Synthesis and Application of New Ruthenium-Based Olefin Metathesis Catalysts

Development of ruthenium-*N*-heterocyclic carbene catalysts for ring-closing metathesis at low catalyst loading and for redox-triggered ring-opening metathesis polymerization

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Teile dieser Arbeit sind bereits veröffentlicht oder zur Veröffentlichung eingereicht:

Papers

1. Roman D. Savka, Herbert Plenio, *"A hexahydro-s-indacene based NHC ligand for olefin metathesis catalysts", Journal of Organometallic Chemistry* **2012***, 710,* 68-74.

2. Lars H. Peeck, Roman D. Savka, Herbert Plenio, *"Fast Olefin Metathesis at Low Catalyst Loading", Chemistry – A European Journal* **2012**, *18*, 12845–12853.

3. Pavlo Kos, Roman Savka, Herbert Plenio, *"Fast Olefin Metathesis: Synthesis of 2-Aryloxy-Substituted Hoveyda-Type Complexes and Application in Ring-Closing Metathesis", Advanced Synthesis & Catalysis* **2013***, 355,* 439–447.

4. Roman Savka, Sabine Foro, Markus Gallei, Matthias Rehahn, Herbert Plenio, *"Oxidation-triggered Ring-opening Metathesis Polymerization" Chemistry – A European Journal* **2013**, *19*, 10655–10662.

5. Roman Savka, *"2-(Pentafluorophenyl)imidazolidines". Synlett* **2013,** *24*, 1735–1736.

European patent application

Kos P., Savka R., Plenio H. Ruthenium-based metathesis catalysts, precursors for their preparation and their use. Application date: 29.10.2012. Eur. Pat. Appl. EP12190416.3. Applicant: Umicore AG & Co. KG.

Content

Abbreviations

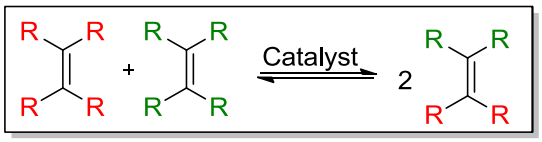
Ac	acetyl
Ar	aryl
Bu	butyl
COD	*cis*-cyclooctadiene
Cy	cyclohexyl
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
Dip	2,6-diisopropylphenyl
Et	ethyl
Fc	ferrocene
Fc*	decamethylferrocene
FT-IR	fourier transform infrared spectroscopy
*i*Pr	isopropyl
IMes	1,3-bis(2,4,6-trimethylphenylimidazol)-2-ylidene
L	ligand
Me	methyl
Mes	mesityl
MIC	mesoionic carbene
NaHMDS	sodium bis(trimethylsilyl)amide
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
PAG	photoacid generator
PBM	*p*-methoxybenzyl ether
Ph	phenyl
Py	pyridine
r.t.	room temperature
SIMes	1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
SIPr	1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
TBS	*tert*-butyldimethylsilyl
TCQ	tetrachloroquinone
TFA	trifluoroacetic acid
THF	tetrahydrofuran
UV/Vis	ultraviolet–visible spectroscopy

1. Introduction

Carbon-carbon bond formation is a fundamental reaction in organic chemistry. Among the metal-catalyzed transformations, cross-coupling reactions and olefin metathesis have been attracting a special attention. This is evidenced from 2005 Nobel Prize given to Robert H. Grubbs, Richard R. Schrock and Yves Chauvin for the development of the metathesis method in organic synthesis and 2010 Nobel Prize awarded to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for palladium-catalyzed cross couplings in organic synthesis.

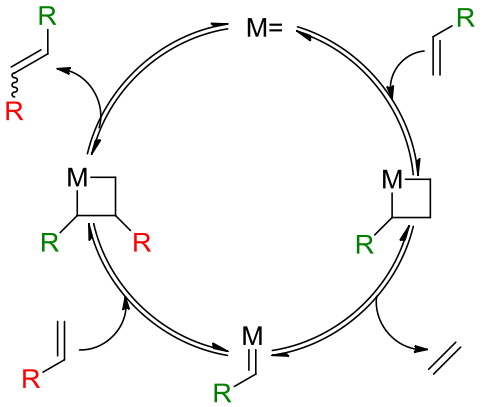
Over the last two decades, olefin metathesis has become a powerful tool for straightforward formation of carbon-carbon double bonds. It has been used for synthesis of heterocycles[1] and in total synthesis[2], in pharmaceutical[3] and supramolecular chemistry,[4–6] for green chemistry[7] and for protein modifications.[8,9]

In general, olefin metathesis is a chemical reaction between two olefins in which two carbon-carbon double bonds exchange with one another, forming new olefins with another substitution pattern around the double bond (Scheme 1).



Scheme 1. General representation of olefin metathesis reaction.

In 1971, Yves Chauvin and Jean-Louis Hérisson proposed the mechanism for olefin metathesis generally known as “Chauvin mechanism” (Scheme 2). As seen in Scheme 2, the catalytic cycle is a set of [2+2] cycloaddition and cycloreversion reactions. First, the initial metal alkylidene (M=) reacts with an olefin, forming a metallacyclobutane intermediate. Next, this intermediate undergoes cycloreversion, forming either the initial metal alkylidene or, productively, ethylene and a new metal alkylidene (M=CHR). The new metal alkylidene (M=CHR) reacts with second molecule of olefin to give metallacyclobutane intermediate which then cycloreverts to form the product and original metal alkylidene species.



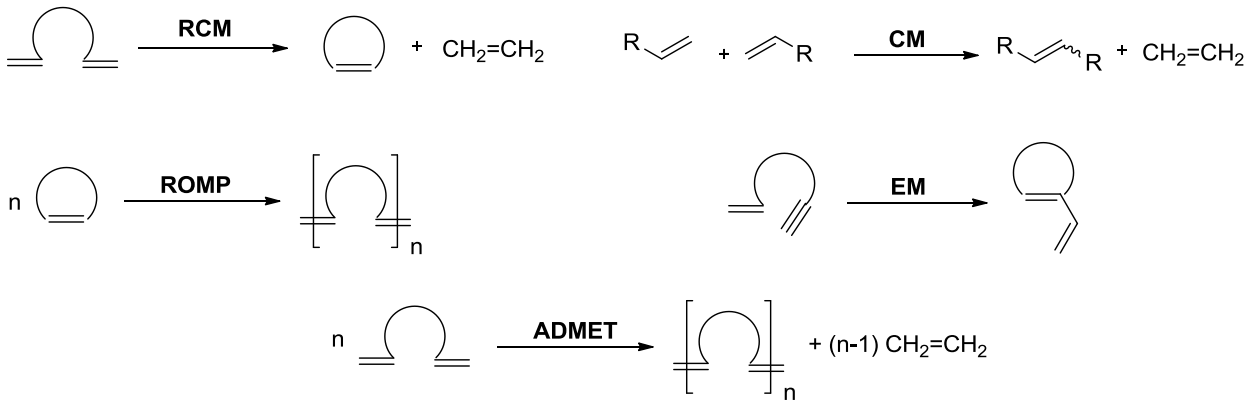
Scheme 2. Mechanism of olefin metathesis proposed by Chauvin.

Some fields of olefin metathesis, in particular ring-closing metathesis at low catalyst loading, ring-closing metathesis of hindered olefins, switched control over ring-opening metathesis polymerization, selective formation of *Z*-olefins via cross-metathesis, metathesis of renewable raw materials and efficient catalyst recycling are of great interest to scientific community because of their potential application.

Consequently, the presented dissertation deals with the development of fast initiating ruthenium catalysts for ring-closing metathesis at low catalyst loading, efficient catalysts for ring-closing metathesis reactions of challenging substrates and redox-switched catalysts for ring-opening metathesis polymerization which undergo electrochemical activation under mild conditions.

1.1. Types of Olefin Metathesis Transformations

Among the various types of metathesis reactions the most practically important are: Ring-Closing Metathesis (**RCM**), Cross Metathesis (**CM**), Enyne Metathesis (**EM**), Ring-Opening Metathesis Polymerization (**ROMP**) and Acyclic Diene Metathesis (**ADMET**) (Scheme 3).

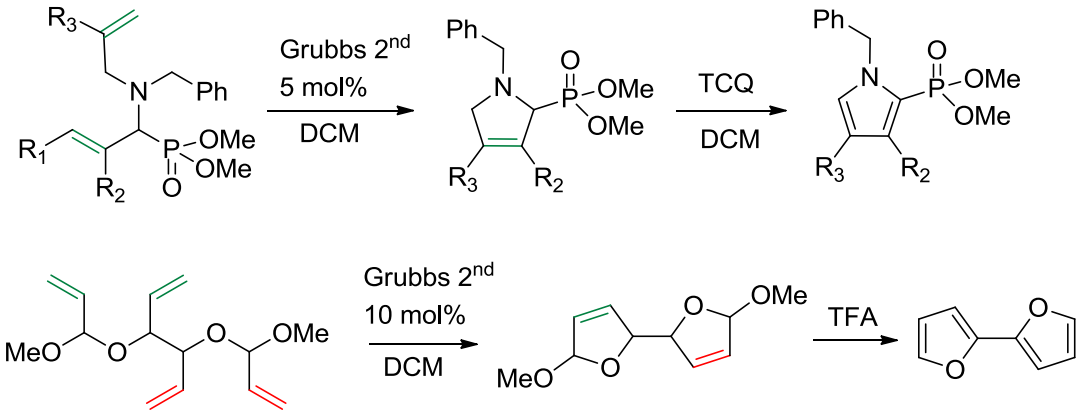


Scheme 3. Some types of olefin metathesis transformations.

Ring-closing metathesis is thermodynamically favorable for the formation of medium-sized cycles (C_5-C_7). The probability of encounter between reactive double bonds decreases for large cycles. This partitioning depends on substrate, catalyst, and reaction conditions.[10] Ring-opening metathesis polymerization is thermodynamically favored for strained ring systems, such as norbornene derivatives, dicyclopentadiene, cyclooctene, cyclooctadiene etc. The ROMP reaction often occurs rapidly to form polymers with good yields. The cross metathesis reaction between two different olefins usually results in the formation of a statistical mixture of predominantly *E*-olefins. However, the chemo- and stereoselectivity of cross-metathesis can be adjusted by the appropriate selection of the catalyst and substrates as well as by the use of an excess of the more readily available olefin.

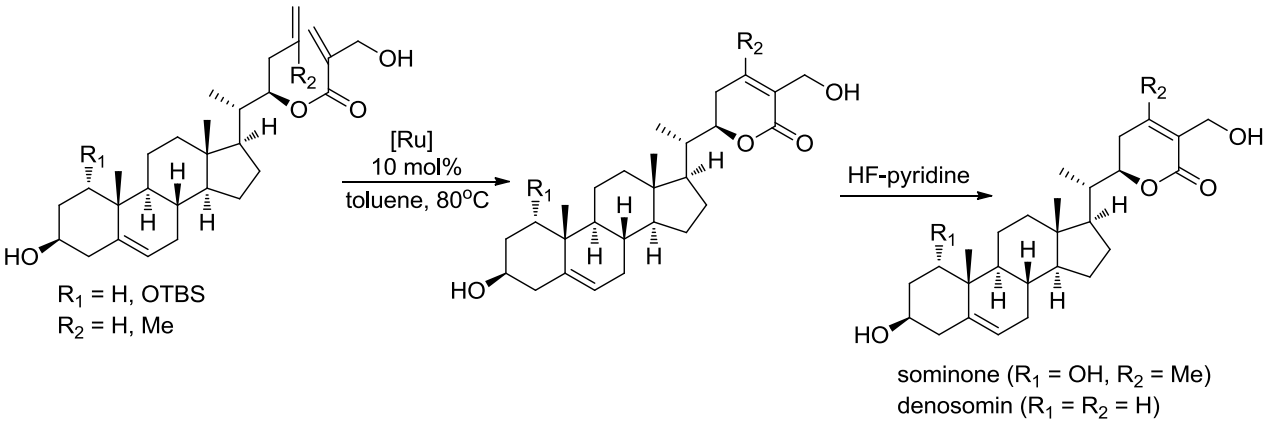
1.1.1. Ring-Closing Metathesis

Ring-closing metathesis was found to be an excellent synthetic tool providing straightforward approach to aromatic heterocycles.[11] As an example the synthesis of 2-phosphonopyrroles[12] via a one-pot RCM/oxidation sequence and the preparation of furnished bis-furan[13] via the tandem cyclisation of bis-allylic acetal are highlighted in Scheme 4.



