Latent olefin metathesis catalysts

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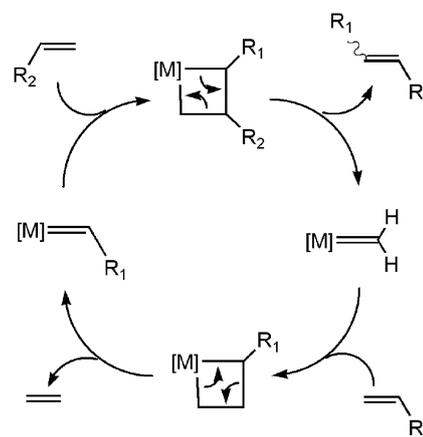
Olefin metathesis is a versatile synthetic tool for the redistribution of alkylidene fragments at carbon–carbon double bonds. This field, and more specifically the development of task-specific, latent catalysts, attracts emerging industrial and academic interest. This *tutorial review* aims to provide the reader with a concise overview of early breakthroughs and recent key developments in the endeavor to develop latent olefin metathesis catalysts, and to illustrate their use by prominent examples from the literature.

Introduction to olefin metathesis

Carbon–carbon double bonds constitute important building blocks towards the synthesis of many natural and synthetic products and olefin metathesis, a carbon–carbon double bond breaking and reforming sequence, has availed itself to synthetic organic and polymer chemists as an elegant method for making them.[1,2] The elucidation of the olefin metathesis mechanism by Chauvin and the development of well-defined Mo and Ru catalysts by Schrock and Grubbs, respectively, have transformed olefin metathesis to a versatile, user-friendly methodology. Accordingly, these researchers have gained most prominent recognition as they were awarded with the Nobel Prize for Chemistry in 2005.[3]

The olefin metathesis transformation can be understood in terms of a transition-metal-catalyzed redistribution of the

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Scheme 1

alkylidene fragments at carbon–carbon double bonds between two olefins (Scheme 1). Chauvin recognized that metal carbenes are the key intermediates during this transformation,

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.

Stijn Monsaert

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the mechanism comprising the formation and subsequent breaking of a metallacyclobutane ring *via* a [2+2]-cycloaddition/-cycloreversion of an alkene with a transition-metal alkylidene.[4]

With this in mind, several modes of olefin metathesis can be classified (Scheme 2); *e.g.*, an intramolecular olefin metathesis reaction results in a carbo- or heterocyclic olefin, referred to as ring-closing metathesis (RCM).[5a] The reverse reaction is known as ring-opening (ROM) or ring-opening cross metathesis (RO/CM).[5b] Cross metathesis is defined as an intermolecular metathesis reaction of monofunctional alkenes.[5c]

Alternatively, strained cyclic olefins can repeatedly react with metal carbenes resulting in the formation of a polymeric material, denominated as ring-opening metathesis polymerization (ROMP).[6a,b] In addition, the step-wise condensation of acyclic α,ω-dienes can lead to the formation of polymers with
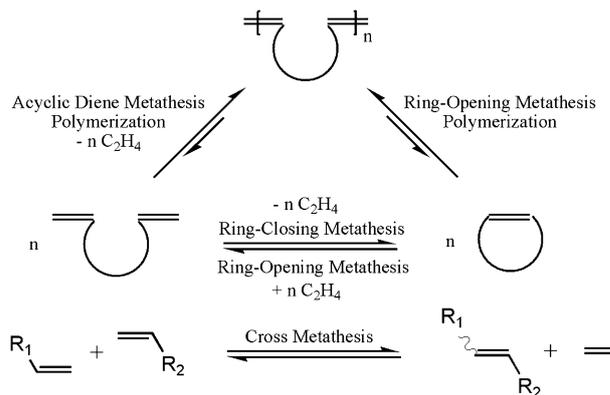
Scheme 2

well-defined characteristics as well, and is designated as acyclic diene metathesis polymerization (ADMET).[6c]

Furthermore, olefin metathesis catalysts exhibit catalytic activity towards closely related types of metathesis reactions, *e.g.* enyne metathesis,[7a] and even towards non-metathetical transformations.[7b,c]

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. Research by Schrock *et al.* on the development of high oxidation state, early transition-metal alkylidene complexes culminated in the discovery of the highly active olefin metathesis catalyst **1** (Scheme 3).[8] A major break-through was established by the development of air and moisture stable ruthenium alkylidene complexes which are tolerant towards most functional groups and thus straight-forwardly applicable in organic synthesis. The synthesis of the first generation ruthenium benzylidene catalyst **2**[9a] (Scheme 3) established a milestone in the history of olefin metathesis and laid the foundation for the further development of related complexes bearing an N-heterocyclic carbene ligand,[10a] the

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Renata Drozdzak (1969, Poland) obtained her MS in chemistry from the University of Wroclaw (Poland) in 1994. In 1999, she received her PhD degree in inorganic chemistry from the University of Wroclaw under the tutelage of Prof. A. Keller. From 1999 until 2002 she held a postdoctoral position at the same university. From 2003 until 2004 she conducted post-doctoral studies at the Ecole Nationale Superieure de Chemie, Laboratoire de Catalyse de Lille (France) under the direction of Prof. A. Mortreux. Currently she is working in collaboration with Prof. F. Verpoort of Ghent University on ruthenium-based Schiff base bearing catalysts.

Pascal Van Der Voort

Pascal Van Der Voort is a professor at the Department of Inorganic and Physical Chemistry, COMOC, Ghent University, Belgium. He obtained his PhD at the University of Antwerp (Belgium) in 1993 on the modification and characteriza-tion of silica and held several postdoctoral research positions on materials synthesis and characterization. Since 2006 he has been leading, together with Francis Verpoort, the research group COMOC (Center for Ordered Materials, Organometallics and Catalysis). He is the author of more than 90 Web-of-Science publications and two books.

Francis Verpoort

Francis Verpoort (1963, Belgium) received his PhD for his work on the develop-ment of heterogeneous tungsten based olefin metathesis catalysts from Ghent University in 1996. From 1996 to 1998 he was an assistant professor at Ghent University, and in 1998 he was promoted to full professor at the same university at the Department of Inorganic and Physical Chemistry, Division of Organometallic Chemistry and Catalysis. His main research interests concern the structure and mechanisms in organometallic chemistry, homogeneous and heterogeneous hybrid transition-metal catalysts, Schiff bases as co-ligands in metal complexes, enol–ester synthesis, olefin metathesis and ring-opening metathesis polymerization and atom transfer radical polymerization.

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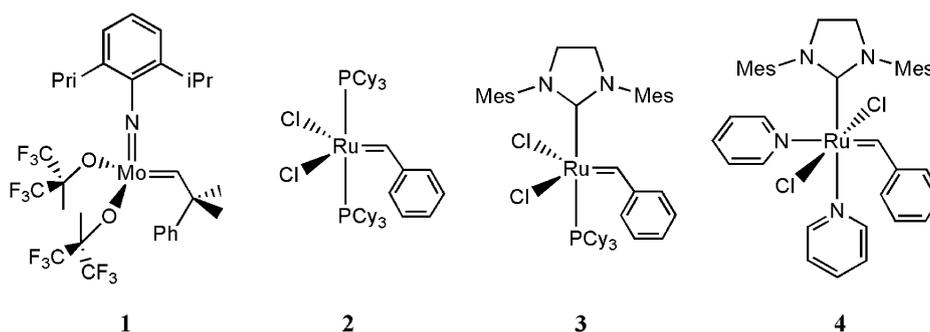
Scheme 3

so-called second generation Grubbs' catalyst **3**[9b] (Scheme 3), which generally gives rise to higher catalytic activities[10b] and increased thermal stability. It was shown that these ruthenium precatalysts enter the metathesis cycle after phosphine dissociation. The corresponding 14-electron complexes are highly electron-deficient and are stabilized by coordination of an olefin and subsequent formation and decomposition of the ruthenacyclobutane ring.

