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Ruthenium-Based Olefin Metathesis Catalysts Derived from Alkynes

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1. Introduction to Olefin Metathesis

The formation of carbon−carbon bonds has been the subject of intense research by synthetic organic chemists, and in view of this endeavor, olefin metathesis, the exchange of alkylidene units at carbon−carbon double bonds, has matured from a "black box" laboratory curiosity to a useful synthetic methodology for the synthesis of carbon−carbon double bonds.[1] The awarding by the Nobel Prize Committee to Chauvin for postulating the now generally accepted olefin metathesis mechanism and to Schrock and Grubbs for availing a significant number of efficient and easy-to-handle early transition-metal and ruthenium olefin metathesis catalysts, respectively, attests to the immense impact of this reaction on the academic and industrial chemical community.[2]

While at that time the olefin metathesis reaction was predominantly believed to proceed according to a pairwise mechanism in which two olefins enter the metal's coordination sphere,[3] Hérisson and Chauvin postulated a nonpairwise mechanism in which metal carbenes and metallacyclobutanes represent key intermediates, the overall mechanism being understood in terms of a [2 + 2]-cycloaddition/-cycloreversion sequence of an olefin to a metal carbene species (Scheme 1).[4] Further experimental support for the proposed mechanism was later provided by Katz[5] and Grubbs.[6]

From a mechanistic point of view, the outcome of the olefin metathesis reaction is strongly dependent on the olefin feed (Scheme 2). Indeed, strained cyclic olefins undergo ring-opening metathesis polymerization (ROMP), while cyclohexene remains unaltered.[7] On the other hand, α,ω-dienes will ring-close (RCM) to form five-, six-, or higher-membered hetero-[8] or carbocyclic olefins in presence of suitable olefin metathesis catalysts.[9] In high substrate concentrations, however, longer-chain acyclic α,ω-dienes are subjected to a stepwise acyclic diene metathesis (ADMET) ethylene condensation polymerization.[10] Under ethylene atmosphere or in presence of acyclic olefins, cyclic olefins form acyclic dienes, a process known as ring-opening metathesis (ROM)[11] or ring-opening/cross metathesis (RO/CM). The intermolecular alkylidene exchange between two distinct olefins is designated as cross metathesis (CM).[12]

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Ana María Lozano Vila was born in San José, Costa Rica, in 1978. She received the B.S. degree in chemistry and the Ph.D. degree in inorganic chemistry from Universidad de Extremadura, Spain, in 2001 and 2006, respectively, being awarded with both Extraordinary University Degree and Extraordinary Doctoral Prizes. From 2006 to 2007, she was involved in food research and technology in the Instituto Tecnológico Agroalimentario (INTAEX), Badajoz, Spain. Currently she is a postdoctoral researcher under the tutelage of Prof. F. Verpoort at Ghent University, Belgium, where she is studying ruthenium-based indenylidene Schiff base-bearing catalysts.

Stijn Monsaert (1982, Belgium) received his Master of Industrial Sciences in 2004. His undergraduate research involved the study of acid-activated Schiff base ruthenium catalysts relevant to the reaction injection molding (RIM)−ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD). In 2005, he joined ViaCatt NV as a research scientist and further developed and optimized the use of latent ruthenium olefin metathesis catalysts for application in RIM−ROMP of DCPD. In 2006, he started his doctoral research at Ghent University under the supervision of Prof. F. Verpoort. Ever since, he has been occupied with the study of new ruthenium indenylidene catalysts for olefin metathesis reactions.

Agata Bajek was born in Rzeszów in 1983. She received her M.S. degree in chemical technology from Rzeszow University of Technology (Poland) in the group of G. Groszek. She joined the research group of Prof. F. Verpoort at Ghent University and Prof. S. Wolowiec at the Rzeszow University of Technology as a Ph.D. student in 2008. Her research focuses on Ru−*N*-heterocyclic carbene complexes, dendrimers, and catalysis.

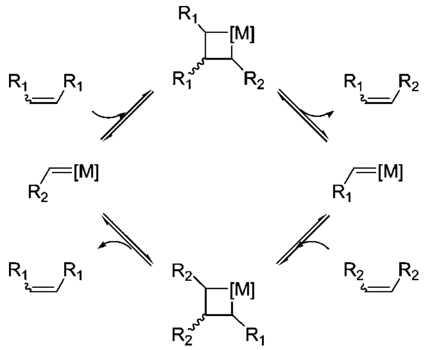
Francis Verpoort (1963, Belgium) received his D.Phil. for his work on the development of heterogeneous tungsten-based olefin metathesis catalysts from Ghent University in 1996. From 1996 to 1998, he was an assistant professor at Ghent University. In 1998, he was promoted to full professor at the same university in the Department of Inorganic and Physical Chemistry, Division of Organometallic Chemistry and Catalysis. In 2004, he founded ViaCatt NV, a spin-off company of Ghent University based on (latent) ruthenium olefin metathesis catalysts. In 2008, he became Editor of Applied Organometallic Chemistry. In 2010, he was appointed as visiting professor at the College of Chemistry, Liaoning University, China. His main research interests concern the structure and mechanisms in organometallic chemistry, homogeneous and heterogeneous hybrid transition metal catalysts, Schiff bases as coligands in metal complexes, enolester synthesis, olefin metathesis, ring-opening metathesis polymerization, and atom transfer radical polymerization.

The versatility of the olefin metathesis method has significantly contributed to its success as a synthetic methodology. Moreover, olefin metathesis catalysts are reported to be efficient catalysts for various mechanistically related reactions, that is, enyne metathesis[13] and ring-rearrangement metathesis (RRM).[14] In addition, selected olefin metathesis catalysts exhibit catalytic activity toward nonmetathetical transformations[15] such as Karash addition reactions[16] or have been applied in tandem catalysis.[17]

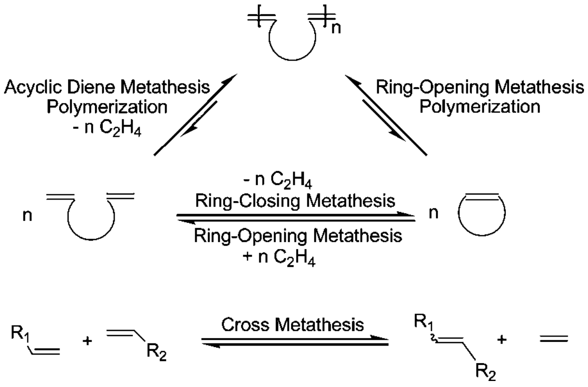
Development of efficient catalysts for the olefin metathesis reaction, originally observed for olefins in presence of transition-metal salts with main group metal alkyl cocatalysts, initially focused on the activity of ill-defined early transition-metal catalyst systems. In this regard, Calderon reported on the highly active $WCl_6/EtAlCl_2/EtOH$.[1n] Although these systems did not contain a carbene unit, it is supposed that the carbene ligand was formed in the initial stage of the reaction. These catalytic systems turned out to be cheap; however, the application of harsh reaction conditions, strong Lewis acids, and the occurrence of side reactions limited their scope. The lack of reaction control prompted the development of well-defined early transition-metal catalysts.

As soon as the Chauvin mechanism was accepted, it was clear that highly active, well-defined single-component catalysts had to be found among stable transition-metal alkylidenes or metallacyclobutanes. Early examples in this respect were the pentacarbonyl tungsten diphenylcarbene by Katz in 1976[18] and the titanocyclobutane by Grubbs in 1980.[19] The development of synthetically modular high oxidation state tungsten, tantalum, and molybdenum alkylidene complexes by Schrock evoked the discovery of the highly active olefin metathesis catalyst **1**[20] (Figure 1).[21] The

Scheme 1. Chauvin Mechanism for Olefin Metathesis

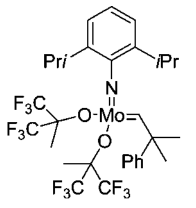


Scheme 2



sensitivity of molybdenum alkylidene complexes to air and moisture and their intolerance toward functional groups long impeded their widespread applicability in organic synthesis.[1g,9c] However, recent developments have yielded molybdenum alkylidene analogues exhibiting functional group tolerance[21c] while maintaining a high degree of enantiomeric selectivity.[22]

Nevertheless, tolerance to functional groups improves with the group number of the incorporated metal.[1b] Seminal reports by Novak and Grubbs illustrated not only that ruthenium serves as an interesting candidate for executing olefin metathesis reactions but also that the reactions were successful in water.[23] This suggested that the catalytically active ruthenium compound might be tolerant toward moisture. Indeed, it was later confirmed that Grubbs catalysts tolerate a wide array of functional groups, such as alcohols, amides, carboxylic acids, and aldehydes and are easier to handle than Schrock's catalysts. Moreover, recent developments remain to focus on performing olefin metathesis reactions in water.[24] A major breakthrough in ruthenium-based olefin metathesis catalysis was established during the mid-1990s with the synthesis of ruthenium benzylidene compounds.[25] In its most widely known embodiment, two tricyclohexylphosphines and two chlorides coordinate to the ruthenium benzylidene moiety (**2**, Figure 2). Commercialization of this catalyst, commonly known as the Grubbs first generation catalyst, elicited an emerging interest from synthetic organic and polymer chemists and allowed organometallic chemists to fine-tune the ligand environment. Related to the latter aspect, the replacement of one phosphine ligand in the first generation Grubbs catalysts with a bulky *N*-heterocyclic carbene (NHC) ligand established a novel milestone, allowing an increase in catalytic activity and selectivity in several olefin metathesis reactions.[26] Systems incorporating an imidazol(in)-2-ylidene[27] ligand are known as Grubbs second generation catalysts (Figure 2).[26a,28]



Schrock's Catalyst

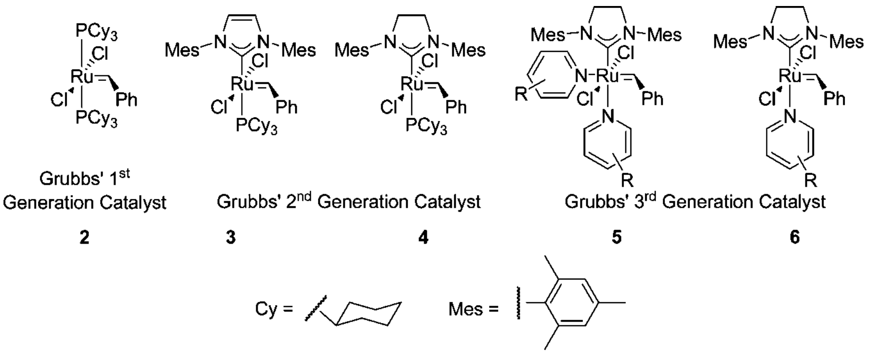
1

Figure 1. Schrock's catalyst.

Exchange of the other phosphine in the second generation Grubbs catalyst with pyridine afforded higher initiation rates (Grubbs third generation catalysts, **5** and **6**, Figure 2).[29] The fortuitous incorporation of a chelating carbene ligand by Hoveyda resulted in a family of fairly stable aryl-ether chelated complexes, **7** and **8**, with high activity and improved selectivity compared with Grubbs catalysts in CM and RCM reactions (Figure 3).[30]

Modification of the isopropoxy fragment with a more bulky chelating group resulted in very high initiation rates indicating that this bulky moiety forces the decoordination of the leaving group.[31] Grela et al. introduced a strong electron-withdrawing group on the phenyl ring of the aryl-ether ligand obtaining a much higher catalytic activity (Figure 3).[32] These successful modifications are evidence that catalytic activity can be adapted by fine-tuning the structure and the electronic properties of the ligands.

Nowadays, more active, efficient, and highly selective catalysts are continuously developed leading to a large number of metathesis catalysts described in literature.[7c,33] In addition, many aspects related to latent catalysts,[34] chiral catalysts,[35] catalyst immobilization[36] or use in alternative reaction media[24d,37] or chemical biology[38] have been studied. The current review focuses on the aspects related to the



Grubbs' 1st Generation Catalyst

Grubbs' 2nd Generation Catalyst

Grubbs' 3rd Generation Catalyst

2 **3** **4** **5** **6**

Figure 2. Grubbs catalysts.

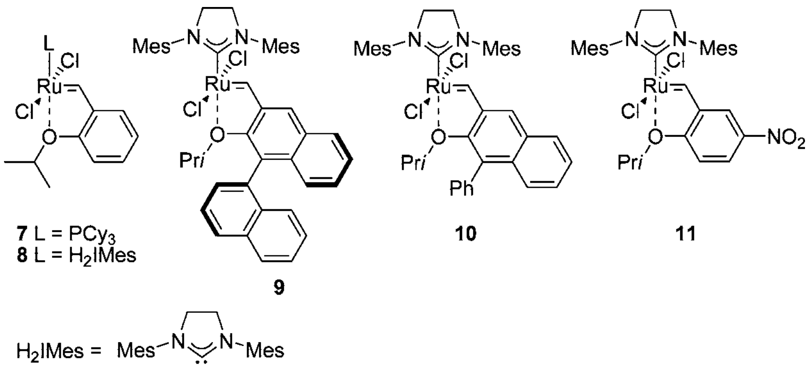
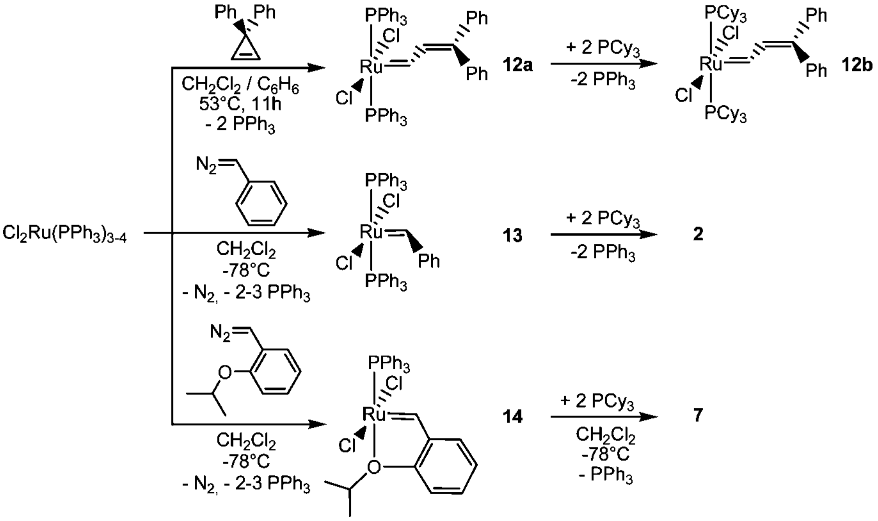


Figure 3. Hoveyda–Grubbs-type catalysts.

Scheme 3



preparation of well-defined ruthenium olefin metathesis catalysts featuring a ruthenium–carbon double bond and more specifically on alternative ruthenium-based olefin metathesis catalysts derived from alkyne precursors such as the vinylcarbenes (allylidenes), vinylidenes, allenylidenes, and indenylidenes. These families of compounds are receiving growing interest from both academia and industry during the last years, but to the best of our knowledge, until now no other review has focused on these families together systematically covering the specific contribution of every group of compounds toward olefin metathesis.

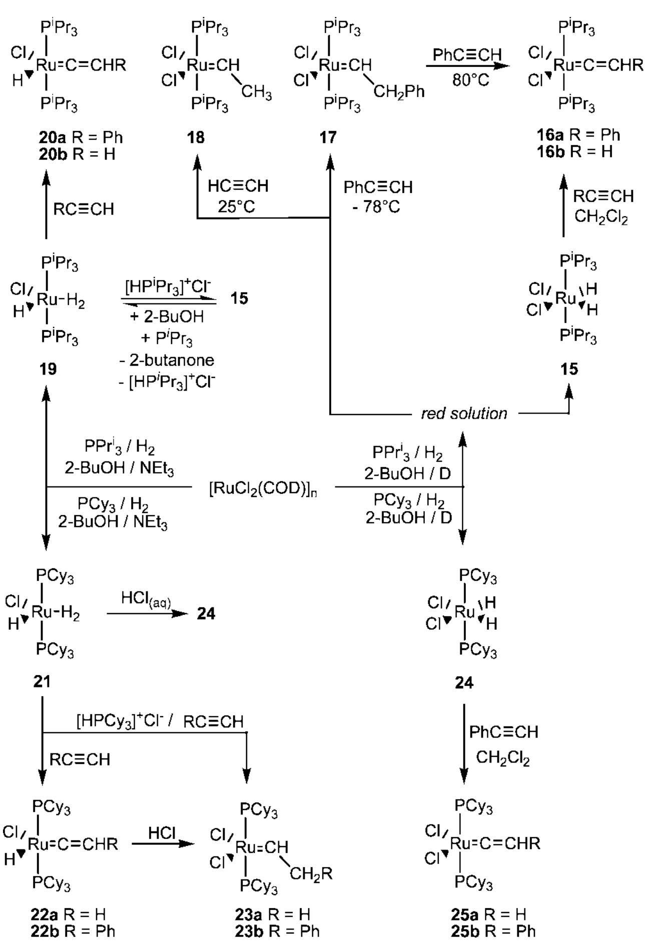
To provide a solid background against which the development of ruthenium vinylidene, allenylidene, and indenylidene olefin metathesis catalysts should be regarded, the following section covers the efforts toward the efficient preparation of ruthenium complexes bearing an alkylidene ligand that are relevant to the field of olefin metathesis.

2. Preparation of Well-Defined Ruthenium Olefin Metathesis Catalysts

The seminal report on the isolation of a stable ruthenium carbene complex by Grubbs et al. upon the reaction of the commercially available ruthenium precursor $Cl_2Ru(PPh_3)_{3-4}$ with 3,3-diphenylcyclopropene afforded the first well-defined olefin metathesis active ruthenium catalyst **12a** (Scheme 3).[39] The observation that ruthenium salts were active for the ROM polymerization of strained cyclic olefin such as norbornenes[23] was of paramount importance in this respect, and it was anticipated that the active ruthenium alkylidene compound could be caught in the first stage of the reaction in case of the extremely strained cyclopropene. This complex exhibited activity toward the ROMP of strained cyclic olefins, that is, norbornenes, in organic media, and it was soon thereafter recognized that exchange of the coordinatively labile PPh_3 ligands by stronger electron-donating trialkyl phosphines (**12b**) significantly improved its catalytic activity, thus making it capable of polymerizing unstrained cyclic olefins and forming five- to eight-membered olefinic hetero- and carbocycles[40] However, difficulties associated with the large scale synthesis of the cyclopropene precursor contained the germ for further research toward more straightforward procedures for the preparation of five-coordinate ruthenium alkylidene complexes.

As soon as 1995, the same laboratory reported on the synthesis of olefin metathesis active ruthenium catalysts upon reaction of phenyl diazomethane with $Cl_2Ru(PPh_3)_3$. The accordingly obtained catalyst **13**, after ligand exchange with PCy_3, is now generally known as the Grubbs first generation catalyst, **2** (Scheme 3).[25a,b] The comparable ease of preparing the synthetically modular diazo carbene precursors allowed for the synthesis of a family of well-defined ruthenium-based olefin metathesis catalysts, which were found to exceed the activity of the Grubbs–Nguyen catalyst **12** significantly.[25a,b] Later, Hoveyda applied a similar procedure for the preparation of the so-called Hoveyda first generation catalyst **14** (Scheme 3).[30a] However, handling of the hazardous diazo compounds requires special care, and new, more accessible routes toward well-defined ruthenium olefin metathesis catalysts remained the focus of subsequent research.

Scheme 4

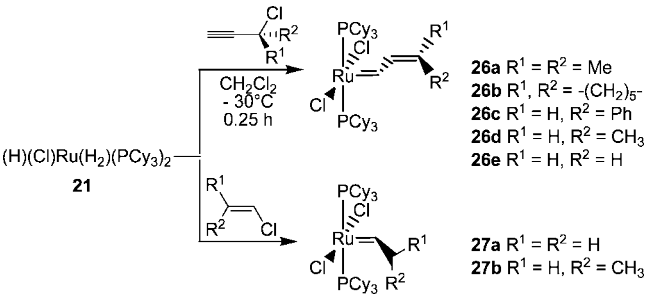


In view of these demands, Werner et al. developed a procedure for the preparation of vinylidenes and alkylcarbenes. Treatment of $[(RuCl_2(COD)]_n$ with P^iPr_3 under H_2 atmosphere in refluxing 2-propanol yielded a *red solution*, which upon recrystallization from diethyl ether afforded the expected dichloro dihydrido ruthenium compound **15** in high yield (93%, Scheme 4).[41] Importantly, the compound in the *red solution* was obviously different from the isolated product and was tentatively taken for a monohydride dihydrogen complex **19**. The isolated complex **15** was found to be an efficient precursor for the development of a ruthenium vinylidene compound **16a** upon reaction with phenyl acetylene at room temperature in dichloromethane (Scheme 4). The benzylcarbene compound **17**, found as a side product in a 10:1 ratio, was the exclusively formed product when the red solution was treated at −78 °C with 2 equiv of phenyl acetylene and was efficiently converted to the ruthenium vinylidene complex **16a** upon reaction with phenyl acetylene at 80 °C. Treatment of the red solution with acetylene at room temperature afforded a ruthenium methylcarbene **18** as the sole product (Scheme 4).[41] In sharp contrast, reaction of the isolated complex **15** with acetylene did not afford the methyl carbene complex **18** but rather the ruthenium vinylidene compound **16b**.

Interestingly, it was also found that reaction of propargylic alcohols or their derivatives, typically used for the synthesis of allenylidene complexes (*vide infra*), yields vinylcarbenes analogous to **12b** upon reaction with the dichloro dihydro ruthenium compound **15** (Scheme 4).[42]

Under otherwise identical conditions but in presence of NEt_3, $[RuCl_2(COD)]_n$ is converted to a hydrido dihydrogen ruthenium complex **19**, which yields a hydridovinylidene compound **20** upon reaction with terminal acetylenes (Scheme 4).[43] Of note, complex **15** can also be converted to compound **19** in 2-butanol with loss of butanone and P^iPr_3 as hydrochloride scavenger. The reverse reaction is mediated by $[HP^iPr_3]^+Cl^-$ as a chloride and proton source.

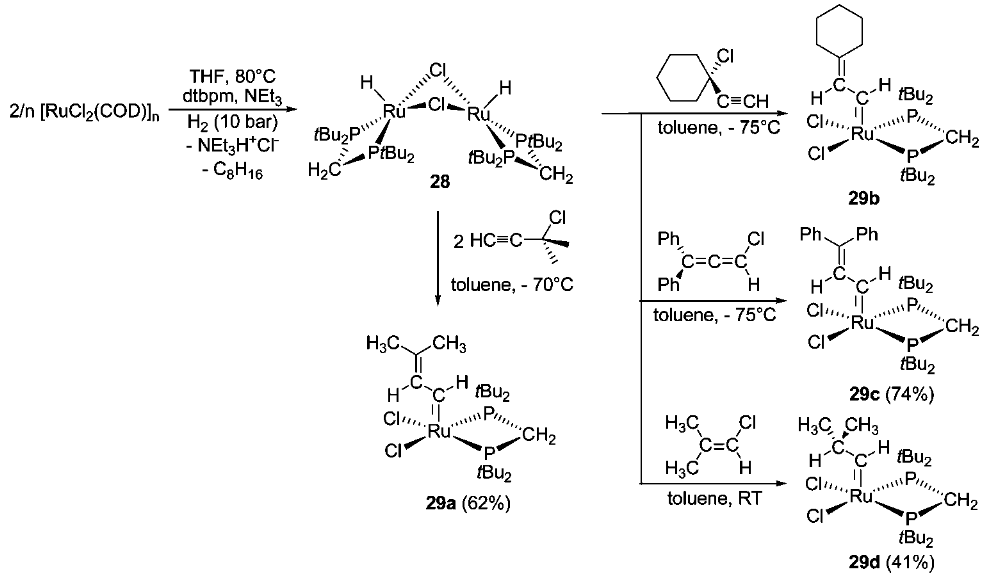
Scheme 5



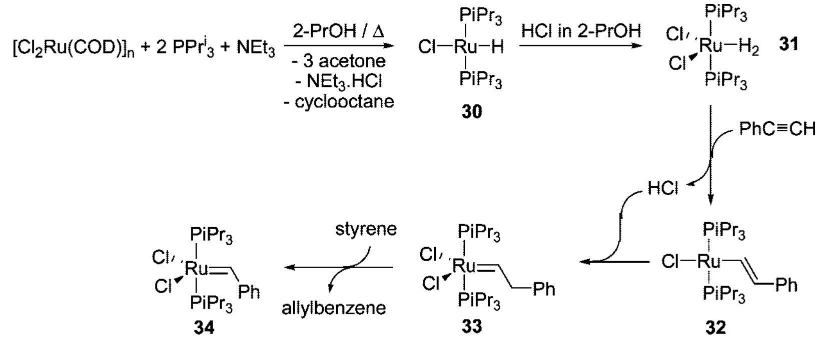
Later, Werner et al. further demonstrated that the bistricyclohexylphosphine hydrido dihydrogen ruthenium compound **21** reacts with terminal acetylenes to afford the analogous hydridovinylidene complexes **22a** and **22b**. However, when the reaction was performed in the presence of $[HPCy_3]^+Cl^-$, ruthenium alkylidenes **23a** and **23b** are isolated. Reaction of the hydrido vinylidenes **22** with hydrochloric acid or $[HPCy_3]^+Cl^-$ also affords the corresponding alkylidene complexes **23**. It was assumed that addition of HCl occurs across the carbon−carbon double bond in the vinylidene ligand, followed by a carbene insertion into the ruthenium hydride bond with subsequent α-chloride shift to form **23**. In a similar way as described above, a ruthenium dichloro dihydrido complex **24** bearing two PCy_3 ligands was prepared, which affords the analogous ruthenium vinylidene complexes **25a** and **25b**.[44] Additionally, a one-pot procedure that affords the desired carbene ruthenium catalyst **23a** in about 75% yield was developed starting from the commercially available $RuCl_3 \cdot 3H_2O$. Reduction of the ruthenium precursor in presence of PCy_3 and Mg/$ClCH_2CH_2Cl$ under H_2 atmosphere at 60−85 °C and subsequent addition of 2 equiv of acetylene and a small excess of water at −40 °C yielded the desired ruthenium alkylidene **23a** upon warming to room temperature.[44] At the same time, Grubbs reported on a resourceful strategy to prepare the air-sensitive $ClHRu(H_2)(PCy_3)_2$, **21**, from $[RuCl_2(COD)]_n$, PCy_3, H_2, and NEt_3 in 94% isolated yield, the former compound being a rewarding precursor for the preparation of ruthenium vinylcarbene complexes. Compound **26a** was formed quantitatively at −30 °C within 10 min upon reaction with the commercially available 3-chloro-3-methyl-1-butyne and could be isolated in 95% yield (Scheme 5). Other propargylic halides were found to be suitable carbene precursors, albeit with the formation of trace amounts of complex **24** as a byproduct as the steric bulk of the propargylic halide decreases. To account for the carbene formation, an insertion of the alkyne in the ruthenium−hydride bond with a subsequent rearrangement and a formal addition of the chloride to ruthenium was proposed. Although alkylcarbene complexes **27** were observed during the reaction of **21** with an excess vinyl chloride, it should be stated that these reactions were significantly less productive and yielded various ruthenium carbene complexes and complex **24** as a side product (Scheme 5).[45]

Caulton et al. showed that ruthenium hydride dihydrogen chloride or iodide complexes bearing 2 P^tBu_2Me ligands react

