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The Versatile Alkylidene Moiety in Ruthenium Olefin Metathesis Catalysts

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Dedicated to Professor Benzion Fuchs

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Ruthenium olefin metathesis is without doubt one of the most thriving fields in modern synthetic chemistry. Applications in industry and recent developments in basic research make the study of alkylidene ruthenium compounds both exciting and rewarding. As usually recurrent in organometallic catalysis, the development of novel ligands, in particular alkylidene ligands, has had a pivotal role in the tremendous success of the area. This microreview details the evolution of the alkylidene ruthenium compounds, including simple alkylidenes, benzylidenes, Fischer carbenes, vinylidenes, allenylidenes, indenylidenes and the important sub-class of chelated alkylidenes, and includes a discussion of the significant effects these ligands have had on the precatalysts properties.

Introduction

The chemistry of ruthenium olefin metathesis has been laden with unprecedented success. More than 160 reviews[1] have been published on the subject just during the last decade and the usefulness of olefin metathesis has been applied in almost every possible aspect. Most achievements in the area can be attributed to the flexibility of the ligand shell around the Ru^{II} alkylidenes; perhaps above all to the versatility of the alkylidene ligand itself (Scheme 1). In this microreview we briefly outline the evolution of ruthenium alkylidene ligands starting from the first well-defined ruthenium olefin metathesis catalysts, through the development of simple benzylidenes, vinilydenes, indenylidenes up to the important sub-class of chelated benzylidenes and alkylid-

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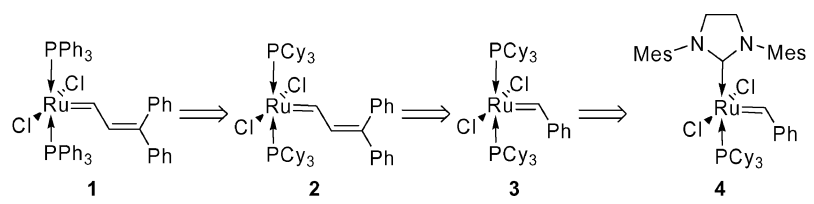
Gabriel Lemcoff finished his undergraduate studies at Tel-Aviv University where he also received his PhD degree in Chemistry in 2002 on novel macromolecular diacetal systems under the supervision of Prof. Benzion Fuchs. He then joined Prof. Steven C. Zimmerman's group at the University of Illinois at Urbana-Champaign where he stayed for almost three years working on molecularly imprinted dendrimers and developing intramolecular cross-linking strategies using the Grubbs' catalysts. In 2004 he joined Ben-Gurion University of the Negev as a Senior Lecturer where he works on new methods in catalysis and the design of novel macromolecular architectures.

Eyal Tzur studied at Ben-Gurion University of the Negev where he received his undergraduate and MSc degrees. In 2005 he joined the Lemcoff research group as a PhD student, where he worked on the synthesis of bis-N-heterocyclic carbenes and bimetallic ruthenium olefin metathesis catalysts. He has also worked on the area of strongly chelated ruthenium complexes and synthesized novel N-, S-, P- and Se-chelated ruthenium complexes.

Charles E. Diesendruck was born in Palo Alto, CA, USA in 1980. After obtaining his BSc in Chemistry from Ben-Gurion University of the Negev in 2003, he became a project manager at Chemada Fine Chemicals. In 2005 he returned to BGU for his PhD under the supervision of Dr. N. G. Lemcoff. His research interests are in the preparation of bimetallic catalysts and their use in the preparation of ladder polymers. He also works on the development of latent olefin metathesis catalysts.



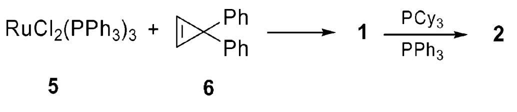
Scheme 1. Evolution of Ru dative ligands.

enes. We also summarize the influence these chelated carbenes have had on the catalysts' general performance, their activities in water, recyclability and latency properties.

Non-Chelated Carbenes

The First Alkylidenes

The first well-defined, metathesis active vinylalkylidene ruthenium complex **1** was synthesized by Grubbs et al.[2] as a mixture of *cis*- and *trans*-bis(phosphane) isomers by the addition of diphenylcyclopropene (**6**) to $RuCl_2(PPh_3)_3$ (**5**) (Scheme 2). Initiator **1** polymerized norbornene effectively even in the presence of water or ethanol.[2] Although the initiation behavior and functional group tolerance of **1** were exciting, its activity was limited to the ROMP of highly strained monomers. Replacement of PPh_3 by PCy_3 (Cy = cyclohexyl), led to complex **2** (Scheme 2) and to a fortuitous discovery; the larger and more basic the phosphane, the higher the metathesis activity.[3] Although **2** was not as active as early metal catalysts, it was much more versatile due to its functional group tolerance. For example, even in the presence of common protecting groups, compound **2** was able to cyclize α,ω-dienes to five-, six-, and seven-membered carbo- and heterocycles in good yields.[4] This robust catalyst was air-stable as a solid and retained its activity even when exposed to traces of water, alcohols, or acids. These characteristics made catalyst **2** ideal for a wide range of synthetic organic applications.[3,5]



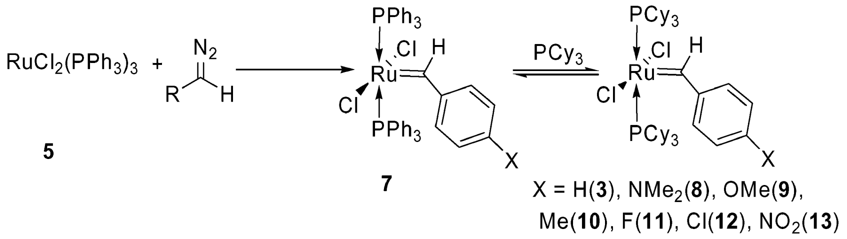
Scheme 2. Synthesis of vinylalkylidene complexes **1** and **2**.[2]

Benzylidene Complexes

The difficulty of synthesizing diphenylcyclopropene initially limited the availability of these complexes, conveniently, the happy discovery by Grubbs et al. of the reaction of **5** with aryldiazoalkane compounds (as carbene sources) led to readily accessible substituted benzylidenes, as shown in Scheme 3.[6]

This family of complexes were air-stable in the solid state and did not show any signs of decomposition even in the presence of nucleophiles, including water. Although no general trend about the electronic influence of aromatic substituents on the initiation rates of these complexes could be discerned, perturbations to the parent aromatic π-system (i.e. X ≠ H) curiously resulted in a decrease of the initiation rate.[6] Thus, the replacement of vinylalkylidenes by benzylidenes was a great accomplishment not only because of the simplicity of their synthesis, but mainly due to the fact that complex **3** initiated metathesis reactions approximately 1000 times faster than complex **2**. For example, catalyst **3** underwent metathesis with ethylene within minutes at room temperature. In contrast, the diphenylvinyl derivative **2** reacted slowly with ethylene, even under forcing conditions, and was only partially converted into the methylidene product (20% after a few hours). Noteworthy, the methylidene complex is the actual active catalytic species in most ring-closing metathesis (RCM), cross-metathesis (CM) and acyclic diene metathesis polymerization (ADMET) reactions. This difference in initiation properties was also reflected in the molecular-weight distributions of ring-opening metathesis polymerization (ROMP) products, which was naturally broader for **2** than for **3**.[6]

Towards the end of the millenium, Grubbs and Herrmann reported an additional breakthrough, the synthesis and activity of ruthenium complexes containing N-heterocyclic carbene ligands (NHC) such as the second-generation Grubbs catalyst **4** (Scheme 1), where the NHC has a satu-

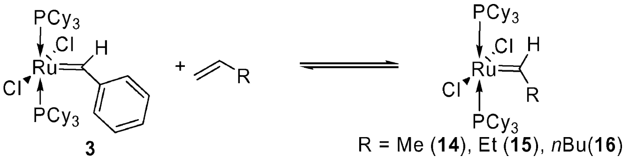


Scheme 3. Synthesis of benzylidene complexes **3** and **8**–**13**.

rated backbone.[7] The replacement of a phosphane ligand by an NHC generated a reactivity performance that rivalled the most active early metal systems. The superior activity of **4** included high rates for ROMP of low-strain substrates and even ROMP of sterically hindered substrates containing trisubstituted olefins such as 1,5-dimethyl-1,5-cyclooctadiene.[8] Complex **4** was also able to perform RCM of sterically demanding dienes to form tri- and tetrasubstituted olefins[7] and produced the first example of CM to yield a trisubstituted olefin.[9] In addition, this catalyst has also been used to extend the scope of alkene-alkyne cross metathesis to cases where the alkyne is disubstituted and contains a coordinating functionality.[10] Remarkably, complex **4** remained effective at loadings as low as 0.05 mol-% for RCM reactions and 0.0001 mol-% (monomer/catalyst ratio: 10^6) for ROMP.[7] Certainly, compelling reasons for making the Grubbs second-generation catalyst commercially available and one of the most widely used olefin metathesis precatalysts.

Alkylidene Moiety Complexes

Other than the ubiquitous methylidene complex (vide supra), simple alkylidene complexes may be obtained by cross metathesis (CM) reactions of 1-alkenes with benzylidene compounds. Although olefin metathesis is usually considered an equilibrium process, kinetic products may be isolated under certain conditions. For example, complex **3** may be quantitatively converted into the alkylidenes $(PCy_3)_2Cl_2Ru{=}C(H)R$ [R = Me (**14**), Et (**15**), *n*Bu (**16**)] when treated with a tenfold excess of 1-propene, 1-butene, or 1-hexene, respectively (Scheme 4).[6] When 3-methylbut-1-ene was used the reaction was very slow and the expected product could only be fleetingly observed in the NMR, emphasizing the difficulty in obtaining sterically hindered olefins with **3**. The isolated compounds **14**–**16** were comparable to precursor **3** in terms of reactivity, stability and solubility. In the presence of a large excess (30–50 equiv.) of styrene, these complexes could also be reconverted to **3**.