In the search for 2nd generation type catalysts with higher initiation rates, Choi and Grubbs reported complex **4** (Scheme 3) which turned out to be an ideal candidate for "living" ring-opening metathesis polymerizations, yielding polymers with remarkably low PDI's.[9c]

The success of the olefin metathesis reaction can thus be greatly attributed to its versatility and the development of well-defined catalysts stable to demanding reaction conditions. As these catalysts became commercially available and were exposed to a myriad of potentially interesting applications, the field was faced with renewed challenges, e.g. catalysts yielding high enantioselectivity in reaction products, catalysts with enhanced thermal stability or catalysts immobilized on heterogeneous supports were strongly demanded.

A class of task-specific olefin metathesis catalysts which has recently attracted increased attention is that of latent catalysts. Several key concepts should be kept in mind during the design of potential latent olefin metathesis catalysts. Firstly, the ideal latent olefin metathesis catalyst exhibits no catalytic activity in the presence of monomer or substrate at room temperature, but can be triggered quantitatively to a highly active form by thermal, chemical or photochemical activation to initiate the metathesis reaction. Most metathesis catalysts are operative at room temperature and are therefore not well-suited for applications where catalyst latency is beneficial. Additionally, catalyst stability towards decomposition or thermal degradation should be guaranteed by the rigorous choice of ligand environment.

In the past decade, ring-opening metathesis polymerization attracted increasing interest from polymer chemists since it is a straightforward method for the synthesis of functionalized, polymeric materials in a "living" way.[6a,b] Additionally, ruthenium-based olefin metathesis catalysts are easy to handle and the catalytically active species are relatively stable compared to those used in classical living polymerizations. The advantages of latent initiators for anionic polymerizations or controlled radical polymerizations are widely recognized,

and the use of similar methodologies for ring-opening metathesis polymerization is justified therefrom.

The advent of latent olefin metathesis catalysts was driven mainly by the need for ring-opening metathesis polymerization catalysts that can be mixed with the monomers without concomitant polymerization, which should allow for longer handling of the catalyst–monomer mixtures or even storage of the formulation for longer periods.

Furthermore, commercially available catalysts suffered from considerable degradation during metathesis reactions and it was anticipated that the elaboration of latent catalysts, which generally exhibit higher thermal stabilities, could yield *a catalyst that lives forever*.[11]

With this review, we wish to provide a comprehensive introduction to the state-of-the-art of latent ruthenium olefin metathesis catalysts, and to serve as a guide for further reading to the interested reader. In order to allow for a straightforward comparison of the catalytic behavior of the discussed catalysts, we have compiled representative catalytic data in Tables 1–3.

Ill-defined latent catalysts

Contrary to well-defined latent olefin metathesis catalysts, ill-defined latent catalysts can be defined as transition-metal complexes without an alkylidene fragment. In the case of ruthenium, the active alkylidene is formed *in situ* by the addition of a carbene source or it is formed by coordination of the substrate to the coordinatively unsaturated complex and subsequent 1,2-H-shift. Although these ill-defined systems were originally used due to a lack of well-defined catalysts, they regained interest, having several advantages compared to the former ones. For example, these catalysts are generally cheaper and readily commercially available or easily prepared from commercially available compounds. Furthermore, they sometimes exhibit comparable performance and allow for straightforward synthetic procedures.

In the late 1980s, it was shown that $Ru(H_2O)_6(tos)_2$ polymerizes norbornenes within minutes and low-strain cyclic olefins were readily polymerized when ethyl diazoacetate was added to the reaction.[1b] Noels *et al.* reported on the use of trimethylsilyl diazomethane (TMSD) as a more efficient carbene precursor in combination with ruthenium arene complexes **5** (Scheme 4, L = PCy_3, $PPhCy_2$, P^iPr_3), either preformed or prepared *in situ* upon mixing [$RuCl_2$(*p*-cymene)]$_2$ with the corresponding phosphine, to form the highly active
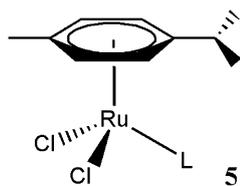
Scheme 4
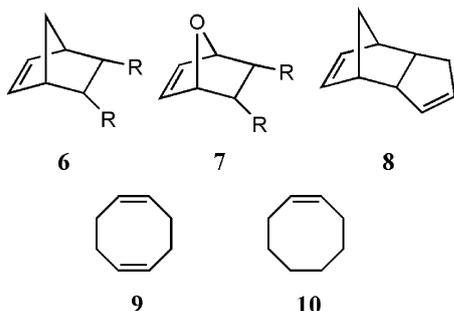
Scheme 5

[Ru]=CHSiMe$_3$ *in situ* for the polymerization of functionalized norbornenes (Scheme 5, **6**) and cyclooctenes (Scheme 5, **10**). Gelation occurred within minutes after activation of the complexes with TMSD and TON higher than 2000 were readily reached. Interestingly, proof of the formation of the [Ru]=CHSiMe$_3$ complex and the propagating species derived therefrom upon addition of monomer could be observed by ^{1}H and ^{13}C NMR spectroscopy, and the content of original ruthenium activated accordingly was determined to be 15–20%. Metathesis activity was attributed to the highly active, coordinatively unsaturated ruthenium monophosphine complex formed upon the TMSD induced release of the *p*-cymene ligand.[12]

In 1997, Hafner *et al.* described the use of osmium and ruthenium arene complexes bearing various phosphine ligands.[13] Type **5** osmium complexes (Scheme 4, L = PCy$_3$, P^{i}Pr$_3$) are highly active ROMP catalysts when irradiated by UV (200 W Hg lamp, 5 min), while inactive towards thermally induced polymerization. In contrast, similar complexes based on ruthenium mostly exhibited room temperature activity towards the polymerization of norbornene. However, clear-cut photoactivity was determined for complex **5** (Scheme 4, L = P^{n}Bu$_3$), yielding traces of poly(NBE) after 1 h at 80 °C but affording 80% conversion upon irradiation for 5 minutes at room temperature. Furthermore, complex **5** (Scheme 4, L = PCy$_3$) exhibited latent properties towards the polymerization of dicyclopentadiene (Scheme 5, **8**, DCPD), being stable for weeks as a solution in DCPD and thermally activated upon heating to temperatures above 80 °C. This was an important precedent since poly(DCPD) is an attractive, oxidatively stable thermoset with exquisite electrical and mechanical properties, and no ruthenium catalysts for the ROMP of DCPD were available at that time. In fact, poly(DCPD) was classically obtained using early transition-metal catalysts and the observation that ruthenium complexes are suitable catalysts opened the field of poly(DCPD) chemistry to the incorporation of filler materials and additives.

Additionally, this complex, either preformed or formed *in situ*, exhibits high catalytic activity towards the RCM synthesis of small to large, functionalized cyclic olefins when heated to reflux in CH$_2$Cl$_2$ and exposed to neon light or strong daylight.[14]

De Clercq and Verpoort reported the incorporation of a bidentate κ^2-(O,N) Schiff base ligand in complex **5**. Results showed that these complexes exhibit rather low activity towards the ROMP of norbornene and cyclooctene but high activity is observed after chemical activation with TMSD.[15]

The isolation of N-heterocyclic carbenes in the early nineties[10a] marked an important milestone when incorporated in olefin metathesis catalysts since they function as strong electron-donating and sterically demanding phosphine mimics. Delaude *et al.* reported the visible light-induced ROMP of cyclooctene with complexes **5** (Scheme 4, L = IMes = 1,3-dimesitylimidazol-2-ylidene, Dipp = 1,3-di(2,6-diisopropyl-phenyl)-imidazol-2-ylidene).[16] These complexes exhibited high catalytic activity, even at room temperature and without the addition of TMSD as a carbene precursor. However, the need for photochemical activation was indisputably evidenced from experiments in darkness (22%), normal daylight (93%), on irradiation with neon light (99%) or with a 250 W incandescent light bulb (>99%), being of possible interest when thinking of dental applications or surface modification. Surprisingly, these complexes exhibit no photochemical activity for the RCM of diethyl diallylmalonate. Although the mechanism of ruthenium alkylidene formation remained elusive, UV-Vis and NMR spectroscopy confirmed the release of the *p*-cymene ligand (absorption at 450 nm) after visible light irradiation of the complex in PhCl, thus forming a highly coordinatively unsaturated ruthenium complex.