Scheme 4. Synthesis of heterocycles via ring-closing metathesis.

Ring-closing metathesis is often applied in synthesis of natural compounds and their analogues.[14–16] Nemoto and co-workers described the synthesis of sominone starting from dehydroepiandrosterone on the basis of an RCM strategy for the construction of a δ-lactone side chain.[17] In addition, this synthetic protocol was applied for design of several analogous derivatives including 1-deoxy-24-norsominone (denosomin), which was revealed to exhibit notable bioactivities for new antidementia chemotherapy (Scheme 5).

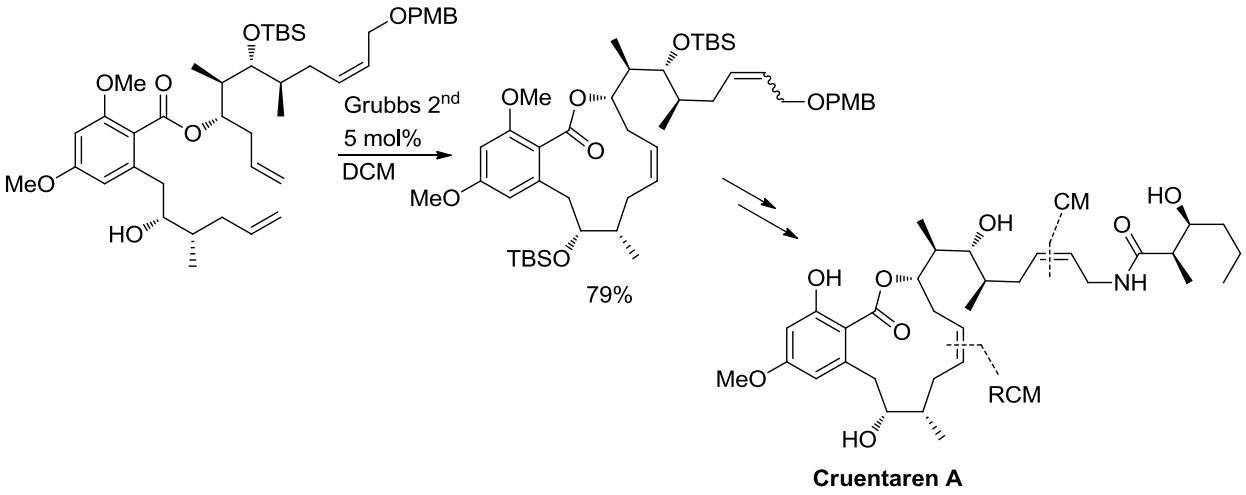


Scheme 5. Ring-closing metathesis in synthesis of sominone and denosomin.

1.1.2. Cross-Metathesis

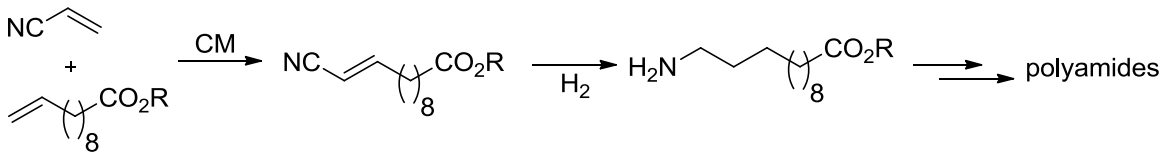
Like ring-closing metathesis, cross-metathesis is often utilized in total synthesis of natural products.[18–21] A convergent and efficient synthesis of cruentaren A, an antifungal benzolactone produced by the

myxobacterium *Byssovorax cruenta*, was reported based on ring-closing metathesis and cross-metathesis as the key steps (Scheme 6).[22]



Scheme 6. Cross-metathesis in synthesis of cruentaren A.

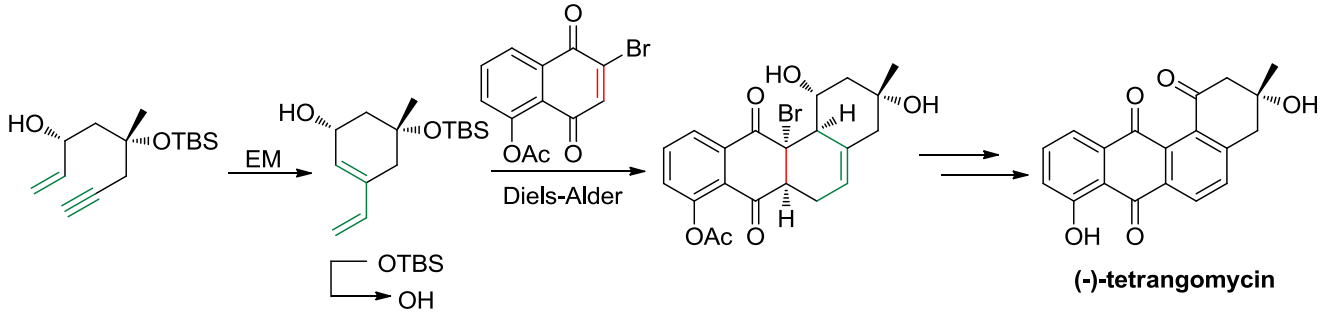
Cross-metathesis has become a powerful method for the production of fine chemicals from renewable raw materials.[23–26] The synthesis of α,ω-aminoesters, the precursors of polyamides, from acrylonitrile and unsaturated fatty acids, derivatives of plant oils, via tandem cross-metathesis/hydrogenation sequence was published by Couturier et al. (Scheme 7).[27]



Scheme 7. Cross-metathesis of a renewable raw materials.

1.1.3. Enyne Metathesis

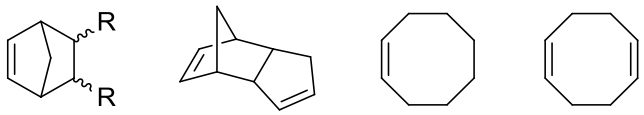
Enyne metathesis is particularly useful synthetic method for the construction of complex molecules, such as fused bicycles and polycycles.[28–30] In combination with Diels-Alder cycloaddition reaction enyne metathesis opens an easy access to otherwise difficult available polycycles. For example, the synthesis of (–)-tetrangomycin, the angucycline antibiotic, have been recently reported based on enyne metathesis and Diels–Alder reaction as key steps (Scheme 8).[16]



Scheme 8. Enyne metathesis in synthesis of (–)-tetrangomycin.

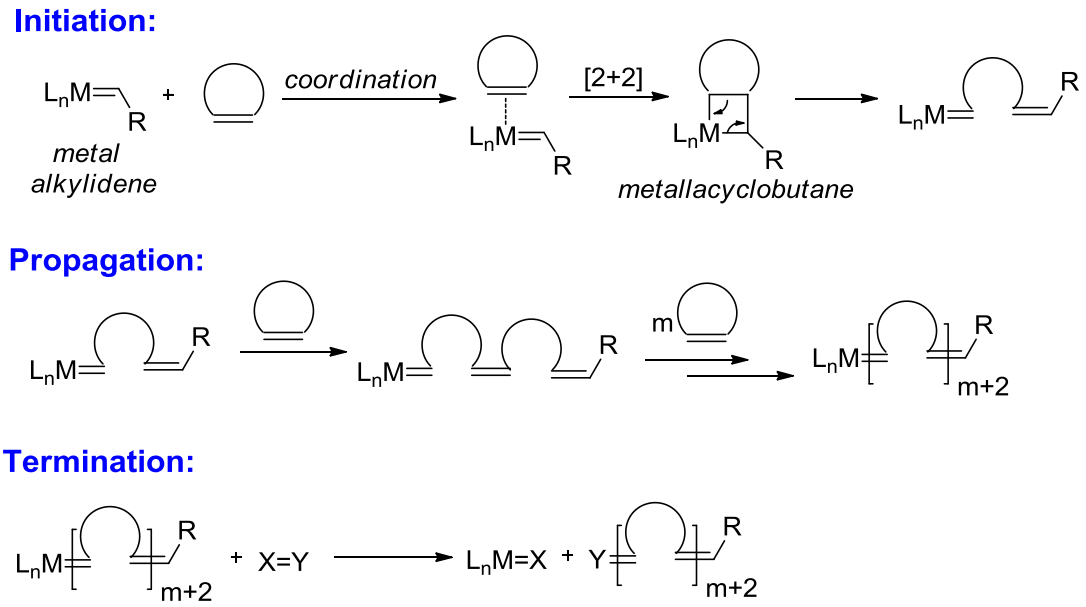
1.1.4. Ring-Opening Metathesis Polymerization and Acyclic Diene Metathesis Polymerization

Ring-opening metathesis polymerization (ROMP) turned out to be powerful tool for synthesis of polymers with various architectures and useful functions.[31–36] Recently, Grubbs and co-workers have found a potential application of ROMP reaction in photolithography.[37] The most common monomers used in ROMP are cyclic olefins possessing high ring strain, such as norbornene derivatives, *cis*-cyclooctene, cyclooctadiene and dicyclopentadiene (Scheme 9).



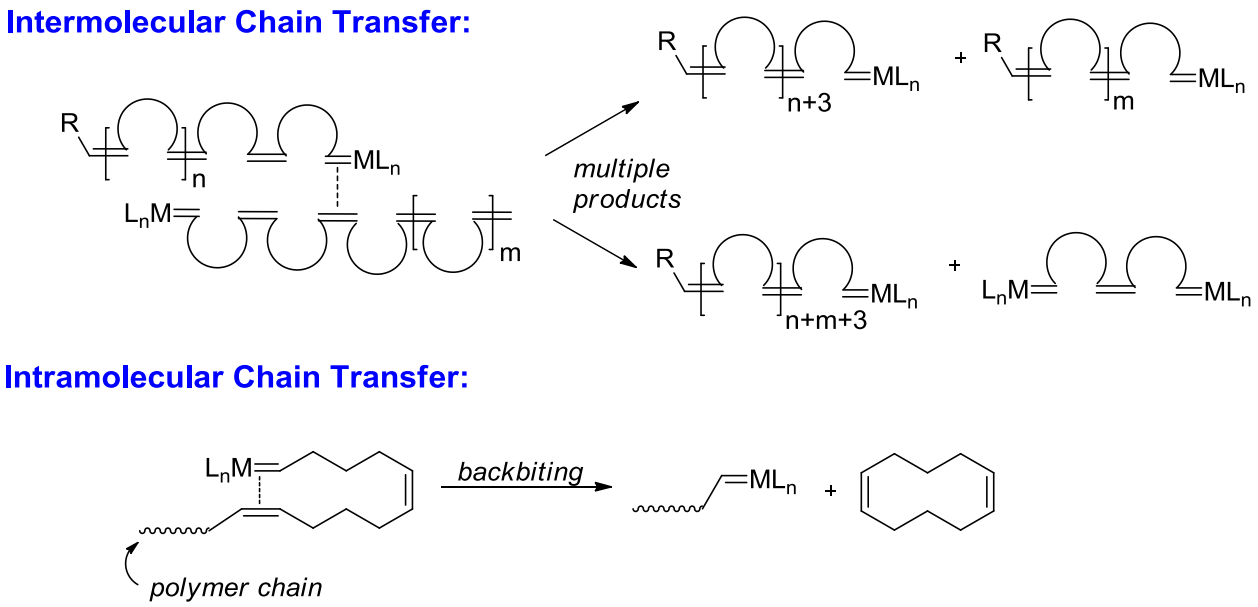
Scheme 9. ROMP monomers.