Scheme 6



Scheme 7



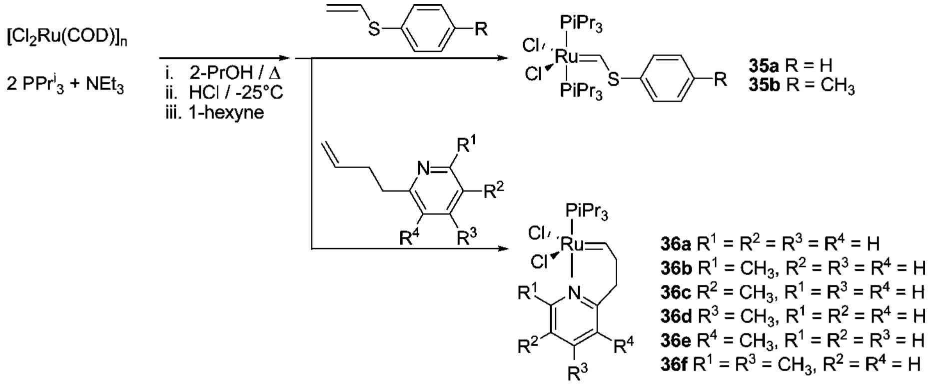
in a 1:2 stoichiometric amount with terminal alkynes, RCCH (R = Ph; R = $SiMe_3$), 1 equiv of alkyne serving as carbene precursor and 1 equiv of alkyne serving as hydrogen acceptor, to afford hydridovinylidene ruthenium complexes analogous to **22** and 1 equiv of the corresponding alkene. The reaction of $HIRuH_2(P^tBu_2Me)_2$ with DCCPh showed that the only products formed are *cis*-HDC=CHPh and $(P^tBu_2Me)_2DIRu(=CCHPh)$, which is consistent with a mechanism comprising addition of the Ru−H across the alkyne forming a π-acetylenic complex and subsequent α-D migration.[46]

Hofmann et al., in search of olefin metathesis catalysts bearing a chelating bisphosphine ligand, which are relevant to the experimental investigation of the phosphine ligand dissociation behavior in Grubbs first generation catalyst, applied a similar procedure for the reduction of $[RuCl_2(COD)]_n$ in presence of bis(di-*tert*-butyl-phosphanyl)-methane (btbpm) instead of PCy_3 and obtained an electronically unsaturated dihydride ruthenium dimer **28**, which formed a ruthenium vinylcarbene complex **29a** with a *cis*-dichloro arrangement upon reaction with 2 equiv of propargyl chloride at −70 °C in toluene as an air-stable green powder in 62% yield (Scheme 6).[47] Initial screening of the catalyst's activity toward the ROMP of norbornene and cyclopentene showed that complex **29** was significantly less active than the Grubbs catalysts **2**, as can be rationalized by the strongly decreased tendency to phosphine ligand dissociation due to the chelate effect. Later, it was shown that allenyl and vinyl chlorides were also suitable precursors for the preparation of ruthenium complexes featuring a metal−carbon double bond, **29c**,**d**.[48] Of note, biscationic bimetallic ruthenium carbene complexes obtained from **29** after chloride abstraction using trimethylsilyl triflate were found to be highly active catalysts toward the ROMP of cyclooctene.[48]

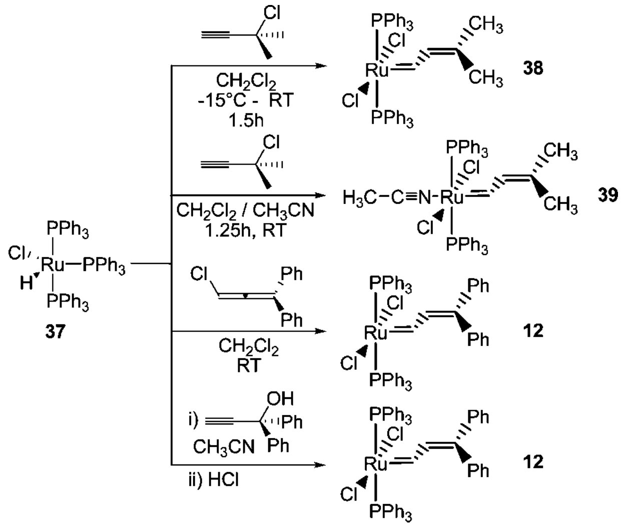
In 2000, van der Schaaf et al. reported on a one-pot procedure for the preparation of Grubbs first generation catalyst **34**. Most importantly, the reduction of $[RuCl_2(COD)]_n$ was successful in refluxing 2-propanol in presence of 2 equiv of P^iPr_3 and 1 equiv of NEt_3 without use of dihydrogen gas. Upon slow cooling of the obtained red solution previously described by Werner et al.,[41] orange crystals formed, which turned out to be a tetracoordinate, 14-electron ruthenium monohydride species, $HClRu(P^iPr_3)_2$, **30**, as determined by single-crystal X-ray analysis. Simultaneously, 3 equiv of 2-propanol were converted to acetone as a result of ruthenium hydride formation (1 equiv) and reduction of cycloocta-1,5-diene to cyclooctane (2 equiv). Cooling of the red solution to −20 °C, addition of 1 equiv of hydrochloric acid to form the proposed ruthenium dichloro dihydrogen complex **31**, and subsequent addition of 1 equiv of phenyl acetylene and 2 equiv of styrene led to the isolation of Grubbs first generation catalyst **34** in 75% yield on a multigram scale. The proposed mechanism is depicted in Scheme 7.[49]

Interestingly, a similar procedure using 1-hexyne instead of phenyl acetylene was successfully applied for the synthesis of complexes **35a** (78%), **35b** (72%), and **36a**−**f** (55−68%)

Scheme 8



Scheme 9

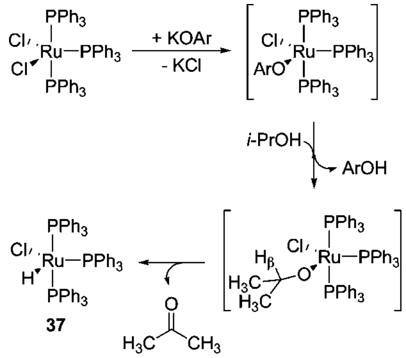


(Scheme 8), which were found to be latent catalysts for the controlled polymerization of dicyclopentadiene.[50]

Hofmann et al., acknowledging its accessibility and ease of handling, showed that the Wilkinson's hydride, ClHRu(PPh$_3$)$_3$, **37**,[51] a 16-electron analogue to the 14-electron hydride intermediate reported by van der Schaaf, readily reacts with propargyl chlorides in CH$_2$Cl$_2$ to yield the vinylcarbene **38** in good yield (75%, Scheme 9). Alternatively, the reaction is performed with subsequent addition of PCy$_3$ or the sterically demanding dtbpe (1,2-bis(di-*tert*-butylphosphino)ethane) in a one-pot process. When the reaction was performed in CH$_2$Cl$_2$/CH$_3$CN in a 3:1 ratio, a hexacoordinate ruthenium alkenylcarbene complex **39** was isolated as a yellow-green powder in 69% yield bearing a labile CH$_3$CN ligand *trans* to the carbene moiety. Although vinyl chlorides did not react in a similar way, the reaction was successful in the case of 3-chloro-1,1-diphenyl-1,2-propadiene to afford Grubbs–Nguyen catalyst **12a** (Scheme 9).[52]

Hill et al. showed that reaction of **37** with propargylic alcohol in acetonitrile presumably forms a γ-hydroxyvinylidene compound, which, upon workup with hydrochloric acid, yields compound **12a** (83%), as well.[53]

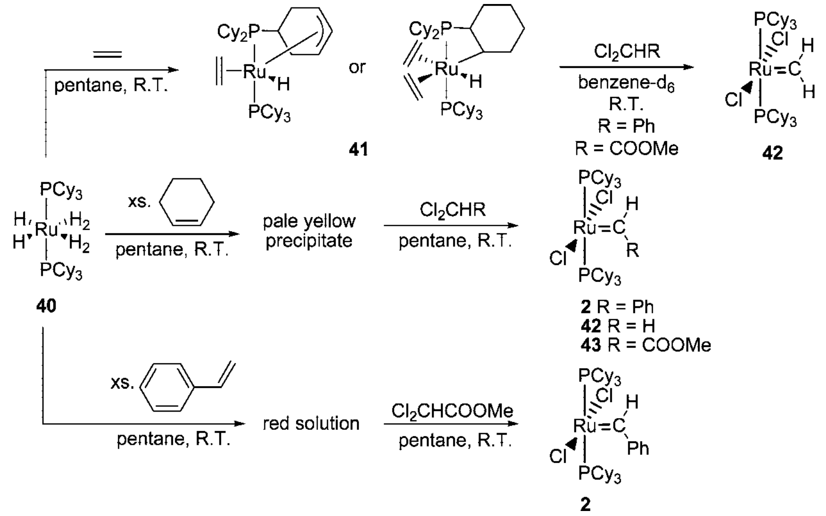
Scheme 10



An optimized procedure for the preparation of the Wilkinson's hydride complex **37** from RuCl$_2$(PPh$_3$)$_3$ and 1 equiv of 4-*tert*-butyl-aryloxide in refluxing benzene/2-propanol was later reported by Fogg et al. and afforded the desired complex in quantitative yield (97–99%). A mechanism was postulated comprising metathesis of the aryloxide for the chloride, protonolysis of the formed aryloxide complex with 2-propanol, and subsequent β-H elimination in the isopropoxide ligand, thus eliminating acetone, the driving force of the reaction (Scheme 10). The obtained complex **37** was later converted to Cl$_2$Ru(PCy$_3$)$_2$(=CHCHCMe$_2$), **38**, upon reaction with 1 equiv of 3-chloro-3-methyl-1-butyne at room temperature in CH$_2$Cl$_2$ within 30 min (Scheme 9), and subsequent phosphine ligand exchange in a one-pot reaction afforded a metathesis-active ruthenium compound in 88% isolated yield.[54] Of note, a ruthenium alkenylcarbyne complex was formed as a minor side product during the reaction of **37** with 3-chloro-3-methyl-1-butyne, and this carbyne complex was isolated in 75% yield when the reaction was performed in THF with a 4-fold excess of 3-chloro-3-methyl-1-butyne.[54]

Oliván and Caulton reported on the first double oxidative addition of dichloromethane, a *geminal* dihalocompound, to a single ruthenium center using [(H)$_2$Ru(H$_2$)$_2$(PCy$_3$)$_2$] as a formal source for the coordinatively unsaturated Ru^0 compound, [Ru(PCy$_3$)$_2$], after reductive elimination of the hydride ligands and loss of the H$_2$ ligands. Accordingly, [(Cl)$_2$Ru(=CH$_2$)(PCy$_3$)$_2$] was obtained in good yields upon reaction of [(H)$_2$Ru(H$_2$)$_2$(PCy$_3$)$_2$] with a small excess of dichloromethane after merely 15 min at 60 °C (67%) or after 3 h at room temperature using a 4-fold excess of dichloromethane (63%).[55] When the reaction was performed in a closed NMR-tube, however, [(Cl)$_2$Ru(=CH$_2$)(PCy$_3$)$_2$] further reacted with the released H$_2$ to give HClRu(H$_2$)(PCy$_3$)$_2$, and no reaction occurred when the reaction was performed under a 1 atm H$_2$ atmosphere, indicating dissociation of H$_2$ as the initial step of the reaction and (H)$_2$Ru(H$_2$)(PCy$_3$)$_2$ as the actual reactive partner. Alternatively, [(H)$_2$Ru(N$_2$)$_2$(PCy$_3$)$_2$] readily affords [(Cl)$_2$Ru(=CH$_2$)(PCy$_3$)$_2$] upon reaction with 4 equiv of CH$_2$Cl$_2$ within 20 min at room temperature precluding inhibition and side reactions. In case of vinylic *gem*-dichloride as carbene precursor, a ruthenium ethylidene

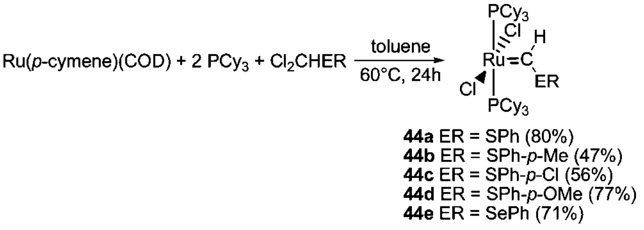
Scheme 11



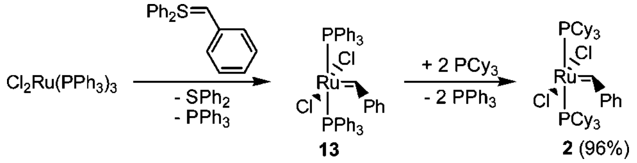
compound is observed, a result of a double oxidative addition with subsequent selective reduction of the vinylic C−C double bond. Reaction of benzylidene chloride with $[(H)_2Ru(N_2)_2(PCy_3)_2]$ yields the formation of Grubbs first generation catalyst **2** in 65% with $(H)_2(Cl)_2Ru(PCy_3)_2$ (7%) and $ClHRu(H_2)(PCy_3)_2$ (28%) as side products. The isolation of $Cl(PhCH_2)Ru(H_2)(PCy_3)_2$ from the same reaction with benzyl chloride suggests a two-step mechanism with "Cl-RuCHRCl" as an intermediate. A ruthenium propylidene, initially formed during the reaction of 1,1-dichloropropane with $[(H)_2Ru(N_2)_2(PCy_3)_2]$, appeared to be the thermodynamically unfavored product since $HClRu(N_2)(PCy_3)_2$, the product of a β-hydride migration after the first oxidative addition of a C−Cl bond, is exclusively obtained after 24 h while no traces of the ruthenium propylidene could be observed.[56]

Independently from the research of Oliván and Caulton, Grubbs et al. reported on the preparation of Grubbs first generation catalyst **2** upon reaction of $Ru^0(COD)(COT)$ with $PhCHCl_2$ in presence of 2 equiv of PCy_3 according to a mechanism that was designated as an oxidative addition−α-chloro elimination sequence. However, the preparation of Ru(COD)(COT) was quite tedious, and the procedure could not be applied to the synthesis of other carbenes. Alternatively, the hydrido alkyl complex **41**, a formal source of a Ru^0 species upon reductive elimination of the hydride and alkyl ligand obtained from $(H)_2Ru(H_2)_2(PCy_3)_2$ under ethylene atmosphere, reacts with Cl_2CHR (R = Ph, COOMe) to afford a ruthenium methylidene complex **42** instead of the expected benzylidene **2** or methylester carbene **43**, obviously the result of subsequent metathesis of the latter compounds with ethylene (Scheme 11). Indeed, styrene and methyl methacrylate were observed in the reaction mixture. In the case where cyclohexene is used instead of ethylene, a pale yellow precipitate, presumably a bis(hydrido)(olefin)-Ru^{II} compound, is obtained, which affords the Grubbs first generation catalyst **2**, the methylidene complex **42**, and the methylester carbene complex **43** in near to quantitative yields upon reaction with Cl_2CHPh, CH_2Cl_2, and $Cl_2CHCOOMe$, respectively. The methylester carbene complex **43** further reacts with styrene to afford **2**, and in the case where styrene is used instead of ethylene or cyclohexene, a red solution is obtained that reacts with $Cl_2CHCOOMe$ to afford Grubbs first generation catalyst **2** in 54% yield on a multigram scale.[57] Of note, ester carbene complexes were found to be active in the thermodynamically unfavored ring-opening metathesis of cyclohexene and metathesis of trisubstituted olefins and acrylates.[58]

Scheme 12



Scheme 13



Ozawa and co-workers showed that Fischer-type ruthenium carbene complexes are straightforwardly accessible from Ru^0(*p*-cymene)(COD) and dichloromethyl chalcogenides in presence of 2 equiv of PCy_3 (Scheme 12). In contrast to Ru(COD)(COT), the comparably air- and moisture-stable Ru(*p*-cymene)(COD) is readily obtained from commercially available products in 83% isolated yield. Other Ru^0 complexes, that is, Ru(benzene)(1,3-cyclohexadiene), proved to be successful precursors to ruthenium carbene complexes as well. Ozawa et al. further exemplified the use of catalysts **44a** and **44e** as highly selective catalysts for ring-opening/cross metathesis of norbornene and oxanorbornene derivatives with thio and seleno vinyl substrates.[59]

A distinct and general methodology for the incorporation of carbene ligands in transition-metal complexes was elaborated by Gandalman et al. Diphenyl sulfur ylide, prepared upon the deprotonation of a benzyl diphenylsulfonium salt with 1 equiv of $KN(SiMe_3)_2$, was reacted with $RuCl_2(PPh_3)_3$ at −30 °C. Subsequent exchange of PPh_3 ligands with PCy_3 afforded Grubbs first generation catalyst **2** in 96% yield.[60] In addition, the reaction was also successful in a polymer-assisted solution-phase (PASP) synthetic approach (Scheme 13).[61]

The preparation of transition-metal alkylidene complexes has long been limited to α-elimination from a transition-metal alkyl complex or the use of diazo precursors. The seminal finding that ruthenium carbene complexes are active olefin metathesis catalysts prompted the search for straightforward synthetic strategies toward these compounds. Despite the above-summarized developments, many of these strategies remain unattractive in terms of toxicity, stability, or accessibility of the ruthenium or hydrocarbon precursor. In the following sections, we will focus on the development and application of ruthenium-based olefin metathesis catalysts derived from alkynes and their derivatives. In contrast to the above-described approaches, it will be demonstrated that these systems are readily obtained from cheap and commercially available resources in near to quantitative yields under soft reaction conditions. In addition, these catalysts are readily modified by ligand exchange reactions to afford new ruthenium-based olefin metathesis catalysts with specific characteristics. As such, they have gained much industrial and academic interest, and their performance in olefin metathesis reactions is exemplified by prominent examples from literature.

3. Vinylidene Complexes

3.1. Introduction

The chemistry of vinylidene complexes displays a representative example of how highly reactive, short-lived organic molecules may be effectively stabilized by coordination to transition metals and therefore give them novel chemical properties that are useful for organic transformations[62] The coordination and organometallic chemistry of ruthenium–vinylidene complexes have been examined in some reviews hitherto by Bruneau and Dixneuf,[63] Katayama and Ozawa,[64] Cadierno and co-workers[65] and Dragutan.[66] They provide important information on the preparation, structure, and reactivity of this class of transition metal complexes as well as on their wide application profile in catalysis and organic synthesis. Moreover, the mechanistic aspects regarding the formation of metal vinylidenes from alkynes have been published by Wakatsuki.[67]

Reactivities of metal vinylidene complexes are rationalized by taking the electrophilicity of vinylidene α-carbon, the nucleophilicity of vinylidene β-carbon, and the highly unsaturated structures of the vinylidene ligands into consideration.[68] The representative examples for using vinylidene complexes include cycloaromatization of conjugated enediynes,[69] dimerization of terminal alkynes,[70] and addition of oxygen, nitrogen, and carbon nucleophiles to alkynes.[71]

Some vinylidene complexes have been used as catalyst precursors for olefin metathesis.[1b] Although the efficiency of the vinylidene complexes as initiator is lower compared with the well-known Grubbs' alkylidene and indenylidene complexes, the polymerization rate is fast enough for practical use and more importantly, they are readily prepared from conventional terminal alkynes. Another important feature is the rearrangement of the vinylidene ligand ([M]═C═CHR) to an alkylidene moiety ([M]═CHR) in the presence of an olefin.[72] This enlarges the application field of vinylidenes to valuable, easily accessible precursors for selective cross-metathesis (CM), ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), and also poly-cyclization reactions and synthesis of natural compounds with important biological activity.[72a]

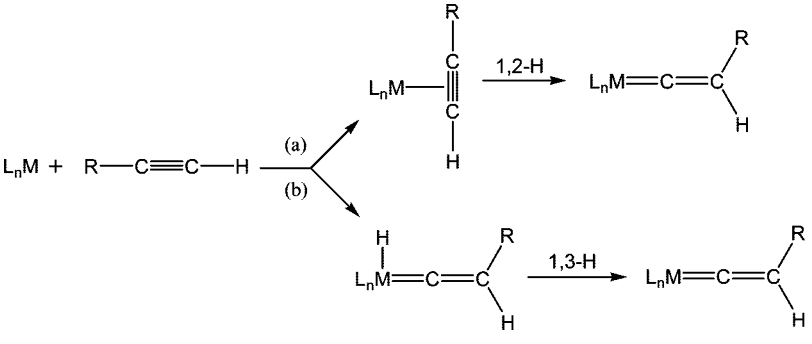
3.2. Synthesis and Structures

A groundbreaking report by Bruce et al. in 1979 showed that [CpRuCl(PPh$_3$)$_2$] reacts in the presence of NH$_4$PF$_6$ with phenyl acetylene to form a cationic vinylidene complex [CpRu(═C═CHPh)(PPh$_3$)$_2$][PF$_6$] (**45**) in 88% yield.[73] Following upon this event, several ruthenium vinylidene complexes have been prepared using terminal alkynes as vinylidene sources. Thus, vinylidene complexes responsible for catalysis are afforded by tautomerization of alkyne ligands, which may occur through two alternative pathways either by η^2-coordination of the triple bond followed by a 1,2-hydrogen shift (path a, Scheme 14)[74] or by oxidative addition of the alkynes yielding an alkynyl metal intermediate, which rearranges via 1,3-hydrogen shift or protonation (path b, Scheme 14).[63b,75]

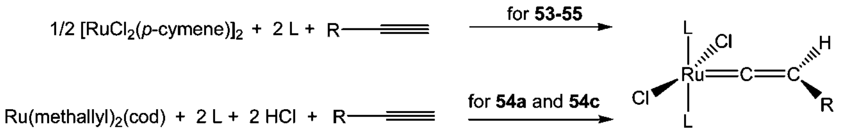
The mechanistic aspects of these reactions have been perfectly explained based on molecular orbital discussions.[67] The energy diagram obtained with DFT calculations predicts the formation of the vinylidene complex by 1,2-H shift vs the hydride-alkynyl by the oxidative addition in [CpRu(PH$_3$)$_2$-(HCCMe)]$^+$ complex.[76] However, an easier oxidative addition is obtained when replacing PH$_3$ with the more electron-releasing PMe$_3$ ligand, explaining the competition between both processes.[77] Quite similar relative energies of the η^2-acetylene and hydride-ethynyl isomers are also calculated by combinations of QM and MM computations to estimate the electronic and steric influence of the ligands.[75]

A convenient method to synthesize vinylidenes was described by Wakatsuki et al. in 1991.[78] Treatment of [RuX$_2$(PPh$_3$)$_3$] (X = Cl, Br) with ^{t}BuC≡CH yielded a 16-electron species with the general formula [RuX$_2$-(═C═CH^{t}Bu)(PPh$_3$)$_2$] (X = Cl, Br) (**46**, **47**). Later, Werner and co-workers achieved the synthesis of the P^{i}Pr$_3$-coordinated analogue [RuCl$_2$(═C═CHPh)(P^{i}Pr$_3$)$_2$] (**48**), which was conveniently prepared from [RuH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$] using PhC≡CH.[41,44,79] Grubbs et al. reported the synthesis of [RuCl$_2$(═C═CH$_2$)(PCy$_3$)$_2$] (**49**) by the reaction of

Scheme 14



Scheme 15



53: L = PPh$_3$, R = *t*-Bu
54a: L = P*i*-Pr$_3$, R = *t*-Bu
54b: L = P*i*-Pr$_3$, R = Fc
54c: L = P*i*-Pr$_3$, R = Ph
54d: L = P*i*-Pr$_3$, R = *p*-MeO$_2$CC$_6$H$_4$
54e: L = P*i*-Pr$_3$, R = *p*-MeOC$_6$H$_4$
55a: L = PCy$_3$, R = *t*-Bu
55b: L = PCy$_3$, R = Fc
55c: L = PCy$_3$, R = Ph

[RuCl$_2$(=CHPh)(PCy$_3$)$_2$] with 1,2-propadiene/allene,[25b] and Caulton presented the synthesis of [RuHCl(=C=CHR)(P^{t}Bu$_2$Me)$_2$] (R = Ph, SiMe$_3$) (**50**, **51**), formed by insertion of terminal acetylenes RC$\equiv$CH into [RuH$_3$XL$_2$] complexes (X = Cl, I; L = P^{t}Bu$_2$Me).[46] In 1998, Ozawa reported a vinylidene ruthenium complex bearing a hydridotris(pyrazoyl)borate ligand, TpRuCl(=C=CHPh)(PPh$_3$) (**52**), which serves as catalyst precursor for the ROMP of norbornene.[80] Ozawa and co-workers have developed two synthetic routes to vinylidene ruthenium complexes bearing basic and bulky tertiary phosphine ligands with the general formula [RuCl$_2$(=C=C{H}R)L$_2$] (Scheme 15).[81] In a first approach [Ru(methallyl)$_2$(COD)] is reacted with P^{i}Pr$_3$, HCl, and RC$\equiv$CH via a [RuCl$_2$(P^{i}Pr$_3$)$_2$]$_n$ intermediate. In a second procedure, a toluene solution of [RuCl$_2$(*p*-cymene)]$_2$, L (2 equiv/Ru), and RC$\equiv$CH (1 equiv/Ru) is heated at 80 °C and leads to the selective formation of the vinylidene complexes.

Furthermore, treatment of [RuCl$_2$(*p*-cymene)]$_2$ with PCy$_3$ and PhC$\equiv$CSiMe$_3$ gives the β-silylvinylidene complex **56** [RuCl$_2$(=C=C{SiMe$_3$}Ph)(PCy$_3$)$_2$] as a result of a 1,2-silyl migration.[81] In the case where a less bulky phosphine is employed, for example, PMe$_2$Ph instead of PCy$_3$ or P^{i}Pr$_3$, the coordinatively saturated complex **57** is formed (Figure 4).[64]

Only a few papers point out the synthesis of Ru–vinylidene complexes containing the pincer-type tridentate ligands (**58a**, **58b**, **59**) and tridentate ligand 2,6-bis[(dimethylamino)methyl]pyridine κ^3-(*N*,*N'*,*N*) (Figure 5).[72a,74,82]

In 2000, Peruzzini and co-workers reported the successful synthesis of water-soluble ruthenium(II) vinylidene species. The water-soluble complex [{RuCl$_2$(TPPMS)$_2$}Na$_2$]·4H$_2$O (TPPMS = Ph$_2$P{2-OS(O)$_2$C$_6$H$_4$}$^-$Na$^+$) reacts with phenylacetylene in THF at room temperature to give the water-soluble unsaturated carbene [{RuCl$_2${=C=CHPh}(TPPMS)$_2$}]Na$_2$ (**60**) (Figure 6). The ability of this complex to catalyze the homogeneous ring-opening metathesis of cyclic olefins with methyl acrylate as chain transfer reagent was discussed, and it was proven that they promote the cross-olefin metathesis of cyclopentene with methyl acrylate to generate polyunsaturated esters. Recently, in 2004, they described some vinylidene complexes (**61**, **62a**, **62b**) derived from glycoynitols as new precursors for water-soluble unsaturated carbenes.[83] Moreover bi- and trimetallic vinylidene complexes (**63**, **64**) were prepared by different research teams (Figure 6).[81,84]

In addition, Sun and co-workers were able to isolate the first ruthenium bis(vinylidene) complex (**65**) and a vinylvinylidenemetal complex (**66**) obtained from the reaction of [$\eta^5\sigma$-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru(NCCH$_3$)$_2$ with silylalkyne (Scheme 16).[85]

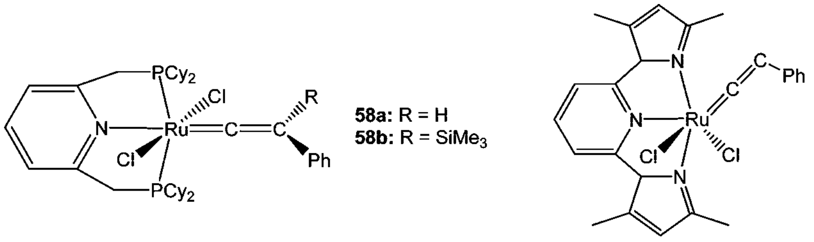
It was also reported by Keller et al. that the *cis*-dichlororuthenium complex [RuCl$_2$(dppene)(bpy)] (dppene = Ph$_2$PCHCHPPh$_2$, bpy = 2,2'-bipyridyl) reacts with terminal alkynes in the presence of NaPF$_6$ to give a *cis*-chloro(vinylidene)[(dppene)(bpy)ClRu=C=CHPh]PF$_6$ (**67**) complex in 88% yield.[86]

In addition, the synthesis and spectroscopic properties of ruthenium derivatives containing the macrocyclic amine ligand 16-TMC (1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) have also been described.[87] Reaction of [Ru(16-TMC)Cl$_2$]Cl and HC$\equiv$CR in the presence of zinc amalgam in refluxing methanol afforded the vinylidene ruthenium complexes with the general formula *trans*-[Cl(16-TMC)Ru=C=CHR]PF$_6$, (R = C$_6$H$_4$X^{-4}, X = H, Cl, Me, OMe) (**68a**–**68d**) (Scheme 17).