Buchmeiser *et al.* studied complexes **5** (Scheme 4, L = PPh$_3$, PCy$_3$, IMes, SIMes) where the chlorines are replaced by trifluoro acetate ligands and subjected them to thermally induced polymerization of enantiomerically pure norbornene derivatives.[17] *Exo*-norbornene derivatives were polymerized faster than their *endo*-congeners, but the non-quantitative nature of the initiation of the ruthenium precatalysts yielded "non-living", though controlled polymerizations. Replacement of the chlorine ligands by trifluoro acetate ligands, as well as the incorporation of N-heterocyclic carbene ligands, furthermore proved to be of capital importance for the straightforward *in situ* formation of the active catalyst. In addition, quantum chemical calculations supported the idea that the active catalyst is formed upon coordination of norbornene and a subsequent 1,2-H-shift, and allowed for rationalization of discrepancies in catalytic activities observed.
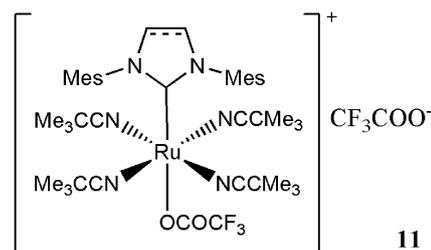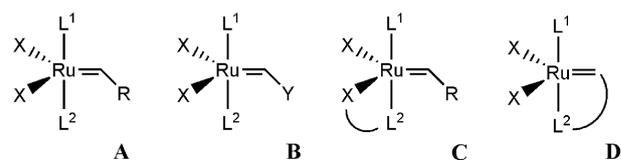

Scheme 6

Hafner *et al.* studied the use of cationic (half-)sandwich Ru[II] and Ru[II] nitrile complexes as potential photoinitiators since they are known to possess a high activation energy barrier towards the dissociation of an arene or nitrile ligand and therefore were suspected to exhibit high thermal latency. Indeed, a mechanistic study revealed the release of arene ligands upon UV irradiation to form solvated Ru[II] complexes, $[Ru(solvent)_6]^{2+}$, which are ought to be responsible for high polymerization activity. A similar study using ^{1}H NMR spectroscopy for the ruthenium nitrile complexes in D_2O revealed the release of acetonitrile from $[Ru(NC-Me)_6]^{2+}$ to form $[Ru(NC-Me)_{6-x}(D_2O)_x]^{2+}$ complexes. Experimental results illustrated that indeed only weak activity was observed for the thermally induced ROMP of norbornene and 7-oxa-2-norbornene-6,7-dicarboxylic acid dimethyl ester (Scheme 5, **7**) in ethanol using different nitrile complexes. However, activity of the complexes increased effectively upon irradiation with a 200 W Hg lamp. More importantly, ruthenium sandwich complexes exhibited no thermal activity at all, but proved to be highly active catalysts upon short irradiation. Analysis of the polymers thus obtained revealed high PDI's (typically higher than 2.0) for both ruthenium (half-)sandwich and nitrile complexes, basically indicating that the polymerization is not "living". Additionally, their cationic character limited their applicability to polar solvents such as water and ethanol.[18]

Only recently, Buchmeiser *et al.*,[19] elaborating the initial efforts of Hafner *et al.*, reported on the incorporation of an N-heterocyclic carbene ligand (Scheme 6, NHC = IMes, SIMes) in cationic Ru[II] nitrile complexes, illustrating the use of such complexes as photoactive initiators for ROMP of functionalized norbornenes, DCPD and 1,5-cyclooctadiene (Scheme 5, **9**, COD). Analogous to the results obtained by Hafner *et al.* no catalytic activity was observed upon mixing these photocatalysts with cyclic olefins (after 24 h at room temperature). However, a 308 nm light source clearly induced catalytic activity when the catalyst–monomer mixtures in $CHCl_3$ were exposed. Interestingly, yields increased significantly when a 254 nm Hg lamp was used instead. Furthermore, the newly explored methodology proved applicable for the surface functionalization of glass plates with poly(DCPD).

A quantum chemical study provided mechanistic understanding of the photo-formation of the ROMP-active species. Thus, it was explained that in accordance with mechanistic studies by Hafner *et al.*, irradiation induces the dissociation of one ^tBu-CN ligand. Although, either dissociation of a second ^tBu-CN ligand or coordination of a monomer proved to be energetically unfavored, excitation to the triplet state by UV irradiation weakens the Ru–N bond and consequently enables decoordination of a second ^tBu-CN. Coordination of an olefinic substrate molecule to form a π-complex and subsequent 1,2-H-shift allows for the formation of the ruthenium alkylidene and consequent polymerization. In addition, theoretical studies were supported by laser flash and steady-state photolysis experiments.

Well-defined latent catalysts

A major shortcoming of ill-defined catalyst systems is their lack of initiation efficiency which results in broad molecular
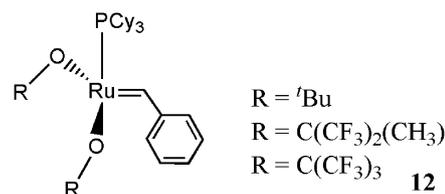

Scheme 7

weight distributions of the obtained polymers and the need for high catalyst loadings which limits commercial applications. Polymerizations with ill-defined latent catalysts can therefore not be considered as "living" polymerizations. However, the advent of well-defined, highly active ruthenium catalysts and the fact that they were commercially available, urged the development of latent catalysts incorporating a ruthenium alkylidene motif. Different approaches towards the design of well-defined latent catalysts are presented in Scheme 7.[20]

A first class of catalysts retain the classic morphology of Grubbs' first and second generation catalysts (class A). When applying heteroatom substituted carbene ligands, so-called Fischer carbenes, no catalytic activity is observed. However, these catalysts can be activated thermally or photochemically (class B). Catalysts with motif C or D make use of the chelate effect to reduce catalyst initiation. When activated, class C catalysts open the coordination site by the dissociation of L^2. Although this approach can stabilize the catalyst towards decomposition, a competitive coordination between the dangling ligand and olefinic substrates can reduce the propagation speed. Such a competition is avoided when using catalysts with motif D.

Latent Grubbs type catalysts

In the search for the isolation of highly reactive, 14-electron ruthenium alkylidene intermediates, Grubbs *et al.* reported coordinatively unsaturated, trigonal pyramidal ruthenium complexes after exchange of both chlorine ligands in the first generation Grubbs' catalyst by more π-donating and sterically demanding tertiary alkoxide ligands (Scheme 8; Table 1, entries 1 and 2).[21] Although highly electron-deficient, these complexes exhibit no catalytic activity for the RCM of diethyl diallylmalonate at room temperature, and only moderate activity is obtained after 12–96 h at 60 °C. Furthermore, substantial catalyst decomposition is observed after entering the catalytic cycle. However, catalysts **12** can be triggered by the addition of 2 equiv. of hydrochloric acid, yielding almost quantitative conversions for the RCM of diethyl diallylmalonate at room temperature after about 1 h. The idea that HCl could protonate the alkoxide moieties with subsequent release of those ligands and post-end coordination of the two chlorines to ruthenium was supported by ^{19}F NMR spectroscopy and

R = ^tBu
R = $C(CF_3)_2(CH_3)$
R = $C(CF_3)_3$ **12**

Scheme 8

Table 1 Activity of latent Grubbs type catalysts (entries 1–6) and latent catalysts bearing electron-rich carbene ligands (entries 7–10)