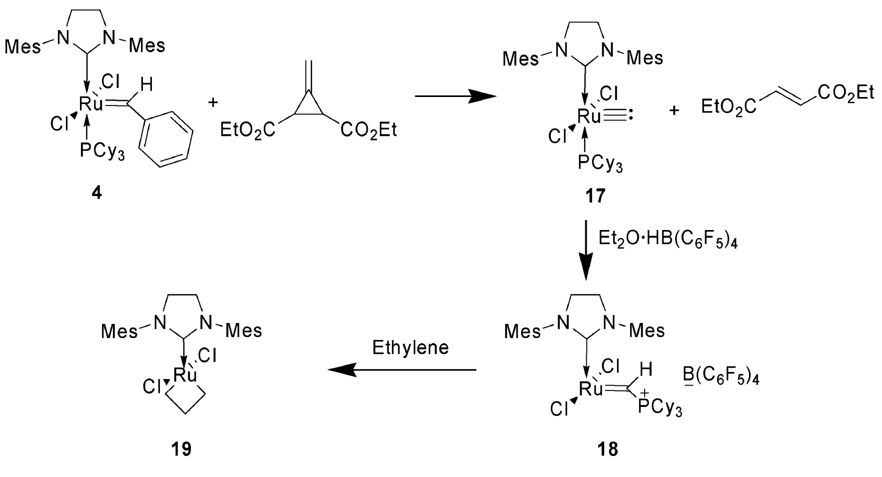


Scheme 4. Synthesis of alkylidene complexes **14**–**16**.[6]

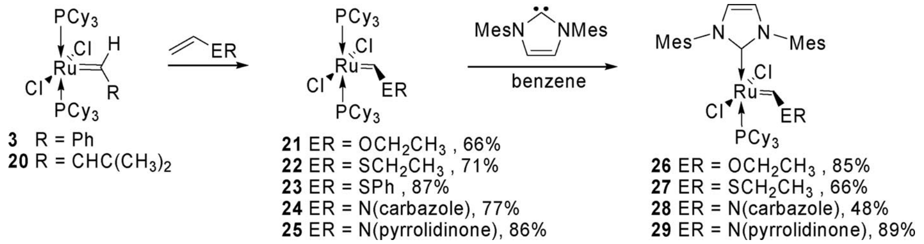
An additional important type of alkylidene ruthenium compounds was developed by Piers,[11] exploring the protonation by a super-acid of ruthenium carbides **17**.[12] The obtained 14e⁻ species **18**, as opposed to the methylidene active species, was unusually stable and could be readily isolated and characterized (Scheme 5). Complex **18**, having an empty coordination site *trans* to the NHC ligand, showed an exceptionally high initiation rate, making this complex very active in simple RCM reactions. More importantly, its reaction with ethylene made it possible for the first time to observe the ruthenacyclobutane species in solution.[13] This important development was later used to study the kinetics of metallocyclobutane formation and decomposition.[14]

Fischer Carbene Complexes

An additional class of alkylidene ligands attached to ruthenium olefin metathesis catalysts are Fischer-type carbenes. Although not classical alkylidenes due to their different reactivity and electronic configuration, we have included Fischer carbenes here because of the role they play in ruthenium metathesis catalysis. At the turn of the millennium, the Grubbs group synthesized a series of electron-rich (ER) carbene complexes in order to explore their stability and reactivity.[15] Thus, the addition of excess $H_2C{=}C(H)ER$ to $(PCy_3)_2Cl_2Ru{=}C(H)R$ afforded a series of Fischer-type carbene complexes in good yields (Scheme 6). Interestingly, no methylidene byproducts ($[Ru]{=}CH_2$) could be observed in any of these reactions. Previously, the Ozawa and van der Schaaf groups had also made a few appealing chalcogenide Fischer alkylidene complexes and even showed their properties as chain-terminating agents in some ROMP reactions.[16]



Scheme 5. Observation of metallocyclobutane **19** using phosphonium alkylidenes.[13]



Scheme 6. Synthesis of electron-rich carbene complexes **21**–**29**.[15]

Thus, treatment of the bis(phosphane) complexes **21**, **22**, **24**, and **25** with 2 equivalents of the free carbene IMes [*N*,*N′*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] in benzene afforded (IMes)$(PCy_3)Cl_2Ru{=}C(H)ER$ (**26**–**29**) in 48–89 % yield (Scheme 6).

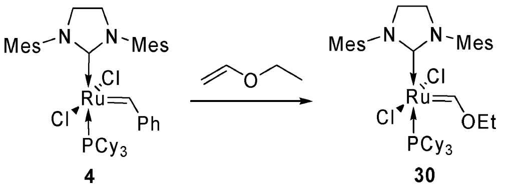
X-ray structure analyses suggested that Ru Fischer-type carbene complexes were structurally similar to those of the parent alkylidene complex **3**,[17] however the heteroatomic carbene moiety (ER) had strong effects on the chemical shifts of relevant NMR resonances (Table 1). The distinctive α-^{1}H [Ru]=C(*H*)ER resonances strongly shifted upfield and appeared to be *inversely* proportional to the electronegativity of the α-heteroatom on the carbene moiety.[15] ^{13}C NMR spectroscopy also indicated that the chemical shifts for the carbene carbon atoms [(Ru)=*C*(H)R] (228–282 ppm) were upfield relative to those of typical Ru alkylidenes.

Table 1. ^{1}H and ^{13}C NMR chemical shifts for different Ru=**CH**–R carbenes.[15]

Entry[a]	Complex	R	^{1}H NMR[b]	^{13}C NMR[b]
1	**3**	Ph	20.02	294.7
2	**18**	Et	19.12[c]	322.6[c]
3	**21**	OEt	14.49	276.9
4	**22**	SEt	17.67	281.6
5	**23**	SPh	17.79	280.4
6	**24**	N(carbazole)	17.59	228.0
7	**25**	N(pyrrolidinone)	16.64[c]	–
8	**26**	OEt	13.81	277.5
9	**27**	SEt	17.07	281.2
10	**28**	N(carbazole)	16.94	230.0
11	**29**	N(pyrrolidinone)	16.12[c]	246.8[c]
12	**4**	Ph	19.16	294.2
13	**30**	OEt	13.63	276.8

[a] CD_2Cl_2 was used as solvent unless stated otherwise. [b] In ppm relative to TMS. [c] C_6D_6 as solvent.

In addition, an important Fischer carbene complex, $(H_2IMes)(PCy_3)Cl_2Ru{=}C(H)OEt$ (**30**), could be prepared in 93 % yield by adding excess ethyl vinyl ether to **4** (Scheme 7).



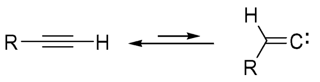
Scheme 7. Synthesis of electron-rich carbene complex **30**.

Fischer-type complexes at equilibrium predominated over the alkylidene analogues. However, the order of thermal stability of $(PCy_3)_2Cl_2Ru{=}C(H)ER$ complexes generally followed the trend ER = $NR_2 > CR_3 > SR > OR$. In addition, complexes coordinated with an NHC ligand were thermally more robust than their bis(phosphane) analogues. All Ru Fischer-type carbene complexes initiated the ROMP of norbornene (a very reactive substrate) at room temperature and afforded quantitative yields of polymer. Although the polymerizations were rapid ($t_{1/2}$ in the range of minutes), they were significantly slower than those initiated by the parent alkylidenes ($t_{1/2}$ in the range of seconds).[2,8,15,17] In contrast to the polymerization of highly strained cyclic olefins, when 1,5-cyclooctadiene (COD) was the monomer, a range of reactivities were observed with differing carbene substituents (ER). Unfortunately, these effects could not be correlated to NMR or crystal structure data and thus suggested a complex relationship between catalyst electronic structure, activity, and stability. Even though most Ru Fischer-type complexes were somewhat RCM active, the rates of the reaction were highly dependent on the α-heteroatom. Collectively, the rates of ROMP and RCM suggest that the relative activities of $L(PCy_3)Cl_2Ru{=}C(H)ER$ complexes follow more or less the same reactivity pattern as the thermal stability trend (more stable, higher activity), only that NR_2 and CR_3 are exchanged. As expected, complexes ligated with IMes or H_2IMes displayed higher activities than their bis(phosphane) analogues.

An important caveat to keep in mind is that, traditionally, ROMP and other metathesis reactions are typically quenched by the addition of ethyl vinyl ether;[18] however, the resulting Fischer carbene complex may still be metathesis active under some conditions. Low temperatures, rapid workup, and an excess of the vinyl ether minimizes the formation of byproducts and more importantly, the addition of sulfur- or nitrogen-functionalized olefins [$CH_2{=}C(H)SR$ and $CH_2{=}C(H)NR_2$] should not be used as quenching agents, because the resulting Ru complexes could still exhibit considerable activity.

Vinylidene Complexes

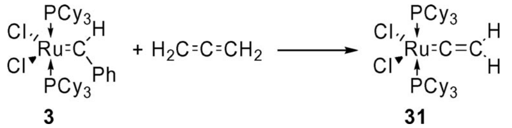
Vinylidene moieties are well-known metal carbene ligands. Vinylidene (:C=CHR) by itself is a very high-energy tautomer of alkyne (RC≡CH) (Scheme 8), nevertheless, it may be duly stabilized on binding with most transition metals.



Scheme 8. Terminal alkynes and the tautomeric vinylidenes.

In 1979, Bruce disclosed the reaction of phenylacetylene with $CpClRu(PPh_3)_2$ in the presence of NH_4PF_6 to afford a cationic vinylidene complex $[(PPh_3)_2CpRu(=C=CHPh)]^+$ $[PF_6]^-$ in 88% yield.[19] Following this report, a variety of vinylidene ruthenium complexes were prepared using terminal alkynes as vinylidene sources.[20] Most of these contained Cp and related ligands, and were coordinatively saturated, 18-electron species. However, for more than a decade, only scattered reports for 16-electron complexes could be found, despite their obvious potential reactivity advantages. In 1991, Wakatsuki reported an early example of a 16-electron complex with the general formula $L_2X_2Ru=C=CHR$.[21] Wakatsuki prepared the PPh_3 complexes $(PPh_3)_2X_2Ru=C=CH\text{-}t\text{Bu}$ (X = Cl, Br) by the treatment of $RuX_2(PPh_3)_3$ with $t\text{BuC}{\equiv}\text{CH}$. Later Werner and co-workers synthesized the $P(i\text{Pr})_3$ analogue with $\text{PhC}{\equiv}\text{CH}$[22] and Caulton reported that $(P\text{-}t\text{Bu}_2\text{Me})_2\text{-}HClRu=C=CHPh$ was formed by the insertion of $\text{PhC}{\equiv}\text{CH}$ into polyhydride $RuH_3Cl(P\text{-}t\text{Bu}_2\text{Me})_2$.[23]

Already in 1996 Grubbs first recognized the metathesis activity of the unsubstituted vinylidene complex **31**, synthesized from allene and **3** (Scheme 9). Even though **31** polymerized norbornene, it was inactive for metathesis of acyclic olefins.[6] After this study, preparations of many other metathesis active vinylidene complexes were reported. For example, heating a toluene solution of $[RuCl_2(p\text{-cymene})]_2$ (**32**), PCy_3 (2 equiv./Ru), and $\text{RC}{\equiv}\text{CH}$ (1 equiv./Ru) at 80 °C led to selective formation of the vinylidene complexes **33**–**35**. Complex **36** could be obtained by the use of $\text{PhC}{\equiv}\text{CSiMe}_3$ as the alkyne source.[24] As in most metathesis active P ligated complexes, displacement of one of the PCy_3 with 4,5-dihydroimidazol-2-ylidene (H_2IMes) could be carried out, affording complexes **37**–**39** (Figure 1).[25]



Scheme 9. Synthesis of vinylidene complex **31**.