Furthermore, the neutral ruthenium(II) vinylidene complexes containing a bis(3,5-dimethylpyrazol-1-yl)acetato ligand (bdmpza) have been prepared by Kopf et al. in 2006. Treatment of [Ru(bdmpza)(Cl)(PPh$_3$)$_2$] with a variety of alkynes afforded the vinylidene complexes [Ru(bdmpza)-

56 **57**

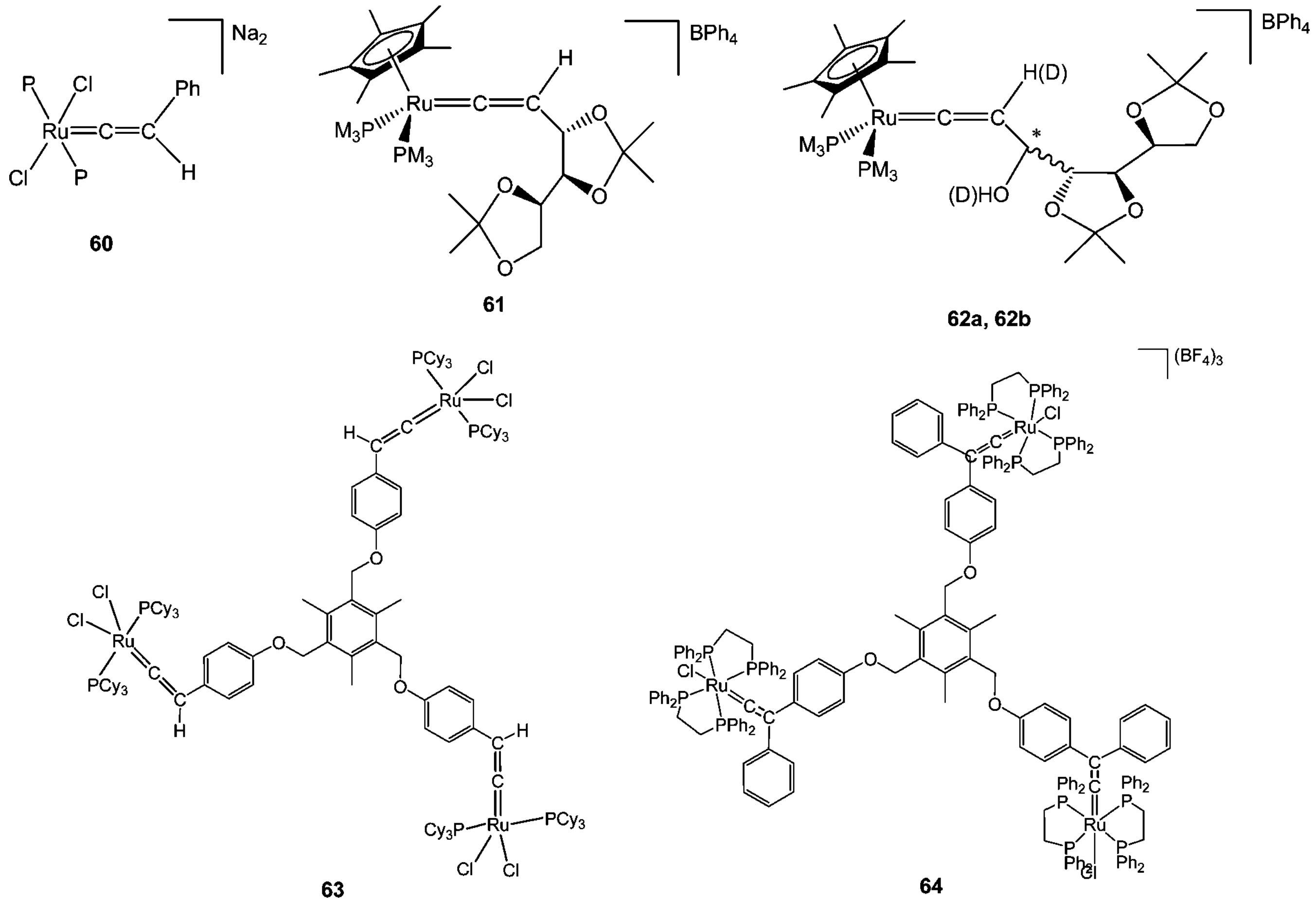
Figure 4.



58a: R = H
58b: R = SiMe$_3$

59

Figure 5.



60

61

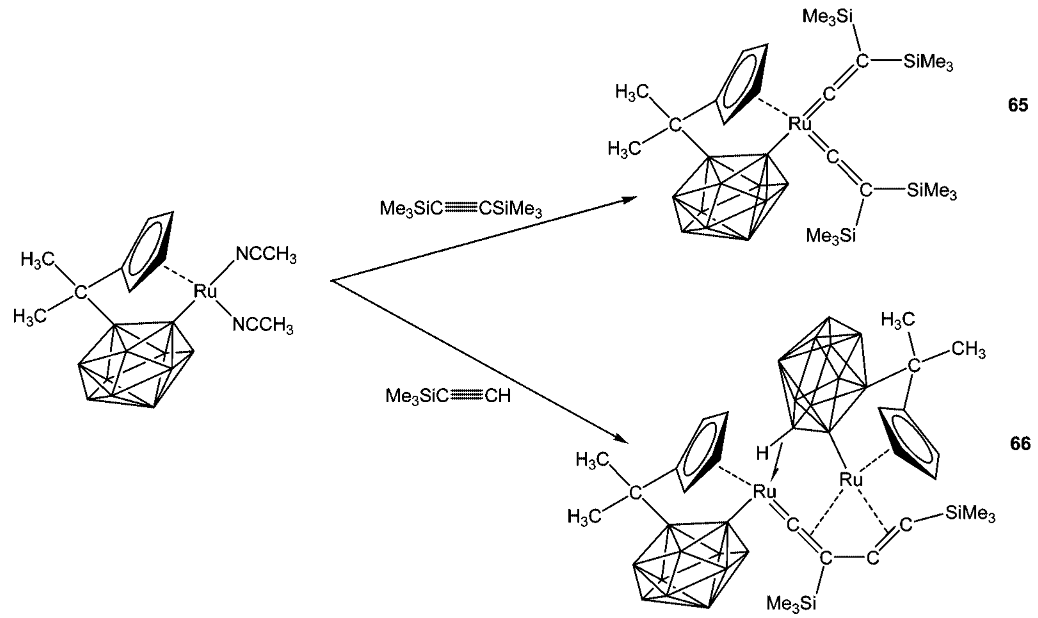
62a, 62b

63

64

Figure 6.

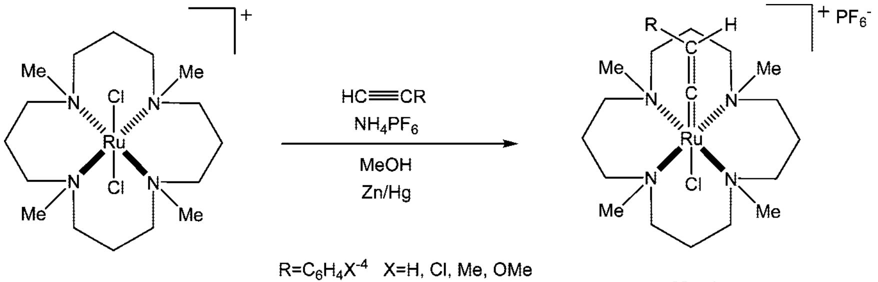
Scheme 16



(Cl)(=C=CHR)(PPh$_3$)], (R = Ph, *p*-Tol, Pr, Bu) (**69a−d**) (Scheme 18).[88]

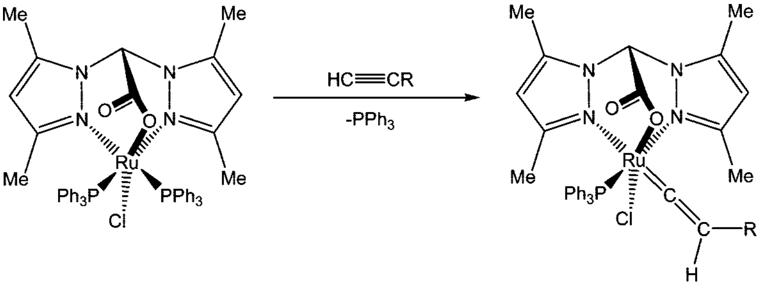
Activation of propargylic alcohols with hydrogen atoms at the carbon atom adjacent to the one bearing the hydroxyl group is another possible way for the preparation of vinylvinylidenes. However, the dehydration step can lead to the allenylidene derivative, but this only occurs in the minority of the cases.[68,89] This also have been demonstrated with theoretical calculations since the vinylvinylidene tautomer is ca. 2.1 kcal/mol more stable than the allenylidene.[90] Pavlik et al. studied the reaction of RuTp(COD)Cl with PR$_3$ (PR$_3$=PPh$_2{}^i$Pr, P^{i}Pr$_3$, PPH$_3$) and propargylic alcohols HC≡CCPh$_2$OH, HC≡CCFc$_2$OH (Fc = ferrocenyl), HC≡CC(Ph)MeOH, and 1-ethynylcyclohexanol. The 3-hydroxyvinylidene complexes [RuTp(Cl)(PPh$_2{}^i$Pr)(=C=CHC(Ph)$_2$OH)] (**70a**) and [RuTp(Cl)(P^{i}Pr$_3$)(=C=CHC(Ph)$_2$OH)]

Scheme 17



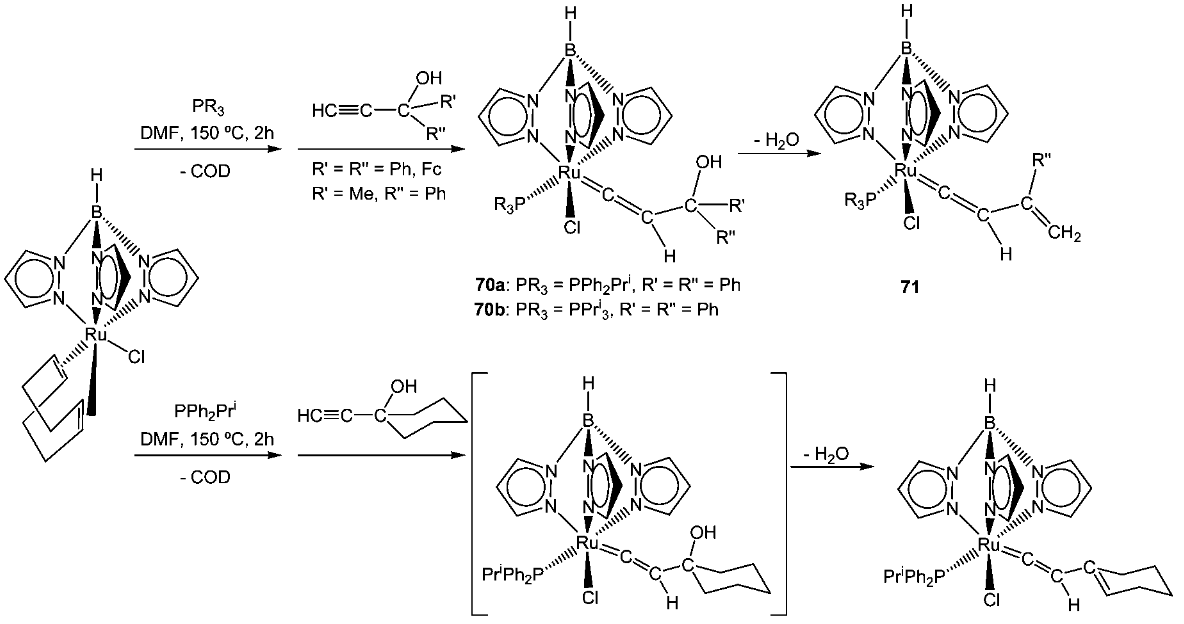
68a-d

Scheme 18



69a: R = Ph
69b: R = *p*-Tol
69c: R = Pr
69d: R = Bu

Scheme 19

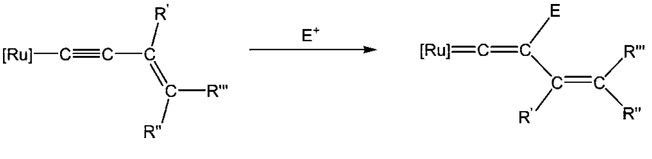


70a: PR$_3$ = PPh$_2$Pr^i, R' = R'' = Ph
70b: PR$_3$ = PPr$^i_3$, R' = R'' = Ph

71

72

Scheme 20



(**70b**) were isolated efficiently, and some vinylvinylidene complexes were obtained (**71**, **72**) (Scheme 19).[91]

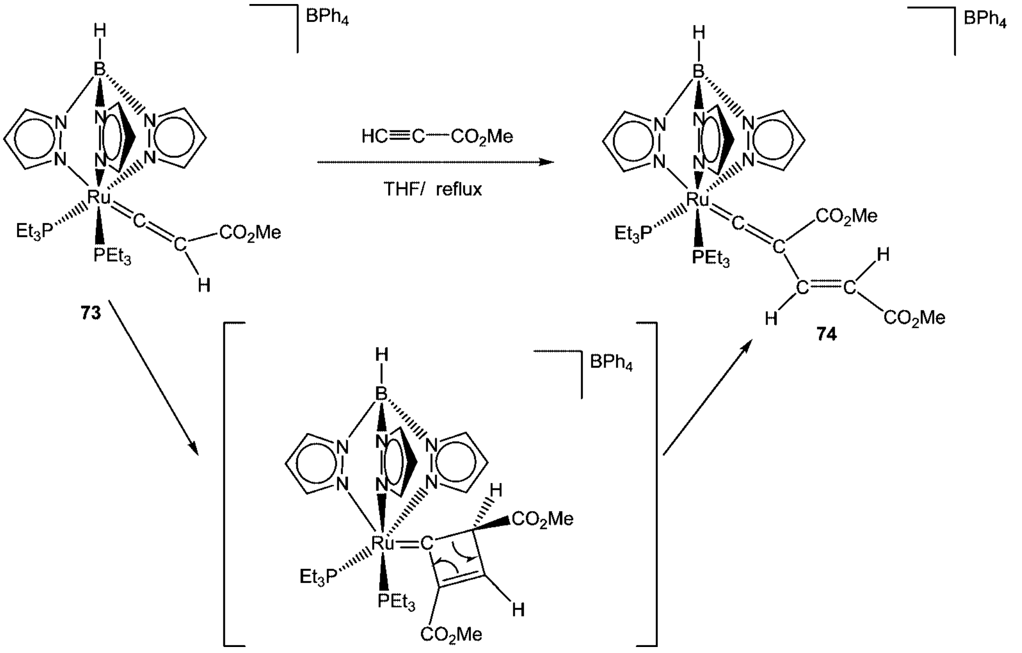
Besides, terminal 1,3-enynes $HC{\equiv}CC(R^1){=}CR^2(R^3)$ and σ-enynyl derivatives $[Ru]{-}C{\equiv}CC(R^1){=}CR^2(R^3)$ are also general methods to prepare vinylvinylidenes. In the first case, the reaction proceeds by the classical tautomerization of the alkyne followed by a 1,2-hydrogen shift or a 1,3-hydrogen shift. On the other hand, the vinylvinylidene is formed due to the addition of one electrophile to the C_β atom of the σ-enynyl compound (Scheme 20).[68,89]

Puerta and co-workers have also generated one vinylvinylidene through addition of $HC{\equiv}CCO_2Me$ to the cationic vinylidene complex $[Ru\{{=}C{=}C(H)CO_2Me\}\{HB(pz)_3\}(Pet_3)_2][BPh_4]$ as it is shown in Scheme 21.[92]

A new and alternative approach to synthesize γ-substituted vinylidenes via allenylidene/alkenylcarbyne complexes has been described as well (Scheme 22).[93] As can be observed in Scheme 22, a nucleophilic addition occurs to the $C_\beta{-}C_\gamma$ double bond of an allenylidene compound or to the double bond of an alkenylcarbyne complex. Protic nucleophiles in the case of reaction with allenylidenes and aprotic nucleophiles with alkenylcarbynes were tested as the most appropriate to react.

Ample Ru−vinylidene complexes were formed by ligand exchange of the $[RuCl_2({=}C{=}CHR)L_2]$-type complexes (L

Scheme 21



= P^iPr_3, PCy_3; R = Ph, ^tBu, Fc, p-$MeO_2CC_6H_4$, p-$MeOC_6H_4$). Grubbs and Verpoort reported a new catalyst obtained by exchange of one of the PCy_3 with *N*-heterocyclic carbene (NHC) ligands: 1,3-dimesitylimidazol-2-ylidene (IMes), **82**, and its saturated analogue 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (SIMes), **83a−c** (Figure 7).[94]

Similarly, the κ^2-(*N*,*O*)-chelate complex **84** was formed by displacement of the PCy_3 with 2-acetylpyridine (Figure 8).[64]

The various Schiff base complexes were synthesized using Tl-salts of the appropriate Schiff bases (**85a−f**, Figure 9).[94b−f,95]

The synthesis of Ru−vinylidene complexes bearing sulfur donor ligands was also described.[96] Treatment of $[Ru({=}C{=}CHPh)(PCy_3)_2Cl_2]$ with $K[N(PPh_2S)_2]$ affords *cis*-$Ru({=}C{=}CPh)(PCy_3)[N(PPh_2S)_2]_2$ (**86**) (Figure 10). On the other hand, the reaction of $[Ru({=}C{=}CH^tBu)(PCy_3)_2Cl_2]$ and $[Ru({=}C{=}CHPh)(P^iPr_3)_2Cl_2]$ with sterically demanding diphosphane $1,2\text{-}C_2H_4(PCy_2)_2$ gives the chelating complexes $[RuCl_2({=}C{=}CH^tBu)C_2H_4\{PCy_2\}]$ and $[RuCl_2({=}C{=}CHPh)\text{-}C_2H_4\{PCy_2\}]$ (**87a**,**b**), respectively, by displacement of the two monodentate phosphane ligands (Figure 10).[97]

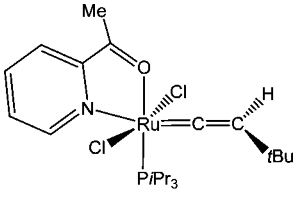
Vinylidene ruthenium derivatives have been also studied; these are the intermediates to other types of catalysts, for example, carbyne complexes,[98] Grubbs-type ruthenium carbenes, using hydrido(vinylidene) complexes, $RuHCl({=}C{=}CHR)(PCy_3)_2$ (R = H, Ph), as precursors.[99]

3.3. Catalytic Activity in Olefin Metathesis

Catalytic activity in olefin metathesis chemistry has not been proven for all the above-mentioned complexes. Following the discovery of the Grubbs-type catalysts, various vinylidene ruthenium complexes have been examined as precursors for the olefin metathesis. In addition to easy accessibility, the vinylidene complexes have the advantage of high stability. They are fairly stable in solution, as well as solid, samples, which can be stored in air for several months at ambient temperature. Their second advantage is their ease of preparation and electronic and steric fine-tuning.

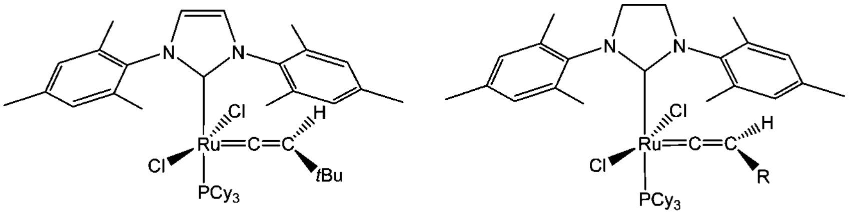
3.3.1. Ring-Opening Metathesis Polymerization (ROMP)

Table 1 summarizes the results of the best-performing vinylidene ruthenium complexes as catalysts in ROMP of norbornene. Catalytic reactions using **54a**, **55a**, or



84

Figure 8.

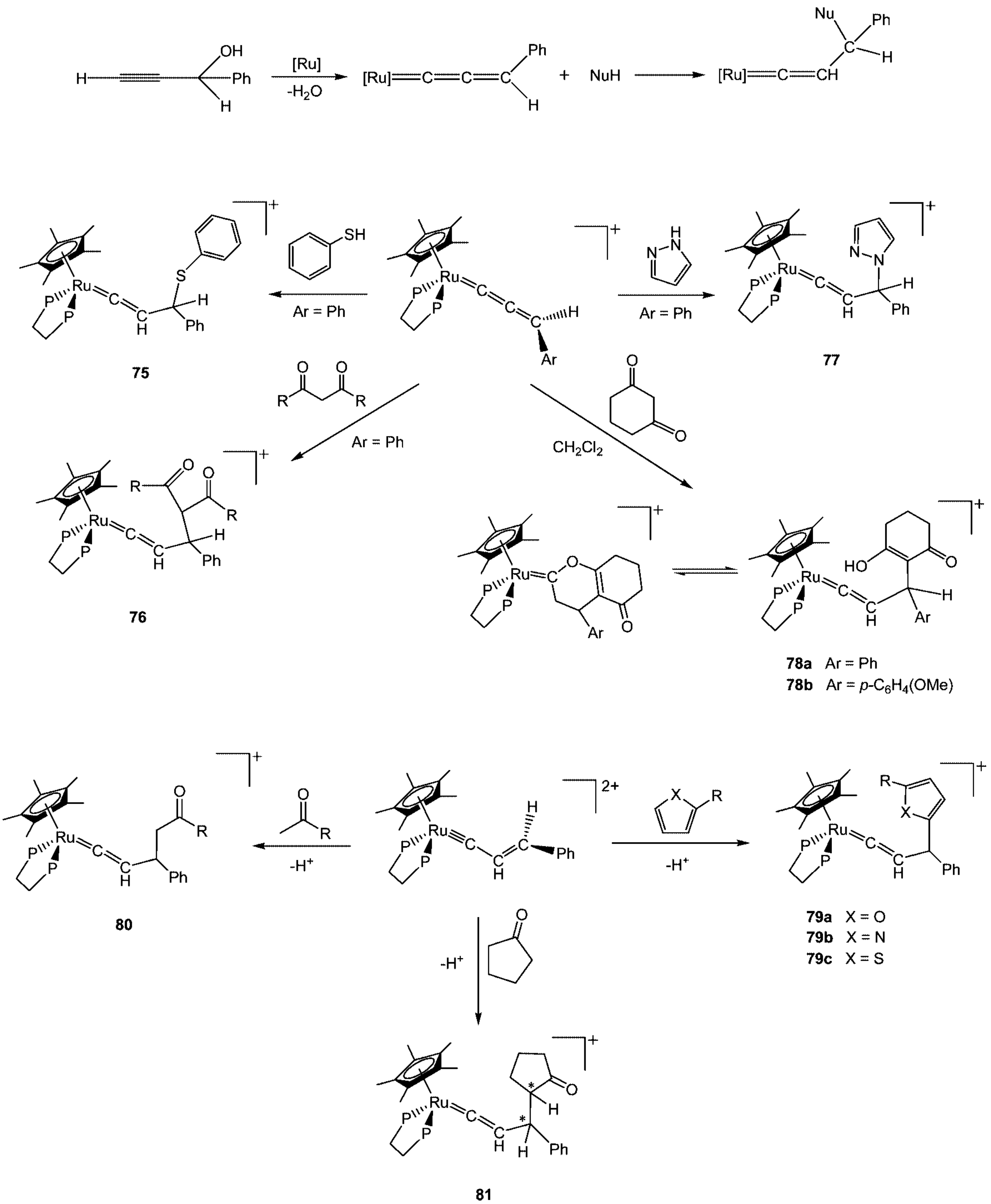


82

83a: R = Ph
83b: R = $SiMe_3$
83c: R = *t*Bu

Figure 7.

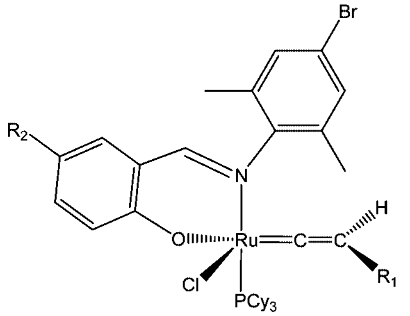
Scheme 22



85a−c were completed within a few minutes at room temperature affording almost quantitative polymer yield with high molecular weight. The catalytic activity of these systems is comparable to other highly active ruthenium catalysts for ROMP of norbornene.

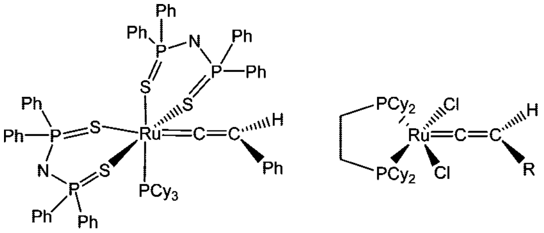
Vinylidene ruthenium complexes were tested on their ROMP activity toward different cyclic olefins and the results are summarized in Table 2.

From these results, it is obvious that low- and high-strained cyclic monomers are converted with excellent yields (except for **85a** and **85b** in ROMP of cyclooctene where the yield is not higher than 15%). However, significant differences were observed in their behavior. All reactions depicted in Table 2 were carried out at higher temperatures, whereas ROMP reaction of entry 2 using **54a** as catalyst proceeded at room temperature. The silylvinylidene ruthenium complexes (**85c** and **85d**) proved to be the best performing systems in this series. Studying the substitution pattern of the Schiff base ligand, it is clear that the highest activity is obtained with the electron-withdrawing nitro group in the *para*-position.[86] Molecular weights are exceedingly higher than theoretically expected from the monomer to catalyst precursor ratios. The slow initiation compared with the propagation is typical for vinylidene complexes and indicates low initiation efficiency of these catalysts as initiators as a considerable amount of the vinylidene catalysts remained unreacted in the reaction solutions after the polymerization.[72b]



85a: R_1 = Ph, R_2 = H
85b: R_1 = Ph, R_2 = NO_2
85c: R_1 = $SiMe_3$, R_2 = H
85d: R_1 = $SiMe_3$, R_2 = NO_2
85e: R_1 = *t*-Bu, R_2 = H
85f: R_1 = *t*-Bu, R_2 = NO_2

Figure 9.