Entry	Catalyst	Reaction	Substrate	Temperature/°C	Co-catalyst (equiv.)	TON^a/mol × mol^{-1}	TOF^b/mol × mol^{-1} × h^{-1}	Ref.
1	**12** (R = C(CF$_3$)$_2$(CH$_3$))	RCM	DEDAM^c	60^d	—	3.5	0.036	21
2				25^d	HCl (2)	>4.8	>7.38	21
3	**2** + 2 equiv. inhibitor^e	ROMP	**6** (R = H)	25^f	—	<20	<0.28	22
4				25^f	85% H$_3$PO$_4$ (5)	>900	>216 000–54 000	22
5			**10**	25^f	—	<20	<0.28	22
6				25^f	85% H$_3$PO$_4$ (5)	>900	>30 857–9818	22
7	**13**	ROMP	**8**	n.d.^{g}	—	>11 760^h	>70 560–58 800^h	24
8				60^f	—	>11 760^h	>1 058 400^h	24
9	**14**	ROMP	**9**	60^d	—	10–50	25–0.53	25
10		RCM	DEDAM^c	60^d	—	1.65–33	33–1.16	25

^{a} Turn-over number, calculated based on literature data. ^{b} Turn-over frequency, calculated based on literature data. ^{c} Diethyl diallylmalonate. ^{d} Solvent: C$_6$D$_6$. ^{e} See text for details. ^{f} No solvent. ^{g} Not determined. ^{h} Calculation based on assumption of >98% conversion.

the fact that Grubbs' first generation catalyst was regenerated upon consecutive acid (2 equiv.) and PCy$_3$ (1 equiv.) addition.

In 2007, P'Pool and Schanz reported the use of Grubbs' first generation catalyst in a reversible inhibition–activation sequence with readily available N-donors such as methyl imidazole (MIM), dimethylamino pyridine (DMAP) and pyridine as inhibitors and phosphoric acid as activator.[22] A high degree of latency was found since no activity was observed after 24 h at room temperature for the ROMP of 50 equiv. of cyclooctene upon addition of 1–5 equiv. of MIM or DMAP, while successful reactivation occurred upon addition of an excess of H$_3$PO$_4$. In addition, a dramatic increase of initiation rate was found for the reactivated complexes compared to non-inhibited Grubbs' first generation catalyst. Interestingly, an in-depth NMR investigation allowed the study of the equilibria governing the inhibition and reactivation processes and the experimental results observed could thus be clarified (Table 1, entries 3–6).

In another study focused on Grubbs' first generation catalyst, Kunkely and Vogler[23] have shown that UV-Vis irradiation of the square pyramidal complex induces a geometrical distortion which increases steric hindrance between phosphine and chlorine ligands, thus facilitating phosphine dissociation. Such a methodology was recognized to be of potential interest for less efficient or latent first generation Grubbs' catalyst analogues.

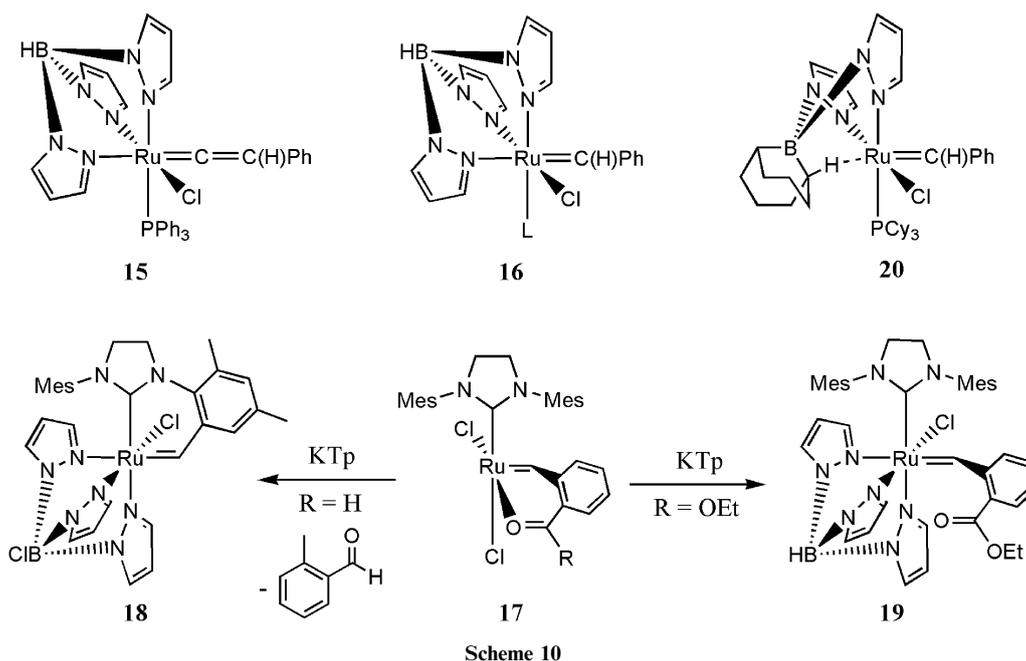### Catalysts bearing electron-rich carbene ligands

Although heteroatom substituted ruthenium carbenes were initially believed to be inactive for olefin metathesis reactions, van der Schaaf et al. illustrated that ruthenium complexes bearing arylthio substituted carbene ligands, **13** (Scheme 9; Table 1, entries 7 and 8), efficiently polymerized 12 000 equiv. DCPD, with gel times ranging from 10 to 12 min, thus allowing for adequate handling of the monomer–catalyst mixture in contrast to Grubbs first generation catalyst.[24] Additionally, reactions were completed within 60 seconds by application of these catalysts in a plate polymerization experiment using a preheated mold at 60 °C and monomer–catalyst ratios of 4700/1, allowing for fast polymerization and high exotherms, a semiquantitative indication for conversion.

13 R = H
     R = Me

14 L = PCy$_3$, IMes, SIMes
     ER = OEt, SEt, SPh,
     N(carbazole),
     N(pyrrolidinone)
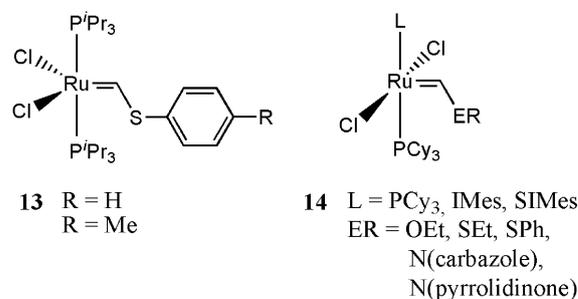
Scheme 9

This approach was further elaborated by Grubbs and Louie with the synthesis of complexes **14** (Scheme 9; Table 1, entries 9 and 10).[25] These complexes proved applicable for the ROMP of norbornene at room temperature, albeit with significantly decreased initiation rates; $\tau_{1/2}$ ranges within minutes whereas $\tau_{1/2}$ ranges within seconds for comparable complexes bearing alkylidene or benzylidene ligands, thus allowing for rigorous mixing of catalyst and monomer. In contrast to the IMes and SIMes (4,5-dihydro-1,3-dimesitylimidazol-2-ylidene) substituted catalysts, ROMP of the more challenging COD revealed only moderate to low activity for the phosphine bearing analogues, even when heated to 60 °C. Interestingly, all complexes were active for the RCM of diethyl diallylmalonate and a distinct reactivity trend was concluded; activity of (L)(PCy$_3$)Cl$_2$Ru=C(H)ER catalysts increased in the series E = C > N > S > O.

Catalysts bearing dangling ligands

Although application of the discussed catalysts exhibits notable advantages for certain applications, efforts were directed towards the exploration of different catalyst designs which are more readily altered. In this discussion, the use of hemilabile ligands is of major importance. Hemilabile ligands occupy two or more coordination sites at the metal center via donating groups with preferably significantly different steric and electronic properties. Thus, one coordinating group can dissociate from the catalytically active center to yield a coordination vacancy for substrate molecules while the other donor group remains attached to the transition metal and consequently stabilizes the reactive species. Furthermore,

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Scheme 10

steric and electronic properties of these ligands are easily varied over a wide range by the proper choice of the constituting coordinating groups, thus allowing for advanced fine-tuning of the properties of the precatalyst.