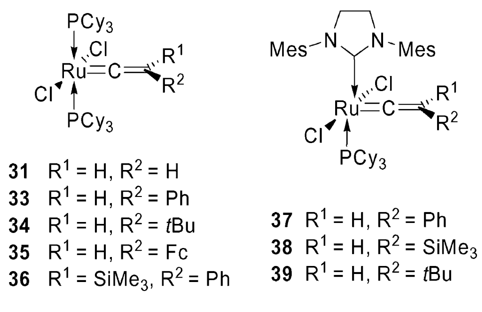
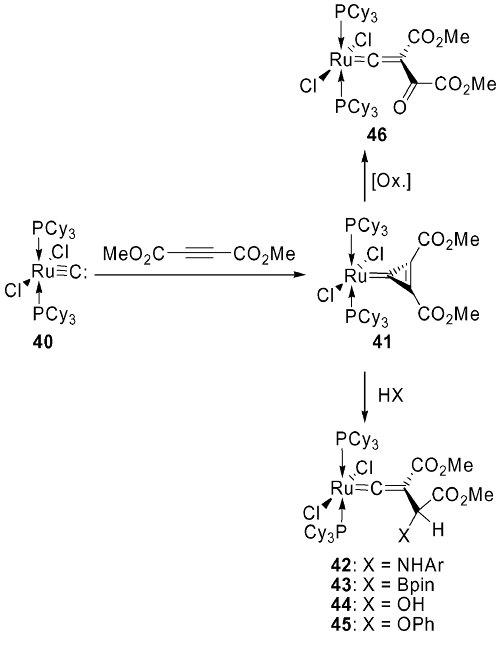


Figure 1. Vinylidene complexes.

Bis(phosphane) vinylidene complexes **33**–**36**[20a,24,26] and especially vinylidene NHC ruthenium complexes **37**–**39**[25,27] operated as excellent metathesis catalysts for polymerization of several cyclic olefins, such as cyclooctene, dicyclopentadiene and norbornene derivatives and also for the preparation of appealing RCM products. For example, complex **35** (2 mol-%) catalyzed RCM of 1,6- and 1,7-dienes in more than 90% yield in $CDCl_3$ at 60 °C, whereas enynes and dienynes could also be cyclized into alkenyl cycloalkenes using this complex.[16b] The order of the activity for NHC vinylidenes in ROMP and RCM was: **38**>**39**>**37**. Johnson et al. reported[28] some noteworthy unique vinylidine complexes **42**–**46**. These complexes were prepared starting from the rare neutral terminal carbido complex **40** which is surprisingly stable[12] and undergoes [2+1] addition with dimethyl acetylenedicarboxylate (DMAD) to yield the cyclopropenylidene complex **41**. Protic reagents HX [X = OH, OPh, $NHC_6H_3(3,5\text{-Me}_2)$] as well as pinacolborane and pyridine *N*-oxide (oxygen atom addition) added in a 1,1 manner to **41**, forming vinylidene complexes **42**–**46** in high yield (Scheme 10). Like the "parent" vinylidene complex **31**; **42**–**46** did not catalyze ring-closing metathesis of diethyl diallylmalonate, but they could polymerize norbornene.

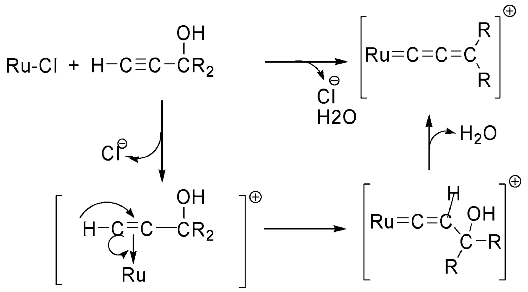


Scheme 10. Synthesis of vinylidene complexes **42**–**46**.

In summary, although less reactive than the corresponding benzylidene analogues, vinilydene complexes are attractive for practical purposes: they are readily available from commercial products such as alkynes, PCy_3, imidazolium salts and $[RuCl_2(p\text{-cymene})]_2$, the corresponding polydispersities in ROMP products are comparable to well-established olefin-metathesis catalysts, the complexes are long-lived even at elevated temperatures and they are extremely tolerant towards air, heat and moisture.

Allenylidene Complexes

Since their first discovery,[29] the chemistry of metal-allenylidenes has been steadily expanding,[30] mainly due to the seminal discovery by Selegue[31] of a straightforward, very general preparation method by simple activation of propargylic alcohols (Scheme 11). The electron density of the allenylidene ligand strongly impacts the general reactivity of allenylidene complexes. The C1 and C3 carbon atoms are electrophilic, while the C2 carbon is nucleophilic. Increased electrophilicity and nucleophilicity of these carbon atoms naturally affect the complex stability and its ability to produce efficient and functional group tolerant olefin metathesis catalysts.[32]



Scheme 11. Formation of allenylidene complex by propargylic alcohol.

The neutral, 16-electron ruthenium allenylidene complex **47** was first synthesized by Nolan and co-workers[33] by reacting a mixture of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$ with commercially-available 3,3-diphenylpropyn-3-ol (also easily obtained by the reaction between benzophenone and acetylide), followed by phosphane-ligand exchange with PCy_3 (Scheme 12).

Synthesis of complex **47** may also conveniently start from the commercially available ruthenium dimer **32**, which reacts with the corresponding propargyl alcohol and two equivalents of PCy_3. Other allenylidene complexes may be obtained by further substitution of a neutral ligand. For example, the replacement of a phosphane group with IMes readily afforded the ruthenium NHC allenylidene complex **48** (Scheme 12). Single-crystal X-ray studies of **47** and **48** (Figure 2), provided significant information about bonding in the solid state and the similar electronic environment at the metal center.[33] Also, upon reaction of H_2IMes (1.5 equiv.) with Ru allenylidene **47** at 50 °C, both mono(NHC) complex **49** and bis(NHC) complex **50** were formed (Scheme 13).[27]

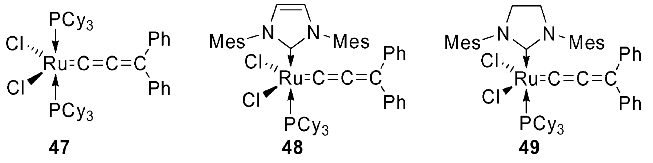
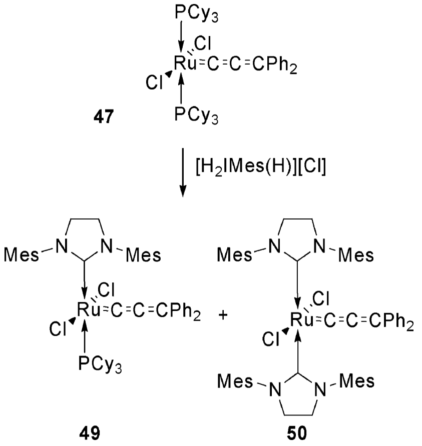
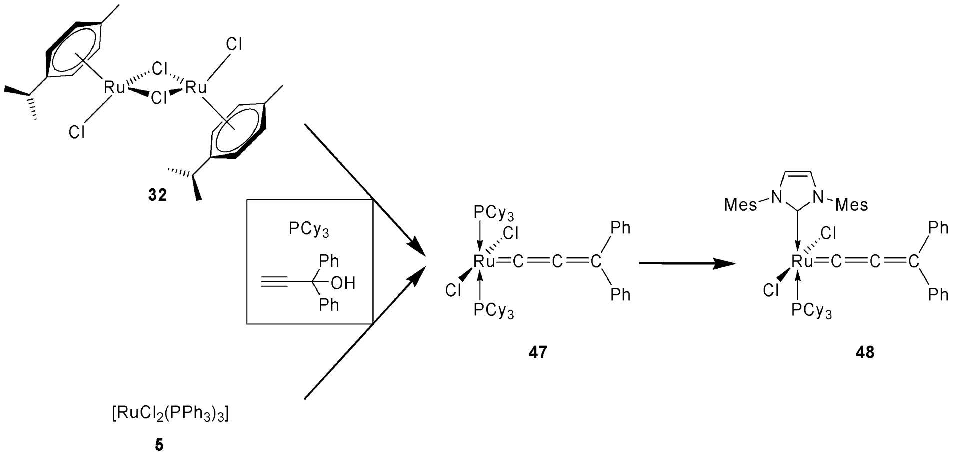


Figure 2. Allenylidene complexes.



Scheme 13. Synthesis of complexes **49** and **50**.

Unfortunately, the catalytic RCM activity of complexes **47**–**50** was somewhat low, although the complexes were stable under the reaction conditions. At a temperature of 40 °C, complexes **47** and **49** showed substantial ROMP activity (complex **48** was not tested for ROMP), but were still less active than the Grubbs catalysts. Interestingly, the bis(NHC) complex **50** was inactive at 40 °C, and active at 80 °C for ROMP of cyclooctadiene, opening up possibilities

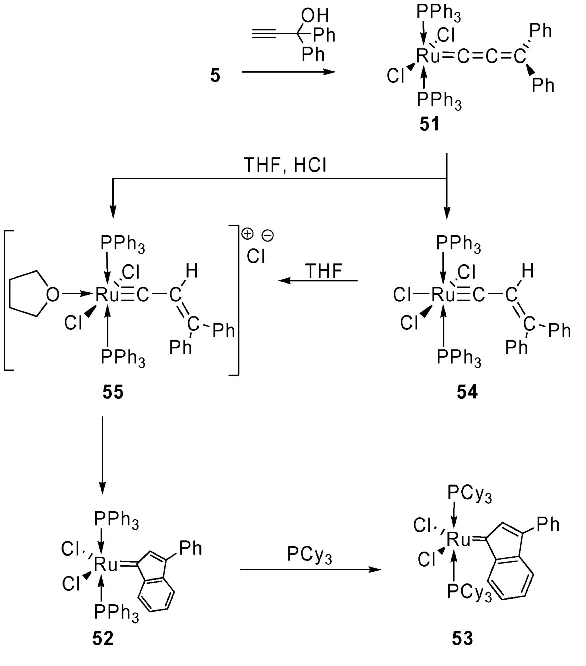


Scheme 12. Synthesis of vinylidene complexes **47** and **48**.

for latent catalysis applications (vide infra).[27] Notwithstanding their poor activity, the lessons learned in the development of ruthenium allenylidene complexes ultimately led to the discovery of the more useful indenylidene compounds.