86

87a: R = *t*Bu
87b: R = Ph

Figure 10.

3.3.2. Ring Closing Metathesis (RCM)

Next to their activity toward ROMP, vinylidene ruthenium complexes also exhibit catalytic activity toward RCM reactions. Among other α,ω-diolefins, all catalysts were subjected to RCM of diethyl diallylmalonate (DEDAM). Experimental results are summarized in Tables 3 and 4.[72b,86]

The RCM of DEDAM proceeded with excellent yield using complexes **55b**, **83a−c**, or **85a−f** at reasonably low catalyst loadings (2−5 mol %). However, catalysts **55b** and **83a−c** required lower temperature, and the reactions were quantitative within 2 h. Catalysts **54a** and **54b** also performed the RCM of DEDAM, albeit using significantly longer reaction times.

A variety of dienes and dienynes were easily converted into the corresponding cyclic alkenes in high yields, while no detectable side products were observed. On the other hand, the ring-closing reaction of enynes involved the formation of several unidentified compounds. The catalytic activity of complexes **85a−f** toward RCM decreases in the series **85d** > **85c** > **85f** > **85e** > **85b** > **85a**.

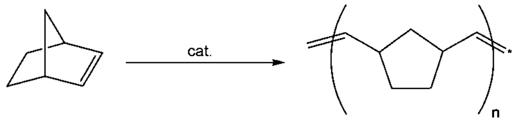
3.3.3. Other Types of Metathesis Reactions

The isolation and characterization of the first water-soluble Ru(II) vinylidene and allenylidene complexes have allowed demonstration that such compounds could be successfully applied as catalysts in olefin metathesis. The catalytic performance of $[\{RuCl_2\{=C=CHPh\}(TPPMS)_2\}]Na_2$ (**60**) (TPPMS = $Ph_2P\{2\text{-}OS(O)_2C_6H_4\}^-Na^+$) in homogeneous ring-opening cross metathesis (ROCM) reveals that this carbene is an active catalyst in promoting the cross-olefin metathesis of cyclopentene with methyl acrylate to give polyunsaturated esters (Scheme 23).[83b]

The selective formation of the ester $C_7H_{11}CO_2Me$ ($n = 1$) proceeds within 2 h in a homogeneous methanolic system at room temperature with 64% yield.

Several examples have been reported for catalytic alkyne−alkyne and alkyne−alkene coupling reactions probably through a [2 + 2] cycloaddition of vinylidene ruthenium intermediates.[100]

Table 1. ROMP of Norbornene Using Vinylidene Ruthenium Complexes As Catalysts



entry	catalyst	*T* (°C)	*t*	yield (%)	M_n[a] ($\times 10^4$)	M_w/M_n[a]	TON	ref
1	$[TpRu(=C=CHPh)(PPh_3)]$	80	24 h	76	3.0	5.01	100	80
2	**53**	40	24 h	83	10.6	2.31	100	72b
3	**54a**	[b]	10 min	98	59.9	1.44	100	72b
4	**55a**	[b]	10 min	>99	48.3	2.03	100	72b
5	$[Ru(=C=CHPh)(NN'N)(PPh_3)][BF_4]_2$	80	1 h	100	96.8	1.16	795	72a
6	**83a**	[b]	5 min	100	103	2.1	2000	94b
7	**83b**	[b]	5 min	100	93	1.9	2000	94b
8	**83c**	[b]	5 min	100	98	2.3	2000	94b
9	**85a**	80	0.5 h	94	67.6	1.53	800	94b
10	**85b**	80	0.5 h	98	62.6	1.60	800	94b
11	**85c**	80	0.5 h	100	63.4	1.70	800	94b
12	**85d**	80	4 h	100	65.6	1.68	800	94b
13	**85e**	80	4 h	100	58.2	1.39	800	94b
14	**85f**	80	4 h	100	60.0	1.48	800	94b

[a] Determined using gel permeation chromatography (GPC) based on PS standards. [b] Room temperature.

Scheme 23

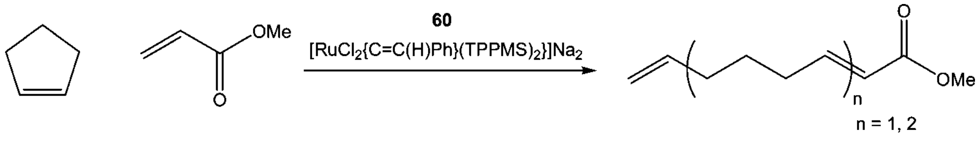
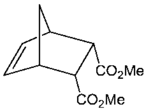
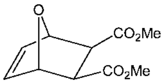
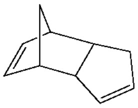
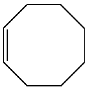
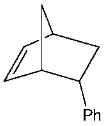
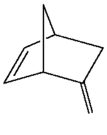
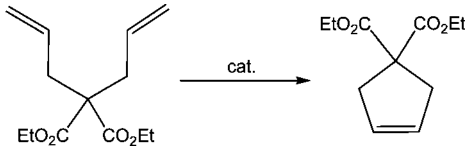


Table 2. ROMP of Other Cyclic Olefins Using Vinylidene Ruthenium Complexes As Catalysts

Entry	Monomer	Catalyst	T (°C)	Time (h)	Yield (%)	M_n[a] ($x10^4$)	M_w/M_{na}[a]	TON	Ref
1		**54a**	60	24	87	18.0	2.81	100	72b
2		**54a**	r.t.	24	97	66.5	2.14	100	72b
3		**54a**	60	12	>99	-	-	100	72b
		83a	60	2	74	-	-	2000	94b
		83b	60	2	100	-	-	2000	94b
		83c	60	2	97	-	-	2000	94b
		85a	80	10	90	-	-	800	94b
		85b	80	10	96	-	-	800	94b
		85c	80	10	100	-	-	800	94b
		85d	80	10	100	-	-	800	94b
		85e	80	10	95	-	-	800	94b
		85f	80	10	97	-	-	800	94b
4		**54a**	60	12	>99	-	-	100	94b
		83a	60	0.5	54	379	1.66	5000	94b
		83b	60	0.5	99	434	1.60	5000	94b
		83c	60	0.5	90	474	1.54	5000	94b
		85a	80	15	10	34.7	1.70	250	94b
		85b	80	15	15	30.5	1.84	250	94b
		85c	80	15	93	37.9	1.54	250	94b
		85d	80	15	100	28.9	1.76	250	94b
		85e	80	15	80	30.5	1.70	250	94b
		85f	80	15	88	27.9	1.83	250	94b
5		**83a**	60	2	71	150	1.69	2000	94b
		83b	60	2	94	202	1.54	2000	94b
		83c	60	2	87	214	1.67	2000	94b
		85a	80	4	74	46.8	1.93	800	94b
		85b	80	4	80	43.9	2.08	800	94b
		85c	80	4	95	60.7	1.89	800	94b
		85d	80	4	98	63.5	1.99	800	94b
		85e	80	4	89	48.3	1.88	800	94b
		85f	80	4	92	51.5	1.80	800	94b
6		**83a**	60	0.5	90	187	1.75	2000	94b
		83b	60	0.5	100	190	1.77	2000	94b
		83c	60	0.5	100	209	1.90	2000	94b
		85a	80	10	100	83.6	1.90	800	94b
		85b	80	10	100	79.6	1.98	800	94b
		85c	80	10	100	82.8	2.3	800	94b
		85d	80	10	100	94.1	1.91	800	94b
		85e	80	10	100	91.5	1.93	800	94b
		85f	80	10	100	84.9	1.78	800	94b

[a] Determined using GPC based on PS standards.

Table 3. RCM of DEDAM Using Vinylidene Ruthenium Catalysts



entry	catalyst[a]	solvent	T (°C)	t (h)	yield[b] (%)	ref
1	**54a**	$CDCl_3$	60	24	83	72b
2	**54b**	$CDCl_3$	60	24	75	72b
3	**54c**	$CDCl_3$	60	24	55	72b
4	**54d**	$CDCl_3$	60	24	10	72b
5	**55b**	$CDCl_3$	60	24	96	72b
6	**82**	toluene-d_8	80	12	95	94a
7	**83a**	C_6D_6	60	2	90	94b
8	**83b**	C_6D_6	60	2	100	94b
9	**83c**	C_6D_6	60	2	100	94b
10	**85a**	C_6D_6	80	24	96	94b
11	**85b**	C_6D_6	80	24	98	94b
12	**85c**	C_6D_6	80	24	100	94b
13	**85d**	C_6D_6	80	24	100	94b
14	**85e**	C_6D_6	80	24	100	94b
15	**85f**	C_6D_6	80	24	100	94b

[a] The amount of catalyst precursors: 2 mol % (**55b**), 5 mol % (others). [b] Determined by ^1H NMR analysis using mesitylene as an internal standard.

4. Allenylidene Complexes

4.1. Introduction

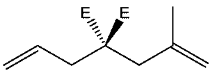
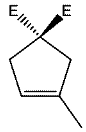
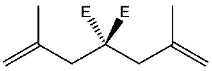
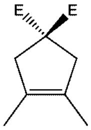
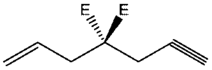
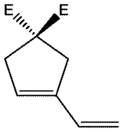
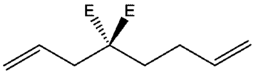
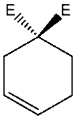
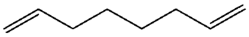
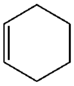
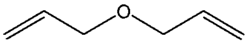
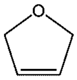
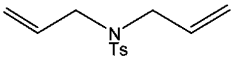
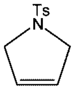
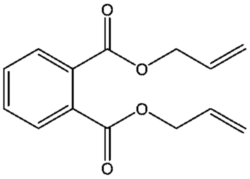
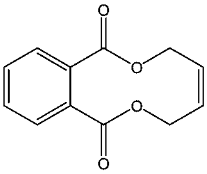
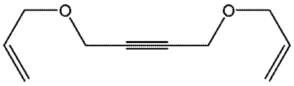
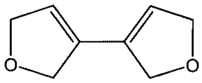
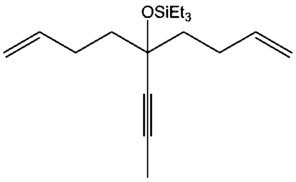
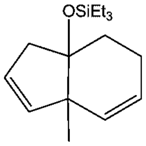
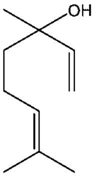
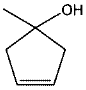
The organometallic chemistry of allenylidene systems has attracted a great deal of interest and reached a faster development since Selegue reported a simple general method for the preparation of ruthenium allenylidene complexes by activation of alkynols with the dimer $[(p\text{-cymene})RuCl_2]_2$.[101] Rapidly, their use as catalysts has increased drastically, resulting in a versatile, useful, and powerful tool for modern organic synthesis, polymer chemistry, and homogeneous catalysis.[83b,94g,102]

These unsaturated carbene derivatives belong to the cumulenylidene family $[M]{=}C({=}C)_n{=}CR^1R^2$ ($n > 0$) with $n = 1$, so the allenylidene moiety is formed by three carbon atoms constituting a linear σ-donor$-\pi$-acceptor double-bond chain. Experimental and theoretical studies[103] demonstrated that C_α and C_γ carbon atoms are electrophilic centers, while the C_β carbon atom is nucleophilic. To control the regioselectivity during the nucleophilic additions at C_γ, bulky or electron-donating properties or both of the auxiliary ligands are used, leading to α-alkynyl complexes.[89a,104] Although less common, neutral or nucleophilic allenylidene complexes can be protonated at C_β to give alkenylcarbyne compounds.[105] Posterior studies demonstrated that the reaction further continued in acid or thermally promoted conditions until the formation of the indenylidene counterpart.[106] These three reactive centers in the η^1-chain ligand allow the straightforward construction of organic skeletons, which would require a multistep preparation method in traditional organic synthesis. Thus, the extensive reactivity of allenylidene complexes has been shown in a wide range of reactions like the addition of neutral nucleophiles as alcohols, amines, or phosphines. The nucleophilic addition of an alcohol yields Fischer-type α,β-unsaturated alkoxycarbene derivatives of the general type $[Ru]^+{=}C(OR^1){-}CH{=}CR^2R^3$.[89a,107] The addition of primary or secondary amines to a cationic allenylidene ligand affords azoniabutadienyl, aminoallenyl, and azabutadienyl ruthenium species.[108] However, because of steric reasons, the addition of tertiary phosphanes takes place at the C_γ of the allenylidene group forming phosphonioalkynyl complexes that, subsequently, isomerize very slowly to afford the thermodynamically more stable phosphonioallenyl derivatives at ambient temperature.[109] Addition of anionic nucleophiles leading to neutral alkynyl complexes $[Ru]{-}C{\equiv}C{-}C(Nu)R^1R^2$[103c,110] and cyclization reactions by addition of organic molecules containing two nucleophilic heteroatoms and one electrophilic hydrogen atom were studied as well.[111] Additionally, in allenylidenes bearing a $-C_\gamma HRR'$ group, reactions of deprotonation can take place in the presence of a weak base to form ruthenium alkenyl acetylides.[105a,112] Regarding catalytic reactions, ruthenium allenylidene complexes have been improved considerably since in 1992 Trost and Flygare published the first ruthenium allenylidene system participating in a catalytic cycle.[113] These complexes have been used as catalysts or intermediates in catalysis, for instance, in dimerization of tin hydrides,[114] transetherification of vinyl ethers,[115] and hydrogen transfer reactions.[116] However, the largest and most important application is olefin metathesis reactions since Fürstner, Dixneuf, and co-workers reported for the first time the catalytic activity of a cationic arene allenylidene ruthenium complex, $[RuCl({=}C{=}C{=}CPh_2)(p\text{-cymene})(PR_3)][PF_6]$ ($PR_3 = PCy_3$, P^iPr). In RCM, these complexes are highly effective, exhibiting an activity comparable to the Grubbs-type alkylidene complexes known at that time.[102a] Eversince, this family of compounds has been gratifyingly used in skeleton rearrangement of enynes[102b,c,117] and ring-opening metathesis polymerization (ROMP).[102f,106,118] In addition, there are interesting cases related to green chemistry, for example, catalysts operating in ionic liquids, water-soluble catalysts, or heterogeneous catalysts.[83b,102l,m,119] More importantly, these complexes tolerate an array of functional groups like amides,[102a,d] sulfonamides,[102a,d,k] ketones,[102a,d] esters,[102k] ethers, silyl ethers, aryl halides, acetals, glycosides,[102a,d] fluorinated carbamate, and phosphonate groups,[120] even including unprotected secondary hydroxyl groups[102a,d] when performing as catalysts in olefin metathesis reactions. Moreover, they are quite robust compounds at high temperatures (80 °C), some of them being stable even after 32 h heating.[121] Worth noting is that in some cases they even lead to good yields in olefin metathesis reactions at room temperature.[102c]

The amphoteric character of ruthenium allenylidene complexes renders them versatile precursors for synthesis of organometallic compounds. Reversible protonation and deprotonation affords alkenylcarbyne and alkenyl acetylide ruthenium derivatives, respectively,[105a] with the possible further formation of the indenylidene analogue.[106,118b,c,122] Interesting are also the redox characteristics of ruthenium(II) allenylidenes.[123] For instance, in (bis)allenylidene complexes, the π-conjugated bridges afford the communication of electronic information between the metal centers, useful in materials science for electronic devices.[124] Moreover, optoelectronic applications as nonlinear optical materials and molecular wires are possible due to the interaction between the ruthenium metal and the allenylidene ligand upon electronic transitions.[87]

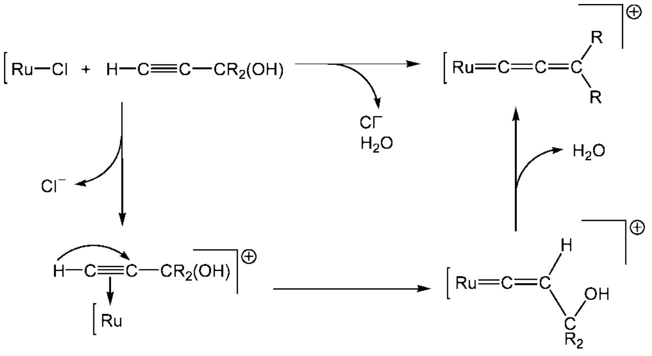
Focusing on the performance of these complexes as catalysts in olefin metathesis reactions, being the field with the most academic and industry interest, we here cover the topic of ruthenium allenylidene olefin metathesis catalysts up to present.

Table 4. RCM of α,ω-Diolefins Using Vinylidene Ruthenium Catalysts

Substrate ^{a}	Product ^{a}	Catalyst ^{b}	T (°C)	t (h)	Yield ^{c} (%)	Ref
		**82**	80	10	98	94a
		83b	60	2	76	94b
		83c	60	2	71	94b
		83d	80	24	69	94b
		**83b**	60	10	44	94b
		83c	60	10	34	94b
		85d	80	24	36	94b
		**55b**	60	96	64	72b
		**55b**	60	16	94	72b
		**83a**	60	1	92	94b
		83b, 83c	60	1	100	94b
		85a	80	10	98	94b
		85b	80	10	99	94b
		85c-85f	80	10	100	94b
		**83a**	60	1	96	94b
		83b, 83c	60	1	100	94b
		85a	80	10	97	94b
		85b	80	10	98	94b
		85c-85f	80	10	100	94b
		**55b**	60	24	90	72b
		**83a**	60	2	71	94b
		83b	60	2	90	94b
		83c	60	2	83	94b
		85c	80	24	72	94b
		85d	80	24	83	94b
		85e	80	24	67	94b
		85f	80	24	80	94b
		**55b**	60	3	99	72b
		**55b**	60	44	91	72b
		**83b**	60	2	89	94b
		83c	60	2	80	94b
		85c	80	24	70	94b
		85d	80	24	81	94b
		85f	80	24	75	94b

[a] E = COOMe. [b] The amount of catalyst precursors: 2 mol % (**55b**), 5 mol % (others). [c] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

Scheme 24



4.2. Synthesis of Ruthenium Allenylidenes Complexes

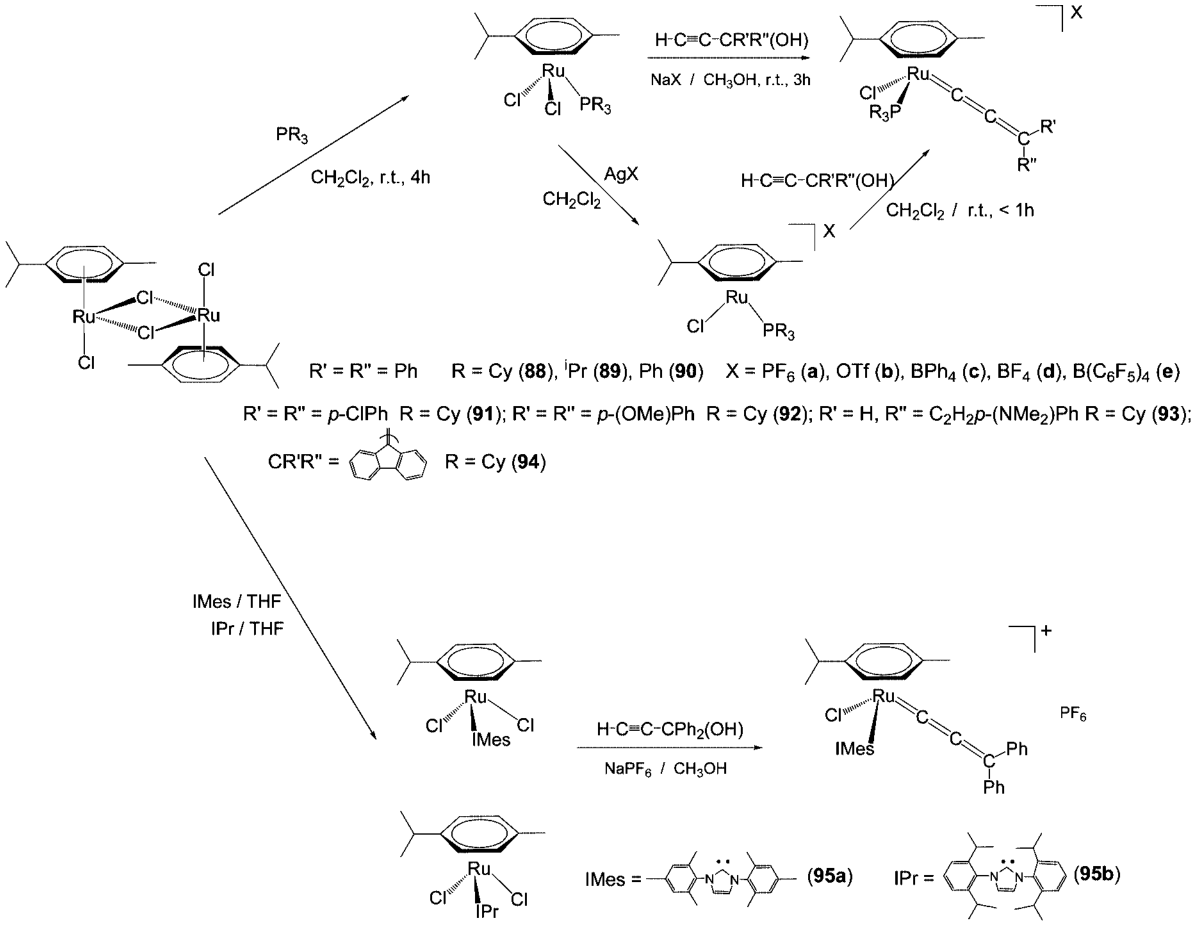
To date, ruthenium allenylidene complexes are most commonly prepared according to Selegue's procedure published as early as 1982.[101] This method comprises the reaction of propargylic alcohols or their derivatives with a suitable 16-electron Ru(II) complex to form the ruthenium−carbon double bond. From a mechanistic point of view, coordination of 2-propyn-1-ol to the metal center is followed by a metal-mediated π-alkyne-to-vinylidene tautomerization with subsequent spontaneous dehydration of the hydroxyvinylidene species generating the allenylidene ligand (Scheme 24).

The catalytically active family of arene ruthenium allenylidene complexes can be obtained either under protic or under aprotic conditions (Scheme 25). In both procedures, the air- and moisture-stable commercially available compound [(p-cymene)RuCl$_2$]$_2$ reacts with phosphine to give [(p-cymene)(PR$_3$)RuCl$_2$]. Under protic conditions, treatment of the monomeric species with propargyl alcohol in the presence of a sodium salt in MeOH at room temperature delivers the allenylidene compounds in high yields as violet powders. Likewise, [(p-cymene)(PR$_3$)RuCl$_2$] reacts with a Ag salt in aprotic media (CH$_2$Cl$_2$) to yield the stable cationic [(p-cymene)(PR$_3$)RuCl]$^+$X$^-$, which subsequently can be treated with propargylic alcohol to form the allenylidene ruthenium complex.[102a,d]

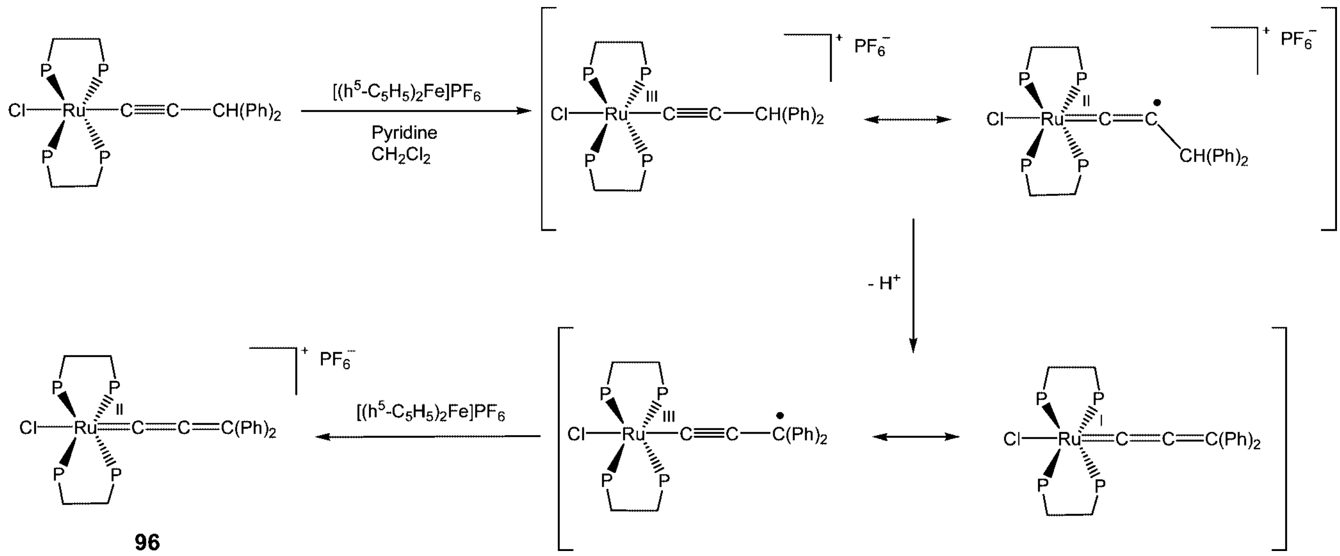
Similarly, this general procedure is also used to produce active arene ruthenium allenylidene complexes bearing N-heterocyclic carbene ligands. Thus, treatment of the Ru-dimer [(p-cymene)RuCl$_2$]$_2$ with IMes or IPr in THF at ambient temperature followed by a posterior reaction of the formed product with propargyl alcohol in the presence of NaPF$_6$ in MeOH generates NHC-bearing allenylidene species (Scheme 25).[121] Modification of the N-heterocyclic carbene or phosphine ligand, the allenylidene substituent, the counteranion, or the arene provides a wide structural variety of ruthenium allenylidene complexes.

An alternative preparative procedure toward allenylidene ruthenium complexes consists of a double oxidation mechanism of ruthenium acetylides carried out with 2 equiv of ferricinium salt in the presence of pyridine. Stabilization of the radical species on C$_\gamma$ allows for H$_\gamma$-elimination and subsequent oxidation to the desired allenylidene complex (Scheme 26).[125]

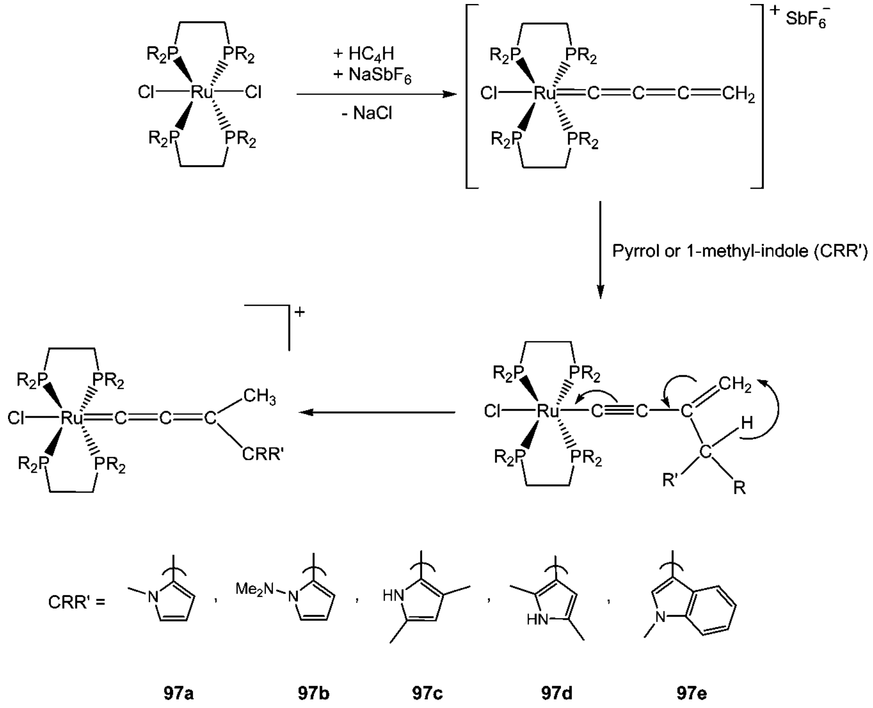
Scheme 25. Synthesis of Cationic Arene-Allenylidene-Ruthenium Complexes Bearing Phosphine or *N*-Heterocyclic Carbene Ligands



Scheme 26



Scheme 27



In addition, pyrrolyl- and indolyl-substituted allenylidene ruthenium complexes have been synthesized by reaction of a cationic primary butatrienylidene intermediate, [Cl(dppm)$_2$-Ru=C=C=C=CH$_2$]$^+$, with pyrrole and 1-methylindole, respectively.[126] The mechanism consists of a regioselective attack of the cumulated electrophile on the electron-rich heterocycle and posterior proton migration to the methylene group of the intermediate σ-complex (Scheme 27).

