **43** and **44**, respectively, in considerable yield⁴⁷ (Scheme 21).



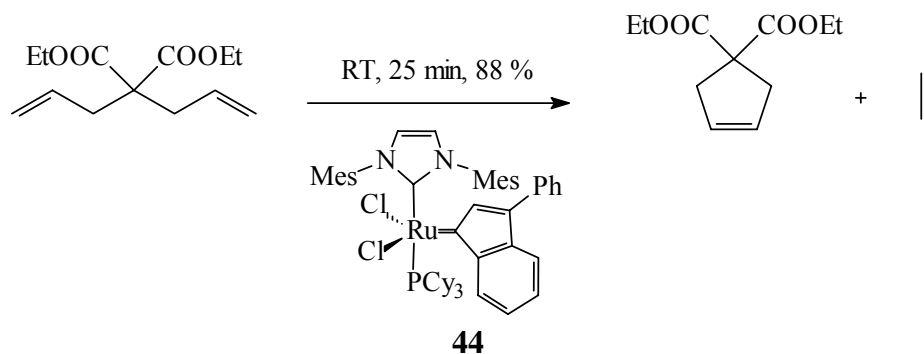
Scheme 21. Synthesis of 1,3-dimesitylimidazolin-2-ylidene ruthenium indenylidene complexes **43** and **44**.

Complex **44** can be best prepared in hot hexane because of an easier isolation of the product by simple filtration *vs.* evaporation of the solvent. By a similar procedure complexes **45** and **46** have been obtained from **40** and **41**, respectively, and 1,3-bis(2,6-di-isopropylphenyl)imidazolin-2-ylidene (Scheme 22).

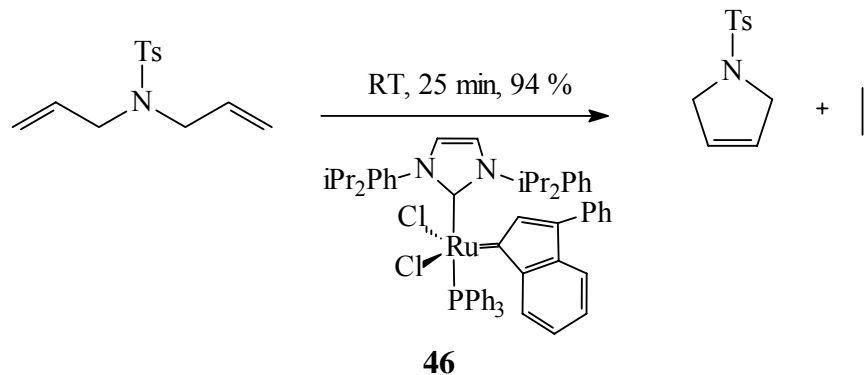


Scheme 22. Synthesis of bis(1,3-diisopropylphenyl)imidazolin-2-ylidene ruthenium indenylidene complexes **45** and **46**.

Thermal stability studies indicated that compounds **44** and **46**, incorporating a PCy₃ ligand, are very stable and do not decompose even after heating to 80°C for several days. RCM experiments using diethyl diallylmalonate and diallyl tosylamine as substrates showed a good catalytic activity and selectivity of the ruthenium indenylidene complexes of this precatalyst family (yields of 88% and 94% were recorded for **44** and **46**, respectively). (Schemes 23 and 24).

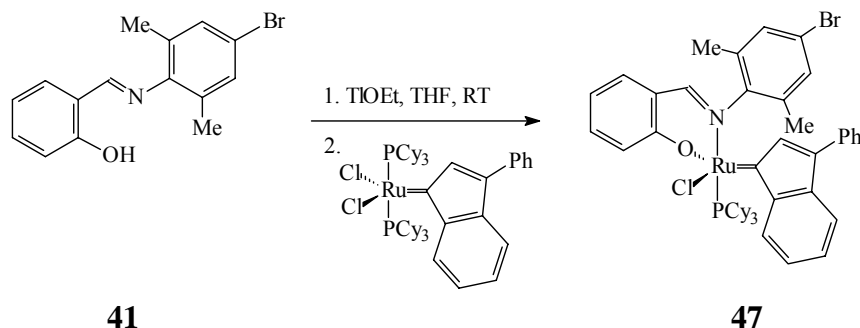


Scheme 23. RCM using ruthenium indenylidene catalyst **44**.