Indenylidene Complexes

The majority of late transition metal indenylidene complexes are synthesized through an intramolecular rearrangement of allenylidene or cumulenylidene complexes.[30d,32b] The general synthetic strategy involves the introduction of a preformed C3 skeleton containing a leaving group. The most common approach, as mentioned above, is to employ the dehydration of 2-propyn-1-ols to obtain the cumulenylidene complexes.[31,33,34] Originally, the product formed from the reaction of $RuCl_2(PPh_3)_3$ **5** and 1,1-diphenylpropargyl alcohol performed by Hill et al. was believed to provide the allenylidene species **51**.[34a] However, shortly after the discovery of the promising catalytic activity of the material thus formed,[34b] Fürstner recognized that the analytical and spectroscopic data of this complex were not in agreement with the proposed structure and that the stable product isolated was in fact rearranged indenylidene ruthenium complex **52** (Scheme 14).[35] It should be noted that **52** can lead to complex **53** by a simple ligand exchange reaction between PPh_3 and the stronger σ-donating phosphane ligand PCy_3,[36] while the in-situ reaction of **5** and 1,1-diphenylpropargyl alcohol with PCy_3 prevented the rearrangement and led to the allenylidene complex **47** (Scheme 12). Recently, Nolan and Schanz have reported more convenient synthetic pathways for the synthesis of these indenylidenes.[37]



Scheme 14. Synthesis of complexes **52** and **53**.

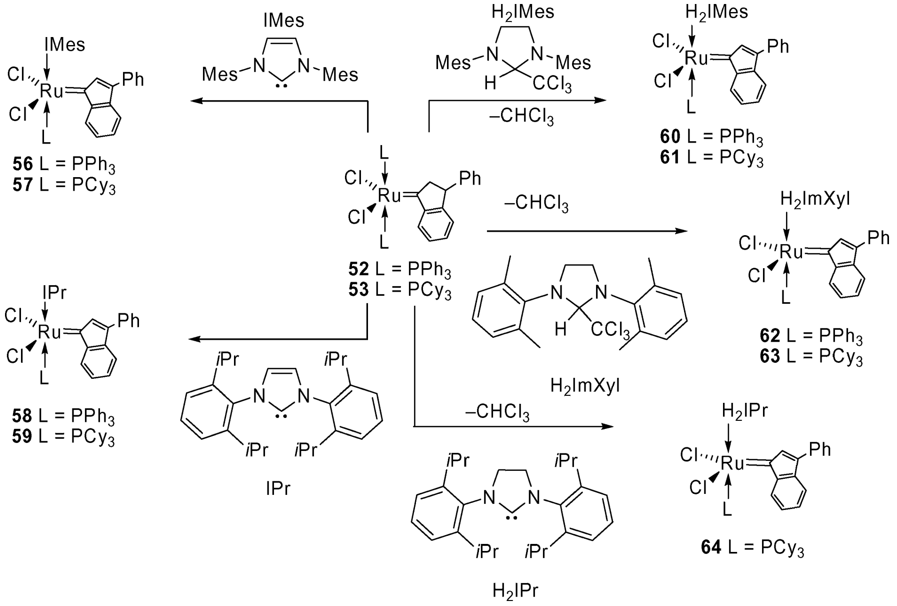
Dixneuf and Castarlenas have elegantly shown that the rearrangement pathway, from allenylidene to indenylidene in 18-electron arene-Ru complexes, is promoted by an acid source.[38] Schanz et al. also succeeded in crystallizing some intermediates that led to the proposed detailed mechanism depicted in Scheme 14.[37b] Allenylidene **51** and carbyne **54** could be isolated and unequivocally characterized by X-ray techniques. It was also proposed that the α-carbon atom of intermediate **55** possessed elevated electrophilicity and thus enabled the observed transformation.

Compared to the phosphane-containing indenylidene complexes which often suffered from degradation due to the lability of the ligand, their replacement by NHC ligands brought about improved thermal stability.[7,39] Hence, precatalysts **56–59** were synthesized by treatment of complexes **52** and **53** with free carbenes IMes and IPr [*N*,*N′*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene].[40] Likewise, saturated NHC-bearing complexes **60–63** were synthesized by Verpoort[41] by treatment of complexes **52–53** with the protected carbene-precursor adducts (Scheme 15).

Of note, this significant report[40] was the first disclosure of the complete and correct characterization of the indenylidene moiety. Complex **57** is now commercially available and is regularly used for several metathesis reactions.

The thermal behavior of complexes **52**, **53** and **56–59** was investigated and it was found that the IPr ligand significantly contributed to the stability of the complex. Moreover, it was shown that precatalysts bearing PCy_3 ligands were much more thermally stable than precatalysts bearing PPh_3 ligands.

Even though allenylidene compound **47** did not present any RCM activity, the indenylidene complexes **56** and **58** showed good catalytic activity with diethyl diallylmalonate and diallyltosylamine as substrates.[40] It should be noted that **56** catalyzed these specific RCM reactions only when heated to 40 °C, whereas **58** did so at room temperature. Sterically hindered diethyl bis(2-methylallyl)malonate does not easily undergo ring-closing metathesis reaction. Even so, catalyst precursor **56** converted 60% of this substrate into the cyclic product after 2 h at 80 °C. Conversion of the same reaction using **58** was only 17% at this temperature. Heating the reaction mixtures for longer periods of time did not increase yields; suggesting that the catalyst is disabled after a certain period of time at higher temperatures. Compounds **53**, **57** and **59**, were reasonably active at room temperature in the RCM of diethyl diallymalonate, however **57** was less reactive with diallyltosylamine as substrate. As expected, the more difficult tetra-substituted olefins afforded low yields with the indenylidene complexes shown.[40] In any case, these complexes showed much higher catalytic activity compared to their allenylidene analogues. When matched up to the benzylidene complexes, **61** exhibited lower activities in RCM reactions as well as in ROMP; clearly a result of decreased catalyst initiation. On the other hand complex **60** shares the activity of the second-generation Grubbs' catalyst **4** for RCM, and it initiates ROMP significantly faster. High and almost identical RCM conversions were obtained for both **60** and **62**. In contrast, com-



Scheme 15. Synthesis of complexes **56**–**64** from complexes **52** and **53**.

plexes **61** and **63** with a stronger coordinating PCy_3 ligand, exhibited slower initiation and reactivity. The need for ligand dissociation again proves to depress PCy_3 containing catalysts, but gives rise to improved catalyst lifetimes. This trend could also be observed in the ROMP of cyclooctadiene.[41a,41b] Moreover, first-generation catalyst **53** afforded higher RCM conversions at shorter reaction times compared to NHC complexes **60**–**63**. An additional important indenylidene complex, **64**, was recently prepared by Nolan.[42] The indenylidene containing H_2IPr[*N*,*N'*-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene] showed the same trend as the benzylidene analogue, being more active in the RCM of unhindered olefins and less active in the RCM of hindered olefins compared to **61**.

The indenylidene ruthenium complexes provide an attractive alternative to the benzylidene compounds. They are readily synthesized from simple starting materials and show enhanced activities in many metathesis reactions. At times they also allow reactions not promoted by many previous Ru catalysts, in particular the convenient synthesis of tri- and tetrasubstituted cycloalkenes (albeit in low yields). These reasons, and the additional fact that they have been much less researched than their benzylidene counterparts, lead us to believe that indenylidene complexes will bring additional exciting developments to the area of ruthenium alkylidene precatalysts in the coming years.

Chelating Benzylidenes

The entropic advantage obtained by multivalent chelating ligands may significantly affect the catalytic activity of the bound metal by modifying stability, initiation rates, propagation rates, etc. The most prominent and influential complex containing a chelating benzylidene is, without a doubt, the Hoveyda–Grubbs catalyst **69** (Figure 3). As often occurs in science, serendipity played its part in the discovery of this complex. Hoveyda, during his studies on the preparation of nonracemic chromenes by a Ru-catalyzed metathesis methodology, cleverly noticed that 2-ethoxystyrene would not react with a cyclooctene derivative (Scheme 16).[43] In this decisive paper, Hoveyda proposed that coordination of the ruthenium metal by the ether oxygen inhibited oligomerization of cyclooctene.

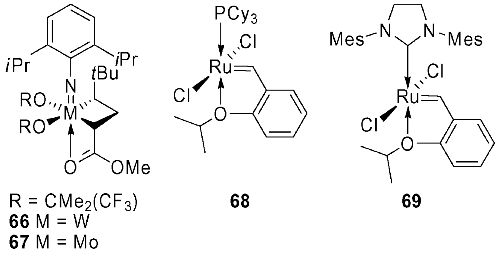
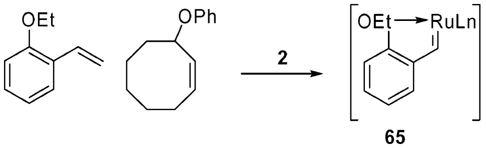


Figure 3. Isolated chelated metallocyclobutane **66** and **67** and commercially available Hoveyda type chelated catalysts **68** and **69**.



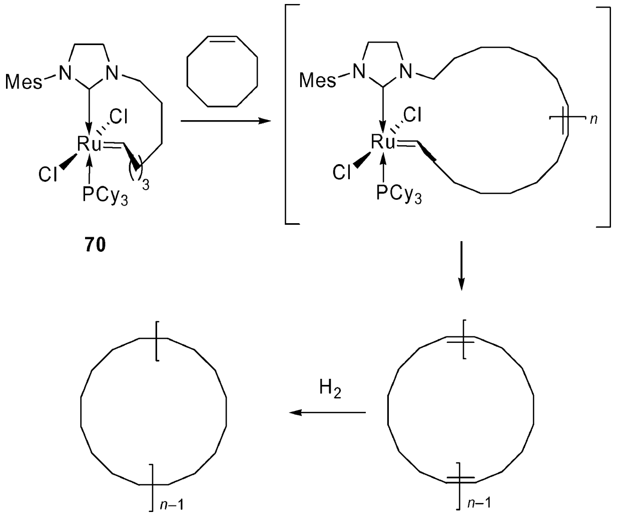
65

Scheme 16. Inhibition of cyclooctene ROMP by *O*-chelation.[43]

At about the same time, Fürstner presented a synthesis of macrocyclic-containing natural products using ruthenium and molybdenum catalysts. Fürstner[44] had observed that the presence of functional groups such as esters, ketones, ethers and urethanes at certain positions in the starting material could significantly influence rates and yields.[45] The lower reactivity was explained by the influence of ligation of the catalytic center with polar groups, forming stable 5- or 6-membered chelate structures. This justification was based on older observations by Schrock,[46] who proposed chelation as the reason for the unreactiveness of highly oxyphilic tungsten-alkylidene complexes. Interestingly, these tungsten and molybdenum complexes could be isolated as the metallocyclobutane intermediates, in support of Chauvin's mechanism for metathesis (Figure 3, **66**–**67**).[47] A few years after these works, Hoveyda isolated the famous 2-isopropoxybenzylidene ruthenium compound **68** and other oxygen-chelated complexes.[48] The *O*-chelated alkylidenes produced complexes more stable towards water, oxygen and other nucleophiles, but also less reactive towards olefins. With the advent of the N-heterocyclic carbenes as superior phosphane surrogates and the 2nd generation of Grubbs' catalysts, it became clear that the additional labile phosphane ligand could also be exchanged, and in less than a year Blechert[49] and Hoveyda[50] isolated and studied the new complex **69** which showed superior activity and stability compared to many of the previously known catalysts.