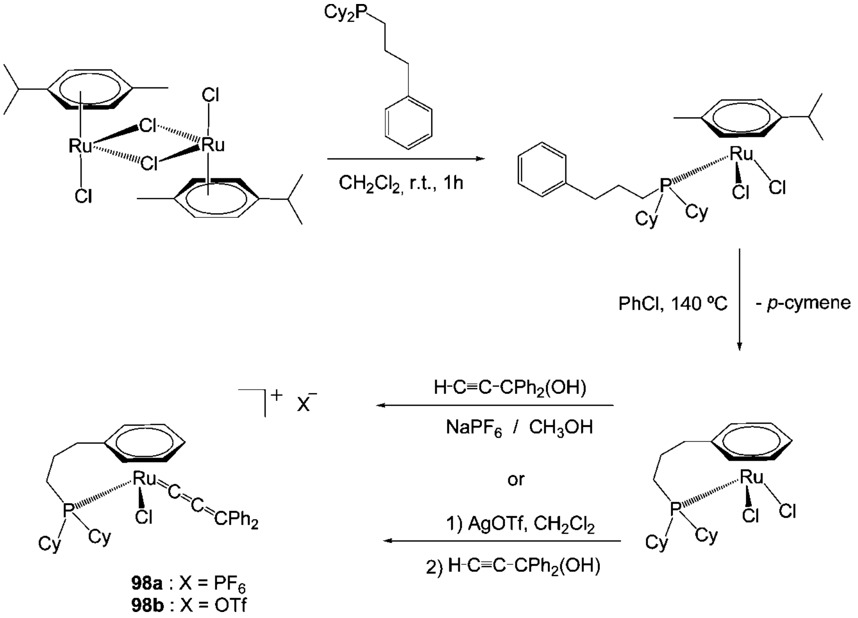
4.3. Ruthenium Allenylidene Complexes as Catalysts in Olefin Metathesis

4.3.1. Arene–Allenylidene–Ruthenium Precatalysts

In the search for enhanced activity and selectivity in olefin metathesis reactions, Dixneuf and Fürstner reported about ten years ago on the first 18-electron cationic allenylidene ruthenium complex of the type [(*p*-cymene)RuCl(=C=C=CR′$_2$)PR$_3$]$^+$X$^-$ and its olefin metathesis activity.[102a] Several studies[102a,c,d] proved that this family of compounds (see Scheme 25) represents a good alternative to alkylidene ruthenium catalysts for olefin metathesis reactions,[40b] constituting an unprecedented example of efficient allenylidene catalysts. Full characterization was presented for all compounds by means NMR, IR, and elemental analysis. In some cases, appropriate size and optical quality crystals were obtained for structural determination by single-crystal X-ray diffractometry. Thus, crystal structures of complexes **89a** and **98b** (see synthesis of this chelate complex in Scheme 28) were published and compared with the neutral arene bischloride ruthenium complex [(η^6-C$_6$H$_5$-(CH$_2$)$_3$-PCy$_2$)RuCl$_2$] and cumulene complexes in CSD (Cambridge Structural Database).[102d]

4.3.1.1. Catalytic Activity in Ring-Closing Metathesis (RCM). Catalytic activity of the cationic 18-electron alle-

Scheme 28. Synthesis of the Chelate Allenylidene Ruthenium Complexes 98a and 98b



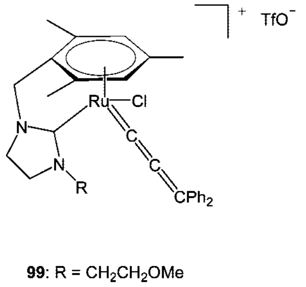
nylidene complexes **88a**, **89a**, and **90a** (see Scheme 25) was first tested in RCM of *N*,*N*-diallyltosylamide to compare the effect of the different phosphine ligands. As can be concluded from results summarized in Table 5 (entries 1−3), catalyst efficiency increases in the case of stronger electron-donating phosphines, $PCy_3 > P^iPr_3 \gg PPh_3$, which is in good agreement with the literature.[25b,40b,127] Due to its better performance, **88a** was subsequently studied in a wide variety of RCM reactions aiming at the formation of various ring sizes and proved to be particularly effective in the macrocyclic series (Table 5), which constitute good mimics for natural products. For instance, the disaccharide formed in excellent yield (entry 36, Table 5) is a pseudointermediate for the synthesis of tricolorin A, a cytotoxic glycoside against human breast cancer.[128]

RCM of *N*,*N*-diallyltosylamide as a model reaction was also selected to study the influence of the counterion on the catalytic activity of these arene complexes. From these results (entries 1, 4−8; Table 5), it can be deduced that reactivity and selectivity are strongly dependent on the counterion, which even in some cases determines the production of byproduct due to collateral isomerization reactions, thus decreasing the yield of the desired ring-closed product (entries 7, 8; Table 5). To mitigate this effect, the addition of selected Lewis or Brönsted acids, for example, $BF_3 \cdot Et_2O$, $HBF_4 \cdot Et_2O$, and F_3CSO_3H, were demonstrated to be highly effective, almost completely eliminating the cycloisomerization reaction. This effect was first explained by the easy decoordination of the phosphine ligand when the P atom reacts with the acid additive to generate the coordinatively unsaturated catalytically active species. However, in the case of strong Brönsted acids, posterior studies demonstrated a most plausible mechanism based on the acid-promoted rearrangement of the allenylidene into the indenylidene followed by decoordination of the η^6-arene ligand.[106] Surprisingly, in the case of **88b** ($^-$OTf as counterion ligand), the RCM reaction could be perfectly performed at ambient temperature, being the first and only example of allenylidene complexes in this regard. When the same RCM reaction was tested using arene ruthenium complexes bearing different substituents in the allenylidene moiety, the influence of the counterion is dramatically correlated with the efficiency and selectivity of the catalyst (entries 9−13, Table 5). Likewise, the RCM reaction in presence of **88a** is accelerated by exposure to UV or neon light.[102b,h] However, enhanced results and stability could not be obtained with chelate complexes **98a** and **98b** (Table 5).

Other important compounds in medicinal chemistry are the α-aminophosphonates and the six- and seven-membered cyclic derivatives, especially when they contain a CF_3 group in the α-position to the phosphonate. As listed in Table 5 from entries 37−40, **88b** was again applied as an *in situ* catalyst for the RCM of various α-aminophosphonates in toluene at 80 °C, gratifyingly giving good results.[120]

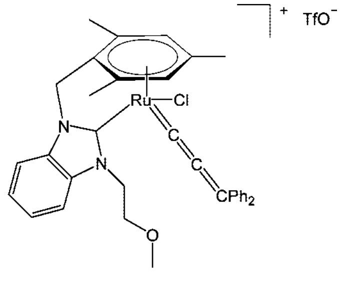
In 2003, Dixneuf and co-workers presented the synthesis and catalytic RCM activity of three chelated η^6-arene,η^1-carbene allenylidene ruthenium complexes (Figure 11).[129]

These compounds were prepared by the typical procedure from the corresponding chelated η^6-arene,η^1-carbene counterpart. To do so, the complexes **99**−**101** were obtained by the displacement of the arene promoted by the 2,4,6-trimethylbenzyl ring of the first coordinated imidazolinylidene or benzimidazole moieties reacting with the dimer $[RuCl_2(arene)]_2$. The obtained compounds were characterized by means of ^1H NMR and IR spectroscopy and comparison with previous known analogous allenylidene ruthenium complexes. However, isolation was not possible due to rapid decomposition. Thus, the catalytic activity was tested with complexes generated *in situ*. From the results listed in Table 6, it can be concluded that the *in situ* generated complex **99**



99: R = CH2CH2OMe

100: R = CH2Mes



101

Figure 11.

Table 5. RCM Reactions Using Arene Allenylidene Ruthenium Complexes As Catalysts

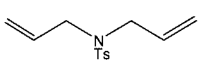
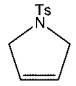
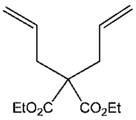
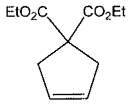
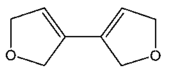
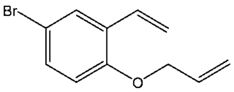
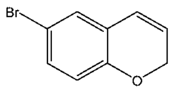
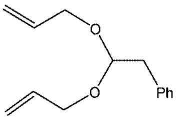
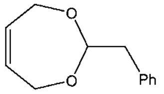
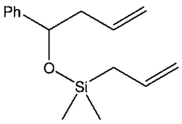
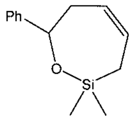
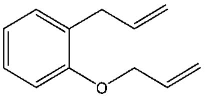
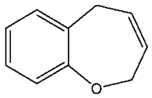
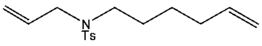
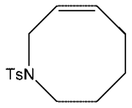
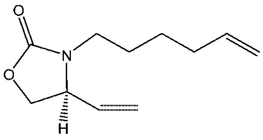
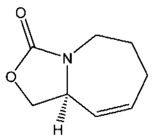
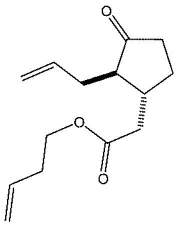
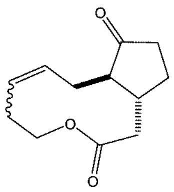
Substrate	Closed-Product	Entry	Cat.	t (h)	T (°C)	Yield (%)	TON	Ref
		1	**88a**	5	80	95	38	102d
		2	**89a**	3	80	66	26	102d
		3	**90a**	3	80	2	0.8	102d
		4	**88b**	5	80	99	40	102d
		5	**88b**	19	20	90	36	102d
		6	**88c**	5	80	91	36	102d
		7	**88d**	5	80	31^b	12	102d
		8	**88e**	5	80	23^b	9.2	102d
		9	**91b**		80	46^b	18	102d
		10	**91d**		80	90^c	36	102d
		11	**92b**		80	85^c	34	102d
		12	**93d**		80	60^b	24	102d
		13	**94d**		80	56^b	22	102d
		14	**98a**	2	80	89	18	102d
		15	**98b**	1	80	92	18	102d
		16	**95a**	27	40	85^d	17	
		17	**88a**		80	86	17-34	102d
		18	**88a**		80	93	19-37	102d
		19	**88**	16	80	93	19	102d
		20	**88a**		80	88	18-35	102d
		21	**98a**	5.5	80	88	18	102d
		22	**88a**		80	77	15-31	102d
		23	**88a**		80	86	17-34	102d
		24	**88a**	2	80	86	17	102d
		25	**98b**	3	80	88	18	102d
		26	**88a**		80	75	15	102d
		27	**88a**		80	66	13-26	102d
		28	**88a**	72	80	30^c	3	102d
		29	**88b**	150	80	47^c	4.7	102d
		30	**88a**		80	40	8	102d

Table 5. Continued

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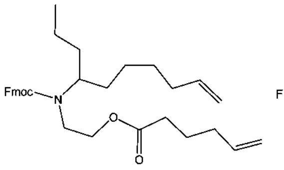
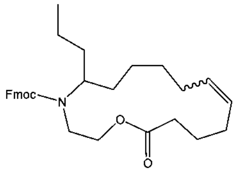
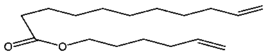
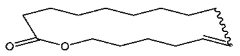
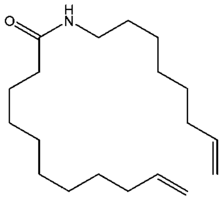
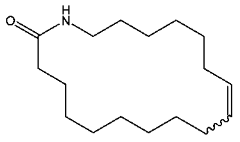
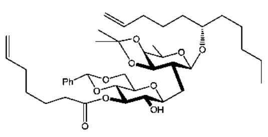
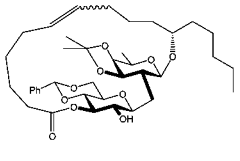
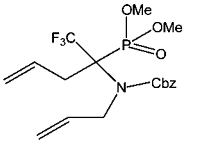
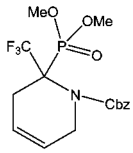
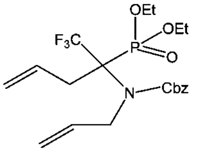
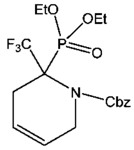
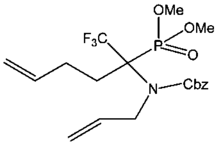
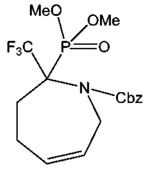
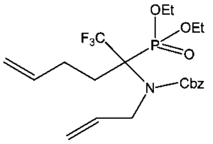
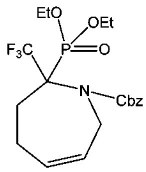
		31	**88a**		80	79	16-32	102d
		32	**88a**	41	80	79	16	102d
		33	**88a**		80	90	18	102d
		34	**88b**	12	80	83	17	102d
		35	**88a**		80	73	15	102d
		36	**88a**		80	85	17	102d
		37	**88b**	6	80	65[e]	6.5	102d
		38	**88b**	6	80	69[e]	6.9	102d
		39	**88b**	6	80	70[e]	7	102d
		40	**88b**	6	80	61[e]	6.1	

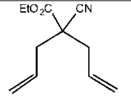
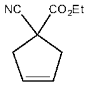
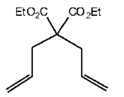
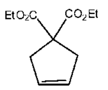
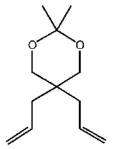
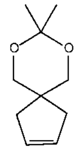
[a] Catalyst loading (2.5−5 mol %) in toluene. [b] Together with the cycloisomerization product and isomerized starting material. [c] Together with the cycloisomerization product. [d] Solvent CD_2Cl_2. [e] Catalyst loading 10 mol %.

displays high activity and selectivity in some RCM reactions, with a strong influence of the diene and the solvent. In case of complexes **100** and **101**, only cycloisomerization products were observed.

Other types of arene allenylidene ruthenium-based systems containing an *N*-(2,4,6-trimethyl-benzyl)benzimidazole ligand (Figure 12) were tested *in situ* for RCM of *N*,*N*-diallyltosylamide. However, no sign of metathesis activity was observed and high percentages of cycloisomeric products were found.[130]

RCM of diethyl diallylmalonate in CD_2Cl_2 at 40 °C using "2nd generation" catalyst **95a** (see Scheme 25) resulted in

Table 6. ROMP Reactions Catalyzed by 99 at 80 °C

Substrate	Product	Solvent	t (h)	Yield (%)	TON	Ref.
		ClPh	5	67	27	129
		CH_3Ph	6	94	38	129
		ClPh	5	87	35	129
		CH_3Ph	5	8	3.2	129
		ClPh	5	-	-	
		CH_3Ph	5	12	4.8	129

high yield (85%) (entry 16, Table 5), which was higher compared with the nonallenylidene analogues under the same conditions.[121]

4.3.1.2. Catalytic Activity in RCM of Enyne Derivatives. The easy one-step preparation by RCM reaction of enyne derivatives lead to useful optically active and Diels–Alder dienes like vinyl-2,5-dihydrofurans. For further investigation on the catalytic activity of cationic 18-electron arene allenylidene ruthenium-based systems, several reactions of this type were tested with a number of catalysts.[102b,c,106] Comparing different reaction conditions, it is clear that a photochemical preactivation considerably increases the reaction rate (entries 1 and 2, Table 7). UV irradiation induced decoordination of the arene ligand to form a highly unsaturated catalytically active species holds as the most plausible explanation for the photoactivation event.

Remarkably, the most active catalyst **88b** with $^{-}$OTf as counterion afforded complete conversion after only 3 h without previous photochemical activation (entry 1, Table 7). Curiously, even a higher conversion was reached when one of the phenyl groups of the allenylidene moiety was replaced by a methyl group (entry 6, Table 7).[106]

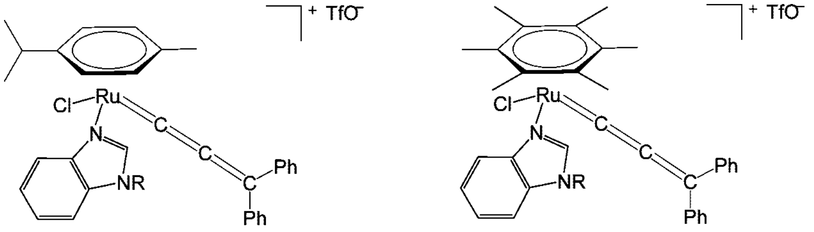
4.3.1.3. Catalytic Activity in Ring-Opening Metathesis Polymerization. In 2002, Dixneuf and co-workers studied for the first time the catalytic performance of the triflate salt **88b** in ROMP reactions of norbornene and cyclooctene (Table 8).[118a] In the case of polymerization of norbornene, a medium yield was reached using *in situ* **88b** at 60 °C. Addition of $N_2CHSiMe_3$ leads to higher yield but also to higher polydispersities. However, polydispersity could be lowered using a more concentrated solution of the pure complex **88b** at ambient temperature. Regarding the cyclooctene polymerization executed by *in situ* formed **88b**, photochemical activation was necessary to yield good performance of this catalyst, whereas isolated **88b**, even with a higher cyclooctene/catalyst ratio, gives quantitative yield and a narrow polydispersity even at room temperature.

One year later, the same group reported on studies supporting the intramolecular rearrangement of the allenylidene into the indenylidene derivative promoted by acid or thermal activation.[118b,c] The first observation was made when an arene allenylidene ruthenium complex was used for the polymerization of cyclooctene with a strong acid. This intramolecular rearrangement led to significantly enhanced TOF values (by 3 orders of magnitude) in remarkably reduced reaction times from 15 h to only a few minutes (Table 9).[118b]

The comparison of different applied catalysts afforded the conclusion that either the less electron-donating phosphine PPh_3 (**90b**) or electron-releasing groups in the aromatic rings of the allenylidene moiety (**92b**) notably reduced the catalytic activity.

Subsequently, other olefin metathesis reactions were evaluated using the catalytic system formed by an arene allenylidene ruthenium complex and the acidic cocatalyst. In the polymerization of cyclopentene, much better results were obtained compared with the commercially available alkylidenes $RuCl_2({=}CHPh)(PCy_3)_2$ and $RuCl_2({=}CHPh)(PCy_3)(H_2IMes)$, even at 0 °C. Furthermore, this *in situ* generated indenylidene catalyst behaved as a highly active system in the acyclic diene metathesis (ADMET) of 1,9-decadiene and RCM of diallyltosylamide and allylpropargylamide.

The activation mechanism of the allenylidene precursors was finally established after the direct observation of the allenylidene-to-indenylidene rearrangement and reaction rates studies by means of NMR spectroscopy. The mechanism was thus understood in terms of a rearrangement, generation of active species, and propagation sequence.[106] To generate active species, the decoordination of one ligand is essential to afford a vacant site for the coordination of the substrate with the metallic center. As shown above, the catalytic activity of arene allenylidene ruthenium-based systems depends on the nature of the phosphine, supporting the thesis that this ligand remains coordinated during the propagation. Additionally, the *p*-cymene ligand is weakly bound to the

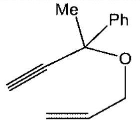
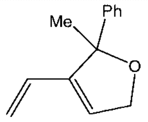
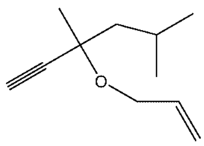
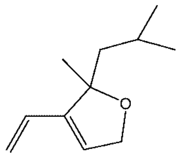
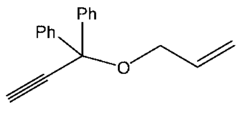
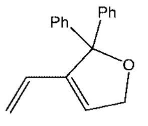
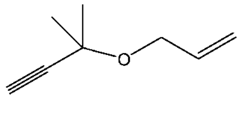
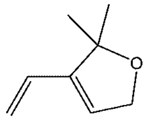
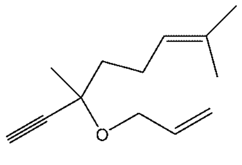
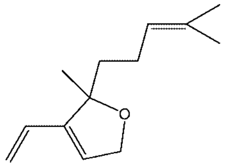
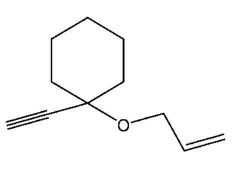
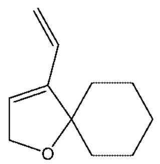
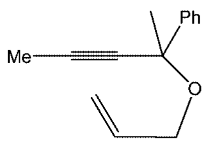
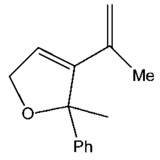


R = *i*Pr (**102a**)
R = *n*Bu (**102b**)
R = CH_2CH_2OMe (**102c**)
R = CH_2-(2,4,6-$Me_3C_6H_2$) (**102d**)

R = *n*Bu (**103a**)
R = CH_2CH_2OMe (**103b**)
R = CH_2-(2,4,6-$Me_3C_6H_2$) (**103c**)

Figure 12.

Table 7. RCM Reactions of Ene−Ynes in the Presence of 88a, 88b, and 104 Catalysts

Entry	Substrate	Closed-Product	Catalyst	t (h)	Isolated Yield	Conversion	TON
1			**88a**	4[a]	84%		34
			88a	24[b]	77%		31
			88b	3[b]	82%		33
2			**88a**	1[a]	62%		25
			88a	6.5[b]	65%		26
3			**88a**	23[a]	67%		27
4			**88a**	63[c]	41%		16
5			**88a**	1[a]	74%		30
6			**88a**	1[a]	63%		25
			88b	3		70% (115)	28
			104	3		85% (115)	34
7			**88a**	24[a]	83%		33

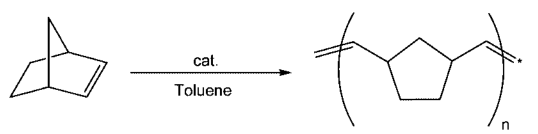
[a] General conditions: photochemical activation (Hg lamp, 300 nm) in toluene at ambient temperature for 30 min using 2.5 mol % catalyst and subsequent heating at 80 °C until full conversion. [b] General conditions: no previous activation with UV irradiation; toluene, 2.5 mol % catalyst loading, and heating at 80 °C until full conversion. [c] UV irradiation followed by reflux in CH_2Cl_2. **104** = [(η^6-*p*-cymene)RuCl{=C=C=C(Me)Ph}(PCy_3)]OTf.

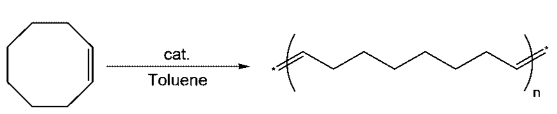
metal center and decoordinates more easily, as previously described in the photochemically promoted activation process. In addition, the free arene has been observed at the initial moment of the reaction using ^1H NMR and GC. From all these indications, it follows that the sterically hindered indenylidene ligand promotes the dissociation of the *p*-cymene more than the allenylidene counterpart. The highly unsaturated 12-electron species formed has to be stabilized by a counterion, which explains the striking correlation between the activity and the nature of the counterion. Finally, the catalytically active species generated begins the Chauvin cycle for olefin metathesis.

4.3.2. Octahedral and Pentacoordinated Allenylidene Ruthenium Complexes

Nolan and co-workers reported in 1999 the first ruthenium allenylidene complex with a 16-electron metal center configuration, $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$ (**106**), and its analogue bearing an *N*-heterocyclic carbene ligand, $(PCy_3)(IMes)Cl_2Ru(=C=C=CPh_2)$ (**107**) (Figure 13).[102e] The first one can be synthesized using the Selegue method by reaction of [(*p*-cymene)$RuCl_2$]$_2$ or $(PPh_3)_4RuCl_2$ with 3,3-diphenylpropyn-3-ol in presence of 2 equiv of PCy_3. The "second generation" complex was obtained by simple exchange of one PCy_3 ligand with IMes. Both complexes were entirely

Table 8. ROMP Reactions Catalyzed by *in Situ* 88b and Pure Isolated 88b





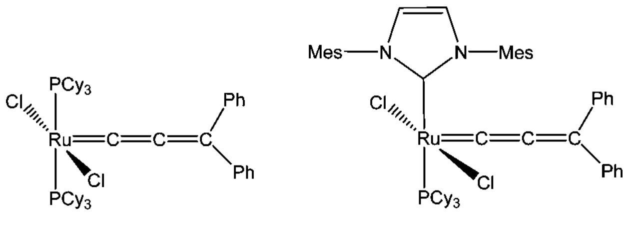
Catalyst	Yield (%)	TON	M n./cat.	t	T(°C)	PDI	Yield (%)	TON	M c./cat.	t	T(°C)	PDI
In situ **88b**	35	105	300 [b]	4 h	60	2.7	12 99	18 149	150 [d] 150 [d]	2 h [e]	r.t. r.t.	- 1.8
88b [a]	90	270	300 [b]	4 h	60	3.4						
Pure **88b**	90	900	1000 [c]	5 min	r.t.	1.8	95 90	950 900	1000 [c] 1000 [c]	15 h 5 min	r.t. 80	1.9 1.4

[a] *in situ* **88b** + $N_2CHSiMe$. [b] 1.5×10^{-5} mol of catalyst. [c] 4.5 mol $\times 10^{-6}$ mol of catalyst. [d] 3×10^{-5} mol of catalyst. [e] 2 h rt + 2 h rt/UV. *n* = norbornene, cat. = catalyst, c. = cyclooctene.

Table 9. ROMP of Cyclooctene in Toluene at Ambient Temperature

entry	catalyst	acid	$M_{\text{cyclooctene/cat.}}$	*t*	PDI[b]	yield (%)	TOF[c]
1	**88b**		1000	15 h	1.9	95	63
2	**88b**	HBF_4 (5 equiv)	1000	1 min	1.7	92	55200
3	**88b**	CF_3SO_3H (5 equiv)	1000	1 min	1.6	95	57200
4	**88b**	CF_3SO_3H (5 equiv)	10000	5 min	1.5	97	116400
5	**88b**	CF_3SO_3H (100 equiv)	100000	5 min	1.4	88	1096000
6	**90b**	CF_3SO_3H (5 equiv)	10000	10 min	1.8	73	43800
7	**92b**	CF_3SO_3H (5 equiv)	10000	8 h	1.9	25	312
8	**105**[a]	CF_3SO_3H (5 equiv)	10000	5 min	1.6	92	110000

[a] **105** = [RuCl(η^6-1,2,4,5-tetramethylbenzene)(=C=C=CPh_2)(PCy_3)]. [b] PDI = polydispersity index, M_w/M_n. [c] TOF = turnover frequency in moles per hour. Cat. = catalyst.