In 1998, Ozawa et al.[26] and Grubbs et al.[27] described the use of a tridentate, 6-electron-donating, anionic hydridotris-(pyrazolyl)borato ligand (κ^3-Tp) to enhance the thermal stability of ruthenium vinylidene, 15, and ruthenium benzylidene, 16, complexes, respectively (Scheme 10). In contrast to Cp-ligands, which are also 6-electron, anionic ligands occupying 3 coordination sites, these Tp ligands are more sterically demanding and stronger electron-donors.

The 18-electron vinylidene ruthenium complex, 15, described by Ozawa exhibited moderate catalytic activity towards the ROMP of norbornene, however, long reaction times (72 h) and high temperatures (80 °C) were required. More importantly, these complexes were shown to be triggered by the addition of 3 equiv. BF$_3$·Et$_2$O, allowing them to achieve the same results at only 40 °C (Table 2, entries 1 and 2).

The incorporation of a Tp ligand in the first generation Grubbs' catalyst, 2, straightforwardly affords complex 16 (Scheme 10, L = PCy$_3$), which was found not to facilitate the RCM of diethyl diallylmalonate or the ROMP of norbornene, even after several days at 70 °C. Although the addition of phosphine scavenging agents such as HCl, CuCl or AlCl$_3$ yields higher catalytic activity for the RCM of diethyl diallylmalonate, the use of complex 16 (L = PCy$_3$) was restricted by the high catalyst loading required (20 mol%) (Table 2, entries 3–6).

Following the efforts of Ozawa and Grubbs, Slugovc et al. tried to implement Tp ligands in κ^2-(C,O) complexes 17 with a cis-dichloro configuration (Scheme 10).[28] Interestingly, addition of KTp to complex 17 (R = H) led to the formation of the κ^2-(C,C)-κ^3-(N,N,N) complex 18, through a double C–H activation of the o-methyl substituents of the SIMes ligand and the simultaneous elimination of the 2-formylbenzylidene

ligand as 2-methylbenzaldehyde. Additionally, the proton in the Tp-ligand appeared to have been substituted by a chlorine which was originally coordinated to ruthenium. In the case of 17 (R = OEt), the rather expected κ^3-(N,N,N) complex 19 was obtained. Monitoring the catalytic activity of complexes 18, 19 and 16 (L = SIMes) towards the ROMP of norbornene-2,3-dicarboxylic acid diethyl ester using DSC revealed that high 'switching temperatures' (the temperature at which the initiation of the polymerization reaction is observed) were reached (109 °C, 128 °C and 138 °C for catalysts 18, 19 and 16 (L = SIMes), respectively) (Table 2, entries 7 and 8).

Another approach, reported by Patel et al., involved the incorporation of an anionic, bidentate bis(pyrazolyl)borate ligand (κ^2-Bp) in Grubbs first generation catalyst, 20 (Table 2, entries 9–11).[29] Interestingly, single-crystal structure determination revealed the presence of an agostic interaction from the Bp ligand to ruthenium. Furthermore, complex 20 exhibited high thermal stability in solution, even in acetone; no indication of decomposition was observed over several weeks. When subjected to catalyst 20, no traces of RCM of diethyl diallylmalonate were detected after 1 h in toluene at 80 °C, and only moderate conversion (36%) was obtained after 1 h at reflux. Addition of CuCl increased the catalytic activity substantially (81%), but the need for high catalyst loadings (8 mol%) render this methodology unfavorable.

As can be concluded from the experimental results discussed above, Tp- and Bp-type ligands induce a high degree of catalyst stability and latency towards RCM of dienes and ROMP of strained cyclic olefins. However, thermal activation of Tp- and Bp-based catalysts proved to be difficult, an inconvenience often remedied by the use of higher catalyst loadings. For these reasons, these type of complexes are unsuitable candidates as potential latent catalysts, hence other approaches are required.

In this respect, a series of latent olefin metathesis catalysts bearing bidentate κ^2-(O,O) and κ^2-(O,N) ligands were

Table 2 Activity of latent olefin metathesis catalysts bearing dangling ligands

Entry	Catalyst	Reaction	Substrate	Temperature/°C	Co-catalyst (equiv.)	TON^a/mol × mol^{-1}	TOF^b/mol × mol^{-1} × h^{-1}	Ref.
1	**15**	ROMP	**6** (R = H)	80^c	—	99	1.38	26
2				40^d	BF$_3$·OEt$_2$ (3)	97	1.35	26
3	**16** (L = PCy$_3$)	RCM	DEDAM^e	70^d	—	—^{f}	—^{f}	27
4				25^d	HCl (1)	5	1.25	27
5				25^d	CuCl (10)	5	0.28	27
6				25^d	AlCl$_3$ (1)	4.1	0.17	27
7	**18**	ROMP	**6** (R = COOEt)	109^{g,h}	—	—	—	28
8	**19**			128^{g,h}	—	—	—	28
9	**20**	RCM	DEDAM^e	80^i	—	—^{f}	—^{f}	29
10				Δ^i	—	4.5	4.5	29
11				Δ^i	CuCl	10.1	10.1	29
12	**21** (L = SIMes, R = ^{t}Bu)	ROMP	**10**	25^d	PAG^j (2)-hν^k	>19	>9.5	31
13		RCM	DEDAM^e	25^d	PAG^j (2)-hν^k	>19	>9.5	31
14	**22** (L = SIMes)	ROMP	**6**	70^i	—	2000–440	500–110	33a
15			**10**	70^i	—	800–632	200–158	33a
16			**9**	25^d	—	—^{f}	—^{f}	33b
17				90^i	—	300	100–12.5	33b
18				25^l	HSiCl$_3$ (70)	3000	12 000	33c
19				25^i	HSiCl$_3$ (1000)	630 000	1 260 000	33c
20		RCM	DEDAM^e	55^m	—	20	5	33a
21	**23** (L = SIMes)	RCM	DEDAM^e	100^i	—	1000–1500	111–167	34
22				25^l	PhSiCl$_3$ (0.5–50)	>800	>267	34
23	**24** (L = ICy)	ROMP	**6** (R = H)	25^i	—	57–65	114–130	36
24				60^i	—	98–100	392–400	36
25		ROMP	**10**	25^d	—	−90^f	—^{f}–90^f	36
26				60^d	—	360–400	864–960	36
27	**24** (L = PCy$_3$)	CM	1-Octene	35^g	—	1143	163	37
28				80^g	—	10 119	1446	37
29	**24** (L = SIMes)	CM	1-Octene	35^g	—	379	54	37
30				70^g	—	10 428	1490	37
31	**25**	RCM	DEDAM^e	20^d	HCl (2)	20	10	38
32			DAA·HCl^n	40°	HCl (2)	14	1.27	38
33	**26**	RCM	DEDAM^e	35^d	—	<0.012	<0.005	39
34				25^d	HCl (xs.)	65	>650	39
35	**27**	RCM	DEDAM^e	40^m	—	30–50	30–50	40
36				70^m	—	100–180	200–360	40
37			DAC(CN)$_2^p$	40^d	—	34.5–47.5	2.88–3.96	40
38				80^i	—	63–98	10.5–16.3	40

^{a} Turn-over number, calculated based on literature data. ^{b} Turn-over frequency, calculated based on literature data. ^{c} Solvent: CH$_2$ClCH$_2$Cl. ^{d} Solvent: dichloromethane. ^{e} Diethyl diallylmalonate. ^{f} No activity observed. ^{g} No solvent. ^{h} 'Switching temperature', see text for details. ^{i} Solvent: toluene. ^{j} Photoacid generator. ^{k} Sub-300 nm light. ^{l} Solvent: CDCl$_3$. ^{m} Solvent: C$_6$D$_6$. ^{n} Diallylamine hydrochloride. ^{o} Solvent: CD$_3$OD. ^{p} Diallylmalononitrile.