Blechert's studies on CM uncovered that the new catalyst **69** showed a higher tendency for cross-metathesis over RCM[51] in comparison to the non-chelated Grubbs 2nd generation catalyst **4**. Furthermore, this new complex could efficiently perform CM of electron-poor olefins. Certainly one of the most interesting properties of chelated benzylidenes is Hoveyda's "boomerang effect"[48] i.e. the almost quantitative recovery of the complex after RCM. Additionally, Hoveyda's complex **69** shows an impressive stability and, to a certain extent, survives heating at 90 °C for three days in a biphasic tetrachloroethane/water system.[52]

Also worthy of note in this section is the development by the Grubbs' group of chelated alkylidenes such as **70**,[53] first prepared by Fürstner,[54] to promote the novel ring-expansion metathesis polymerization. By this clever strategy, exclusively cyclic polymers could be prepared (Scheme 17).[53]

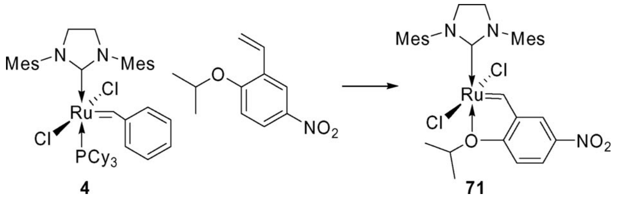


Scheme 17. Ring-expansion metathesis polymerization.

As a consequence of the added stability, activity and other properties, chelating benzylidenes were intensively developed for various goals, which will be further described herein.

Activity

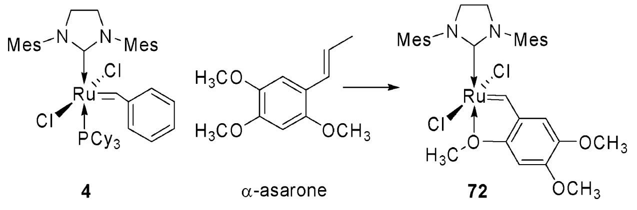
Improving catalyst activity is indisputable the *raison d'être* impelling most research on metal catalysts and their ligand sphere. The development of the benzylidene moiety is no exception and after determining its significant influence, several steric and electronic modifications were studied to advance the catalysts efficiency. The fact that the benzylidene moiety in most cases is not part of the catalytically active species (but part of the precatalyst) means that alterations of the benzylidene may allow for changes in the initiation of the reaction and contribute a smaller role on the propagation steps. The rate-limiting step in H_2IMes-containing ruthenium complexes (such as **4**) is thought to be the dissociation of the coordinating phosphane or chelating atom.[55] This naturally allowed to promote significant changes on reactivity by probing the influence of sterics and electronics on the chelating oxygen–ruthenium bond strength in analogues of **69**. The most marked electronic effect was immediately realized by Grela and proved to be extremely efficient – a nitro electron-withdrawing group (EWG) *para* to the chelating oxygen diminished the electron density on the oxygen weakening the Ru–O bond (Scheme 18).[56]



Scheme 18. Preparation of Grela's EWG-chelated catalyst.[56]

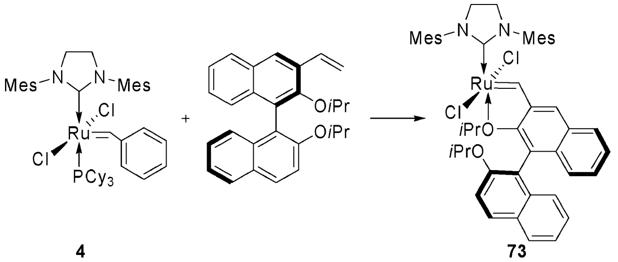
However, further studies proved that the electronic effects may not be so easily predicted; probably due to the intrinsic relationship between sterics and electronics and the influence of EWGs or EDGs on both the chelating heteroatom and the alkylidene carbon. For example, it was discovered that an electron-donating methoxy group in the *para* position, also improved catalyst activity and stability; contrary to the expected reduced activity due to increased electron density on the chelating oxygen. This led to the use of cheap α-asarone as starting material for compound **72**, a relatively active ruthenium metathesis initiator (Scheme 19).[57]

Grela additionally probed the electronic effects on oxygen-chelated benzylidenes and prepared several nitro-substituted derivatives.[58] Although some guidelines could be set regarding the effect of the partial charges of the chelating oxygen and carbene atom on reactivity, this study elegantly highlighted the complexity of the issue, showing that no single complex outperformed all others in all possible



Scheme 19. Inexpensive preparation of a chelated catalyst from natural α-asarone.[57]

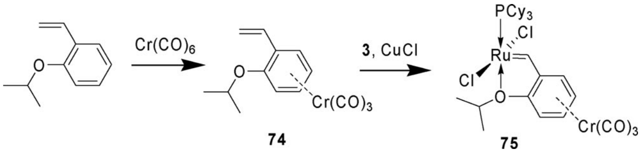
applications and that no clear trend based on electronic effects could be set. Nonetheless, a recent review by Grela makes a valiant effort to provide a guide for the selection of the right catalyst for the right reaction.[59] Parallel to Grela's work, and based on the fact that the substitution of the *i*Pr group in the Hoveyda–Grubbs complex **69** for a methyl group resulted in a less stable and less reactive catalyst,[48] Blechert attempted to weaken the Ru–O bond by steric effects. His influential first work on the subject employed a binol derivative as a starting material, with the intention of obtaining asymmetric olefin metathesis (Scheme 20).[60] While no enantiomeric excess could be observed, complex **73** proved to be much more stable and active than catalysts **4** and **69**.



Scheme 20. Preparation of a steric-hindered chelated catalyst **73**.[60]

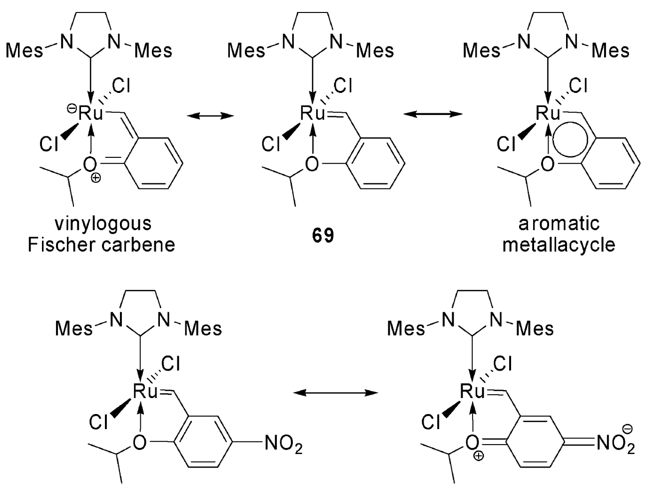
Blechert proposed steric effects as the cause and went on to prepare a simpler complex with just a phenyl group *ortho* to the chelating oxygen.[61] Indeed, this novel molecule turned out to be one of the fastest initiating catalysts to date and showed improved stability and reactivity in RCM, as well as a significant improvement in ROMP initiation. In a key contribution by the Blechert group, eight different styrene ethers were synthesized and their ruthenium benzylidenes secured, with the purpose of determining the influence of steric and electronic effects in oxygen-chelated ruthenium olefin metathesis catalysts. Blechert concluded that in the case of NHC-based catalysts (analogues of **69**), increased electrophilicity at either the chelating oxygen moiety or at the carbene atom leads to faster reaction rates, with the electronic character of the Ru=C bond being the dominant factor. However, some puzzling effects regarding relative activities of electron-donating methoxy vs. methyl groups could not be fully explained by this hypothesis.[62]

Following the trend of activation by weakening the chelating Ru–O bond, a recent creative publication from the Butenschön group, details the synthesis of bimetallic complex **75** where a strongly electron-withdrawing chromium atom bound η^6 to the benzylidene ring provided an air-stable extremely active precatalyst (Scheme 21).[63]



Scheme 21. Preparation of a bimetallic-chelated catalyst **75**.[63]

In an attempt to clarify the diverse, sometimes contradicting, experimental observations, an appealing explanation was recently proposed by Grela: reactivity may be related to the aromaticity of the 5-membered chelate metallocycle.[64] The study of several polyaromatic alkylidenes and comparison to the aromaticity of carbon polyaromatic compounds by the Clar rule,[65] led to the proposal that the chelating oxygen functions not only as a simple chelating ligand, but is an intrinsic part of a conjugated aromatic 5-membered ring. Thus, the stronger the aromatic character of the chelate ring, the less active the metathesis catalyst will become. On the basis of this concept, initial explanations for substituent effects on reactivity are offered, where the decrease of aromaticity, such as in nitro compound **71** (Scheme 22) and out of plane distortion caused by steric hindrance (as in *ortho* substituents) are the determining factors for the increased initiation rates.