106 **107**

Figure 13.

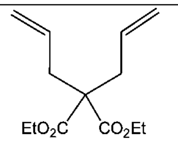
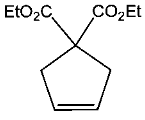
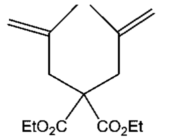
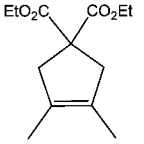
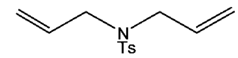
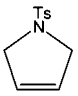
characterized by X-ray diffractometry as square-pyramid structures with the allenylidene moiety occupying the apical position.

The two molecules show very similar Ru−C_α, C_α−C_β, and C_β−C_γ bonds, the first one being in the normal range found for related 16-electron Ru complexes and the other two bonds being also typical distances for allenylidene ruthenium carbenes. However, these bond lengths are much shorter than the ones in the 18-electron allenylidene Ru complexes indicating a stronger link to the metallic atom. Evaluation of the two coordinatively unsaturated 16-electron allenylidene ruthenium complexes in RCM reactions (Table 10) clearly demonstrates a low catalytic activity compared with 18-electron arene allenylidene ruthenium catalysts,[102a] possibly due to the stronger allenylidene moiety bonds in these 16-electron complexes.

In an attempt to find different but useful catalysts for olefin metathesis reactions, a cationic allenylidene ruthenium bearing two hemilabile phosphine ligands, [RuCl(C=C=CPh_2)(κ^2-*P*,*O*-$Cy_2PCH_2CH_2OCH_3$)$_2$]PF_6, was synthesized by Werner and co-workers.[131] The complex was fully characterized by NMR, IR spectroscopy, FAB-MS, and X-ray diffractometry. The catalytic performance of the complex was studied. However, its performance as metathesis catalyst toward ROMP of cyclooctene and RCM of *N*,*N*-diallyltosyl amide was not competitive with the cationic Dixneuf−Fürstner complex [(*p*-cymene)RuCl(=C=C=CPh_2)(PCy_3)]$^+$, since contrary to the total release of the arene ligand only partial dissociation of the chelating ligand occurs, consequently inhibiting diene coordination to the metal center.

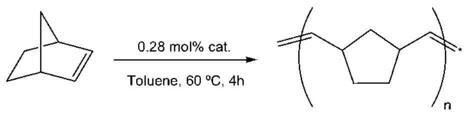
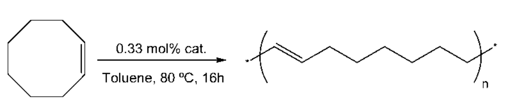
In 2002, Dixneuf and co-workers published the first examples of active allenylidene ruthenium catalysts for ROMP. The family of compounds is constituted by the neutral $RuCl_2$(=C=C=CPh_2)(PCy_3)(dmso)$_2$ (**108**) and $RuCl_2$(=C=C=CAr_2)(PCy_3)$_2$(dmso) [Ar = Ph (**109**), *p*-C_6H_4F (**110**), *p*-C_6H_4Cl (**111**), *p*-C_6H_4OMe (**112**)] and by the cationic derivatives [$RuCl_2$(=C=C=CPh_2)(PCy_3)(dmso)$_2$]OTf (**113**) and [$RuCl_2$(=C=C=CPh_2)(PCy_3)$_2$(dmso)$_2$]OTf (**114**).[102f] All of them were easily obtained from $RuCl_2$(dmso)$_4$ according to the Selegue protocol[101] using AgOTf for the successful formation of the cationic precatalysts. The presence of the allenylidene carbene ligand was evidenced from the characteristic signals corresponding to the C_α, C_β, and C_γ in the allenylidene moiety using ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy. Polymerization of

Table 10. RCM Reactions in Presence of $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$ and $(PCy_3)(IMes)Cl_2Ru(=C=C=CPh_2)$[a]

Entry	Substrate	Closed-Product	Catalyst	Solvent	T (°C)	Yield (%)	TON
1			**106**	CD_2Cl_2	40	12	2.4
			107	CD_2Cl_2	40	8	1.6
2			**106**	CD_2Cl_2	40	4	0.8
			107	CD_2Cl_2	40	0	0
3			**106**	toluene-d_8	80	0	0
			107	toluene-d_8	80	0	0

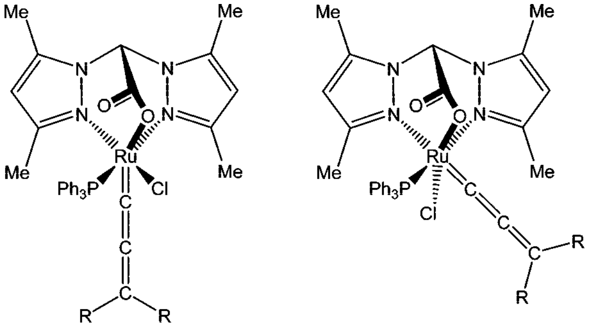
[a] Catalyst loading (5 mol %), diene (0.1 mmol).

Table 11. ROMP Reactions Catalyzed by 109 and 111−114

										
Catalyst	Yield (%)	TON	Mw ($1x10^{-3}$)	Mw/Mn	% *cis*	Yield (%)	TON	Mw ($1x10^{-3}$)	Mw/Mn	% *cis*
109	70	250	149.5	3.97	15	90	273	133.6	1.89	69
111	22	79	66.1	17.0	13	20	61	133.5	1.89	
112	56	200	66.1	15.9		65	197	173.3	1.81	60
113	80	286	53.3	20.0		10	30	70.0	1.68	
114	96	343	73.1	45.2	52	92	279	57.0	1.56	54

norbornene and cyclooctene, selected as metathesis benchmark reactions to depict the catalytic performance of some of these allenylidene complexes, gratifyingly showed that most of them led to desirable yields with the best results found for the cationic complex **113** and the neutral compounds **109** and **112** (considering a good compromise for yield, molecular weight, polydispersity, and percentage of *cis*-CH=CH) (Table 11). From these results, it is evident that electron-donating groups in the aromatic ring, increasing the electron density of the allenylidene moiety, enhance the catalytic activity.

Two isomer couples of ruthenium allenylidene complexes bearing the κ^3-(*N*,*N*,*O*)-heteroscorpionate ligand bis(3,5-dimethyl-pyrazol-1-yl)acetato (bdmpza) were described in 2006 (Figure 14).[88a,108c] The characterization using IR and NMR spectroscopy not only indicated the presence of the allenylidene moiety [$\nu(C=C=C) \approx 1918\ cm^{-1}$ and typical signals of C_α, C_β, and C_γ on ^{13}C NMR] but also could distinguish between the type of isomer with the chloro or the allenylidene ligand in *trans* position to the carboxylate donor. Moreover, ROESY-NMR spectra allowed for distinguishing between the different methyl groups of the heteroscorpionate ligand. Finally, the structure determination by X-ray crystallography of the complexes containing phenyl groups linked to C_γ on the allenylidene carbene ligand was described in detail. However, when these compounds were applied in RCM of diethyl diallylmalonate, they unfortunately exhibited no activity.

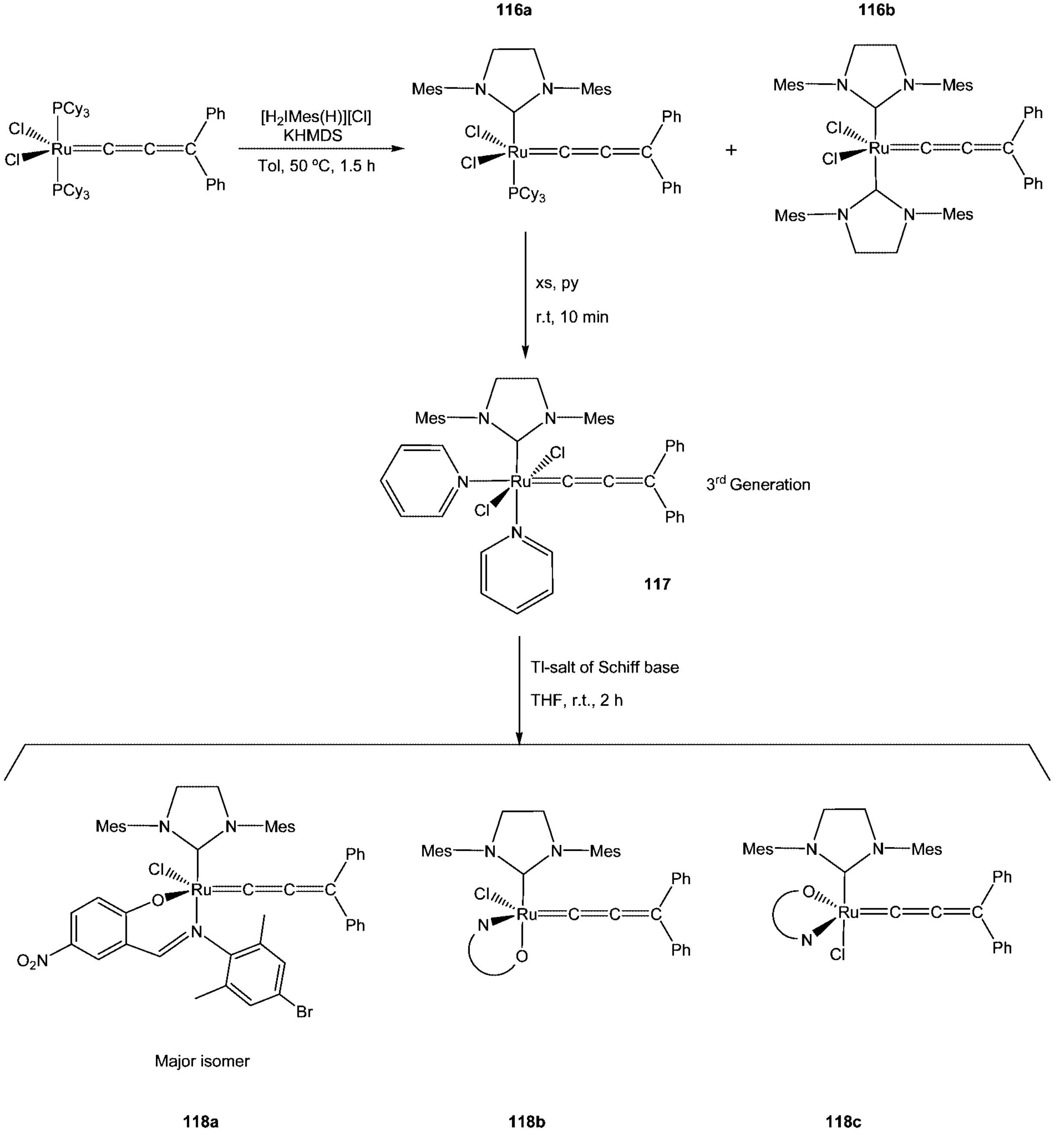


R = Ph, ClPh

115a **115b**

Figure 14.

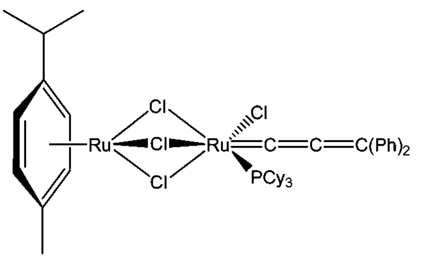
Scheme 29



Recently, our group has published several "second and third generation" allenylidene ruthenium complexes and studied their catalytic behavior, comparing them with other allenylidene and benzylidene catalysts.[94g] Similarly to the NHC-containing allenylidene complex of Nolan,[102e] the SIMes analogue was prepared from the bisphosphine derivative (Scheme 29).

Mono(NHC) complex $(PCy_3)(SIMes)Cl_2Ru(=C=C=CPh_2)$ (**116a**) was well characterized by NMR spectroscopy and X-ray diffractometry, the latter technique showing a slightly distorted square-pyramidal structure the C_γ of the allenylidene ligand being at the apex. All the bond lengths and angles in the Ru coordination sphere were quite similar to those in complexes reported by Nolan, $(PCy_3)_2Cl_2Ru(=C=C=CPh_2)$ (**106**) and $(PCy_3)(IMes)Cl_2Ru(=C=C=CPh_2)$ (**107**). Only Ru−P was shorter in **116a** probably due to the more electron-donating capacity of SIMes in respect to IMes. Tested as catalyst in the ROMP of cycloocta-1,5-diene (COD) and the RCM of diethyl diallylmalonate, the newly described complex was found to be more active than the "first and second generation" vinylidene analogues.

The straightforward reaction from complex **116a** with an excess of pyridine led to the "third generation" related complex (**117**). Subsequently, the NHC−bis(pyridine)-bearing complex **117** reacted with a Schiff base Tl-salt decoordinating the two pyridines to associate the Schiff base as a chelating ligand and forming three isomers (**118a**−**c**). The major isomer (**118a**) was isolated and characterized by means of NMR spectroscopy. When the "third generation" allenylidene complex (**117**) and the major Schiff base isomer (**118a**) were studied in ROMP of COD, both of them performed as good catalysts, being considerably more efficient than the "first and second generation" allenylidene analogues (**116a**,**b**). In contrast, no robust catalytic activity was displayed in RCM of diethylallylmalonate. Compared with Grubbs benzylidene complexes, the allenylidene com-



119

Figure 15.

pounds prepared by Verpoort et al. behaved as less efficient catalysts but still displayed more economical and simple preparation method advantages. Curiously, the formation of an alkenylcarbyne Ru complex was observed when a suitable acid was added to the isomer, causing a decrease in the catalytic activity compared with its benzylidene counterpart. The carbyne intermediate was also detected in some of the Dixneuf and Castarlenas complexes in the rearrangement of allenylidenes into indenylidene derivatives.[106,118b] To prevent this carbyne formation, non-hydrogen-containing Lewis acids, for example, $PhSiCl_3$, were found to be excellent activating additives, significantly enhancing the TON.

4.3.3. Homobimetallic, Heterobimetallic, and Polymetallic Ruthenium Allenylidene Complexes

Starting from the easy to handle and commercially available $[RuCl_2(p\text{-cymene})]_2$ dimer that affords $[(p\text{-cymene})Ru(\mu\text{-Cl})_3RuCl(PCy_3)(\eta^2\text{-}C_2H_4)]$ under ethylene atmosphere, the homobimetallic ruthenium allenylidene complex $[(p\text{-cymene})Ru(\mu\text{-Cl})_3RuCl(PCy_3)({=}C{=}C{=}CPh_2)]$ (**119**) (Figure 15) was further obtained by the general procedure developed by Dixneuf.[102d]

This new complex was well characterized by IR spectroscopy ($\nu_{C=C=C}$ = 1918 cm^{-1}), ^{1}H NMR, and ^{13}C NMR spectroscopy [three allenylidene carbon atoms at $\delta = 301.5$ (C_α), 237.3 (C_β), and 147.1 (C_γ); moreover, showing equivalents phenyl groups in both spectra]. The catalytic performance of this complex was studied in several olefin metathesis reactions showing only some activity in the ROMP of cyclooctene (48% polymer yield). However, the catalyst failed for the RCM of diethyl diallylmalonate and the CM with ethylene. The substantially higher results obtained with the addition of an acid has been explained as the *in situ* rearrangement of the allenylidene into the indenylidene derivative.[102g] In 1999, Fürstner and Hill already published the RCM study of this homobimetallic complex.[102h] However, later investigations revealed that the final products formed were actually Ru-phenylindenylidene compounds but not the allenylidene analogues.[102i,j]

In 2002, Moïse and co-workers published a series of heterobimetallic allenylidene titanium−ruthenium complexes as possible catalysts for ring-closing metathesis.[102k] The general molecular structure of these four complexes is shown in Scheme 30.

The heterobimetallic compounds were prepared *in situ* to prove their catalytic activity in RCM of *N*,*N*-diallyltosylamide. Although no sign of reaction was found with the first three complexes (**122a**−**c**), the cationic Ti−Ru analogue **122d** quantitatively attained ring-closed product in toluene at 80 °C after only 1 h (Table 12). This difference of catalytic performance appeared to be dependent on the phosphine nature and on the length of the alkyl chain between metallic centers. More types of RCM reactions were studied with **122d** catalyst obtaining significantly good results (Table 12).

One year later, in 2003, Dixneuf and Weiss reported the synthesis and characterization of two trisallenylidene ruthenium complexes as possible catalyst initiators for olefin metathesis reactions (**123**, **124**; Figure 16).[84b] Both of them were prepared by the general procedure[102d] from the reaction between the previously synthesized propargylic alcohol

Scheme 30. Synthesis of the Ti−Ru Allenylidene Complexes 122a−d Following the Dixneuf and Fürstner Procedure[102d]

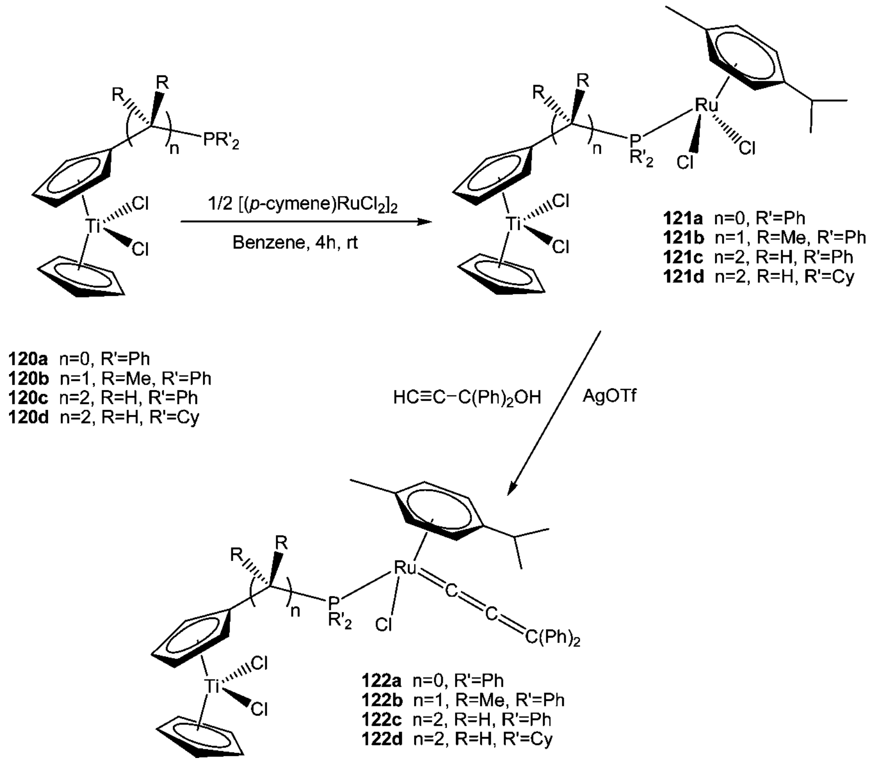
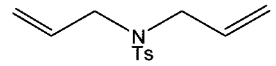
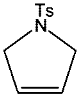
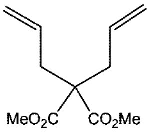
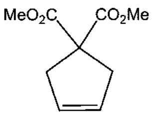
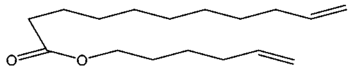
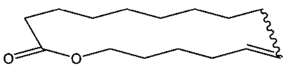
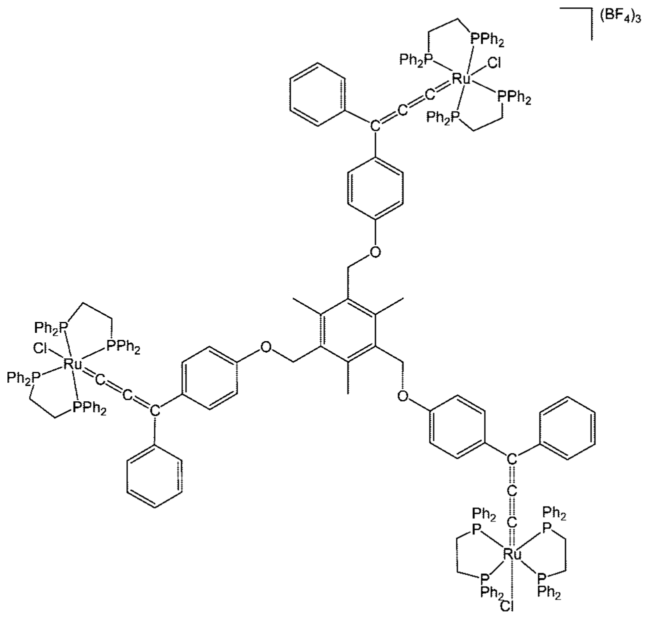


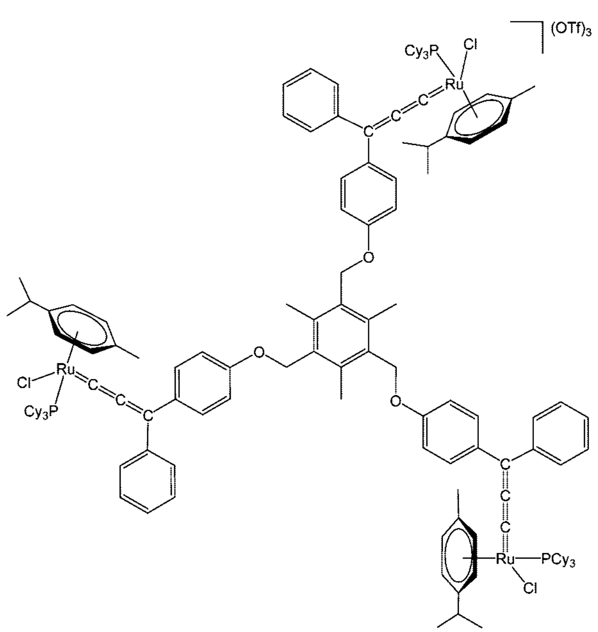
Table 12. RCM Reactions Catalyzed by *in Situ* Generated 122d

Entry	Substrate	Closed-Product	Catalyst loading	Solvent	T (°C)	Yield (%)	TON
1			2.5	Toluene	80	98[a]	39
2			2.5	Toluene	80	63	25
3			5	CH_2Cl_2	reflux	89	18

[a] Less than 10 min.



123



124

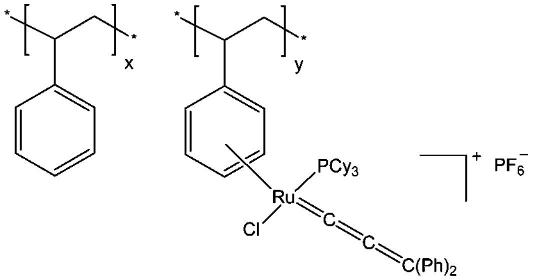
Figure 16.

C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)-PhC(OH)C≡CH]$_3$ and [RuCl(dppe)$_2$]BF_4 or [RuCl(PCy_3)(*p*-cymene)]OTf. Full characterization was carried out by means of ^1H and ^{13}C NMR and IR spectroscopy and subsequent comparison with the respective mononuclear ruthenium complex.

4.4. Green Catalysis of Allenylidene Ruthenium Complexes

4.4.1. Polymer-Supported Arene Ruthenium Allenylidene Complexes

Polymer-supported catalysts are designed to obtain very low or even zero contamination levels in the products, allowing a good recyclability and low-cost procedures. The immobilized catalyst published by Akiyama and Kobayashi[102l] was prepared by the general Selegue method improved by Dixneuf and Fürstner for arene ruthenium allenylidene complexes[102a,d] using the immobilized catalyst [(arene)RuCl$_2$(PR$_3$)]. Benzene rings of polystyrene were used to coordinate the Ru-complex and support the catalyst (Figure 17).

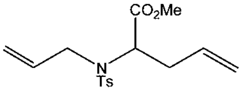
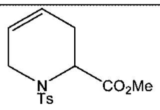
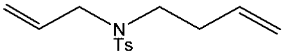
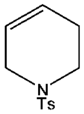
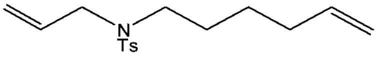
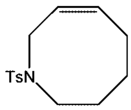
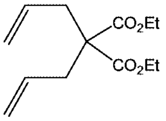
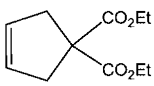
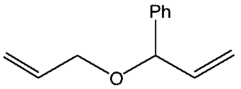
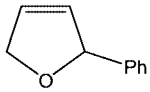
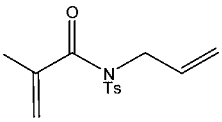
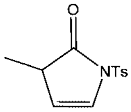


125

Figure 17.

Gratifyingly, the new immobilized arene ruthenium allenylidene catalyst was capable of promoting efficient metathesis transformations (Table 13). Moreover, the catalyst could be recovered in high percentage and reused three times without loss of activity.

Table 13. RCM Reactions Catalyzed by 125 (20 mol %) under Hexane/Toluene (10:1) Reflux[a]

Entry	Substrate	Closed-Product	Time (h)	Yield (%)	TON
1			12	92	4.6
2			12	98	4.9
3			24	57	2.9
4			12	66	3.3
5			12	82	4.1
6			12	72	3.6

[a] Ts = tosyl.

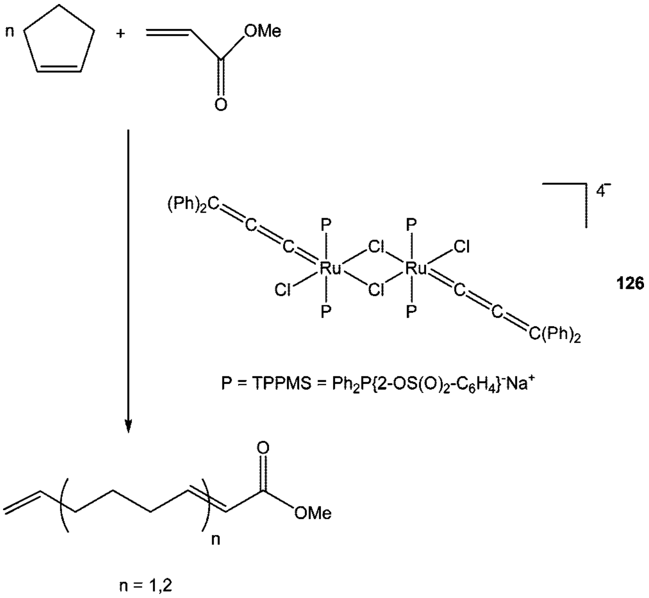
4.4.2. Water-Soluble Allenylidene Ruthenium Complexes

Complexes designed for aqueous metathesis are of great interest due to several advantages related to a cheaper and environmentally cleaner procedure. Peruzzini et al. reported the first example of an allenylidene ruthenium complex that allows cross-metathesis in protic media.[83b] [{RuCl(μ-Cl)(=C=C=CPh$_2$)(TPPMS)$_2$}$_2$]Na$_4$ (**126**), soluble in water and MeOH, has been characterized by means of NMR and IR spectroscopy and FAB-MS, the latter confirming the binuclear structure. After testing the catalytic performance in different olefin metathesis reactions, it was concluded that this complex may be successfully used in the olefin cross-metathesis reaction of cyclopentene with methyl acrylate in water-generating polyunsaturated esters (Scheme 31). However, this water-soluble unsaturated carbene did not promote RCM reactions of some typical model substrates.[115]

4.4.3. Olefin Metathesis in Ionic Liquids

Ionic liquids are considered an alternative to traditional solvents or homogeneous catalysis. The problem of catalyst recycling for an environmentally friendly and cheaper procedure can be solved by tagging the ionic group of the catalyst with an ionic liquid acting as soluble support. Dixneuf and co-workers published for the first time on metathesis reactions in ionic liquids using the cationic precatalysts **88a**, **88b**, and **88d** (see Scheme 25).[102m,119] After several experiments, they discovered that the product yield was dependent on the counteranion of not only the catalyst but also the ionic solvent. Besides, better results were obtained using a biphasic system made of toluene and imidazolium salts by simple extractions of the products from the apolar organic solvent. Table 14 shows the different ring-closing metathesis (RCM) reactions and the ring-opening metathesis polymerization (ROMP) of norbornene studied with the indicated systems.