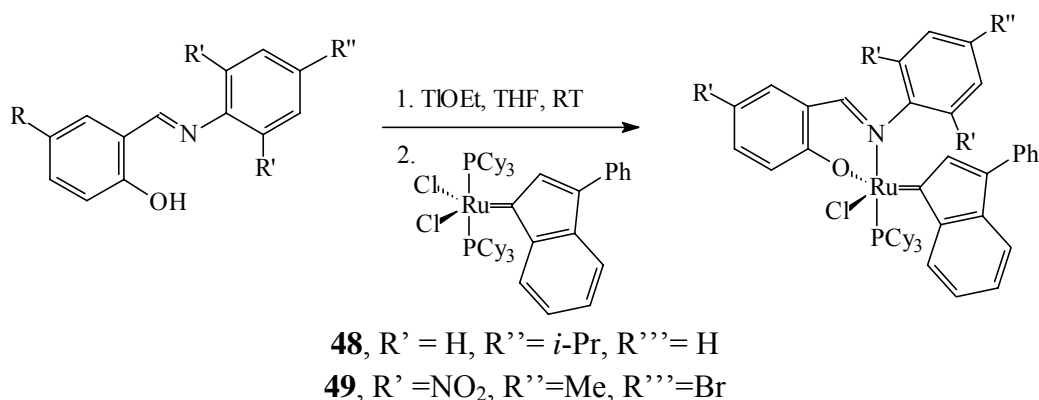
Scheme 24. RCM using ruthenium indenylidene catalyst **46**.

Interesting ruthenium indenylidene complexes containing Schiff-bases as ligands arise from diphosphane ruthenium indenylidene complexes and aromatic salicylaldimines. For instance, complex **47** has been obtained in high yield from **41** (Scheme 25).⁴⁸



Scheme 25. Synthesis of Schiff-base containing ruthenium indenylidene complex **47**.

Complex **47** was characterized by means of ^1H , ^{13}C , ^{31}P -NMR and elemental analysis and successfully applied in enol-ester synthesis (nucleophilic addition of carboxylic acids to terminal alkynes). Importantly, results obtained with catalyst **47** are comparable with those reported for the best metathesis Ru-catalysts.⁴⁹ Related Schiff-base ruthenium complexes **48** and **49** have been prepared analogously and their activity tested in ROMP of cycloolefins and ATRP of vinyl monomers⁵⁰ (Scheme 26).

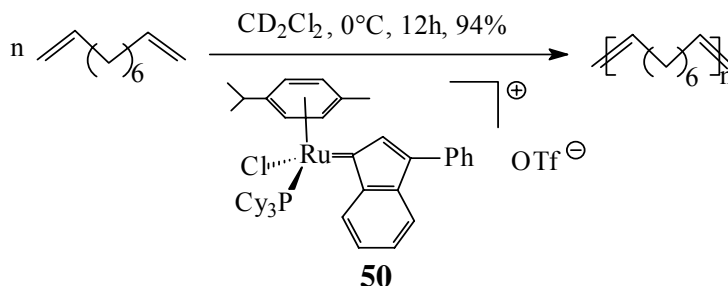


Scheme 26. Synthesis of Schiff-base containing ruthenium indenylidene complex **48**, **49**.

In conclusion, we should mention that bidentate Schiff-base ancillary ligands incorporated into this type of complex pronouncedly influence both their activity and stability.

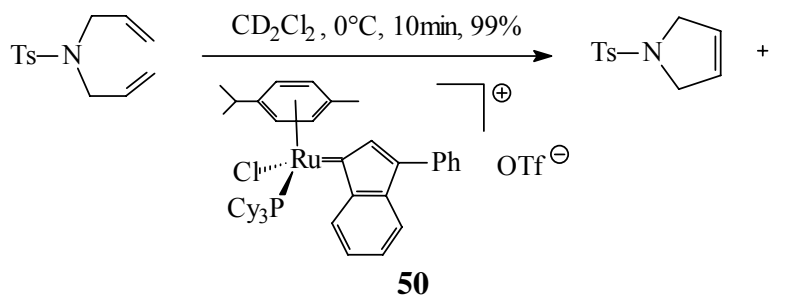
The related arene ruthenium indenylidene complex **50**, generated *in situ* from an allenylidene precursor by treatment with strong acids (*e.g.*, HOTf , HBF_4), displayed a high activity in acyclic diene metathesis reaction (ADMET), RCM of diallyl tosylamide, enyne metathesis reaction of allyl propargyl tosylamide and ROMP of cyclopentene and cyclooctene.⁵¹ For example, in