The general mechanism for ROMP is depicted in Scheme 10. It comprises of three main steps: initiation, propagation and termination.



Scheme 10. Representative mechanism for ROMP reaction.[38]

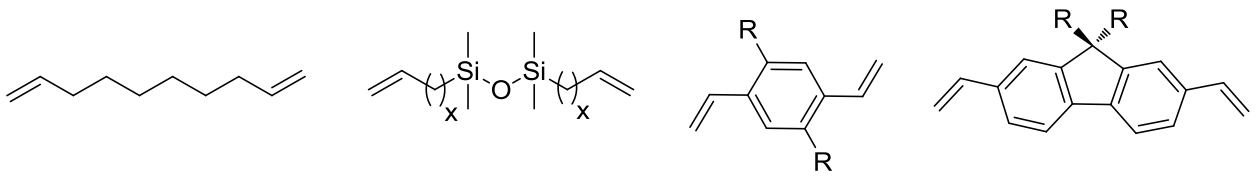
The molecular weight and polydispersity of polymers obtained via ROMP strongly depend on the rate at which the respective catalyst is initiated. Slowly initiating catalysts normally provide polymers with high molecular weights and broad polydispersities. This is due to initiation rate being slow compared to the rate of propagation. In case of polymers with conformationally flexible chains, the polydispersity can also be affected by competing chain-transfer reactions (Scheme 11). When the rate of initiation is faster or comparable to the rate of propagation the ROMP can result in formation of monodisperse low molecular weight material. That is why fast initiating complexes display high activity in ROMP providing polymers with shorter chain length and low PDIs.



Scheme 11. Secondary metathesis reactions in ROMP.[38]

Although secondary metathesis reactions are undesirable in ROMP, they can be controlled by catalyst choice and reaction conditions, thus producing cyclic oligomers.[39]

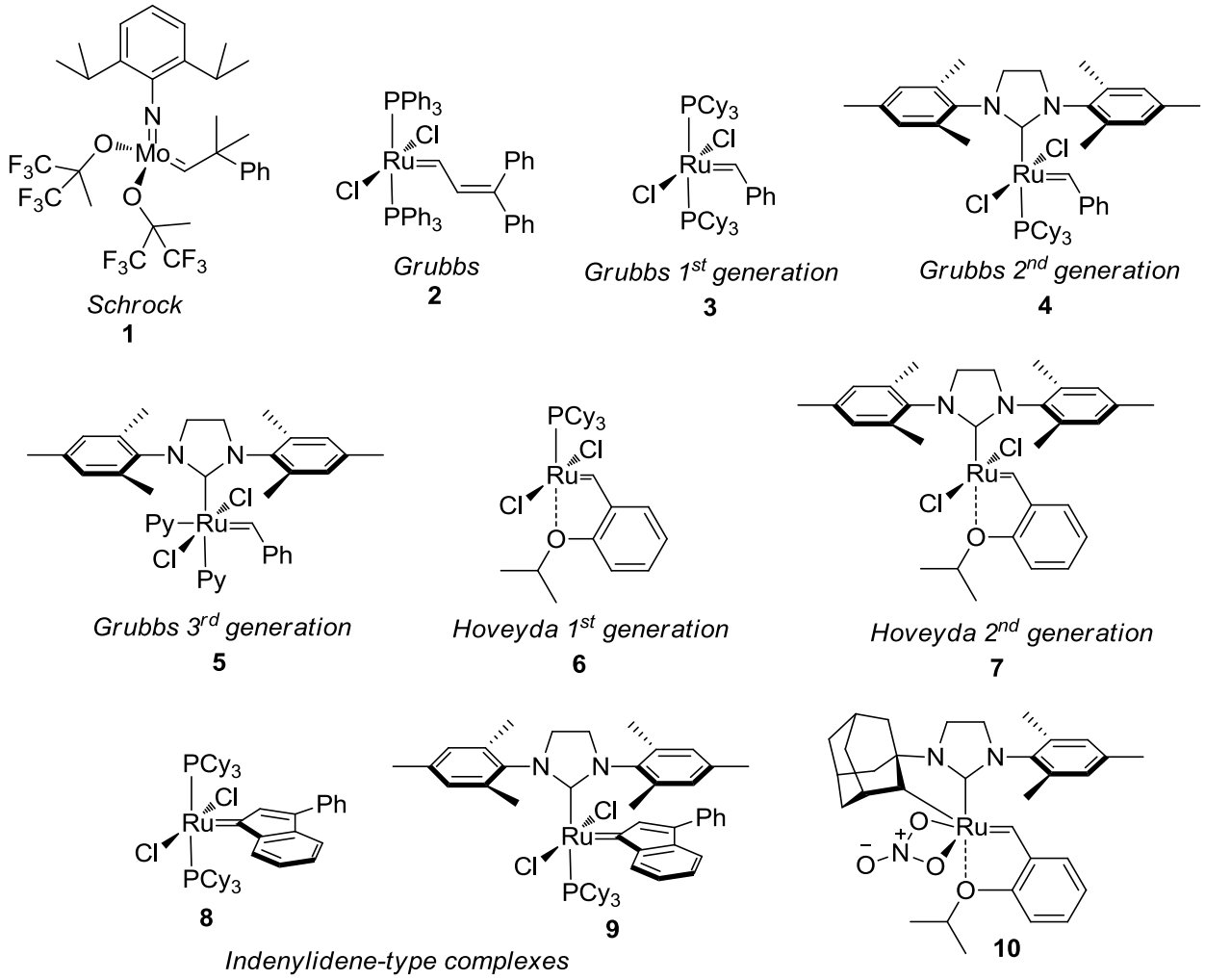
Acyclic diene metathesis polymerization is a step-growth polymerization driven by the release of a condensate, usually ethylene.[40,41] This is why ethylene formed during the reaction has to be removed from the reaction media to shift the equilibrium towards polymer formation. ADMET polymerization affords high molecular weight polymers at high monomer conversion. It is normally performed in bulk to avoid the formation of cyclic oligomers. In acyclic diene metathesis polymerization the non-strained a,ω-olefins are used as monomers instead of the strained cyclic olefins in ROMP. The representative ADMET monomers are given in Scheme 12. The reactive double bonds in these molecules are separated in space to avoid competing RCM reaction.



Scheme 12. Representative ADMET monomers.

1.2. Types of Well-Defined Olefin Metathesis Catalysts

Among various types of olefin metathesis catalysts,[42–45] the complexes summarized below represent common structural motifs.



Scheme 13. Well-defined olefin metathesis catalysts.

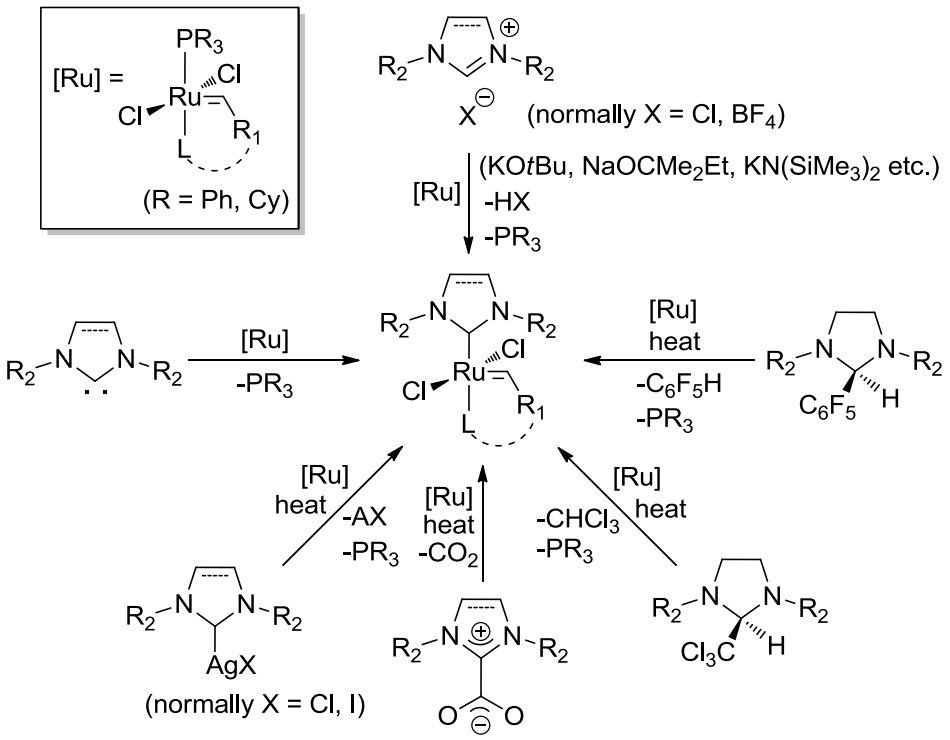
Schrock and Grubbs together with co-workers synthesized numerous important olefin metathesis catalysts. Schrock et al. described well-defined molybdenum alkylidene complexes like catalyst **1** which is one of the most recognizable Schrock-type catalyst. Complex **1** is highly active in olefin metathesis, however, it remains sensitive towards oxygen and moisture and shows low tolerance towards functional groups. Nevertheless, it became the basis for the synthesis of modified Schrock-type catalysts for various metathesis applications. The first well-defined ruthenium-based olefin metathesis catalyst **2** was reported by Grubbs and co-workers in 1992.[46] In 1995, they reported the synthesis of a catalyst **3** which is now known as Grubbs 1st generation catalyst.[47] The ruthenium-based catalysts appear to be more resistant to oxygen and moisture than Schrock-type catalysts. Replacement of one of the phosphine ligand in complex **3** by SIMes carbene led to Grubbs 2nd generation catalyst **4** which turned out to be more active and stable than **3**.[48] In fact, the synthesis of Grubbs 2nd generation catalyst has turned out to be a significant improvement and most of known ruthenium complexes contain *N*-heterocyclic carbene ligands. Complex **5** with two pyridine ligands instead of phosphine is known as Grubbs 3rd generation catalyst.[49] The labile pyridine ligands dramatically increase initiation rate, thus making this catalyst useful for ring-opening metathesis polymerization. In 1998, Hoveyda et

al. reported the synthesis of complex **6** in which benzylidene ligand has a chelating *ortho*-isopropoxy group.[50] The phosphine ligand in **6** was then replaced by SIMes carbene to provide stable and highly reactive Hoveyda 2nd generation catalyst **7**.[51] Ruthenium indenylidene-type complexes **8** and **9** represent a family of robust and efficient catalysts which are quite resistant to harsh reaction conditions (temperature and functional group tolerance).[52] In 2012, Grubbs and co-workers described C-H activated catalyst **10** for Z-selective olefin metathesis.[53]

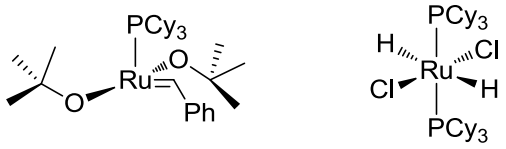
In general, phosphine-based ruthenium complexes like **3**, **6** and **8** are rarely used in catalysis, but they serve as precursors for the synthesis of more active and structurally diverse ruthenium-*N*-heterocyclic carbene catalysts.

1.3. Synthesis of Ruthenium Complexes Bearing *N*-Heterocyclic Carbene (NHC) Ligands

Several methods enable the formation of ruthenium complexes containing *N*-heterocyclic carbene ligands (Scheme 14). The most common method includes deprotonation of the respective azolium salts and subsequent reaction of generated free NHCs with ruthenium precursors. The advantages of this method are the ready availability and stability of azolium salts. The use of strong bases which are incompatible with many functional groups and the formation of typical byproducts (e.g., inorganic salts and alcohols), in some cases, limit the scope of this method. According to Grela and co-workers the reaction between azolium salts and ruthenium precursors is sensitive to the quality of reagents and solvents, reaction scale, and some subtle experimental setup.[54] The reaction between *in situ* generated NHC carbenes and ruthenium precursors sometimes results in low yields and formation of byproducts. The respective ruthenium hydride[55] and alkoxide[56] species act as possible contaminants which can induce side reactions (Scheme 15). Alternatively, NHCs are first prepared and isolated as the free carbenes and subsequently used for the synthesis of ruthenium complexes. This method has advantages, since the reaction is accompanied by the formation of fewer byproducts. However, free NHCs are very sensitive towards moisture and oxygen and need to be handled under inert conditions.