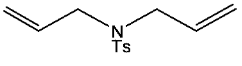
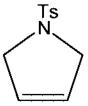
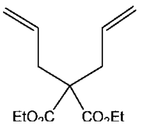
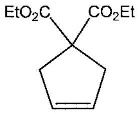
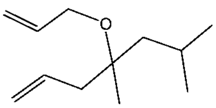
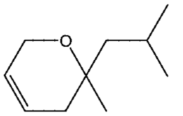
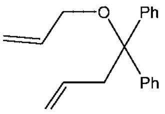
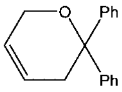
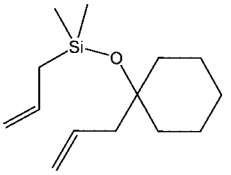
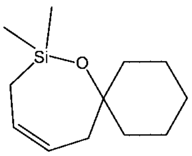
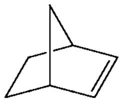
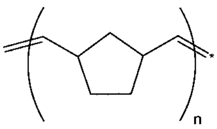
Scheme 31



P = TPPMS = Ph$_2$P{2-OS(O)$_2$-C$_6$H$_4$}$^-$Na$^+$

n = 1,2

Table 14. RCM (Entries 1−5) and ROMP (Entry 6) Reactions Catalyzed by 88b in Ionic Liquid or Ionic Liquid−Toluene Biphasic Medium[102m,119]

Entry	Ionic liquid	Substrate	Product	Time (h)	T (°C)	Yield (%)	TON
1[a]	[bmin][TfO] [b]			2.5	80	97	39
2[c]	[bmin][PF$_6$] [b]			6	80	95	19
3[c]				3.5	80	88	18
4[c]				3.5	80	91	18
5[c]				4	80	93	19
6[d]	[bdmin][PF$_6$] [b]			0.5	40	99	

[a] After the 1st recycling, conditions: diene (0.5 mmol), catalyst (2.5 mol %), [bmin][TfO] salt 2 and 5 mL (3 times) of toluene to extract the product. [b] [bmin] = 1-butyl-3-methylimidazolium; [bdmin] = 1-butyl-2,3-dimethylimidazolium. [c] Conditions: diene (0.5 mmol), catalyst generated *in situ* with 17 mg of [RuCl(PCy$_3$)(*p*-cymene)][TfO] and 5 mg of 1,1-diphenylprop-2-yn-1-ol, biphasic system with 1 mL of toluene and 1 mL of [bmin][PF$_6$]. [d] Conditions: norbornene (4 mmol), catalyst (0.3 mol %), biphasic system with 10 mL of toluene and 2.5 mL of [bdmin][PF$_6$].

The best recycling results were obtained using the biphasic system made from toluene and [bdmin][PF$_6$] salt; both catalyst and ionic liquid could be reused up to 6 times with very good yields.

The cationic allenylidene [RuCl(=C=C=CPh$_2$)(PCy$_3$)(*p*-cymene)][TfO] was also used in the ionic liquid [bmin][PF$_6$]/AlCl$_3$ as catalyst in the RCM reaction of 1,7-octadiene reported by Bayer AG; however only 32% yield was obtained.[132]

5. Indenylidene Complexes

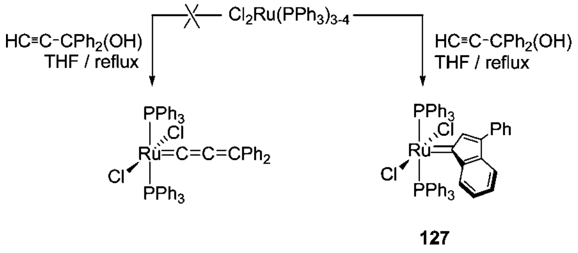
5.1. Introduction

In recent years, the development and application of ruthenium indenylidene type catalysts[133] has received widespread attention due to their high activity in various olefin metathesis reactions and their comparable ease of synthesis.[134] We have previously stressed the importance of straightforward synthetic routes to ruthenium alkylidene complexes, and ruthenium indenylidene complexes, readily prepared upon reaction of propargylic alcohol and Cl$_2$Ru(PPh$_3$)$_{3-4}$, are interesting candidates in this respect. Moreover, most of the reported ruthenium indenylidene complexes exhibit high air and moisture stability, good thermal stability, and excellent tolerance toward functional groups. Furthermore, this class of olefin metathesis catalysts has proved useful for application in the total synthesis of various natural products.[135] In the following sections, we will take a closer look at the discovery and the development of ruthenium indenylidene olefin metathesis catalysts.

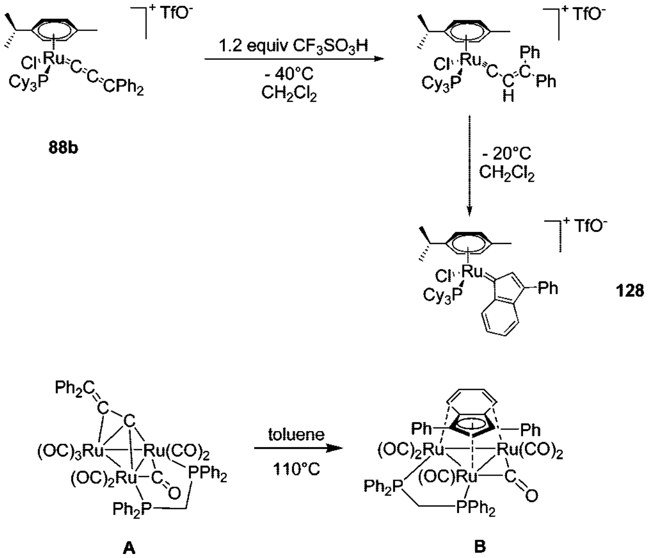
5.2. Synthesis of Ruthenium Indenylidene Complexes: From Allenylidene to Indenylidene

The chemistry of ruthenium indenylidene complexes started with the serendipitous synthesis of the first ruthenium indenylidene complex by Hill and co-workers, who were actually elaborating the synthesis of ruthenium diphenylallenylidene complexes.[136] They found that upon refluxing a mixture of propargylic alcohol and Cl$_2$Ru(PPh$_3$)$_{3-4}$ for 2 h in THF, only one signal was found in ^{31}P NMR spectrum and erroneously attributed this to the corresponding ruthe-

Scheme 32. Serendipitous Discovery of Ruthenium Indenylidene Complex 127



Scheme 33. Formation of Ruthenium Indenylidene Complex 128 from Ruthenium Allenylidene Complex 88b through an Alkenylcarbyne Complex

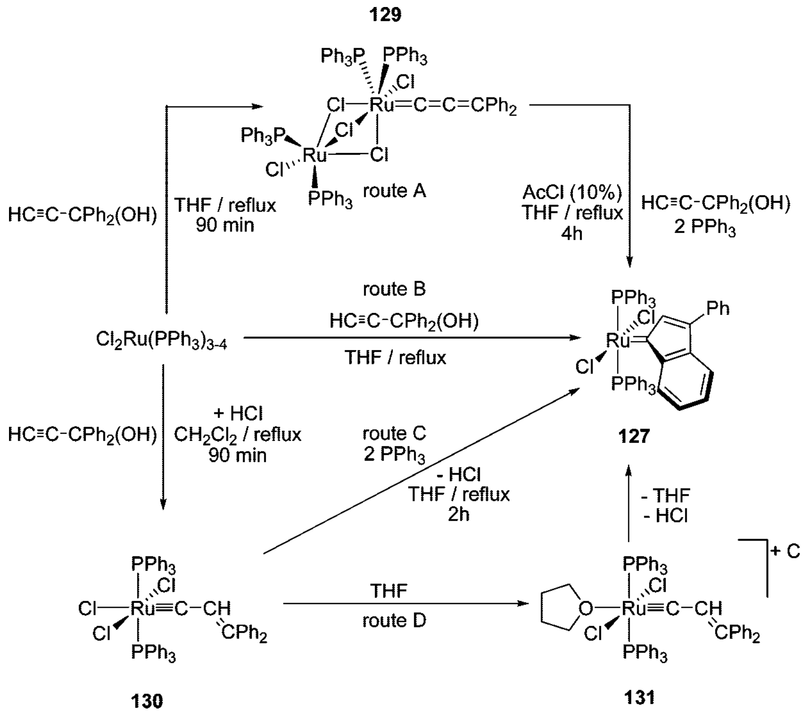


nium allenylidene complex. Later, it was recognized that the obtained complex was not an allenylidene species, but the ruthenium 3-phenylindenylid-1-ene complex, **127** (Scheme 32).[137] Two-dimensional NMR spectroscopy indeed allowed for the unambiguous characterization of the indenylidene moiety. However, details about its synthetic pathway, whether the indenylidene complex is formed through an allenylidene intermediate or generated directly from starting products, could not be discerned. This question was rather relevant indeed since 1,3-diphenylindenyl ligands appeared to form on Ru_3 clusters (see Scheme 33, structure B).[138] Of note, a recent report by Whitwood et al. shows that the formation of an allenylidene complex, and consequently its rearrangement to an indenylidene complex, is prohibited in the case of bisacetate ruthenium complexes due to a hydrogen bond induced charge transfer in the hydroxyvinylidene intermediate.[139]

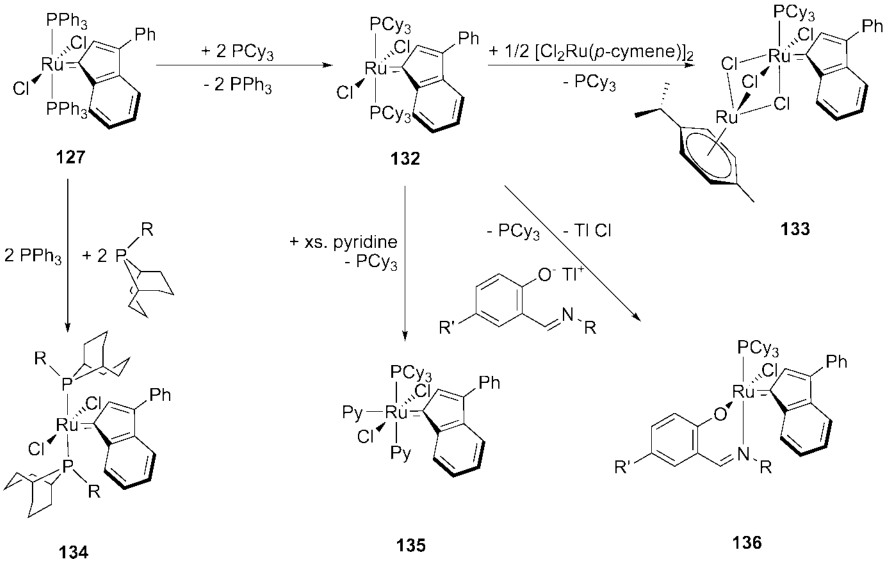
While studying the ring-closing metathesis reaction of *N*,*N*-diallyl tosylamine with cationic ruthenium allenylidene arene complexes at lower temperature (33 °C), Dixneuf et al. observed that the consumption of the substrate is linear in time, indicating that a highly active species is slowly formed *in situ* while the RCM reaction is comparably fast.[140] They proposed a thermally promoted rearrangement of the allenylidene to indenylidene moiety to account for these observations. Indeed, UV−vis studies in toluene at 50 °C revealed the disappearance of the allenylidene band (at 518 nm) and the appearance of new bands at 358 and 409 nm, due to the formation of a new metal alkylidene moiety, presumably a 3-phenylindenylidene moiety. Elaborating these results, bearing in mind that the addition of strong acids such as HBF_4 and CF_3SO_3H significantly enhance the activity of these cationic ruthenium allenylidene arene complexes, Dixneuf et al. found that upon addition of 1.2 equiv of triflic acid to the ruthenium allenylidene arene complex **88b** (Scheme 33) at −40 °C in CH_2Cl_2, color changed from dark red to dark orange, accompanied by the appearance of a new signal in the ^{31}P NMR spectrum at δ 78.6 ppm vs δ 57.6 ppm for the starting complex. ^{13}C and ^{1}H NMR spectra revealed that the newly formed complex is a biscationic ruthenium alkenylcarbyne complex (Scheme 33)[141] derived from the protonation of the C_β of the allenylidene moiety. When temperature was allowed to rise to −20 °C, color changed to violet and the ^{31}P NMR spectrum revealed a new peak at δ 48.3 ppm. Further NMR spectroscopic data were consistent with a ruthenium 3-phenylindenylidene complex **128** (Scheme 33) derived from phenyl substitution by the electrophilic C_α.[106,142] Although very unstable at room temperature, complex **128** and two analogues bearing a PPh_3 and P^iPr_3 ligand, respectively, could be isolated at lower temperature. The isolated catalyst **128** exhibited a lower initial catalytic performance toward the RCM of 200 equiv of *N*,*N*-diallyl tosylamine compared with the acid-activated catalyst **88b** but managed almost quantitative completion of the reaction after 10 min while conversion is abruptly stopped for reactions with the acid activated allenylidene complex after 1 min. The isolated catalyst **128** further operated successfully in the ROMP of cyclooctene and cyclopentene, in RCM, and in enyne metathesis reactions.[106] Interestingly, Bruce et al. previously reported on the cyclization of allenylidene to indenyl ligands on Ru_3 clusters.[138] The Ru_3-allenylidene cluster (Scheme 33) shows a marked resemblance to the biscationic ruthenium alkenylcarbyne complex reported by Dixneuf, therefore giving support to the suggested intermediates.

Although at that time, several ruthenium indenylidene complexes were reported in literature (*vide infra*) and mechanistic details about their synthesis were revealed, Schanz et al. correctly stated that the synthesis of such complexes is not always straightforward and that even though applying the same procedure, sometimes a ruthenium indenylidene species is obtained but more often an unidentified species containing four different kinds of phosphine ligands.[143] The latter species was identified as a μ_3-chloro-bridged bimetallic ruthenium allenylidene complex **129** (Scheme 34). It is worth noting that this complex can be obtained from equimolar quantities of ruthenium allenylidene and starting complex and can be converted to a ruthenium indenylidene complex **127** upon refluxing for 4 h in THF in presence of acetyl chloride (Scheme 34, route A). When a catalytic amount of acetyl chloride is added to $Cl_2Ru(PPh_3)_{3-4}$, forming HCl *in situ* from reaction of the acetyl chloride with water generated upon formation of the allenylidene ligand, to speed up the allenylidene-to-indenylidene rearrangement (*vide supra*), indeed, the indenylidene complex **127** could be isolated directly (Scheme 34, route B). When an excess of HCl is added to the starting product and the mixture is refluxed for 90 min in CH_2Cl_2, a stable yellow compound is obtained, which was characterized as a ruthenium carbyne complex, **130** (Scheme 34), obviously the result of a 1,3-addition of HCl across the proposed ruthenium allenylidene intermediate. Further refluxing of this complex in THF affords ruthenium indenylidene complex **127** (Scheme 34, routes C and D). It should be noted that the same reaction in CH_2Cl_2 did not yield compound **127**,

Scheme 34. Synthetic Pathways to Ruthenium Indenylidene Complex 127



Scheme 35. Ruthenium Indenylidene Complexes Derived from Parent Complex 127



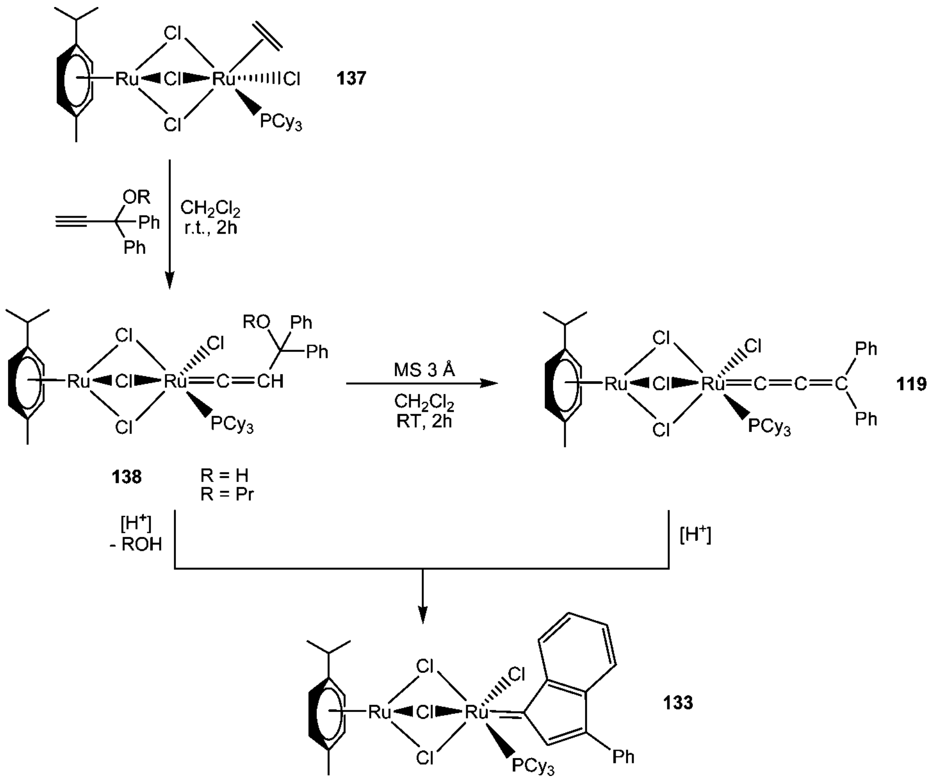
which leads to the assumption of a cationic THF−ruthenium carbyne complex, **131** (Scheme 34), which contains a more electrophilic carbon in the α-position, therefore being more susceptible to nucleophilic attack of the phenyl group. Of note, complexes **129** and **130** were isolated from the reaction mixture, and their structures were determined by single-crystal X-ray analysis.

5.3. Development of Ruthenium Indenylidene Type Catalysts

5.3.2. Ruthenium Indenylidene Catalysts Bearing Phosphine Ligands

As soon as the synthesis of ruthenium indenylidene complexes was well-documented and they were fully characterized, their further application in the development of ruthenium olefin metathesis catalysts was exploited. The first relevant example in this respect was the ligand exchange of PPh_3 with PCy_3. It was known from Grubbs type catalysts that such an exchange had a pronounced influence on catalytic activity and catalyst stability.[40] In this respect, Fürstner reported on the multigram scale synthesis of compound **132** (Scheme 35) and on the synthesis of its bimetallic congener, **133**. Indeed, catalyst **132** was found to be a highly active catalyst, exhibiting high activity toward the RCM of allyl methallyl malonate and the RCM of diallyl tosylamine and its activity was found to be comparable to Grubbs type catalyst. In contrast, catalyst **133** showed limited activity. However, Sauvage et al. later reported on almost quantitative conversion of diethyl diallylmalonate within merely 15 min.[144] Further elaboration of the catalytic activity of these complexes showed that they were tolerant toward a range of polar functional groups, such as ethers, esters, amides, silyl ethers, sulfonamides, ketones, urethanes, alco-

Scheme 36. Synthetic Pathway to Homobimetallic Ruthenium Indenylidene Complex 133



hols, furan, and pyrrole rings.[137b] Of note, the bimetallic ruthenium indenylidene complex was previously also synthesized by Hill, but speciously taken for a homobimetallic ruthenium allenylidene complex.[136] With regard to complex **132**, Kunkely and Vogler reported on the reversible release of the indenylidene ligand after MLCT excitation (λ_{max} = 490 nm), eventually resulting in formation of anthracene and catalyst degradation in air-saturated solvents.[145] Complex **127** undergoes transmetalation in presence of $Hg(ptpy)_2$ with consequent elimination of the indenylidene ligand.[146]

Interestingly, Forman et al. reported on the ligand exchange from **127** to $(PhobCy)_2Cl_2RuC_{15}H_{10}$, the so-called phoban-indenylidene catalyst, **134** (R = Cy) (PhobCy = 9-cyclohexyl-9-phospha-9*H*-bicyclononane).[147] They had previously shown that incorporation of the phoban ligand in Grubbs-type complexes induces a comparably high air and moisture stability and good thermal stability, even in a 2 M HCl solution. Furthermore, they illustrated that this catalyst excels in efficiency and selectivity toward the self-metathesis of 1-decene and methyl oleate, the ethenolysis of methyl oleate, and the RCM of diethyl diallyl malonate compared with Grubbs first and second generation catalysts, **2** and **4**[148] Likewise its benzylidene congener, the phoban-based indenylidene catalyst **134** (R = Cy), exhibited higher catalytic activity toward the self-metathesis and ethenolysis of methyl oleate, enabling substrate-to-catalyst ratios up to 200 000:1 for the self-metathesis reaction and 20 000:1 for the ethenolysis of methyl oleate. In addition, the ethenolysis of methyl oleate with **134** (R = Cy) proved to proceed even at higher temperatures (65 °C) while maintaining its activity.

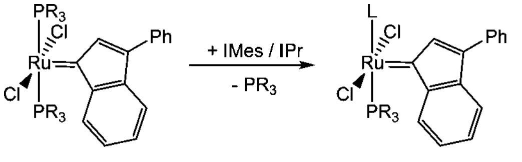
Elaboration of this new class of catalysts, together with comparison of the new isobutyl phoban catalyst **134** (R = ^{i}Bu) in RCM reaction revealed good activity of **134** (R = ^{i}Bu) in RCM of simple five- and six-membered ring substrates, with the exception of enyne metathesis reactions. In general, catalyst **134** (R = ^{i}Bu) performed better than its cyclohexyl-based congener **134** (R = Cy) and, except for the formation of substituted alkenes, good activities were reported for all reactions. During the self-metathesis of 1-octene, however, catalyst **134** (R = Cy) performed notably better.[149]

Nolan et al. reported on the synthesis and catalytic activity of the bis(pyridine) adduct $Cl_2Ru(PCy_3)(py)_2$(3-phenylindenylidene) **135** as an air- and moisture-stable catalyst. This compound, readily prepared upon treatment of **132** with an excess of pyridine, performed well in the initial stage of the RCM reaction of diethyl diallylmalonate. However, catalytic activity dropped significantly after 30 min indicating degradation of the catalytically active species. Similar behavior was concluded for the RCM of more sterically demanding substrates such as diethyl allylmethallylmalonate, eventually resulting in low turnover numbers.[150]

Application of Schiff base ligands has been a well-documented strategy toward the development of thermally stable, efficient catalysts. Verpoort et al. reported on the isolation, characterization, and catalytic activity of ruthenium indenylidene Schiff base complexes, **136**.[94c,151] These catalysts exhibited high thermal stability ($\tau_{1/2\text{-degradation}}$ = 3−6 h at 80 °C in benzene-d_6) with moderate room-temperature activity. However, upon heating to 60 °C, cyclization of diallyl tosylamine is quantitative within 1 h and good to quantitative conversions are reported for the RCM of the more sterically demanding allyl methallyl tosylamine within 3 h under otherwise identical conditions. In addition, rigorous choice of the Schiff base ligands allows for high activity in the cross-metathesis reaction of 5-hexenyl acetate with methyl acrylate. As a result, activities surpassing those obtained with Hoveyda−Grubbs first generation catalyst, **7**, can be achieved.

Sauvage et al., elaborating homobimetallic ruthenium ethylene complexes (Scheme 36), reported on the alternative synthesis of a bimetallic indenylidene complex, **133**, formed

Scheme 37. Synthesis of *N*-Heterocyclic Carbene Ligated Ruthenium Indenylidene Complexes



127 R = Ph
132 R = Cy

139 L = IMes; R = Ph
140 L = IMes; R = Cy
141 L = IPr; R = Ph
142 L = IPr; R = Cy

upon the reaction of propargylic alcohol or its *n*-propyl ether adduct in presence of acid and a drying agent (molecular sieves 3 Å or $CaCl_2$).[144]

X-ray crystallographic data unambiguously proved that the obtained complex **133** was an indenylidene complex, and characterization by means of NMR and IR spectroscopy corresponded to data previously reported by Hill.[136] Interestingly, Sauvage also showed that a bimetallic ruthenium vinylidene complex, **138**, could be isolated upon reaction of the bimetallic ethylene complex with propargylic alcohol or its *n*-propyl ether adduct and that it forms the bimetallic ruthenium allenylidene complex **119** upon addition of drying agents such as molecular sieves. Subsequent addition of trifluoroacetic acid or alternatively *p*-toluenesulfonic acid monohydrate yielded the bimetallic ruthenium indenylidene complex, **133**. Thus, full characterization of key intermediates observed during the transformation of vinylidene-to-indenylidene through a proposed ruthenium carbyne complex was obtained. When applied in characteristic olefin metathesis reactions, **133** exhibited high catalytic activity toward the ROMP of cyclooctene (COE) and the RCM of diethyl diallylmalonate (Table 15). Catalytic tests for the cross-metathesis of styrene yielded poor conversions, attributed to the reduced stability of the corresponding bimetallic ruthenium methylidene complex.

5.3.2. Ruthenium Indenylidene Catalysts Bearing N-Heterocyclic Carbene Ligands

The advent of *N*-heterocyclic carbenes, which act as phosphine mimics, was found to be of paramount importance toward the development of highly active and stable olefin metathesis catalysts.

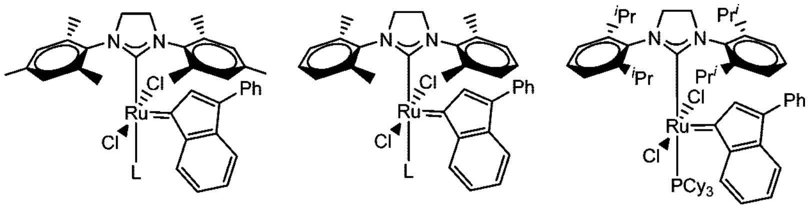
In this respect, Nolan et al. reported on the incorporation of the IMes and IPr ligand in complexes **127** and **132**, respectively (Scheme 37).[102i] Indeed, high thermal stability was observed for the newly obtained NHC ligated catalysts. More importantly, PCy_3 based complexes were more robust compared with their PPh_3-based congeners, basically showing no signs of decomposition after 10 days at 80 °C in toluene. In standard RCM experiments, NHC-ligated catalysts notably performed better than their phosphine-based congeners. RCM of diethyl diallylmalonate and diallyl tosylamine proceeded smoothly with catalyst **142**, whereas catalyst **139** required heating to 40 °C. However, higher conversion was obtained for **140** when applied to RCM of the sterically demanding diethyl di(methallyl)malonate.