ADMET of 1,9-decadiene a polymer yield of 94% has been obtained after 12 hours in CD_2Cl_2 at 0°C , using as catalyst precursors $[\text{RuCl}(p\text{-cymene})(=\text{C}=\text{C}=\text{CPh}_2)(\text{PCy}_3)]$ and HOSO_2CF_3 which generate *in situ* the catalyst **50** (Scheme 27).

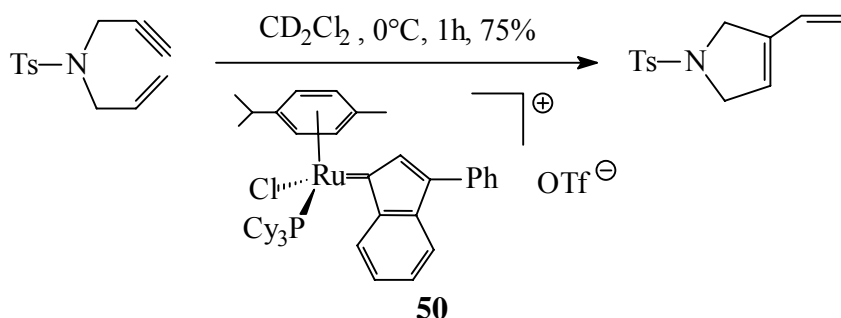


Scheme 27. ADMET reaction initiated by catalyst **50**.

Similarly, when using the same catalytic system, 99% pyrroline N-tosylamide was produced in RCM of diallyl tosylamide, after 10 minutes reaction time (Scheme 28) whereas in enyne metathesis of allylpropargyl tosylamide 75% of 3-vinylpyrroline N-tosylamide was obtained, under the same conditions.⁵¹ (Scheme 29)

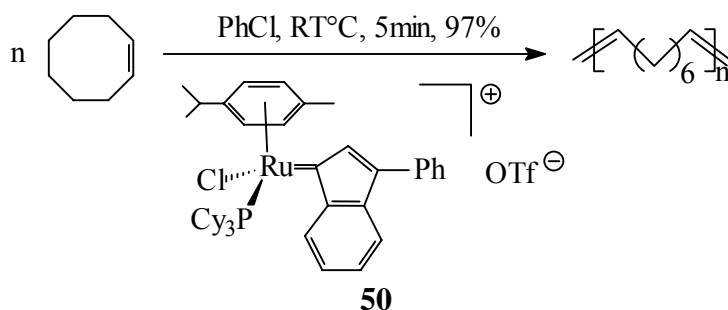


Scheme 28. RCM reaction initiated by catalyst **50**.



Scheme 29. Enyne metathesis reaction initiated by catalyst **50**.

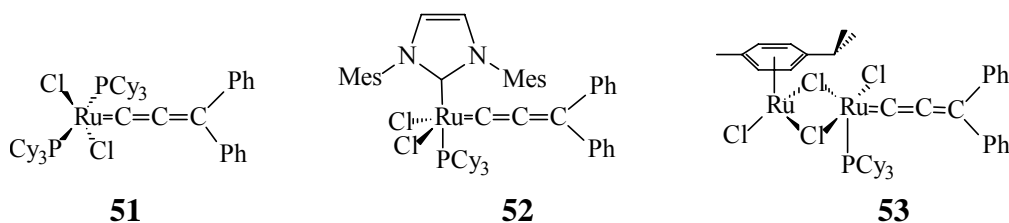
It is important to point out that in ring-opening metathesis polymerization (ROMP) of cyclooctene with the system $[\text{RuCl}(p\text{-cymene})(=\text{C}=\text{C}=\text{CPh}_2)(\text{PCy}_3)][\text{CF}_3\text{SO}_3]/\text{HOSO}_2\text{CF}_3$, in chlorobenzene, an unexpectedly high yield of polyoctenamer was obtained after a short reaction time at room temperature (Scheme 30), whereas when starting from a less reactive monomer, cyclopentene, a maximum yield of 67% could be reached even after 1 hour at 0°C .⁵¹



Scheme 30. ROMP of cyclooctene initiated by catalyst **50**.