Scheme 22. Possible explanation for electronic effects on the activity of chelated catalysts.[64]

Recyclability

One of the unsettled quandaries in olefin metathesis is the difficulty in efficient recycling of the precatalyst. Even though several examples of catalysts which can be reused many times may be found in the literature, much effort is still ongoing in order to prepare the catalyst which will *live forever*.[66] The issue of recyclability is not only important from the economical point of view (ruthenium is a rare and expensive commodity) but also for obtaining metal-free products, due to the relatively high toxicity of ruthenium. In order to prepare biologically relevant compounds, ruthenium concentrations should be below 10 ppm,[67] a level not obtained by simple column chromatography after the use of commercially available catalysts.[68]

Tagged catalysts give to this day the best results in reduction of ruthenium impurities in the products and in recycling of the precatalyst. Tagging has been carried out for all ruthenium olefin metathesis catalyst ligands – the NHC,[69] the anionic ligands,[70] the neutral ligands, such as pyridines,[71] phosphanes[72] and also for alkylidenes. At first hand it would seem that the NHC ligand should be the target of choice for this purpose, since it is the least labile; but their synthesis is generally cumbersome and the ligation with the ruthenium atom involves complicated, and at times harsh, reaction conditions. On the other hand, the preparation of benzylidene-tagged complexes is most straightforward because the functionalized benzylidene may be inserted by a simple metathesis reaction of commercial catalysts with the appropriate styrene derivative. The use of tagged benzylidenes is based on the "boomerang effect" (vide supra) because the tagged ligand "returns" at the end of reaction, restoring the original recyclable complex. Several strategies have been used for separating tagged complexes from the product mixtures: phase separation (ionic liquids,[73] fluorous phase[74]), polar interactions with a solid (such as silica or resin) and polymer supports.[75]

Ionic liquids (ILs)[76] raised interest in both academia and industry as a consequence of their high polarity (which in many reactions stabilized transition states improving reaction rates), negligible vapor pressure and easy recyclability. An interesting feature of ILs is the temperature dependant miscibility with many usual organic solvents, which allows for easy extraction of less-polar organic products after the reaction is over, while leaving the more polar ruthenium complexes dissolved in the IL phase. The introduction of an ionic tag to the benzylidenes proved an effective method to increase solubility of the complex in ILs and improve recyclability. Figure 4 depicts a typical strategy used to attach ionic tags to ruthenium complexes. Untagged catalysts in ILs did not show significant progress in resolving ruthenium contamination and recyclability.[77]

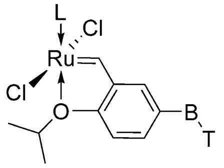
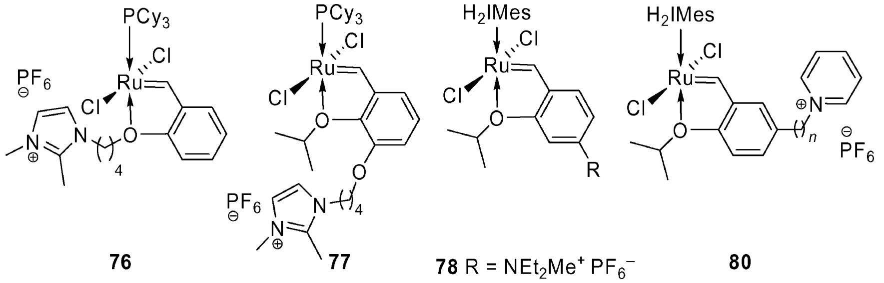


Figure 4. Basic template for most altered chelating benzylidenes.

The work by Mauduit and Guillemin[78] [L = PCy_3 or H_2IMes, B = $–(CH_2)_3–$, T = 3-methyl imidazolium hexafluorophosphate] first showed how a tagged complex in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim] PF_6)/CH_2Cl_2 or toluene could be recycled up to 10 times giving consistent diallyltosylamine RCM conversions higher than 90 %. Yao[79] then developed a very similar complex [L = PCy_3 or H_2IMes, B = $O–(CH_2)_4–$, T = 3-methyl imidazolium hexafluorophosphate] with a slightly longer bridge separating the tag and the metal center. Like the previous work, this catalyst was tested 10 times for the RCM of *N*-allyl-*N*-tosylpent-4-en-1-amine giving satisfactory results. It should be noted that both tests used a biphasic approach and not pure IL as reaction media. Mauduit showed that ruthenium impurities varied between 1 and 22 ppm, depending mostly on the method used for cleaning the toluene phase from IL micro-emulsions. Filtration through silica was used in this case to facilitate the separation (decantation alone was not enough). The scope of these catalysts was expanded to CM, with partial degradation of catalyst activity with new cycles. Interestingly, the obtained products were exclusively *trans*.[80] Some additional examples in the literature that portray IL tagged catalysts are shown in Figure 5.[81] Some of the tags are EWGs, which not only bestows recyclability to the complex but improves its catalytic activity as well. While many of these examples showed remarkable reactivity in multiple cycles, up to now, none can boast catalyst *immortality*; however advances in this area bode well for the near future.

An expensive, but nonetheless viable option, is the use of fluorous phases.[82] The same tagging strategy as the one shown in Figure 4 was used for the fluorous phase experiments as well. The first example was proposed by Yao in 2004[83] [L = H_2IMes, B = COO, T = poly(fluoroalkyl acry-



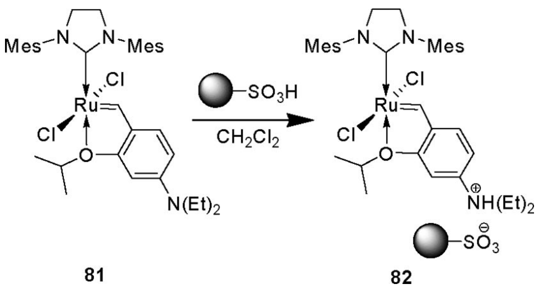
76 **77** **78** R = $NEt_2Me^+ PF_6^−$ **79** R = $NEt_2Me^+ I^−$ **80**

Figure 5. Some benzylidene-tagged catalysts for ionic liquids.[81]

late)] using a biphasic system ($PhCF_3/CH_2Cl_2$). Several RCM reactions, including tri- and tetrasubstitued olefins (with acceptable ca. 50% conversion) were recycled; in some cases more than 20 times! Unfortunately, Ru contamination of the products was not measured, which leaves open the possibility that the high conversions were only a consequence of the higher activity of ruthenium catalysts in the fluorous solvents.[84] In additional studies by Curran, three complexes containing light fluorous tags [L = PCy_3, B = $(CH_2)_2$– or $(CH_2)_3$, T = C_8F_{17} and L = H_2IMes, B = $(CH_2)_2$, T = C_8F_{17}] were prepared.[85] These complexes, while keeping a high activity throughout several rounds, were clearly leaching into the organic phase, and after 7 cycles of RCM almost 90% of the catalyst was lost. Even the resourceful idea of using fluorous silica to remove impurities[74] only achieved a reduction of ruthenium contamination to about 90 ppm, well above the 10-ppm desired threshold.[86]

Finally, the addition of polar groups (such as the ones used for ionic liquids) increases the affinity of the complexes to silica gel, and therefore improves the separation between catalyst and products by chromatographic methods.[81c,87] However, up to this day, simple polar interactions were generally not enough to afford less than 10 ppm Ru in metathesis products. A very interesting recent note by Clavier, Nolan and Mauduit, claims to have obtained less than 6 ppm Ru (some reactions were as low as 2 ppm) in the final products after silica work up by using a modular aminocarbonyl function as the tag. Further work on these aminocarbonyl complexes may definitely lead to very efficient catalysts with high recyclability and low ruthenium contamination.[88]

An alternative related approach using charged resins and ionic interactions has also led to promising results (Scheme 23).[89]



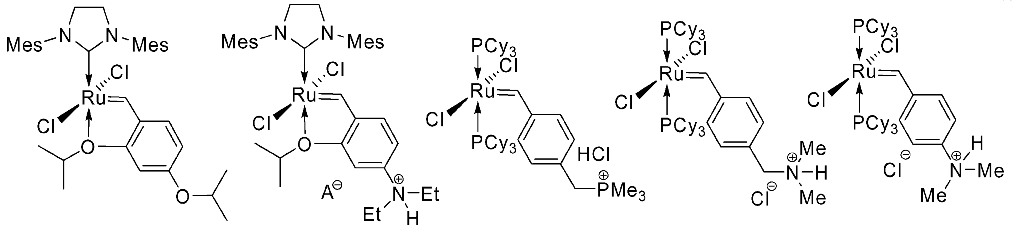
Scheme 23. Non-covalent binding of catalyst to polymer.[89]

Due to the fact that ionic polymers are commercially available and the homogeneous catalysts readily prepared, this method should prove much more economical than preparing a covalently bound catalyst. Moreover the ionic resins may be easily washed and recharged.[89] A classical method to prevent catalyst leaching into the product is to utilize supported catalysts.[90] The original work by Barret, is one of the first examples of supported alkylidene ruthenium compounds on polymers.[91] In this work a first-generation-type complex was bound by metathesis to vinylpolystyrene. The results were fairly good, leaving only 55 ppm Ru in the product after silica work-up. Curiously, when the phosphane ligand was exchanged for an NHC by Barret and Nolan,[92] the ruthenium concentration in the product increased to about 2000 ppm, although, as expected, activity was much improved.

Perhaps one of the salient achievements in this area was the improvement of the "return" of the ruthenium to the polymer, using the "boomerang effect" of the isopropoxy styrene. Hoveyda already in the year 2000 prepared a tetrameric *o*-isopropoxy styrene molecule that could simultaneously bind four ruthenium benzylidenes. This tetramer still reacted as a homogeneous catalyst, but showed improved recyclability compared to the monomeric complex.[50] In 2001, this concept was used in different studies by Blechert,[93] Dowen,[94] and Hoveyda himself.[95] While satisfactory results were attained in many of these studies, Hoveyda's work certainly showed one of the best results in recycling catalysts. In this approach, the ruthenium was bound to rigid monolithic silica discs, and even after 20 cycles of RCM in a wide variety of substrates the catalyst was still active and produced full conversion. However, about a quarter of the ruthenium was lost after 4 cycles (ruthenium contamination in the product was around 500 ppm) and on later cycles ruthenium levels reached up to 10000 ppm (1%!). Furthermore, the reactions had to be conducted under inert atmosphere for the recycling to be efficient after the fourth cycle. Further trials were made after that, including works by Grela, who bound the complex to butyldiethylsilylpolystyrene;[96] Lee, who bound the catalyst to gold clusters;[97] and an inspiring work by Yao, who bound complexes to PEG molecules[98] obtaining 17 cycles of simple RCM and also showed that his catalyst was active in severely hindered tetra-substituted olefins. An additional report by Blechert,[99] achieved 8 metathesis cycles without significant loss of activity, but more importantly, left only 40 ppm of residual ruthenium. Self-supported catalysts could also be obtained by modification of the benzylidene moiety. Lee prepared self supported catalysts with either NHC-bound isopropoxystyrene[100] or di-benzylidenes.[101] Impressive results were presented, where the catalysts reacted for 6 cycles (with increasing reaction time) but Ru impurity in the product was maintained between 15–25 ppm. A related di-benzylidene was prepared later by us in order to prove that two connected ruthenium catalytic centers can bind the same substrate at the same time and to support the dimer ring closing metathesis mechanism.[102]