synthesized (Scheme 11). Complex **21** (Scheme 11, L = PCy$_3$), straightforwardly obtained from first generation Grubbs' catalyst, **2**, and 2 equiv. Tl(alkyl-acac), proved to be inactive for the solvent-free polymerization of DCPD and the polymerization of 7-oxanorbornene-2,3-dimethoxymethyl (Scheme 5, **7**, R = CH$_2$–O–CH$_3$) in methanol at room temperature.[30] However, addition of organic or inorganic acids, e.g. hydrochloric acid, enabled reactivation of the

catalyst and reactions were completed within minutes, basically surpassing the activity of the parent complex **2**. It was furthermore illustrated that complex **21** (Scheme 11, L = PCy$_3$, SIMes) is readily activated upon irradiation of a catalyst–monomer mixture containing a photoacid generator and was found applicable in RCM and ROMP (Table 2, entries 12 and 13).[31] The authors noticed that such behavior could be of supreme interest in a reaction injection molding
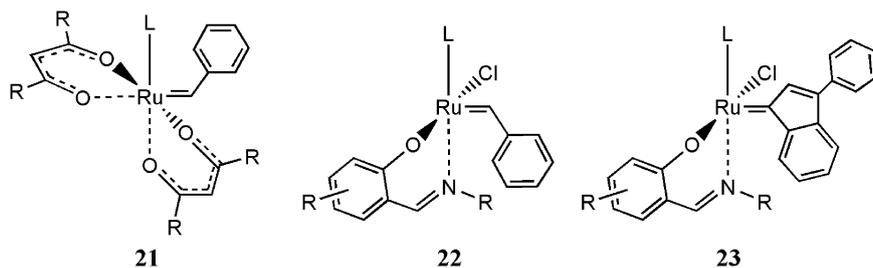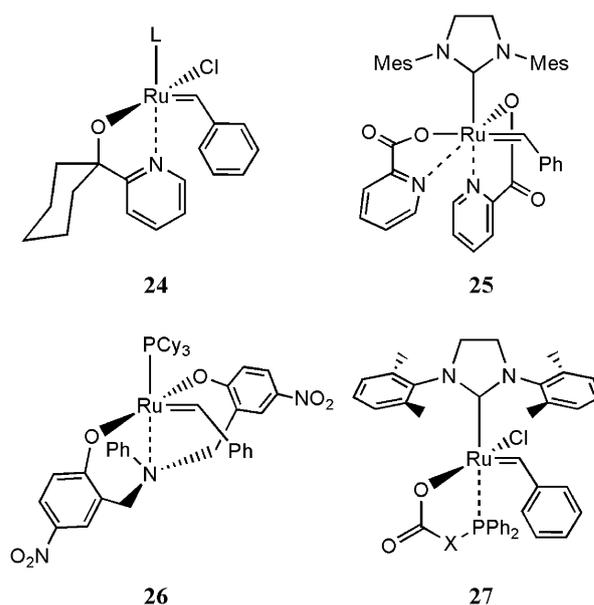
Scheme 11

process where the catalyst can be stored together with the monomer while a second monomer stream contains acid to activate the catalyst.

In another approach towards rationally designed thermally stable olefin metathesis catalysts, efforts were directed towards the development of an O,N-bidentate Schiff base ligated Ru–carbene catalysts.[32] These ligands are especially feasible for fine-tuning of ligand parameters since their steric and electronic environment can be easily tailored by the proper choice of amine and salicylaldehyde. The catalysts thus obtained proved to exhibit high air and moisture stability. Furthermore, the authors noticed that the catalytic activity of these catalysts for the RCM of diethyl diallylmalonate was substantially lower than that of the first generation Grubbs' catalyst, **2**, but that *the reactivity increases dramatically at higher temperatures*. In addition, high activity was observed for the RCM of diallylamine hydrochloride in methanol (catalyst loading: 5 mol%, 40 °C, 12 h, 95% yield).

This type of catalysts was further elaborated by De Clercq and Verpoort, incorporating an N-heterocyclic carbene which generally accounts for enhanced thermal stability combined with a definite increase of catalytic activity (Scheme 11, **22**, L = SIMes; Table 2, entries 14–19).[33a] It was shown that such complexes are extremely inactive at room temperature towards the polymerization of low-strain, cyclic olefins such as 1,5-cyclooctadiene and can be thermally activated to yield high activity for the bulk-polymerization of DCPD.[33b] Quantitative conversions were enabled for ROMP of COD mediated by various Schiff base catalysts; the high temperature (90 °C) and long reaction times (4–24 h) required illustrate that these catalysts combine latency and high thermal stability. Additionally, activation of the catalyst was facilitated by the addition of soft Lewis acids, *e.g.* HSiCl₃,[33c] yielding extremely high catalytic activity for the ROMP of COD and TON's up to 630 000. It was reasoned that coordination of the Lewis acid to the N of the Schiff base ligand yields a vacancy at the ruthenium center thus allowing ROMP, while the dangling phenoxide moiety was believed to prevent or significantly reduce bimolecular decomposition of the activated catalyst. Analogous complexes bearing an indenylidene, **23** (Scheme 11, L = PCy₃, SIMes; Table 2, entries 21 and 22),[34] or allenylidene[35] ligand were also found to exhibit high thermal stability combined with high activity upon thermal or acid activation in various challenging olefin metathesis reactions.

A pyridinyl-alcoholato ligand (Scheme 12, **24**; Table 2, entries 23–26) can be regarded as a 5-membered ring alternative to Schiff base ligands in complexes **22**. Their use was first described by Herrmann *et al.* who reported on enhanced activity for complex **24** (Scheme 12, L = ICy) for ROMP of cyclooctene and norbornene upon thermal activation.[36] Jordaan and Vosloo further elaborated this approach for the self-metathesis of 1-octene by catalysts **24** (Scheme 12, L = PCy₃; L = SIMes; Table 2, entries 27–30) and concluded on an enhanced temperature dependent selectivity.[37] Hahn *et al.* focused on improving the catalyst design by substituting the halide ligands by bidentate pyridine-carboxylato ligands (Scheme 12, **25**; Table 2, entries 31 and 32).[38] This complex showed no activity for the RCM of diethyl diallylmalonate. In contrast, addition of 2 equiv. of hydrochloric acid yielded

Scheme 12

quantitative conversion within 2 hours. Mass spectroscopy elucidated that either one or both Ru–O bonds can be cleaved. When targeting the RCM of diallylamine hydrochloride in methanol, the precatalyst not only proved to be stable in this solvent for weeks, in contrast to second generation Grubbs' catalyst, **3**, which exhibits only limited lifetime, but also a 70% conversion was attained within 12 h at 40 °C upon addition of hydrochloric acid. Alternatively, Jensen *et al.* reported the use of chelating κ³-(O,O,N) amine ligands (Scheme 12, **26**; Table 2, entries 33 and 34) in the RCM of diethyl diallyl-malonate.[39] They concluded a remarkably low room temperature activity of these precatalysts but illustrated the use of Brønsted acids, such as HCl or H₂SO₄, to activate the catalyst. Zhang *et al.* elaborated the possibility of a bidentate phosphino-carboxylato ligand, envisioning the dissociation of the phosphine from the ruthenium at elevated temperatures to initiate olefin metathesis while the carboxylate group remains coordinated to the ruthenium center (Scheme 12, **27**; Table 2, entries 35–38).[40] While these complexes are straight-forwardly obtained from reaction of a second generation Grubbs type complex with the corresponding sodium phosphine-carboxylates, they exhibit medium to high activity for the RCM of diethyl diallylmalonate at 40 °C and 70 °C. Especially complexes with X = CH₂ or X = *o*-C₆H₄ yielded a good combination of high reactivity and catalyst stability at elevated temperatures. Moreover, these complexes excel second generation Grubbs' catalyst, **3**, for the RCM of diallylmalononitrile, a challenging RCM substrate since the cyano-group is known to deactivate olefin metathesis catalysts. Additionally, isomerization of substrate and product is strongly reduced since the phosphine ligand protects the catalytically active center from decomposition.
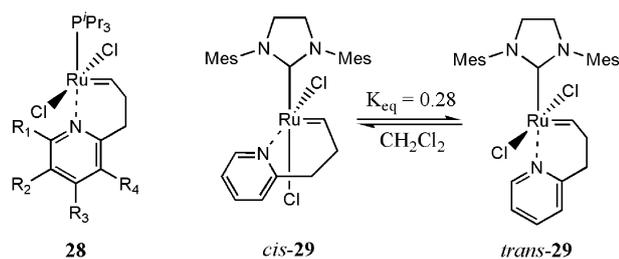
Catalysts bearing chelating alkylidene ligands

Catalysts bearing so-called 'dangling' ligands exhibit desirable characteristics; that is, low to negligible room temperature

activity, high thermal stability of the catalysts and simple activation either through addition of Brønsted or Lewis acids or through application at higher temperatures. When applied in ROM polymerization, however, one can prefer the cleavage of the chelating ligand to prevent its competitive coordination and thus allow for a fast propagation after retarded initiation. Therefore, a class of ruthenium catalysts bearing chelating alkylidene ligands has been developed and gains increased attention.