Determination of catalytic activity of catalysts **132**, **142**, and **143** (*vide infra*) in the cross metathesis reaction of *tert*-butyl(hex-5-enyloxy)dimethylsilane and methylacrylate revealed significantly improved catalytic activity for reactions performed with catalyst **142**, basically conducting the reactions to full conversion under ambient conditions. Further screening of the catalytic activity of **142** in various cross-metathesis reactions showed a definite substrate dependency.[133e]

Elaborating the application of catalyst **140**, Fürstner noted that di-, tri-, and tetrasubstituted small to medium and macrocyclic alkenes are isolated in high yields upon RCM of the corresponding dienes, and it was concluded that catalyst **140** could be regarded as equipotent to its Grubbs-type congener, **3**.[152]

In 2007, Nolan reported on the application of catalyst **143** (Figure 18) bearing a saturated imidazolin-2-ylidene ligand in olefin metathesis reactions.[150] Catalyst performance in RCM experiments using diethyl diallylmalonate as a substrate proved a fast and almost quantitative conversion in the case of catalyst **132**, while NHC-bearing catalysts **143** and **140** needed significantly longer reaction times. However, **143** performed notably better compared with **132** and **140** in the case of RCM of the more sterically demanding diethyl allylmethallylmalonate. Discrepancies in catalytic activities observed were rationalized by the difference in rate-determining step between phosphine- and NHC-based catalysts, respectively. It was reasoned that while NHC-containing catalysts suffer from a reduced initiation rate, phosphine-based catalysts exhibit fast initiation with a reduced propagation rate. Definite causes for the different activity of catalyst **140** and **143** however could not be ruled out. In addition, formation of tetrasubstituted olefins with catalyst **143** was found to proceed with excellent isolated yields, whereas the benzylidene congeners yielded moderate conversions. Further elaboration of the catalytic activity of catalysts **140** and **143** proved that under optimized conditions these catalysts are suitable for RCM of malonate- and tosyl-containing and ether- and amide-based substrates and that high catalytic activity was observed in enyne metathesis reactions. In addition, good activities were obtained in the self-metathesis reaction of undecylenic aldehyde, a renewable derived from castor oil cracking.[135e]

Although the catalytic activity of the ruthenium indenylidene catalyst **143** bearing a saturated *N*-heterocyclic carbene ligand was already reported in the literature, the synthesis and full characterization of complex **143** by means of ^1H, ^{13}C, and ^{31}P NMR spectroscopy, as well as elemental



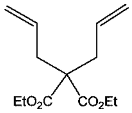
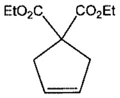
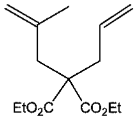
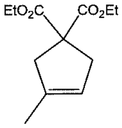
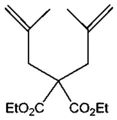
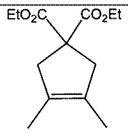
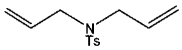
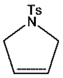
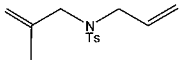
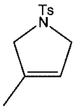
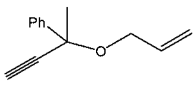
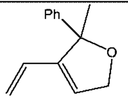
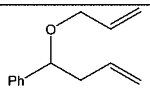
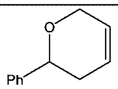
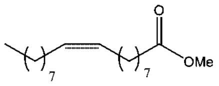
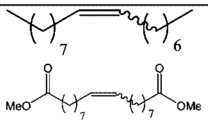
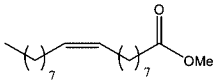
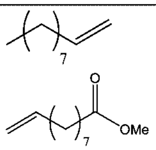
143 L = PCy_3
144 L = py
145 L = PPh_3

146 L = PCy_3
147 L = py
148 L = PPh_3

149

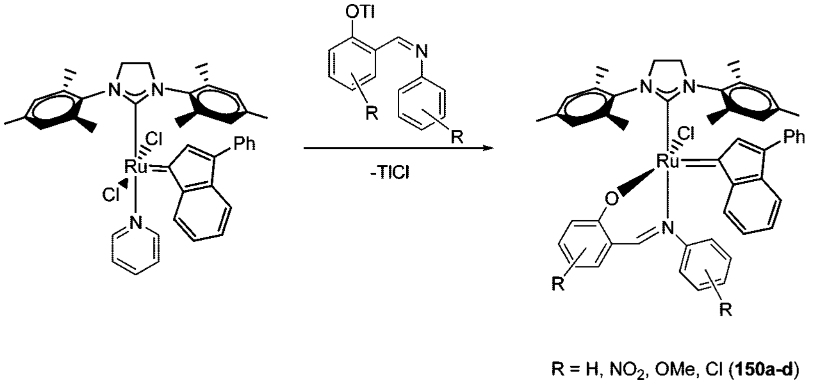
Figure 18. Ruthenium indenylidene type catalysts bearing saturated *N*-heterocyclic carbenes.

Table 15. Catalytic Activity of Phosphine-Based Ruthenium Indenylidene Complexes in Olefin Metathesis Reactions

Entry	Substrate	Product	Cat.	Solvent	t (h)	T (°C)	TON ($mol.mol^{-1}$)	Ref.
1			**127**	CH_2Cl_2-d_2	0.5	40	0	102i
2			**132**	CH_2Cl_2-d_2	0.5	RT	17	102i
3			**133**	CH_2Cl_2	6	20	35	102i
4			**133**	CH_2Cl_2-d_2	0.25	30	98	144
5			**134**[a]	CH_2Cl_2	3	RT	49	149a
6			**134**[b]	CH_2Cl_2	2	RT	47	149a
7			**135**	CH_2Cl_2	10	RT	12	150
8			**136**[c]	$CDCl_3$	10	RT	40	151
9			**132**	CH_2Cl_2-d_2	1	20	> 95	137b
10			**134**[a]	CH_2Cl_2	8	RT	40	149a
11			**134**[b]	CH_2Cl_2	2	RT	49	149a
12			**135**	CH_2Cl_2	10	RT	5.4	150
13			**132**	toluene-d_8	2	80	0	102i
14			**132**	CH_2Cl_2	2	20	98	102i
15			**133**	CH_2Cl_2	17	20	99	102i
16			**136**	$CHCl_3$	1	60	200	151
17			**134**[a]	CH_2Cl_2	8	RT	49	149a
18			**134**[b]	CH_2Cl_2	5	RT	> 49	149a
19			**136**	$CHCl_3$	3	60	200	151
20			**134**[a]	CH_2Cl_2	5	RT	49	149a
21			**134**[b]	CH_2Cl_2	10	40	34	149a
22			**134**[a]	CH_2Cl_2	5	RT	49	149a
23			**134**[b]	CH_2Cl_2	5	RT	49	149a
24			**134**[a]	no	3	50	71603[d]	147
25			**134**[a]	no / 10 bar CH_2Cl_2	2	50	12450[d]	147

[a] R = Cy. [b] R = ^{i}Bu. [c] R = NO_2; R′ = *o*-Cl-phenyl. [d] Productive TON = TON × selectivity to required product.

Scheme 38



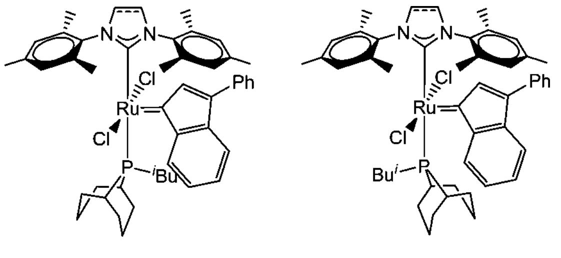
analysis, was not published until 2008 by Verpoort et al.[153] From known methodologies for the introduction of the NHC ligand in ruthenium olefin metathesis catalysts, solely the application of the thermally decomposing SIMes·$CHCl_3$ adduct afforded compound **143** in high isolated yields (82%). In addition, synthesis and characterization of the pyridine- (**144**) and PPh_3-containing (**145**) analogues were reported. In agreement with catalytic data reported by Nolan (*vide supra*), a slow initiation rate was observed for **143** in both RCM and ROMP reactions, a trend that was successfully offset by application at higher temperatures. Catalysts bearing the more labile PPh_3 ligand performed excellent in RCM of diethyl diallylmalonate and ROMP of COD. While the pyridine-containing catalyst **144** exceeded its Grubbs-type congener in ROMP reactions using COD as monomer, moderate activity is obtained when it is applied in RCM reactions. Interestingly, it was evidenced that the Grubbs-type congener suffered from an increased initiation period toward the RCM of diethyl diallylmalonate when higher catalyst loadings were applied, a phenomenon that was not observed with catalyst **144** and for which, to the best of our knowledge, no precedents have been reported so far. An in-depth study of the application of ruthenium indenylidene catalysts **132**, **140**, **143**, **139·py$_2$**, and **144·py$_2$** in ROM polymerizations of COD was later reported by Nolan.[154] In this respect, it is interesting to note that the pyridine-containing complexes reported bear two pyridine ligands, in contrast to reports by Verpoort and Slugovc, who, independent from Verpoort et al., reported on the synthesis of **144** and its application in controlled living ROMP of norbornene and oxanorbornene derivatives.[155] Alternatively, the SIXyl ligand (SIXyl = *N*,*N*′-(2,6-dimethylphenyl)-imidazolin-2-ylidene) was successfully introduced in ruthenium indenylidene type catalysts after reaction with merely 1.15 equiv of its pentafluorobenzene adduct whereas 2 equiv of SIMes·$CHCl_3$ was necessary for the synthesis of **143**. It was concluded that although these catalysts exhibit a roughly similar activity compared with their SIMes-based congeners, slightly lower activity was observed when they were exposed to challenging reactions such as the RCM of diphenyl diallylsilane or cross-metathesis reactions.[156]

Recently, several ruthenium phenylindenylidene complexes bearing a bidentate Schiff base and a SIMes ligand were introduced by Verpoort et al., as effective metathesis catalysts. These new catalysts are easily accessible from the respective pentacoordinated Ru indenylidene complexes **144** and salicylaldimine salts. Activation of this group of catalysts by a Lewis acid, for example, $PhSiCl_3$, resulted in a superior catalytic effectiveness compared with that of the commercially available **132** and **143** indenylidene complexes. This outcome is ascribed to the higher stability of the precatalyst vs that of its phosphine analogues.[157] Intensive, long-term research efforts of Verpoort et al. rewardingly converged into the creation of new Schiff base containing indenylidene complexes (**150a**−**d**, Scheme 38). Since these new systems are very reliable catalysts, they have been commercialized aiming the application by the pharmaceutical industry and polymer industry.[158]

A convenient method for the preparation of ruthenium-based olefin metathesis catalysts bearing an *N*-heterocyclic carbene ligand based on the thermal decomposition of imidazol(in)ium-2-carboxylates was later reported by Sauvage et al. Accordingly, **140** and **143** were prepared in 89% and 86% yield in isolated product.[159]

A useful and practical guide to application of olefin metathesis catalysts was recently availed by Grela and coworkers. They examined the effectiveness of ruthenium indenylidene complexes in standard olefin metathesis reactions and compared their activity to those of Grubbs- and Grubbs−Hoveyda-type catalysts.[160] Indenylidene catalysts **140** and **143** were found to be practically inactive toward the RCM of diethyl diallylmalonate at room temperature using catalyst loadings as low as at 0.05 mol %, in sharp contrast to Grubbs and Hoveyda−Grubbs catalysts. However, conversions dramatically increased when the reaction was performed at elevated temperature (70 °C) rendering them competitive to the most active catalysts reported. Similar conclusions were drawn from experiments aimed at the formation of tetrasubstituted olefins. In contrast, enyne cycloisomerization was significantly more effective using Grubbs- or Hoveyda−Grubbs-type complexes. Cross-metathesis of various olefins with (*Z*)-1,4-diacetoxy-2-butene, however, did not exhibit significant discrepancies in catalytic activity. In addition, application of second generation indenylidene type catalysts, **140** and **143**, to challenging substrates such as diethyl di(methallyl)malonate in fluorinated aromatic hydrocarbon solvents resulted in a remarkable enhancement of catalytic activity. This approach was successfully extended to the RCM of natural products and the cross-metathesis formation of trisubstituted alkenes.[161]

The synthesis and activity of a ruthenium indenylidene complex bearing a saturated IPr ligand was recently reported by Nolan.[162] In contrast to comparable ruthenium indenylidene complexes bearing NHC ligands, **151** (Figure 19) exhibited limited thermal stability, essentially decomposing over the course of 24 h in solution. However, high initial activity was reported, allowing for the fast and complete consumption of sterically unhindered substrates in ring-



***cis*-151** ***trans*-151**

Figure 19.

closing and enyne metathesis reactions, in due contrast to application in RCM of sterically more demanding substrates, eventually affording poor isolated yields.

SIMes·CO_2 and IMes·CO_2 betaines have previously proven their suitability as stable precursors to free *N*-heterocyclic carbenes, which readily coordinate to ruthenium upon phosphine ligand exchange.[163] Upon refluxing a mixture of SIMes·CO_2 or IMes·CO_2 betaines and **134** (R = ^{i}Bu) in THF, Sauvage et al. showed that second generation phoban indenylidene catalysts, **151**, are obtained in high yield. Acquisition of the ^{31}P NMR spectrum at −40 °C allowed for the observation of two distinct peaks, assigned to the *cis*- and *transoidal* conformation of the phoban ligand with respect to the indenylidene moiety. Activity of these catalysts was rather low at room temperature. In contrast, ring closing of diethyl diallylmalonate was quantitative after 3 h at 50 °C. In addition, relatively high TONs were obtained for RCM

Scheme 39. Ruthenium Indenylidene Complexes As Scaffolds for the Synthesis for New Ruthenium Olefin Metathesis Catalysts

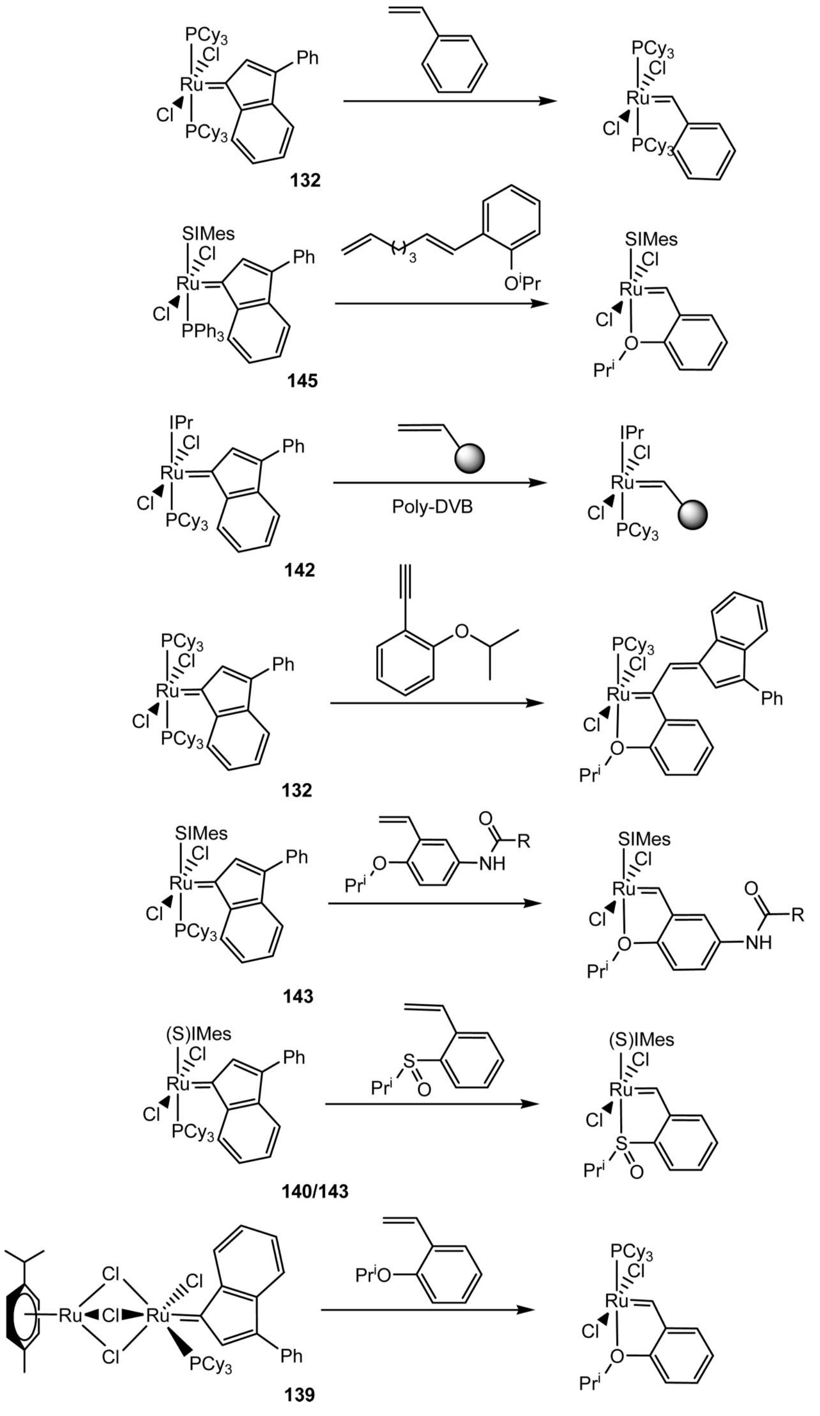


Table 16. Catalytic Activity of *N*-Heterocyclic Carbene-Based Ruthenium Indenylidene Complexes in Olefin Metathesis Reactions

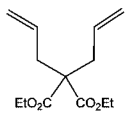
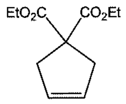
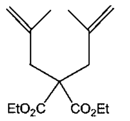
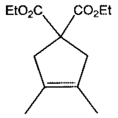
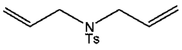
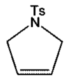
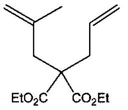
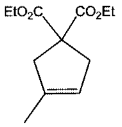
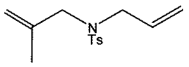
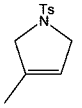
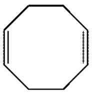
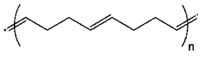
Entry	Substrate	Product	Cat.	Solvent	t (h)	T (°C)	TON (mol.mol^{-1})	Ref.
1			**139**	CH_2Cl_2-d^2	0.5	40	13	102i
2			**140**	CH_2Cl_2-d^2	0.5	20	17.6	102i
3			**141**	CH_2Cl_2-d^2	0.5	40	11.2	102i
4			**142**	CH_2Cl_2-d^2	0.5	20	15	102i
5			**143**	$CDCl_3$	24	rt	178	153
6			**144**	$CDCl_3$	0.5	rt	80	153
7			**145**	$CDCl_3$	3	rt	192	153
8			**146**	$CDCl_3$	24	rt	> 196	156
9			**147**	$CDCl_3$	0.5	rt	20	156
10			**148**	$CDCl_3$	3	rt	170	156
11			**149**	CH_2Cl_2	0.25	rt	48.5	162
12			**150**	toluene-d_8	3	50	> 99	164
13			**139**	toluene-d_8	2	80	13.2	102i
14			**140**	toluene-d_8	2	80	4	102i
15			**141**	toluene-d_8	2	80	3.4	102i
16			**142**	toluene-d_8	2	80	3.8	102i
17			**143**	toluene	5	80	42.5	150
18			**149**	toluene	5	80	4.4	162
19			**151**	toluene-d_8	3	80	10-15	164
20			**139**	CH_2Cl_2-d^2	0.5	40	18.8	102i
21			**140**	CH_2Cl_2-d^2	0.5	20	6	102i
22			**141**	CH_2Cl_2-d^2	0.5	20	18.8	102i
23			**142**	CH_2Cl_2-d^2	0.5	20	17.8	102i
24			**143**	$CDCl_3$	3	rt	0	156
25			**144**	$CDCl_3$	0.5	rt	62	156
26			**145**	$CDCl_3$	1	rt	196	156
27			**146**	$CDCl_3$	3	rt	92	156
28			**147**	$CDCl_3$	0.5	rt	28	156
29			**148**	$CDCl_3$	3	rt	126	156
30			**143**	CH_2Cl_2	5	rt	49.5	150
31			**149**	CH_2Cl_2	0.5	rt	48.5	162
32			**151**	toluene-d_8	3	50	> 99	164

Table 16. Continued

Entry	Substrate	Product	Cat.	Solvent	t (h)	T (°C)	TON (mol.mol^{-1})	Ref.
33			**149**	CH_2Cl_2	0.5	rt	> 49	162
34			**143**	$CDCl_3$	3	rt	2580	153
35			**144**	$CDCl_3$	0.25	rt	98000	153
36			**145**	$CDCl_3$	0.1	rt	2970	153
37			**146**	$CDCl_3$	3	rt	2700	156
38			**148**	$CDCl_3$	0.3	rt	2970	156

Cat. = catalyst, Ref. = reference.

of di(2-methallyl)-malonate at 80 °C in toluene; 15 and 10 for the IMes- and SIMes-based catalyst, respectively.

5.4. Ruthenium Indenylidene Complexes as Scaffolds for the Development of New Ruthenium Olefin Metathesis Catalysts

Besides its direct application in olefin metathesis reactions, advantage has been taken of the synthetically straightforward preparation of ruthenium indenylidene complexes to use as scaffolds for the synthesis of novel olefin metathesis catalysts (Scheme 39).

We have previously stressed the hazardousness of diazo compounds and the fact that their use during the preparation of Grubbs first generation catalyst **2** is therefore to be avoided. Nolan anticipated that Grubbs catalyst **2** can be obtained after cross-metathesis of styrene with first generation indenylidene catalyst **132**.[165] Indeed, high yields in isolated product can be obtained for this reaction using a 20-fold excess of styrene. Interestingly, a one-pot procedure for the synthesis of indenylidene first generation catalyst **132** is reported.

Blechert recognized the utility of ruthenium indenylidene complexes as useful scaffolds for the synthesis of second generation Hoveyda−Grubbs catalyst **8** upon a ring-closing metathesis inspired alkylidene exchange with an alkenyliso-propoxystyrene.[166]

Nolan used polydivinylbenzene (poly-DVB) for the immobilization of **144** on a heterogeneous polymer support.[167] Interestingly, the polymer-supported catalyst exhibits higher catalytic activity for RCM of diethyl diallylmalonate than its homogeneous parent complex, **144**, and leaching after four catalytic cycles was determined to be merely 2% of the initial catalyst loading. Unfortunately, RCM activity was less impressive for diallyl tosylamine and activity for diethyl di(methallyl) malonate was disappointing.

Fürstner adopted the formal insertion of an alkyne into the Ru═C bond for the synthesis of Hoveyda−Grubbs-type catalysts. Addition of 2-isopropoxyphenylacetylene to first generation indenylidene catalyst in the presence of AgCl as a phosphine scavenger indeed afforded the desired κ^2-(*O*,*C*) bidentate complex in moderate yield (59%). Although no catalytic activities were reported for the thus obtained complex, it is worth mentioning that comparable vinylcarbene complexes exhibited good activity toward the RCM of diethyl diallylmalonate in CH_2Cl_2 at reflux.[168]

Cross metathesis of 4-aminocarbonyl-2-isopropoxystyrene derivatives with ruthenium indenylidene catalyst **144** by Mauduit led to the isolation of 4-aminocarbonyl-substituted Hoveyda−Grubbs-type catalysts.[169] An unequivocal influence of the carbonyl substituent was derived from kinetic studies using the RCM of 2-allyl-2-methallyl malonate as a benchmark reaction, thus allowing for fine-tuning of the catalyst activity. More importantly, ruthenium contamination of the reaction products was reported to be significantly below 10 ppm after a single pass through a silica column, a vast advantage when thinking of the synthesis of biologically active compounds.

In search of catalysts with a more controllable activity profile, Grela reported on ruthenium olefin metathesis catalysts bearing a chelating κ^2-(*C*,*S*) sulfoxide ligand.[170] These complexes were obtained in good yields upon adding 2-isopropylsulfinylstyrene to ruthenium (S)IMes indenylidene complexes in presence of CuCl (toluene, 80 °C). Good activity was reported toward RCM of model substrates, but not competitive with the commercially available Grubbs' second generation catalyst, **4**. In addition, the SIMes-containing analogue was slightly more active than its IMes-based congener. Modification of the alkyl substituent on the sulfur atom showed that steric effects conclusively determine the catalytic activity. RCM of diethyl di(methallyl)malonate to form the challenging tetrasubstituted C−C double bond proved satisfactory, albeit only at elevated temperatures (110 °C).

Sauvage et al. successfully converted the bimetallic ruthenium indenylidene complex **139** to the Hoveyda−Grubbs catalyst **7** by means of cross-metathesis of the indenylidene moiety with 2-isopropoxystyrene. Alternatively, a one-pot procedure starting from the homobimetallic ruthenium ethylene complex **137** was availed by subsequent addition of (i) propargylic alcohol, (ii) *p*-toluenesulfonic acid and anhydrous calcium chloride, and (iii) 2-isopropoxystyrene. It is worth noting that the reported procedure excludes the use of a sacrificial phosphine, while the ruthenium dimer side product was effectively recycled.[144]

6. Conclusions and Future Outlook

In conclusion, we have described the rational design, study, and application of olefin metathesis catalysts of ruthenium vinylcarbenes, vinylidenes, allenylidenes, and 3-phenylindenylid-1-enes. Ruthenium vinylidene complexes of the type $[Cl_2Ru\ (=C=CHR)L_2]$ ($L = P^iPr_3$, PCy_3, SIMes, Schiff base) are a convenient alternative to the classical ruthenium bisphosphine catalysts. Due to the particular steric and electronic properties provided by the ligands, some of the vinylidene ruthenium complexes exhibit remarkable activity and selectivity. Those vinylidenes serve as highly efficient catalyst precursors for CM of acyclic olefins, ROMP of cyclic olefins, and RCM of α,ω-dienes. Moreover, these alternatives are easily prepared in high yields from $[RuCl_2(p\text{-cymene})]_2$, combined with neutral donor ligands (L) and terminal alkynes, which are commercially available.

The second group of ruthenium compounds described is ruthenium allenylidene complexes, which have now reached such a state of development that their use as catalysts in olefin metathesis has considerably increased in recent years. These catalysts readily obtained from commercially available products as starting materials are now a modern and useful tool in fine chemistry and polymer production. The use of highly efficient ruthenium allenylidene catalysts has resulted in the generation of functional olefins, macrocycles, fluorinated derivatives, enynes, and polymers by means of RCM, CM, and ROMP reactions. These ruthenium allenylidene complexes not only tolerate an array of functional groups and are quite stable at high temperatures but also tolerate ionic liquids and water as media favoring an environmentally cleaner procedure. Varying the structural characteristics, for example, the phosphine substituents, the nature of the counterion, and the terminal groups on the allenylidene moiety in cationic species significantly increases the number of new possible different catalysts.

Additionally, these allenylidene compounds can be immobilized allowing good recyclability and low-cost procedures.

Regarding ruthenium indenylidene complexes, the mechanism of formation of the indenylidene ligand from reaction between propargylic alcohol and a ruthenium precursor including formation of ruthenium vinylidene, allenylidene, and alkenylcarbene intermediates is now well-understood. This insight led to reliable and reproducible procedures for the synthesis of ruthenium indenylidene complexes under ambient conditions. Prominent characteristics of this class of olefin metathesis catalysts are their ease of preparation, high thermal stability, air and moisture stability, functional group tolerance, and high intrinsic catalytic activity. Altering the application profile of the catalysts is readily obtained by varying or exchange of phosphine ligands, substitution of halide ligands with, for example, Schiff base ligands, incorporation of *N*-heterocyclic carbene ligands, or ultimately a cross-metathesis based exchange of the indenylidene ligand with styrene or its derivatives. Consequently, the class of ruthenium indenylidene type complexes gradually begins to fulfill its potential as viable olefin metathesis catalysts.

7. Acknowledgments

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