5. Ruthenium allenylidene complexes

The family of neutral and cationic ruthenium allenylidene complexes is large but up to now only a limited number of its members have been verified as active metathesis catalysts.⁵² Special attention has been paid to three neutral, coordinatively unsaturated 16-electron ruthenium allenylidene complexes, namely the bisphosphane complex **51**, the imidazolin-2-ylidene complex **52** and the binuclear complex **53** whose catalytic efficiency for alkene metathesis reactions has been investigated extensively (Scheme 31).^{53,54}

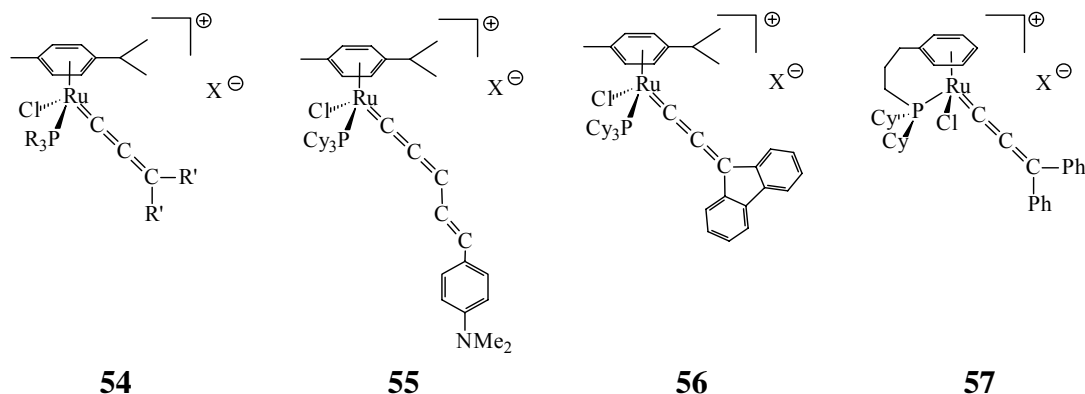


Scheme 31. Neutral ruthenium allenylidene complexes.

Bisphosphane complex **51** is the allenylidene analogue of the Grubbs catalyst **1** with PCy_3 ligands. Its counterpart having PPh_3 groups seems to be rather unstable under normal conditions and to rearrange readily to the indenylidene complex. The more stable but less active, imidazolin-2-ylidene complex **52**, an allenylidene analogue of the benzylidene complex **20**, stems from complex **51**. Binuclear allenylidene complex **53**, a highly active metathesis

ruthenium complex, is related to the binuclear ruthenium benzylidene complex $[\text{Ru}_2\text{Cl}_4(p\text{-cymene})(=\text{CHPh})(\text{PCy}_3)]$ reported by Grubbs and coworkers.²⁷

At variance with the former group of neutral allenylidene complexes, a larger number of cationic, coordinatively saturated 18-electron ruthenium allenylidene complexes have been reported and applied with excellent results in a variety of metathesis reactions.⁵⁵ Essentially, these allenylidene complexes, *e.g.*, **54-57**, contain η^6 -arene ligands associated with additional phosphane and chloride ligands, in conjunction with a “non-coordinating” counterion X^- (Scheme 32).

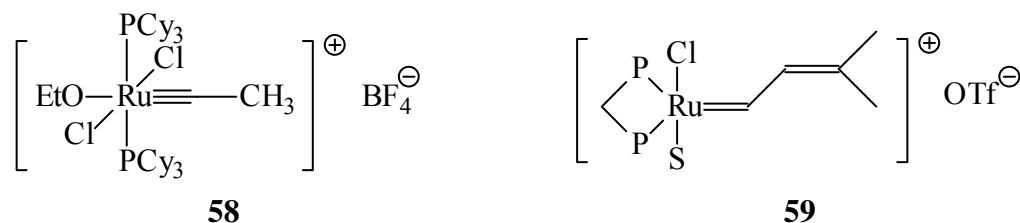


Scheme 32. Cationic ruthenium allenylidene complexes.