A first important report in this respect was the implementation of a substituted 2-pyridylethanyl alkylidene ligand by van der Schaaf et al. (Scheme 13, **28**; Table 3, entries 1 and 2).[24] It was clearly shown that variations in substitution pattern of the pyridine ligand of these catalysts influences gel times and T_gs of the obtained polymers during the bulk-polymerization of DCPD.

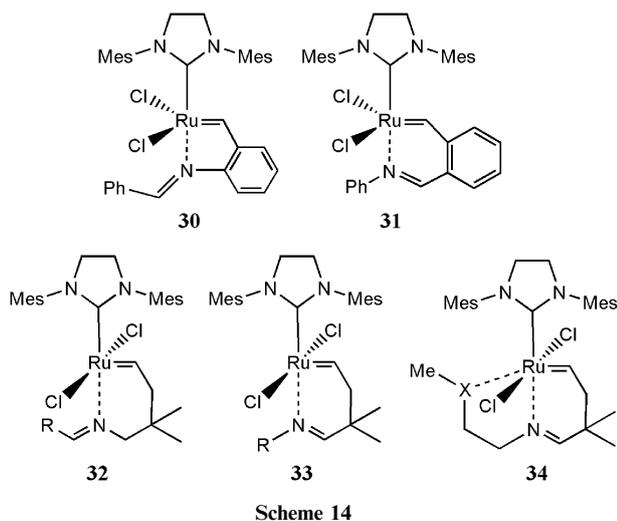Unfortunately, activities of the reported complexes were undesirably low; restricted to 12 000 equiv. DCPD. Consequently, N-heterocyclic carbene ligands, known to induce higher catalytic activities, were adopted in the catalyst design by Schrodi et al. (Scheme 13, **29**; Table 3, entries 3 and 4).[41] Interestingly, the corresponding complex exhibited an isomerization between the cis- and trans-dichloro configuration with a solvent dependent equilibrium (78 : 22 ratio in CD_2Cl_2). More importantly, both isomers could be isolated and the cis-isomer displayed a distinctly higher room temperature latency, i.e. towards the RCM of diethyl diallylmalonate and the ROMP of DCPD. It was reasoned that decoordination of the pyridine moiety, the initial step towards the formation of the catalytically active 14-electron species, is better facilitated by the stronger trans-influence of the N-heterocyclic carbene ligand in the trans-isomer vs. that of the chlorine ligand in the cis-isomer. In addition, mixtures of these isomers allowed the tuning of the induction period in bulk-polymerizations of DCPD, while high catalytic activities were obtained; up to 40 000 equiv. of DCPD were successfully converted.

In search of thermally switchable catalysts which allow for further fine-tuning, Slugovc et al. reported the synthesis of 5- and 6-membered, bidentate Schiff base benzylidene ligands, taking advantage of synthetically modular Schiff base ligands.[20] One member of each family was synthesized (see Scheme 14, **30**, **31**; Table 3, entries 5 and 6) and proved to be stable in solution (solvent = $CDCl_3$) at room temperature for at least 2 months and only moderate activity was observed towards the polymerization of norbornene-2,3-dicarboxylic acid diethyl ester; conversions were 20% and 29% for the polymerization of 50 equiv. norbornene-2,3-dicarboxylic acid diethyl ester with catalysts **30** and **31**, respectively, after 15 days. Additionally, the 'switching temperature' for these

Scheme 13

Table 3 Activity of latent olefin metathesis catalysts bearing chelating alkylidene ligands

Entry	Catalyst	Reaction	Substrate	Temperature/°C	Co-catalyst (equiv.)	TON^a/mol × mol^{-1}	TOF^b/mol × mol^{-1} × h^{-1}	Ref.
1	**28** (R_1 = Me)	ROMP	**8**	—^{c}	—	>11 760^d	>16 036^d	24
2				60^c	—	>11 760^d	>651 323^d	24
3	cis-**29**	ROMP	**8**	30^c	—	>29 400^d	>882 000^d	41a
4	trans-**29**	ROMP	**8**	30^c	—	>29 400^d	>76 696^d	41a
5	**30**	ROMP	**6** (R = COOEt)	48^{c,e}	—	—	—	20
6	**31**	ROMP	**6** (R = COOEt)	55^{c,e}	—	—	—	20
7	**32**	RCM	DEDAM^f	30^g	—	36	>1080	42
8	**33**	RCM	DEDAM^f	40^g	—	24–38	24–38	42
9		ROMP	**8**	30^c	—	>29 400^d	>1 764 000–58 800^d	42
10	**34** (X = C)	RCM	DEDAM^f	60^g	—	38	76	42
11	**34** (X = O)	RCM	DEDAM^f	60^g	—	38	76	42
12	**34** (X = S)	RCM	DEDAM^f	60^g	—	20	40	42
13	cis-**35** (X = N)	RCM	DEDAM^f	25^h	—	3.6	0.15	43a
14	cis-**35** (X = CH)	RCM	DEDAM^f	25^h	—	2.8	0.12	43a
15	trans-**35** (X = N)	RCM	DEDAM^f	25^h	—	7.6	0.32	43a
16	trans-**35** (X = CH)	RCM	DEDAM^f	25^h	—	6.4	0.27	43a
17	**35**	ROMP	**6** (R = COOEt)	110^i	—	129–168	25.8–33.6	43b
18	**37** (R = ^{i}Pr)	RCM	DEDAM^f	25^i	—	—^{j}	—^{j}	44a
19				90^i	—	550	11.5	44a
20	**38**	RCM	Me-DEDAM^{k,j}	25^h	—	<1	<0.17	45a
21				25^h	CSA^l (1)	20	3.33	45a
22	**39**	RCM	Me-DEDAM^{k,j}	28^h	—	~16	~8	45a
23				28^h	Ph_2SnCl_2 (1)	>32	>16	45a
24	**40**	RCM	DEDAM^f	40^h	—	2	1	45b
25				100^h	—	17.6	8.8	45b
26	**40**′	RCM	DEDAM^f	40^h	—	19	0.79	45b

^{a} Turn-over number, calculated based on literature data. ^{b} Turn-over frequency, calculated based on literature data. ^{c} No solvent. ^{d} Calculation based on assumption of >98% conversion. ^{e} 'Switching temperature', see text for details. ^{f} Diethyl diallylmalonate. ^{g} Solvent: C_6D_6. ^{h} Solvent: dichloromethane. ^{i} Solvent: toluene. ^{j} No activity observed. ^{k} Diethyl 2-allyl-2-(2-methylallyl)malonate. ^{l} (−)-Camphor-10-sulfonic acid.

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Scheme 14

Scheme 15

Scheme 16

catalysts was determined by means of DSC to be 48 °C and 55 °C for the 5- and 6-membered Schiff base catalysts **30** and **31**, respectively.