Scheme 14. Synthetic pathways to ruthenium catalysts bearing NHC ligands.



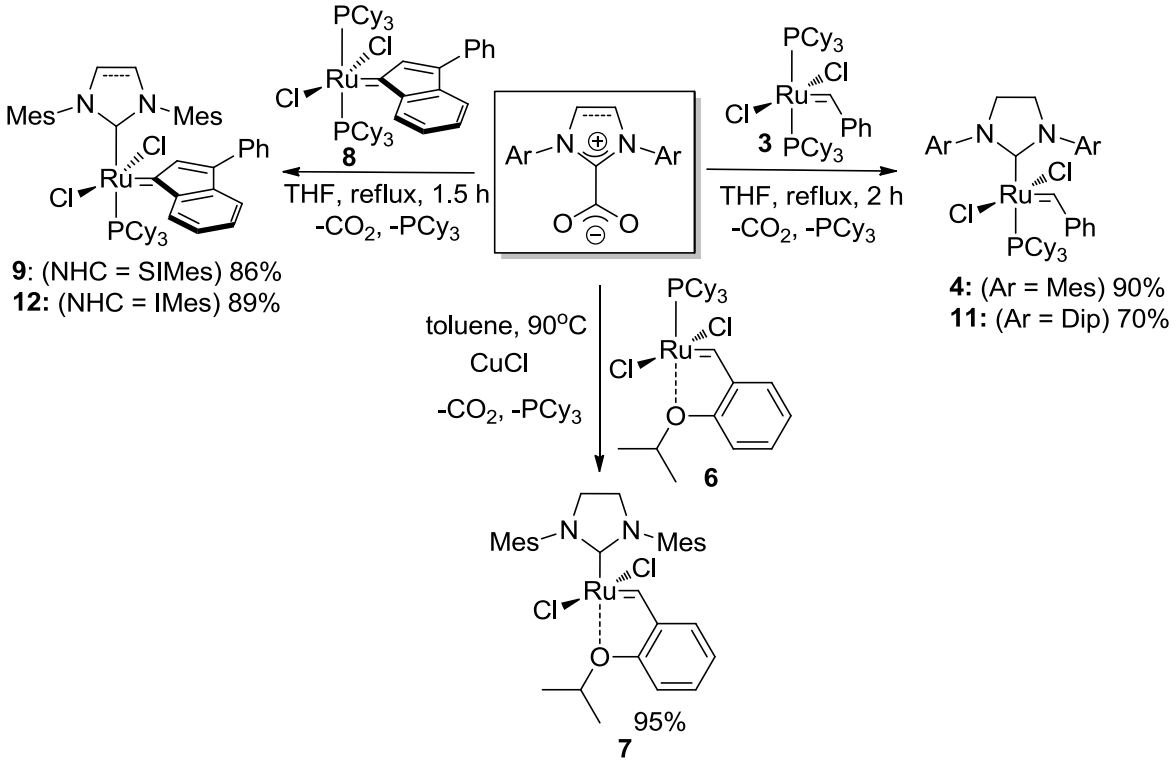
Scheme 15. Hydride and alkoxide species as potential contaminants.

There are several types of reagents, generally known as NHC-transfer reagents or protected carbenes, able to generate free NHCs upon heating. The well-known NHC-transfer reagents are imidazoli(ni)um hydrogen carbonates,[57] imidazole(in)ium-2-carboxylates,[58,59] 2-(trichloromethyl)imidazolidines,[60,61] 2-(pentafluorophenyl)imidazolidines[62] and silver-NHC complexes.[63] These compounds are stable in air and some of them possess high solubility in nonpolar organic solvents such as benzene, toluene and hexane. Imidazolium-2-carboxylates, 2-(trichloromethyl)imidazolidines, 2-(pentafluorophenyl)imidazolidines and silver-NHC complexes were found to be suitable reagents for the preparation of ruthenium-based olefin metathesis catalysts.

1.3.1. Imidazol(in)ium-2-carboxylates

The synthesis of well-known NHC-ruthenium complexes **4**, **7**, **9**, **11** and **12** by phosphane exchange between first generation ruthenium benzylidene-type or ruthenium indenylidene-type complexes and NHCs generated *in situ* from imidazol(in)ium-2-carboxylates was reported in 2009 (Scheme 16).[64]

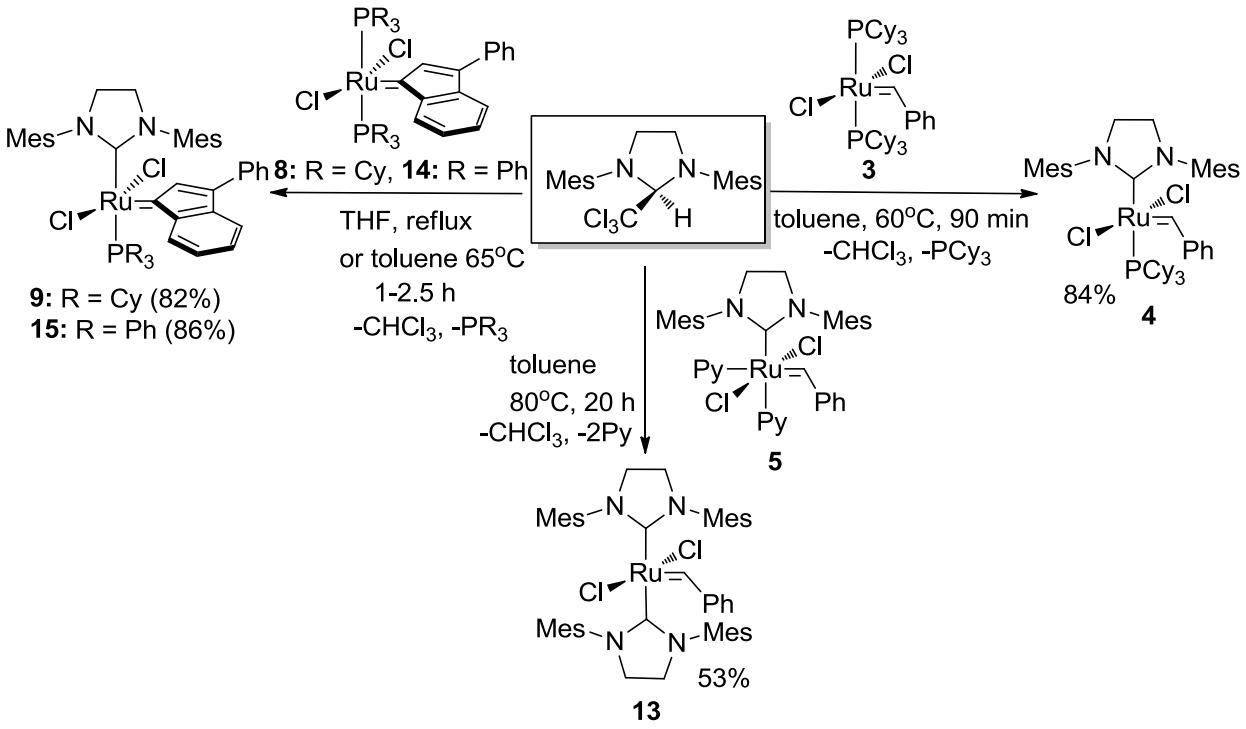
The reactions were run in THF or toluene, but NHC·CO_2 adducts turned out to be better soluble in THF rather than in toluene and their thermolysis in THF at 66°C proceeded faster than in toluene at 80°C.



Scheme 16. Synthesis of ruthenium complexes from imidazol(in)ium-2-carboxylates.

1.3.2. 2-(Trichloromethyl)imidazolidines

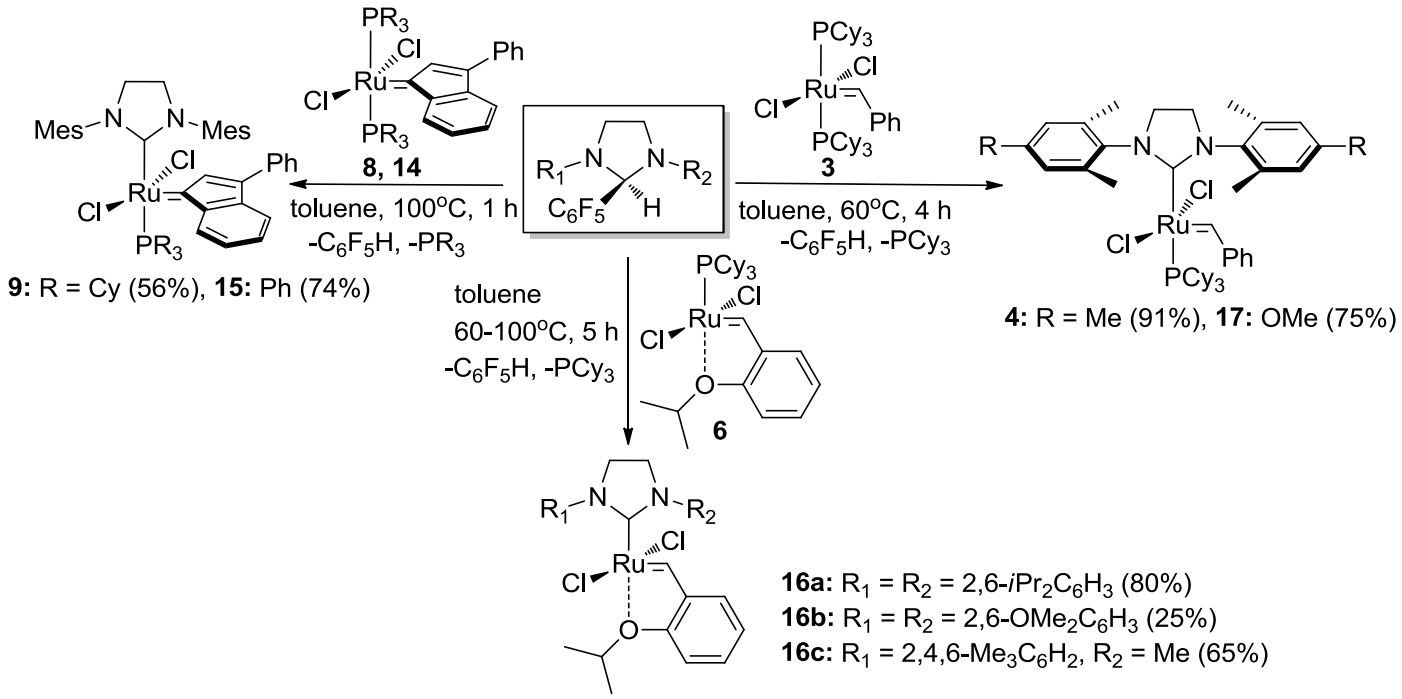
2-(Trichloromethyl)imidazolidines are relatively stable and highly soluble compounds which are normally prepared from imidazolinium salts and chloroform under basic conditions.[60] In 2002, Grubbs and co-workers reported the straightforward and high-yield synthesis of complex **4** from SIMes·$CHCl_3$ adduct which undergoes thermolysis at 60°C in toluene (Scheme 17).[60] The *bis*-NHC-ruthenium complex **13** was also prepared by using SIMes·$CHCl_3$ adduct and Grubbs 3rd generation complex **5** bearing labile pyridine ligands.[60] Verpoort and co-workers followed this method to obtain indenylidene-type complexes **9**, **15** in excellent yields.[65]



Scheme 17. Synthesis of ruthenium complexes from 2-(trichloromethyl)imidazolidines.