By varying the phosphine substituents ($\text{R} = \text{Ph}, \text{Cy}, i\text{-Pr}$), the nature of the counterion X^- ($\text{X} = \text{PF}_6, \text{BPh}_4, \text{BF}_4, \text{OTf}$, etc) and the terminal groups on the allenylidene moiety ($\text{R}' = \text{Ph}, p\text{-chlorophenyl}, p\text{-methoxyphenyl}$, etc), the number of available complexes of this type has been increased. Their potential as metathesis precatalysts was also thoroughly evaluated.

6. Miscellaneous ruthenium complexes

Two very active cationic ruthenium complexes, **58** and **59**, introduced by Werner and coworkers⁵⁶ and Hofmann and coworkers⁵⁷ should also be mentioned. The former has the structure of a hexacoordinated ruthenium carbyne complex while the latter is a ruthenium vinyl carbene bearing a bidentate phosphane ligand. (Scheme 33)

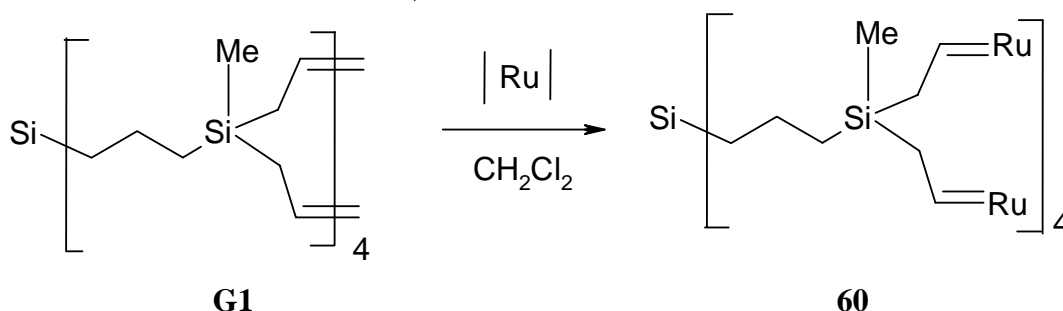


Scheme 33. Ruthenium carbyne and vinyl carbene catalysts **58** and **59**.

Catalysts **58** and **59** are easily accessible and display a quite high activity in ring-closing metathesis reactions.

7. Immobilized ruthenium complexes

Immobilization of ruthenium alkylidene complexes, due to innovative research by Nguyen and Grubbs,⁵⁸ using cross-linked polystyrene-divinylbenzene as the solid support, and by Verdonck *et al.*,⁵⁹ using a dendrimeric carbosilane core, is a further development in metathesis catalysis. The latter catalysts were manufactured by attaching ruthenium alkylidenes to the boundary of the zero-th generation (**G0**) and first generation (**G1**) of the carbosilane dendrimers (Scheme 34).

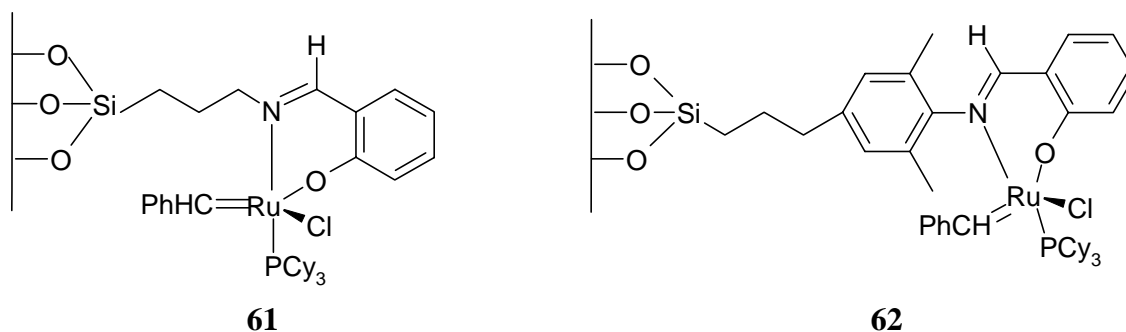


Scheme 34. Immobilized ruthenium complexes using a dendrimeric carbosilane core.