Alternatively, endo- and exocyclic Schiff base alkylidene ligands were applied by Grubbs *et al.* as a structural motif towards latent catalysts (Scheme 14, **32** and **33**; Table 3, entries 7–9).[42] Although the exocyclic Schiff base catalysts did not behave like latent catalysts, performing well at room temperature for the RCM of diethyl diallylmalonate, endocyclic imine catalysts exhibited a distinctly reduced room temperature activity, thus confirming their latent character. The authors further illustrated the versatility of their approach; *i.e.*, when subjected to the polymerization of DPCD, a more pronounced induction of the catalyst was found in the series R = Cy, ^{i}Pr, Ph, without observable influence on the overall catalyst activity. Furthermore, it is worth noting that this particular approach allowed the straightforward synthesis of various latent catalysts with 3-point chelates. Indeed, latency of type **34** catalysts decreases in the series X = S ≫ O ∼ CH$_2$ (Scheme 14; Table 3, entries 10–12).

Grela *et al.* envisaged that more rigid chelates would enhance the catalysts latency and consequently reported the latent properties of quinoline **35** (Scheme 15, X = CH) and quinoxaline **35** (Scheme 15, X = N) alkylidene complexes (Table 3, entries 13–17).[43a] In analogy to the 2-pyridylethanyl alkylidene complexes reported by Grubbs (Scheme 13, **29**), these air stable complexes exhibited *cis–trans*-isomerization, and *cis*-isomers were less active when applied in RCM or enyne metathesis reactions. Additionally, these complexes were found to be excellent latent catalysts for ROM polymerizations of various norbornene derivatives, no activity was observed for at least 2 weeks at room temperature and the catalysts exhibited high activity after thermal activation.[43b]

Finally, we want to conclude with some examples of latent catalysts specifically designed for application in organic synthesis.

A first important achievement in this respect is the development of a S-containing Grubbs–Hoveyda-type catalyst by Lemcoff *et al.* (Scheme 16, **37**; Table 3, entries 18 and 19).[44a]
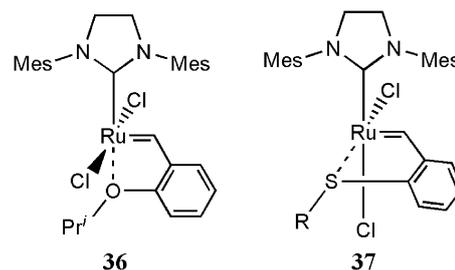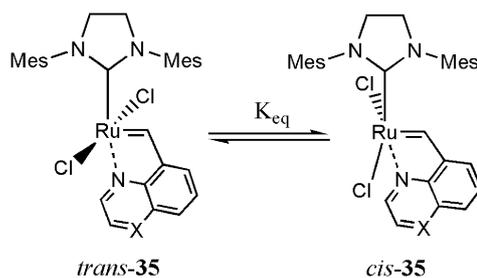
In contrast to the Grubbs–Hoveyda catalyst, **36**, its sulfur-containing congener has a *cis*-dichloro arrangement comparable to previous reports by Grubbs, Slugovc and Grela (*vide supra*). Both of these complexes exhibit high room temperature stability, but contrary to **36**, a highly active olefin metathesis catalyst often used for the synthesis of small or complex molecules, catalyst **37** displays a reversible *thermo-switchable behavior*; high activity is obtained for the RCM of diethyl diallylmalonate upon heating to 80 °C, but activity drops upon cooling the reaction mixture to room temperature. In addition, variation of the S-substituent allowed the activation temperature to be altered.[44b]

Grela *et al.* further elaborated the Grubbs–Hoveyda catalyst motif and introduced acid–base sensitive functionalities on the isopropoxybenzylidene ligand **38**, **39** (Scheme 17; Table 3, entries 20–23).[45a] Activation by Brønsted and Lewis acids, respectively, induced a strong electron-withdrawing effect, thus destabilizing the Ru–O bond and facilitating decoordination of the oxygen atom. In addition, catalyst **38** was straightforwardly immobilized on a polymeric phase containing Brønsted acidic functionalities which resulted in high catalytic activity with minimal ruthenium contamination of the reaction products, a requisite when focusing on the synthesis of biologically active compounds. In another report, Grela *et al.* described the synthesis of a tridentate κ^3-(C,O,O)-complex, **40** (Scheme 17; Table 3, entries 24–26), and its use as a chemically switchable catalyst with high regeneration efficiency.[45b] Catalyst **40** suffers from a strongly diminished activity, but the carboxylate can be cleaved with hydrochloric acid, thus allowing high catalytic activities. More importantly, purification of the reaction mixture on silica gel allowed the selective retention of **40′** (Ru contamination in the reaction products was as low as 48 ppm), while subsequent washing of the silica gel with ethyl acetate gave **40** in 95% yield.
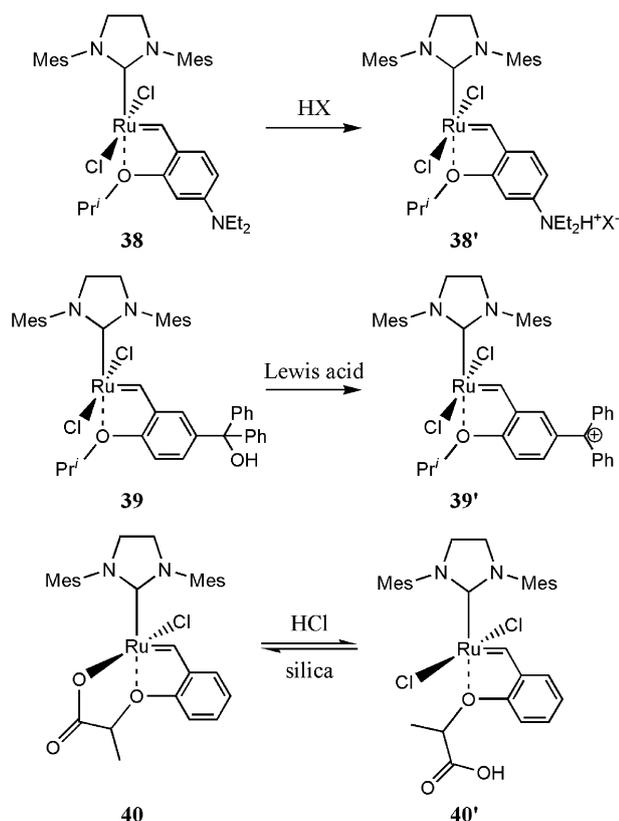
Scheme 17

Conclusions

We have described the rational design, study and application of one- and multicomponent, ill- and well-defined latent ruthenium-based olefin metathesis catalysts. These catalysts are of prominent importance for ring-opening metathesis polymerizations of low- and high-strained cyclic olefins, where they allow for rigorous mixing of monomer and catalyst without concomitant gelation or microencapsulation of the precatalyst, but they are also promising for applications in synthetic organic chemistry, where they give support to the idea of an olefin metathesis *catalyst that lives forever*.

It is now well established that ill-defined catalysts form an alkylidene ligand *in situ* after addition of a carbene precursor or coordination of an olefin to ruthenium and subsequent 1,2-H-shift. Well-defined catalysts bear an alkylidene ligand in their coordination sphere and are straightforwardly isolable. These catalysts are basically inactive towards metathesis of olefins either induced by inhibition, by heteroatom substituted carbene ligands or by chelating ligands occupying the active site of the catalyst, but they can be triggered upon addition of Lewis or Brønsted acids or are activated at higher temperatures.

Regardless of the increasing number of reports on latent ruthenium olefin metathesis catalysts and the advances that are made along these lines, we can state that the development of ill- and well-defined catalysts remains challenging.

Finally, we can conclude that although application of well-defined latent ruthenium olefin metathesis catalysts is often restricted to the advanced organometallic chemists with a profound interest in polymer chemistry, commercialization

of these catalysts will most probably accelerate their use in high profile applications. Furthermore, we hope that this contribution can help to detect synergies in the rational ligand design of potentially interesting latent ruthenium-based olefin metathesis catalysts.

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