1.3.3. 2-(Pentafluorophenyl)imidazolidines

In 2004, Waymouth, Hedrick, and co-workers reported the synthesis of 2-(pentafluorophenyl)imidazolidines as useful NHC-transfer reagents.[66] Later Grubbs expanded the range of available NHC·C_6F_5H adducts and described their application in synthesis of commonly used ruthenium complexes (Scheme 18).[67] In most cases the desired complexes were obtained in moderate to excellent yields with the exception of complex **16b** which was isolated in 25% yield. However, other methods that were attempted to prepare this complex failed. Verpoort with co-workers reported a straightforward synthesis of ruthenium indenylidene-type complexes **9**, **15** from SIMes·C_6F_5H adduct and commercially available ruthenium precursors **8**, **14**.[68]



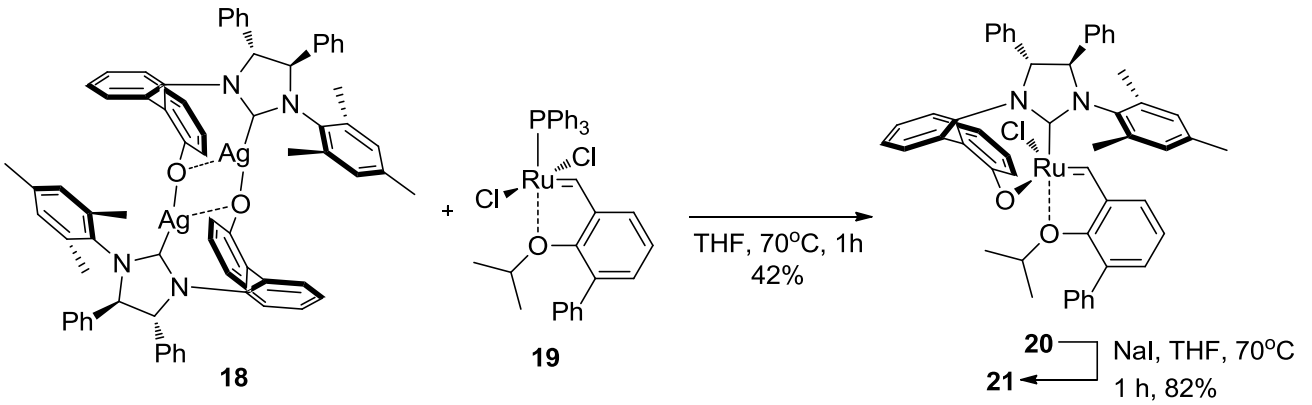
Scheme 18. Synthesis of ruthenium complexes from 2-(pentafluorophenyl)imidazolidines.

1.3.4. Silver-NHC Complexes

Silver-NHC complexes are useful reagents for transferring of NHC carbenes to a variety of other metals.[63] Although they are primarily applied for the synthesis of Au, Cu, Rh, Ir, Pd, Pt, Ni complexes, a few examples of their use in the preparation of olefin metathesis catalysts have been reported.

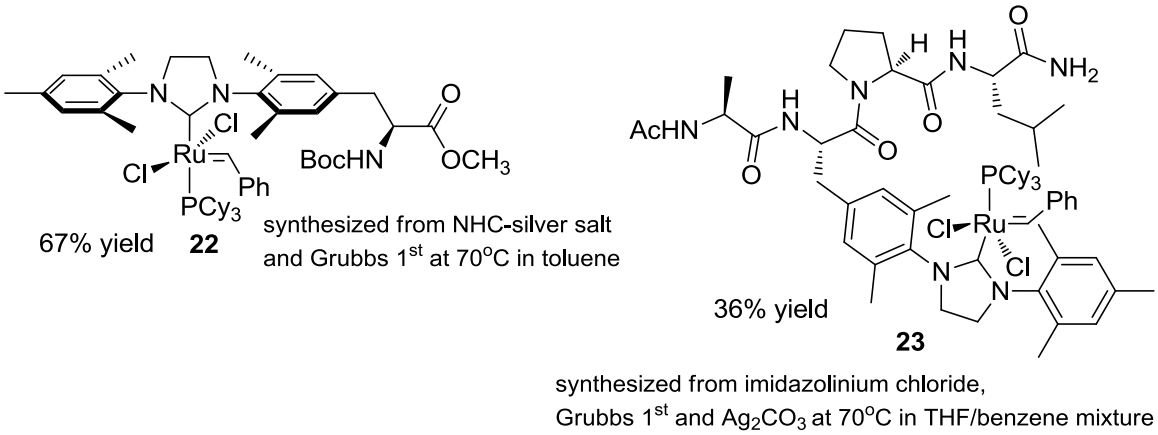
Mono-NHC-ruthenium complexes

In 2005, Hoveyda and co-workers described ruthenium complexes chelated with chiral bidentate *N*-heterocyclic carbene ligand (Scheme 19).[69] These complexes promote highly enantioselective ring-opening metathesis/cross-metathesis reactions. The catalyst **20** was prepared by treatment of chiral silver-NHC complex **18** with ruthenium precursor **19** at 70°C in THF. The Ru-chloride **20** was isolated in 42% yield due to its partial decomposition during purification by column chromatography. Therefore, the chlorine atom in complex **20** was replaced by iodine to give stable Ru-iodide **21**.



Scheme 19. Synthesis of ruthenium catalyst from chiral silver-NHC complex.

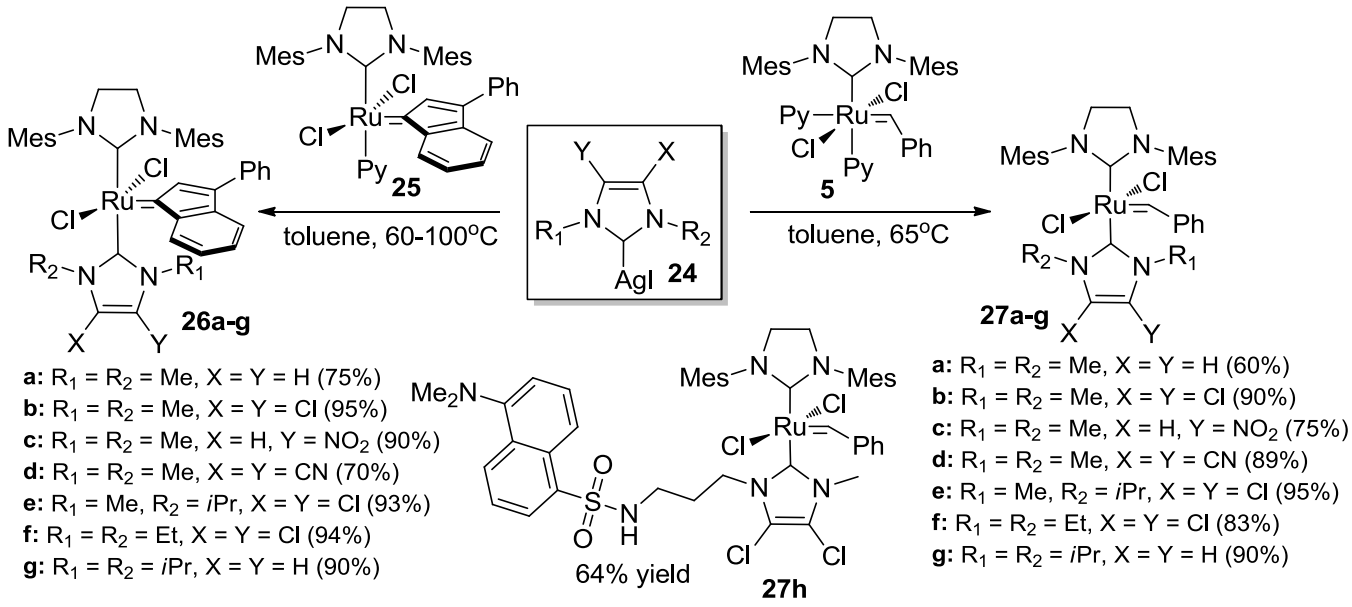
In the same year Gilbertson and Xu reported the synthesis of complex **22** containing SIMes ligand modified with amino acid chain and complex **23** bearing unusual peptide-base SIMes carbene from the corresponding NHC-silver salts and Grubbs 1st generation complex **3** (Scheme 20).[61]



Scheme 20. Ruthenium complexes prepared from silver-NHC complexes.

Bis-NHC-ruthenium complexes

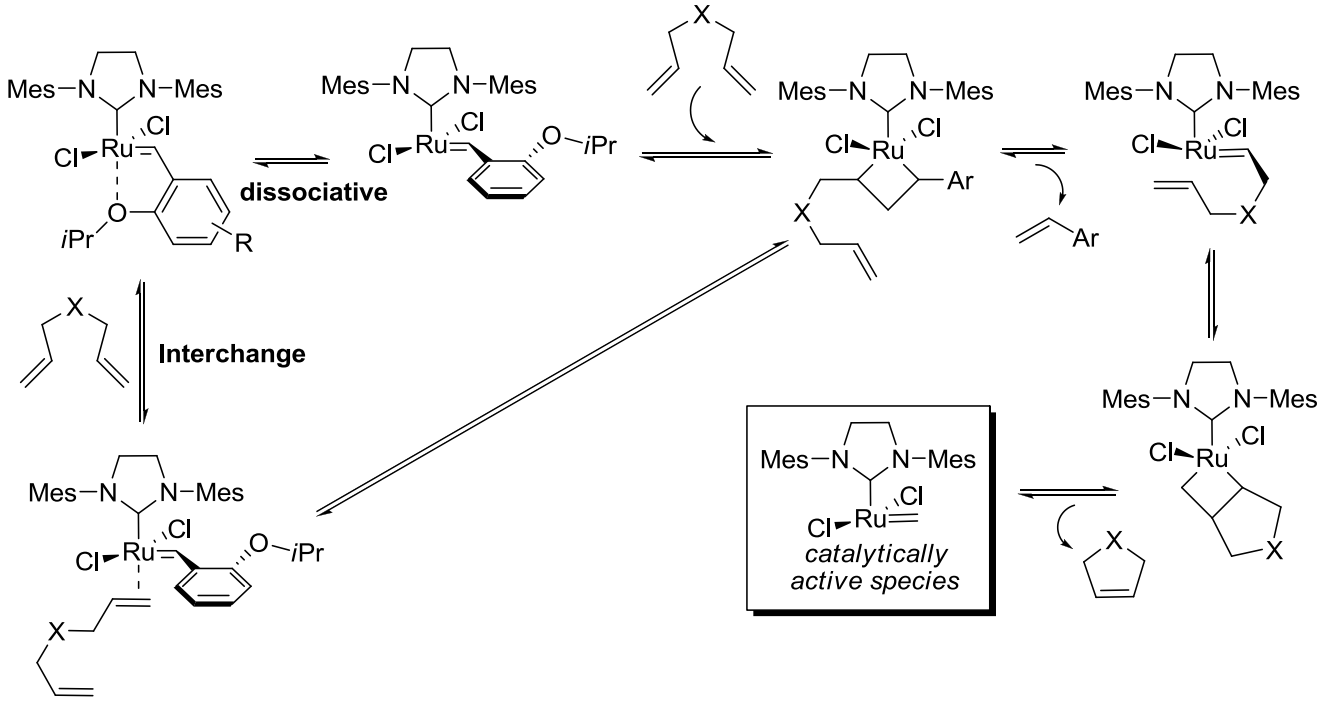
Silver-NHC complexes are particularly useful for the synthesis of bis-NHC-ruthenium catalysts which are not easily accessible by other methods. This simple and straightforward synthetic approach to ruthenium complexes of the general formula (NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)[70] and (NHC)(NHC$_{ewg}$)RuCl$_2$(3-phenylindenylid-1-ene)[71] was explored by Plenio et al. (Scheme 21). The suggested procedure allows to obtain final compounds **26a-g** and **27a-h** in moderate to excellent yields depending on the structure of electron-withdrawing NHC$_{ewg}$ ligand.



Scheme 21. Synthesis of bis-NHC-ruthenium catalysts from silver-NHC complexes.