The catalytic activity of the dendrimeric ruthenium catalyst **60** has been tested in ROMP of norbornene. By means of such complexes, multi-arm star polymers could be produced in a controlled manner.

Barrett and coworkers^{60,61} heterogenized bisphosphane ruthenium complex **1** on polystyrene and evidenced that it was possible to use the supported catalyst in RCM of ethyl diallylmalonate and ROMP of norbornene. Highly efficient immobilized catalysts have been obtained from NHC ruthenium alkylidene complexes deposited on various solid supports. For instance, the saturated imidazolin-2-ylidene ruthenium complex **21** has been directly microencapsulated in polystyrene by Barrett⁶² and Gibson⁶³ or anchored on a polystyrene support by Blechert and coworkers.⁶⁴

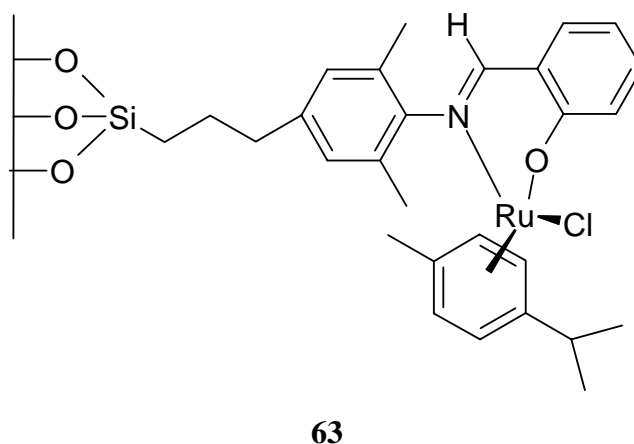
More recently, research efforts in the Verpoort group have been directed to the design, synthesis and implementation of heterogeneous Schiff-base ruthenium catalysts in applications in ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), Kharasch addition, atom transfer radical polymerization (ATRP), as well as in vinylation reactions.⁶⁵⁻⁷² In order to enhance the commercial potential of the above chemical processes, these researchers have achieved synthesis of two multifunctional Schiff-base ruthenium carbene complexes deposited on MCM-41 (**61** and **62**) thus providing recyclable and efficient solid catalysts^{70, 71} (Scheme 35).



Scheme 35. Immobilized Schiff-base ruthenium benzylidene catalysts **61** and **62**.

The methodology followed for preparation of the chemically tethered catalyst onto MCM-41 consisted of immobilizing a previously synthesized precursor containing an anchorable functionality. In the case of **61** and **62**, the mesoporous silica surfaces were treated with the respective tris(alkoxy)silyl-functionalized complex, a commonly applied procedure to tether organometallic compounds onto solid supports. For the solid supported catalysts **61** and **62** two different routes have been employed.⁷¹ Structural examination by Raman spectroscopy, X-ray diffraction, X-ray fluorescence, solid-state NMR and N₂-adsorption analysis showed that in all cases the anchoring of the homogeneous catalyst *via* a spacer onto the MCM-41 surface took place through two or three covalent bonds.⁶⁹

A similar approach has been exploited to synthesize and characterize another new heterogeneous ruthenium catalyst, **63**, that exhibited good stability, reusability and leaching characteristics in both ring-closing metathesis of heteroatom containing dienes giving heterocycles and atom transfer radical addition of halogenated alkanes to olefins yielding polyhalogenated alkanes^{71,72} (Scheme 36).



Scheme 36. Immobilized Schiff-base ruthenium arene catalyst **63**.

Conclusions

During the last decade, the number of ruthenium metathesis catalysts has rapidly expanded owing to their accessibility, remarkable activity and selectivity, encountered generally in conjunction with good tolerance towards polar organic functionalities, air and moisture. A significant advancement in this area was achieved through the introduction of imidazolin-2-ylidene ligands into conventional ruthenium alkylidene complexes. Many of these catalytic systems can be prepared conveniently starting from the classical Grubbs' ruthenium benzylidene catalyst. New trends in process development are currently being opened through design and synthesis of immobilized ruthenium catalysts. Ruthenium complexes enjoy an excellent application profile in metathesis reactions, and particularly in ring-closing metathesis (RCM), cross-metathesis (CM), enyne metathesis (EM), ring-opening metathesis (ROM) and ring-opening metathesis polymerization (ROMP).

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