Metathesis in Water

Ambient conditions are commonly considered as the organometallic chemist's worse enemy – oxygen and water being aggressive molecules which ruthlessly attack reactive carbon–metal bonds. However, especially in the case of ruthenium, this is not always so, and the creation of water- and oxygen-stable ruthenium complexes enables the application of metathesis in biological molecules.[103] Oxygen-stable ruthenium complexes appeared in the very early



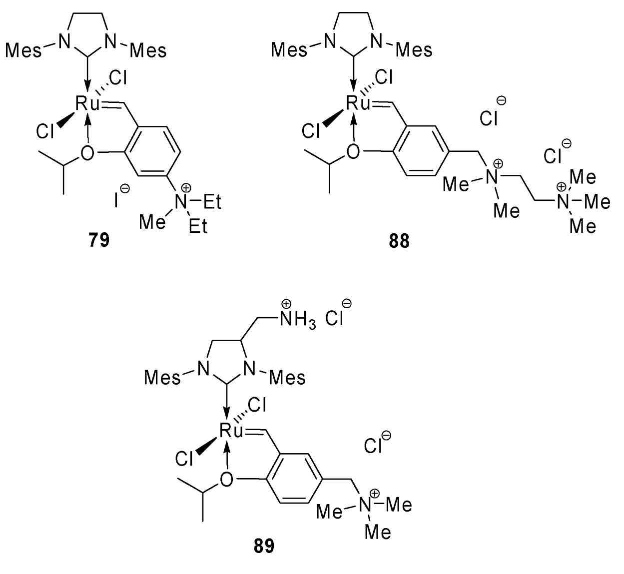
83 **84** **85** **86** **87**

Figure 6. Ruthenium catalysts for use in water.

stages of ruthenium-catalyzed olefin metathesis.[104] Even though these ruthenium catalysts are relatively stable for performing reactions in the presence of water, mostly they are insoluble, impeding their use with biomolecules such as peptides.[105] Thus, mixtures of water and polar organic solvents such as methanol and DMF were typically used. Complex **83** (Figure 6) was found to be very active in RCM and reasonably active in CM in these mixtures.[106] Later, Raines showed that Hoveyda catalyst **69**, when loaded in high quantities in a mixture of DME or acetone and water, also showed satisfying results in RCM reactions.[107]

While several efforts were made in order to use commercially available catalysts – heterogeneous, biphasic, with surfactants, etc. – the design of tagged complexes specifically for performing reactions *in* water certainly proved to be fairly successful. One of the first efforts was carried out by Blechert, binding the complex to a poly(ethylene glycol)-acrylamide copolymer.[108] Several substrates were reacted, both for RCM and CM, however electron-poor olefins gave low yields. Later, several catalysts containing benzylidenes with charged substituents were tried and shown to be active in polar solvents such as alcohols/acids or alcohols/acidic water mixtures (Figure 6).[109]

This concept was further expanded using quaternary amines, including catalysts **79** and **80** which were used in ionic liquids and showed reasonable results also in alcohol/water solutions. The best results in pure water yet have been obtained with catalysts **79**,[87b] prepared by Grela, and **88**, **89**,[110] prepared by Grubbs (Figure 7).



79 **88** **89**

Figure 7. Some tagged catalysts for metathesis in water.[87b,110]

Catalysts **79** and **88** are only slightly soluble in pure water, but at the right concentrations they proved to be very active and efficient in the RCM of even electron-poor olefins and CM of allylic alcohols.

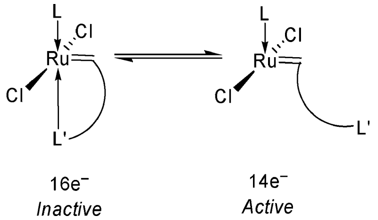
Latent Olefin Metathesis

Latency can be a desirable property in catalysis.[111] Latent precatalysts are usually more stable, an important property for long-term storage, and offer the possibility of complete control of reaction initiation. This latter property, besides the attractive safety attribute, may be essential by itself, for example when completely homogeneous mixtures are necessary before reaction is started (such as in ROMP). Additionally, latent catalysts may offer the possibility to stop a reaction in case of an emergency. It must be said, however, that latency in olefin metathesis is not only dependent on the precatalyst but also on the solvent and substrate, as we discuss in the following section.

Because latency is directly related to initiation rate, and initiation in olefin metathesis takes place through a *dissociative* pathway,[112] complete inhibition of activity may be secured just by strengthening the coordinative Ru–X bond (X = P, O, S, N). While increasing electron density with a methyl group on an *O*-chelated benzylidene was not enough to obtain a sizeable effect, a stronger diethylamine group almost completely stopped the catalyst.[87a] This was ingeniously used to produce a *switchable* system by either microwave heating or adding acid to promote activity.[89a]

The first examples of latency in olefin metathesis can be traced to the Fischer alkylidenes (vide supra). When an oxygen Fischer carbene complex was prepared, the catalytic activity was almost completely discontinued; however, no efficient method for reactivating the complex could be found.[113] Therefore, ethyl vinyl ether became a useful terminating reagent. On the other hand, with sulfur Fischer carbene complexes[15,16d] only partial latency was observed.

Better results for "dormant" species were obtained by using bidentate alkylidenes. Scheme 24 exemplifies the general strategy. Because the first step in the mechanism is ligand dissociation, naturally, the use of bidentate ligands should slow down the initiation rate.



Scheme 24. Activation of chelated catalysts.

Thus, van der Schaaf prepared a series of pyridine-chelated complexes where one of them, complex **92**, showed latency even in the polymerization of very active dicyclopentadiene (Scheme 25).[16d]

Some years later, Grubbs showed that the simple pyridine complex **98** isomerizes to the more stable *cis*-dichlorido complex, especially in more polar solvents, diminishing its initiation rate (Scheme 26).[114]

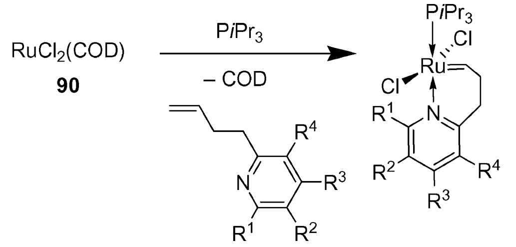
While *cis* and *trans* dichlorido isomers **98** were slow initiators, both still reacted at room temperature. Additional examples of chelating nitrogen alkylidenes are Slugovc's 5- and 6-membered imine rings, which also showed very low rates at room temperature (Scheme 27).[115]

Further development of imine chelates by Grubbs, produced several bidentate (**101**–**108**) and tridentate imine ligands (**109**, **110**) (Scheme 28).[116] The bidentate ligand complexes still showed some reactivity at room temperature, affording conversion of several percents in less than two hours. The complex obtained with sulfur tridentate ligand **110** was the only one which actually showed three-coordinations (the oxygen in **109** did not bind to ruthenium). Unexpectedly, at room temperature, **110** reacted faster than the methylimine-chelated complex **105**.

Grela's quinoline and quinoxaline (Scheme 29)[117] complexes were the first examples of totally inactive precatalysts at room temperature (even after 2 weeks in solution with norbornene substrates) that could still be thermally activated, rapidly producing ROMP products.[118]

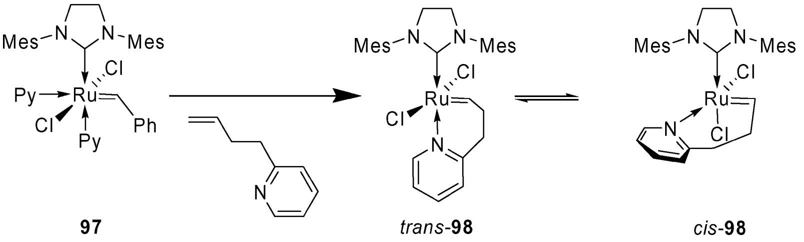
When chelation is achieved by an sp^2 instead of an sp^3 oxygen, the oxygen atom binds stronger to the ruthenium and a higher degree of latency may be obtained. Fürstner first tried to obtain these types of benzylidenes by reacting **3** and **113** (a relative of **4**) with the isopropyl ester of 2-vinylbenzoic acid (Scheme 30).[119] These complexes were shown to be much less active than the Hoveyda type catalysts, indicating that further work along these lines could lead to total latency.

Slugovc expanded this theme by preparing a series of esters and an aldehyde, which all showed the uncommon *cis* dichlorido configuration (Scheme 31).[120] Notably, the aldehyde complex was a substantially slower ROMP initiator than the esters. Still, these complexes presented some metathesis activity at room temperature.

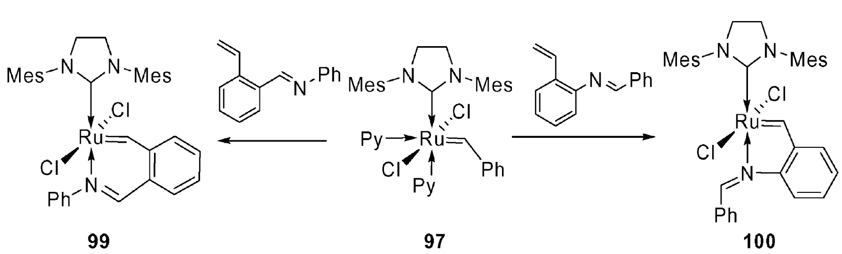


91 $R^1 = R^2 = R^3 = R^4 = H$
92 $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$
93 $R^2 = CH_3$, $R^1 = R^3 = R^4 = H$
94 $R^3 = CH_3$, $R^1 = R^2 = R^4 = H$
95 $R^4 = CH_3$, $R^1 = R^2 = R^3 = H$
96 $R^1 = R^3 = CH_3$, $R^2 = R^4 = H$

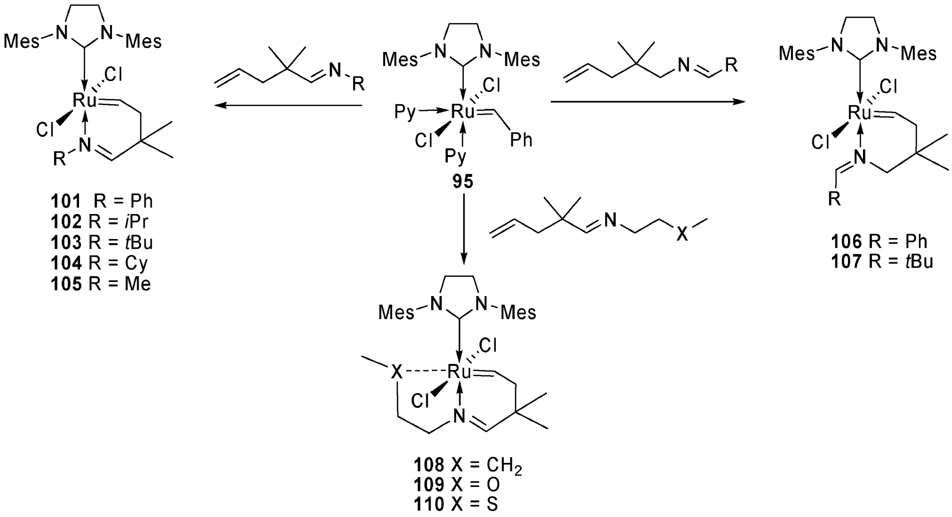
Scheme 25. Preparation of several pyridine-chelated catalysts.[16d]