1.4. Initiation Rate – an Important Parameter Determining the Scope of Catalyst Application

The rate at which catalysts for olefin metathesis are activated has a strong influence on the rate of substrate conversion. Recently, Plenio and co-workers have studied a large number of Hoveyda 2nd generation complexes with differently substituted styrene ligands in various RCM reactions.[72] According to the dissociative or interchange mechanism of initiation for Hoveyda-type catalysts in RCM reactions (Scheme 22), all these catalysts result in the same active species and would exhibit the same catalytic activity. However, it was found that the activity of the catalyst depends on the substituents at styrene ligand. Thus, initiation plays an important role in the reaction outcome.



Scheme 22. Dissociative and interchange mechanisms of initiation for Hoveyda-type catalysts.

The ruthenium-based catalysts can be divided into three types based on their initiation rate (Fig. 1).

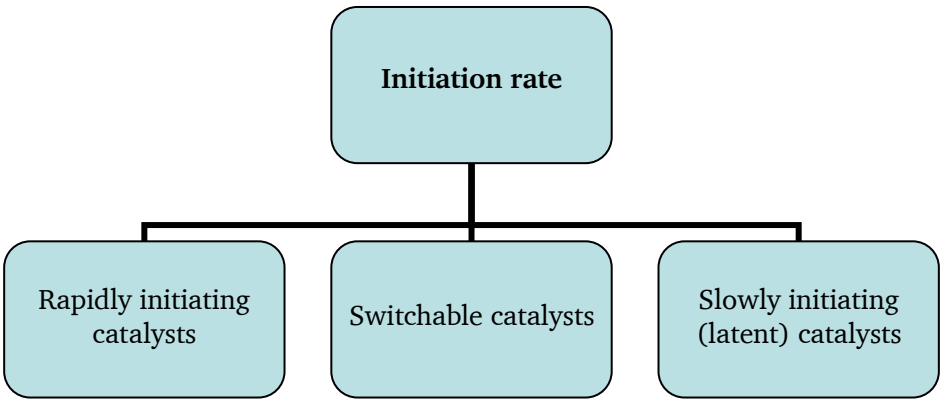


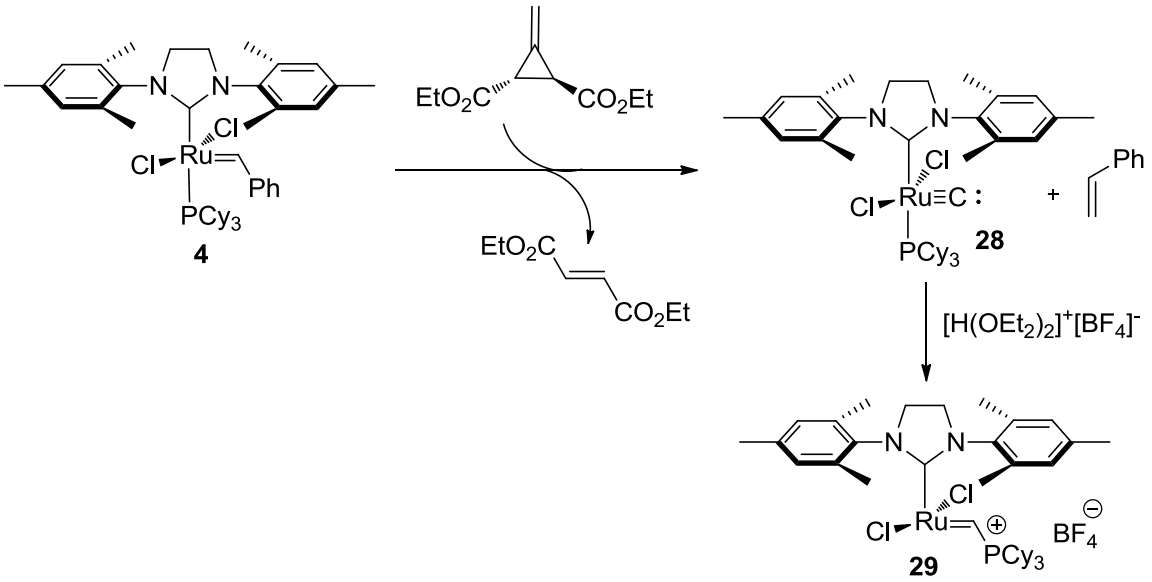
Figure 1. Types of olefin metathesis catalysts based on their initiation rate.

Switchable catalysts combine properties of both rapidly and slowly initiating complexes. It means that they are normally inactive (active) in olefin metathesis and their initiation rate can be increased (decreased) by external stimuli. However, the definition of switchable catalysts is somewhat broader. There are ruthenium complexes containing switched tags that, when exposed to an external trigger, can alter the solubility of the catalyst in nonpolar solvents. Although such catalysts are considered to be switchable, their ability to switch is not related to initiation kinetic.

Rapidly initiating complexes provide good substrate conversion within a short time and low temperatures. These catalysts are useful for the synthesis of low-dispersity polymers by ring-opening metathesis polymerization, which requires a faster rate of initiation than the rate of chain growth. Slowly initiating complexes require high temperatures, and appear to be useful for ring-closing metathesis reactions of sterically hindered substrates. Switchable complexes enable control over olefin metathesis reactions, in particular over ring-opening metathesis polymerization.

1.5. Rapidly Initiating Ruthenium-Based Olefin Metathesis Catalysts

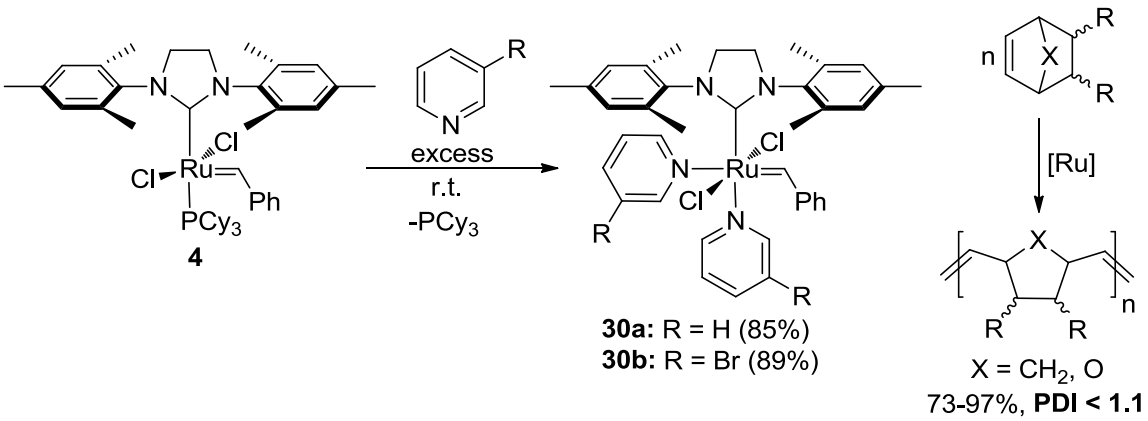
In 2004, Piers and co-workers synthesized four-coordinate cationic complex **29** which does not contain any ligand in *trans*-position to SIMes-carbene and exists as 14-electron specie (Scheme 23).[73]



Scheme 23. Synthesis of Piers 2nd generation catalyst.

This catalyst is initiated very fast, because it doesn't require any ligand dissociation to be activated. Since metathesis reactions often are initiation step limited, complex **29** is exceptionally active in RCM at low temperature in comparison to Grubbs 2nd generation catalyst **4** which requires dissociation of PCy_3 ligand. For example, at 0°C catalyst **4** reaches approximately 25% conversion of diethyl diallylmalonate (DEDAM) after 4h, while Piers catalyst **28** performs much better, providing about 90% conversion after the same reaction time. More importantly, catalyst **29** allowed to observe a ruthenacyclobutane intermediate in an olefin metathesis reaction by NMR at –50 °C.[74]

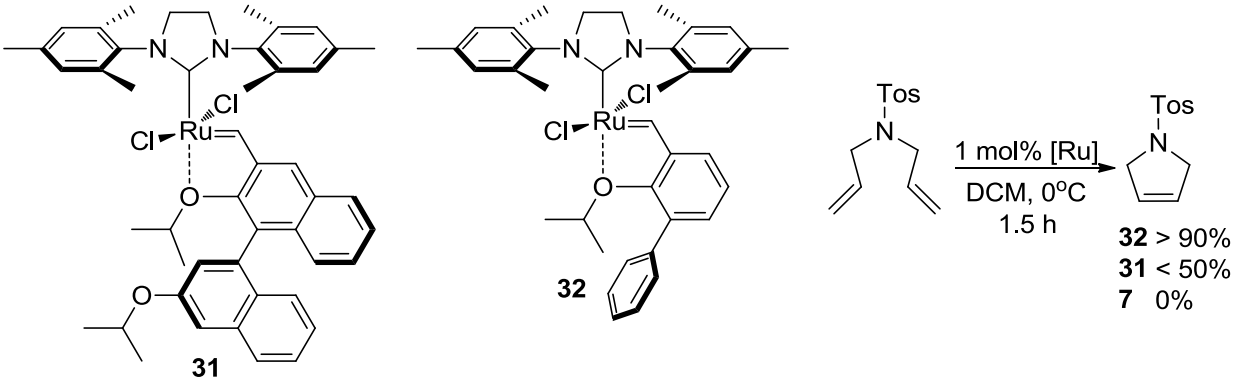
The rate of the initiation step can be drastically increased by replacing the phosphine ligand with more labile pyridine ligands. Grubbs and co-workers reported the synthesis of fast-initiating pyridine complexes **30a,b**, commonly referred to as Grubbs 3rd generation catalysts (Scheme 24).[75] The initiation rates for these catalysts were measured by using both NMR and UV/Vis kinetic studies. Complex **30b** bearing 3-bromopyridine ligand is initiated 20 times faster than pyridine complex **30a** and six orders of magnitude faster than Grubbs 2nd generation catalyst **4**. The high ratio of the rate of initiation to the rate of propagation makes these catalysts useful for the preparation of polymers with narrow polydispersities and for the synthesis of block copolymers. Catalyst **30b** appeared to be extremely effective in ring-opening metathesis polymerization of norbornene and oxa-norbornene derivatives.



Scheme 24. Synthesis of Grubbs 3rd generation catalysts and subsequent ROMP reactions.

Nonetheless, pyridine complexes have been rarely applied in RCM reactions, apparently due to their modest stability under the reaction conditions.

In 2002, Blechert and co-workers showed that aryl group *ortho* to the ether oxygen significantly increased metathesis activity (Scheme 25).[76] Initially, complex **31** was obtained to catalyze enantioselective metathesis reactions, but no asymmetric induction was found. However, this catalyst exhibited superior RCM activity compared to Grubbs and Hoveyda 2nd generation complexes. Thereafter, catalyst **32** with even greater efficiency in metathesis processes was prepared. When the RCM reaction of *N*-tosyl diallylamine was carried out at 0°C in the presence of 1 mol% of the respective catalyst, **32** exhibited higher activity than **31** and Hoveyda 2nd generation complex **7** which turned out to be completely inactive under the reaction conditions.

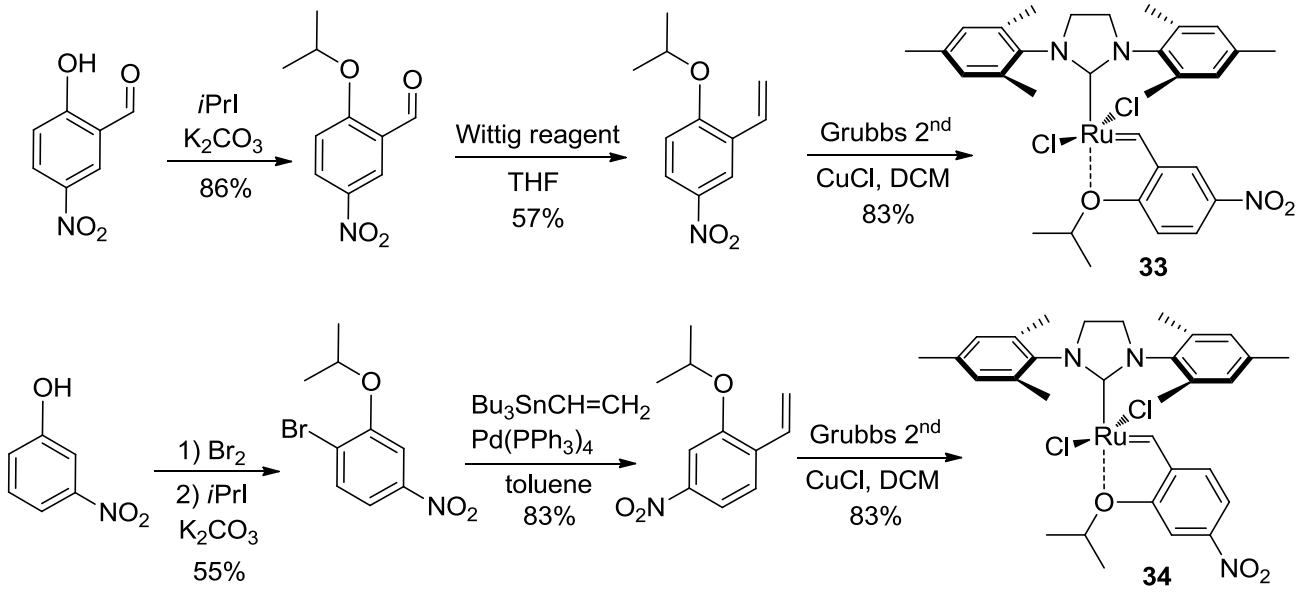


Scheme 25. Synthesis of Blechert catalysts and RCM reaction of *N*-tosyl diallylamine.

In RCM, CM, and ring-opening cross metathesis of miscellaneous substrates complex **32** was more active than Grubbs 2nd generation catalyst **4**. These observations prove that the presence of steric aryl substituents *ortho* to the chelating isopropoxy moiety is responsible for the high initiation rates

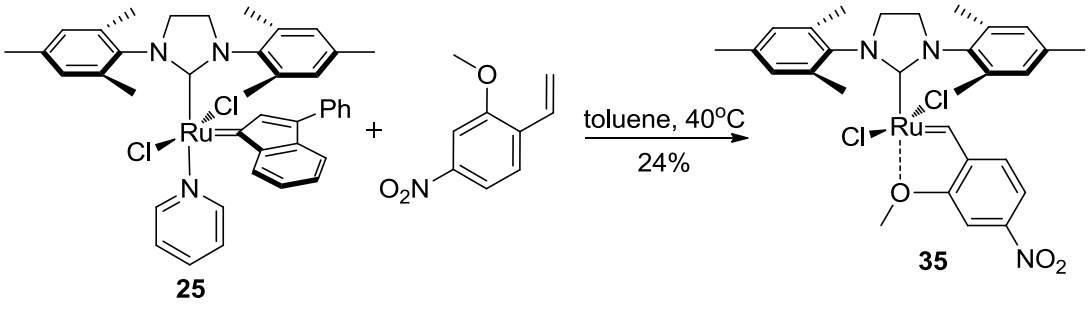
observed and even a small variation in the isopropoxystyrene ligand can result in a massive change in the activity of the catalyst.

Having been impressed by results published by Blechert, Grela and co-workers investigated the role of electronic effects in the isopropoxystyrene ligand. They assumed that strong electron-withdrawing group *para* to isopropoxy group would weaken Ru-O interaction and thus facilitate initiation step. Consequently, complex **33**, commonly known as Grela catalyst, was prepared starting from 2-hydroxy-5-nitrobenzaldehyde and Grubbs 2nd generation catalyst **4** (Scheme 26).[77] The respective 4-nitro isomer **34** was also synthesized using related synthetic pathway.[78] Both complexes turned out to be very active in model metathesis reactions.



Scheme 26. Synthesis of nitro-substituted Hoveyda-type complexes.

Even faster catalyst **35** with 2-methoxy group was synthesized by Plenio et al. (Scheme 27)[79] It was isolated in 24% yield due to its modest stability in solution and partial decomposition during chromatographic purification.



Scheme 27. Synthesis of ruthenium complex with methoxy group.

The reactions of ruthenium complexes with butyl vinyl ether (BuVE) serve as a reasonable model for the initiation reactions. Plenio and co-workers carried out detailed kinetic studies and calculated the respective rate constants (k_{obs}) for the reaction between **33-35** and BuVE using UV/Vis spectroscopy.[79] The results given in Fig. 2 reveal that catalyst **35** initiates much faster than **33** and **34** containing isopropoxystyrene ligands.

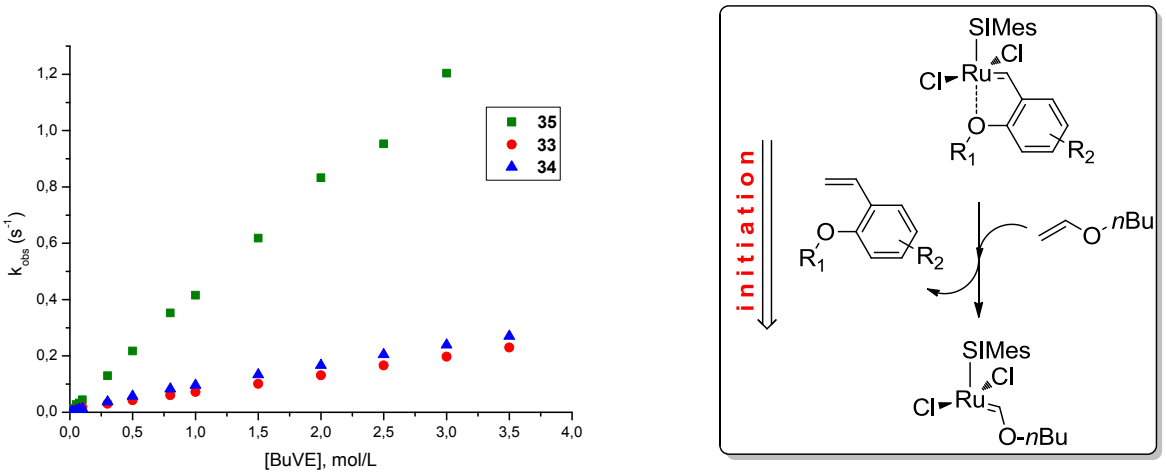
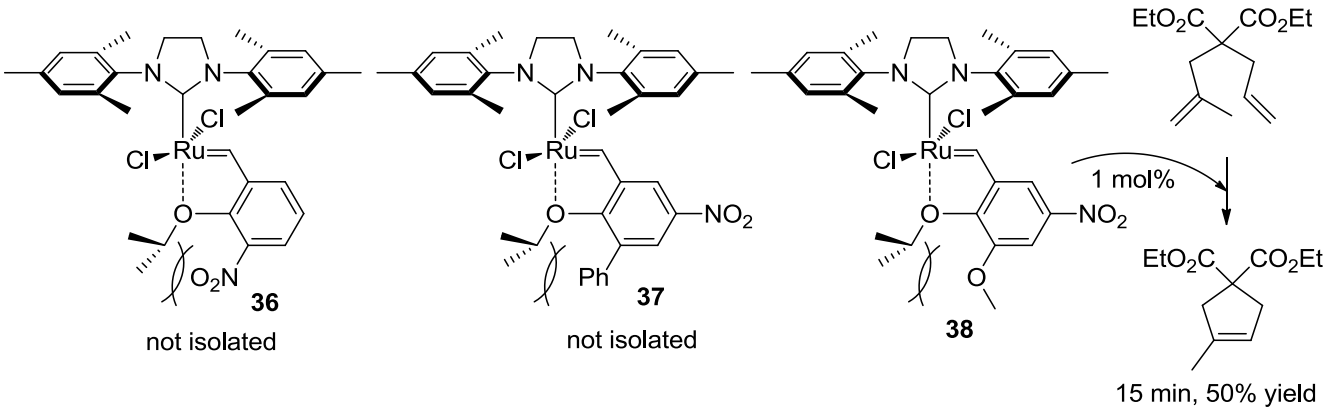


Figure 2. Reaction with BuVE and plot of k_{obs} vs [BuVE] for catalysts **33-35**.

In order to better understand the structure-reactivity relationship, Grela et al. decided to prepare complexes **36-38** (Scheme 28).[78] The design of these complexes was based on the idea that decreasing the electron density in the styrene and simultaneously applying a steric bulk close to the chelating isopropoxy fragment could result in an even higher increase of catalytic activity.

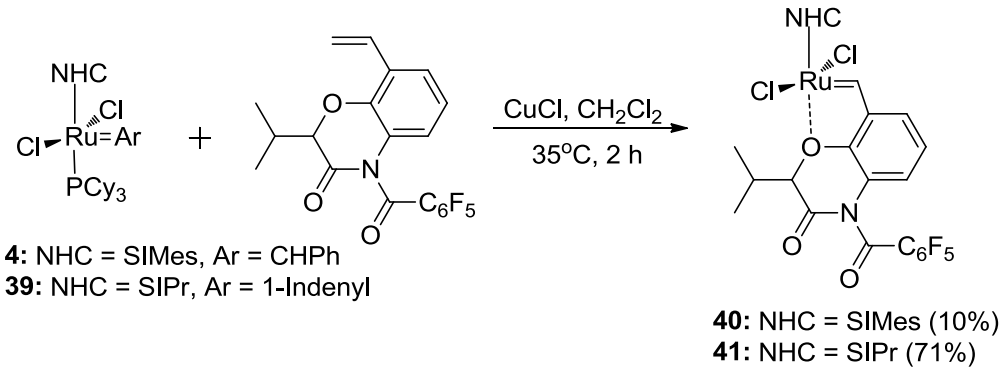
However, all attempts to isolate complexes **36** and **37** failed. Obviously, the combination of two modes of activity, electronic and steric, results in their significant instability. The decrease of the steric bulk *ortho* to isopropoxy group led to a more stable catalyst **38** in 46% yield. In a solid state, this compound can be stored in the fridge for several days, but it decomposes quickly in solution.



Scheme 28. Hoveyda-type complexes with modified styrene ligands.

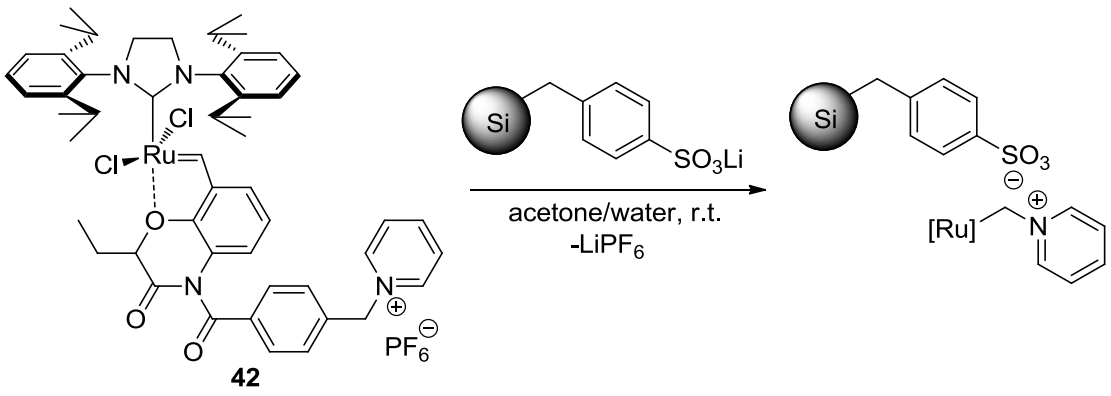
The catalyst **38** is characterized by fast activation rate and converts 50% of 2-allyl-2-(2-methylallyl)malonate into the cyclic product within only 15 min, however, no activity is observed after this time.

The interaction between the NHC and the benzylidene ether ligands can play a role in the catalyst performance. Percy and co-workers investigated the influence of both steric and electronic properties of benzylidene ether and NHC ligands on the initiation rate.[80] The authors proposed an alternative design for a fast-initiating metathesis catalysts, which combine properly balanced steric and electronic properties in a chelating benzylidene ligand (Scheme 29).