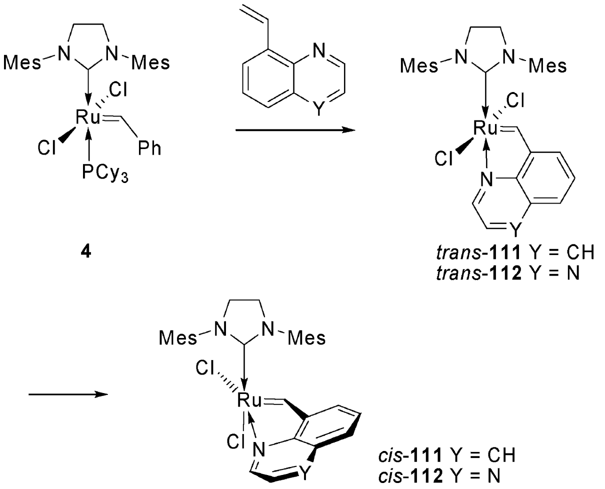
Scheme 26. Preparation of a mixture of *cis*-*trans*-Cl_2 pyridine-chelated catalyst.[114]



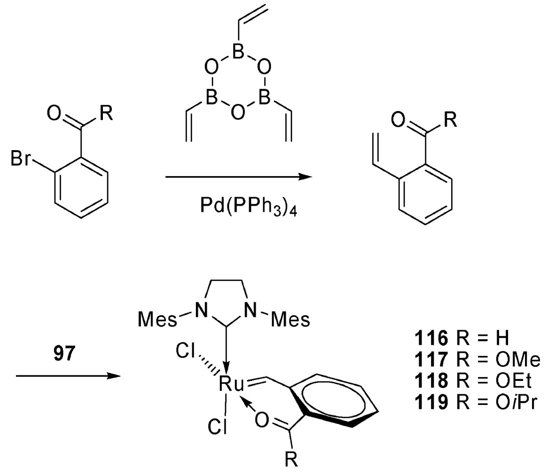
Scheme 27. Preparation of Schiff-base-chelated catalysts.[115]



Scheme 28. Preparation of Schiff base bidentate and tripod-chelated catalysts.[116]

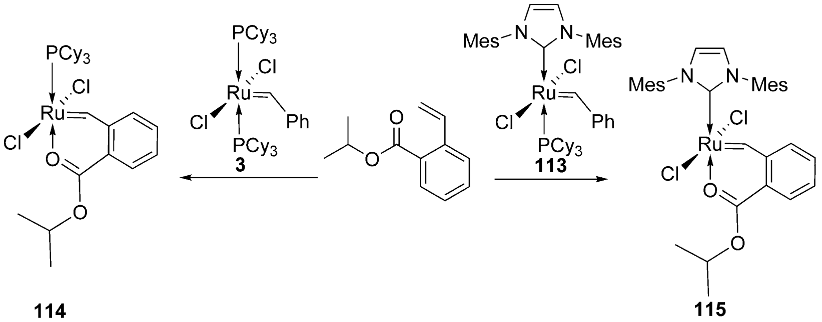


Scheme 29. Preparation of quinoline- and quinoxaline-chelated catalysts.[117]

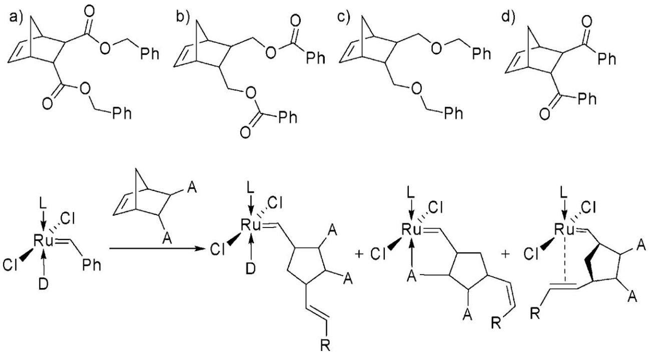


Scheme 31. Preparation of six-membered ring-carbonyl-chelated catalysts.[120]

The influence of chelating sp^2 and sp^3 oxygen atoms in ruthenium benzylidenes was inventively tested by Slugovc in ROMP reactions.[121] A series of norbornenes containing possible chelating oxygen atoms were prepared and initiation and propagation rates checked by NMR (Scheme 32). Propagation rates were reduced by more than an order of magnitude, especially with norbornene d) which contains an sp^2 oxygen.

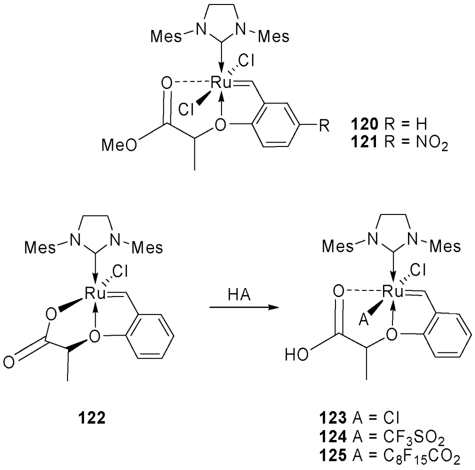


Scheme 30. Preparation of five-membered ring-carbonyl-chelated catalysts.[119]



Scheme 32. ROMP with chelating oxygen-containing norbornenes.[121]

More recently Lavigne, Arlt and Grela prepared new tripod complexes with two chelating oxygen atoms (Scheme 33).[122] While the dichlorido complexes were extremely active, the chlorido-carboxylate complex **122** showed very low reactivity at room temperature. Addition of acids significantly activated the precatalyst and, as expected, HCl gave the best results.



Scheme 33. Tripod oxygen-chelated catalysts and acid activated catalyst.[122]

Catalyst **122** could also be activated without the addition of acids in ionic liquids. In a recent work, Lee[123] showed how different ionic liquid counter anions activated complexes differently. However, none of the oxygen-chelated complexes described were completely inert to reactive olefins at room temperature at these conditions. Grela recently succeeded in obtaining perfectly latent *O*-chelated complexes, by using polyaromatic Hoveyda type derivatives (Figure 8).[64] According to Clar's rule (vide supra), complexes **126**, **127** and **128** have Ru–O bond as part of an aromatic ring, making them extremely strong. Indeed, these complexes were completely inert at room temperature. Unfortunately, activating them proved to be no easy task. At high temperatures, some reduced activity could be observed for **128** exclusively.

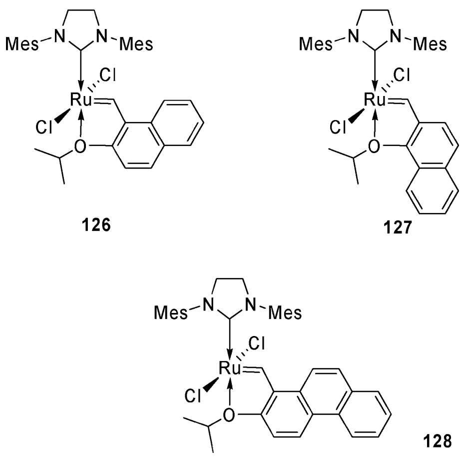
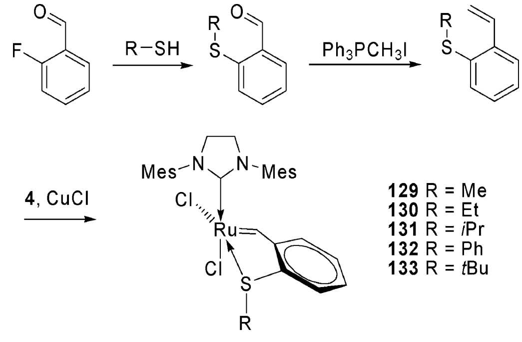


Figure 8. Some polyaromatic Ru-chelated olefin metathesis complexes.

Finally, our group has recently proposed that a simple exchange of the chelating oxygen in **69** by sulfur would fortify the Ru–X bond, since S is a stronger ruthenium ligand.[124] Curiously, these complexes also converted into the *cis* dichlorido conformation (Scheme 34). Our studies showed these compounds to be completely inactive at room temperature for many RCM, CM and even ROMP substrates.[125] These complexes could be activated by heating, giving moderate reactivity, and this activity could be switched on and off by heating and room temperature cycles. Furthermore, the activation temperature could be fine tuned by using steric acceleration effects.



Scheme 34. Preparation of sulfur-chelated catalysts.[124]

More importantly, complexes with aromatic thioethers could also be activated by light through a *cis*-*trans* photoisomerization process – making these complexes the first completely inert photoswitchable metathesis catalysts.[126] Another way of activating S-chelated precatalysts is by oxidation. The sulfoxide derivative also adopts the *trans* dichlorido configuration which is active at room temperature.[127] In synthesis, sulfur-chelated complexes proved to be extremely resourceful latent catalyts, being completely inert at room temperatures towards many metathesis reactions, even to ethyl vinyl ether, and prone to activation by several physical and chemical methods.

Conclusions

The development of the carbene fragment in ruthenium complexes has had a unique impact in olefin metathesis chemistry. Without the ingenious, and at times serendipitous, design of novel alkylidene ligands, olefin metathesis would probably still be relegated to its unclear petrochemical origins. Today, many of the complexes presented in this review are commercially available and serve industry as well as academy. For example, catalysts **3**, **4**, **68**, **69**, **98** may be acquired from Materia, Inc.; catalysts **53**, **61** are prepared by Umicore among other new exciting catalysts this company will be offering soon. BASF-CIBA makes catalyst **23** and Evonik-Degussa commercializes catalyst **57**. The acute interest in olefin metathesis catalysts will undoubtedly lead to new developments in areas covered in this review, such as aqueous metathesis, recyclability and latency. These advancements will be strongly influenced in the future, as they have been until now, by judiciously designed new ligands. Paraphrasing the pioneer and founder of the field Prof. Robert Grubbs: "A number of times along the way, I thought the journey was complete. However, the reaction keeps fooling me. It will be interesting to see where it leads next."[128]

Acknowledgments

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