Scheme 29. Synthesis of benzylidene-chelating ruthenium complexes by Percy et al.

The synthesis of complex **40** from oxazinone-type benzylidene and Grubbs 2nd generation complex **4** appeared to be difficult (<10% isolated yield), confirming the high reactivity of **40** for which initiation rate constant could not be accurately obtained. However, the respective complex **41** with SIPr ligand was isolated in 71% yield. The kinetic profiles of these catalysts were investigated in RCM reaction of benchmark substrates and compared with Hoveyda 2nd generation **7**, Blechert **32** and Grela **33** complexes. Complexes **40** and **41** proved to be more active than Hoveyda 2nd generation and Grela catalysts, but slightly less active than Blechert complex. The related catalyst **42** immobilized onto a silica-based cationic-exchange resin was reported to be recyclable and useful for RCM, CM or enyne metathesis both under batch and circulating-flow conditions (Scheme 30).[81]



Scheme 30. Immobilization of ruthenium complex onto a silica-based cationic-exchange resin.

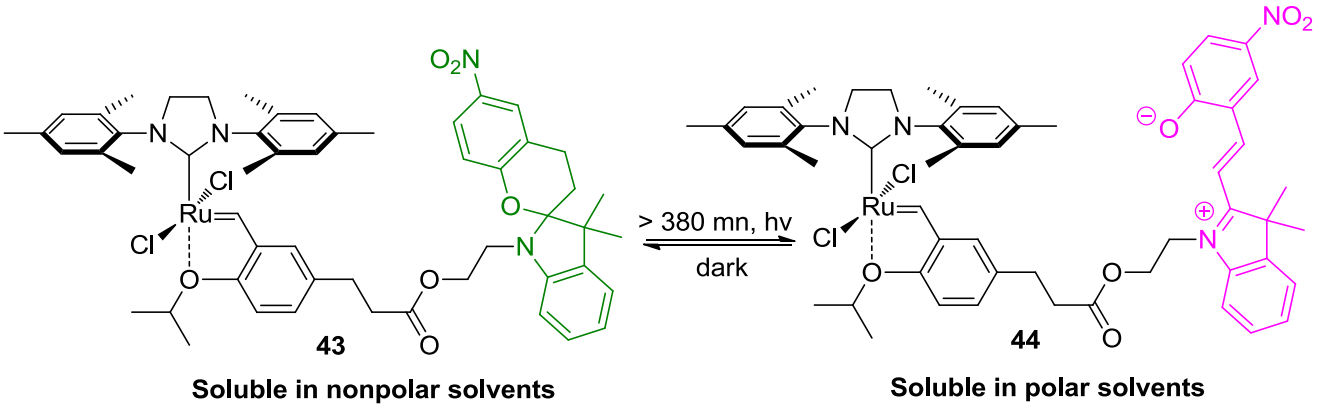
It should be noted that the design of stable rapidly initiating complexes is highly relevant to catalysis, since very rapidly initiating catalysts suffer from a lack of stability under the reaction conditions.

1.6. Switchable Olefin Metathesis Catalysts

The switchable control of chemical reactivity is an important issue in catalysis.[82] The chemical reactivity of ruthenium-based catalysts can be turned on and off by applying some external stimuli. The internal signals may have physical nature (e.g., mechanical force, irradiation, heating) or chemical nature. Stable and switchable initiators are of great interest to polymer chemists, since they provide temporal and spatial control over the polymerization processes.[83]

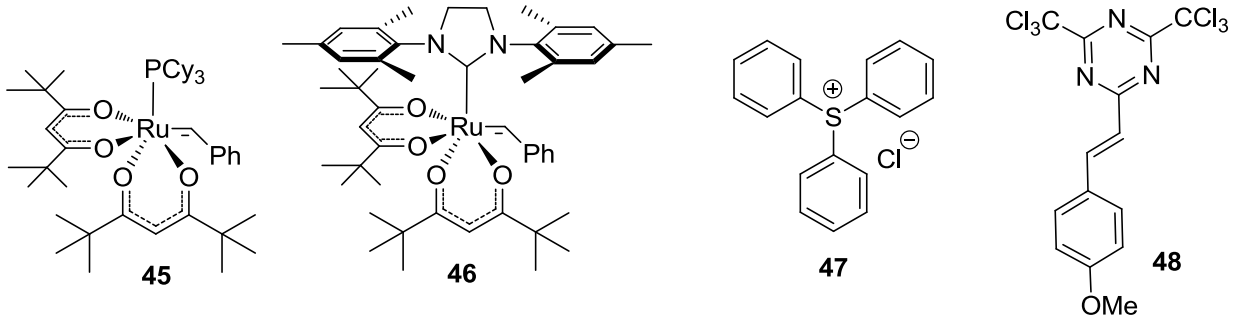
1.6.1. Light Responsive Ruthenium Catalysts

Pretty simple and interesting concept of light-switchable catalysts was proposed by Liu and Wang who prepared Grubbs-Hoveyda-type catalyst **43** bearing light-active nitrobenzospiropyran group (Scheme 31).[84] Irradiation of **43** with light causes the nitrobenzospiropyran tag to convert from its neutral state to the charged state, thus forming catalyst **44**. In the dark complex **44** converts back into **43**. Catalysts **43** and **44** are characterized by different solubility in polar and nonpolar solvents. The neutral form is good soluble in cyclohexane, while the charged form **44** is soluble in polar glycol/methanol mixture. This difference in solubility enabled the separation of homogeneous catalyst from the products and its easy recycling.

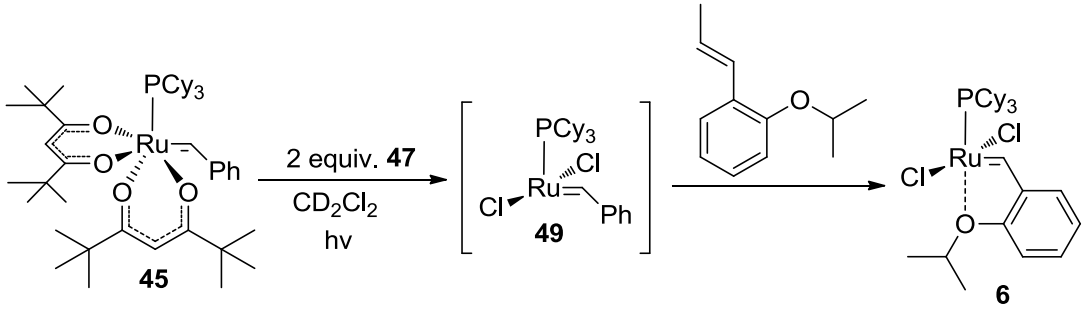


Sheme 31. Solubility switches control catalysis by the photoswitching of spiropyran.

Grubbs et al. demonstrated indirect tandem photoactivation or ruthenium complexes for olefin metathesis (Scheme 32).[85] Combining catalysts **45** and **46** with photoacid generators (PAG) **47** and **48** in the presence of sub-300 nm UV lights resulted in activation of these catalysts by replacement of labile *acac* ligands with chlorine atoms. This activation mechanism is evidenced by the fact that the use of the PAG with non-nucleophilic nonaflate counterion resulted in a complete loss of activity. In addition, one of the possible catalytically active species **49** containing chlorine ligands were trapped with *(E)*-1-isopropoxy-2-(prop-1-en-1-yl)benzene to give well-known complex **6** (Scheme 33).

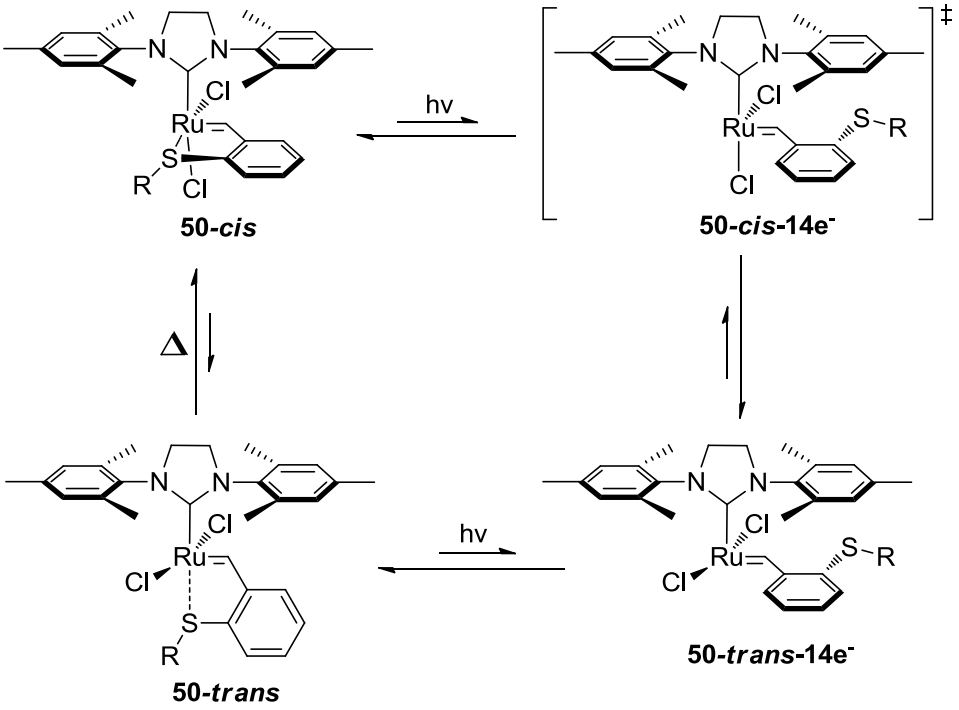


Scheme 32. Ruthenium complexes and photoacid generators used for light induced metathesis.



Scheme 33. Trapping of reactive intermediate.

Lemcoff and co-workers utilized sulfur-chelated ruthenium complexes as photoswitchable catalysts for RCM and ROMP reactions (Scheme 34).[86] The *cis*-chelated complexes were shown to be completely inert at room temperature, but they underwent photoisomerization to active *trans*-dichloro complexes upon irradiation at 365 nm. The thermodynamically more stable *cis*-isomer can be restored by heating of its *trans* counterpart to 80°C in solution.

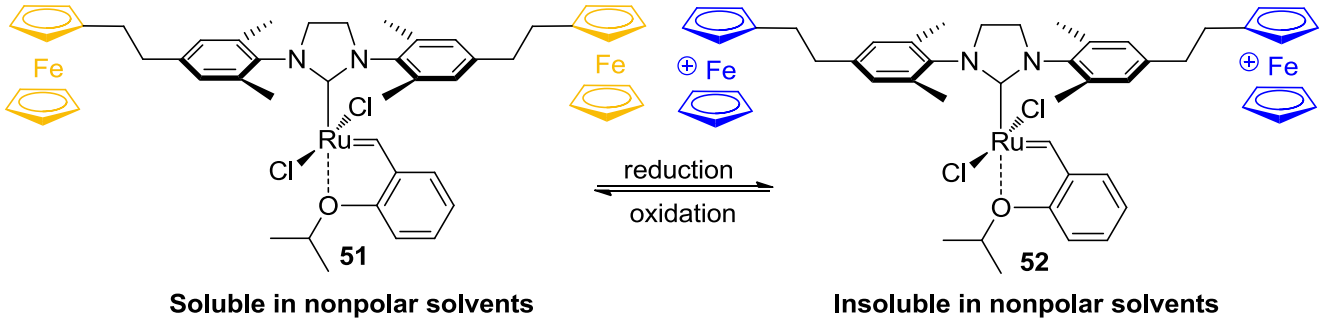


Scheme 34. Proposed mechanism for the photoactivation of *cis*-sulfur-chelated ruthenium complexes.

More examples of light-induced olefin metathesis based on early and well-defined tungsten catalysts and ruthenium-arene complexes have been summarized by Vidavsky and Lemcoff in their review.[87]

1.6.2. Redox-Switched Catalysts

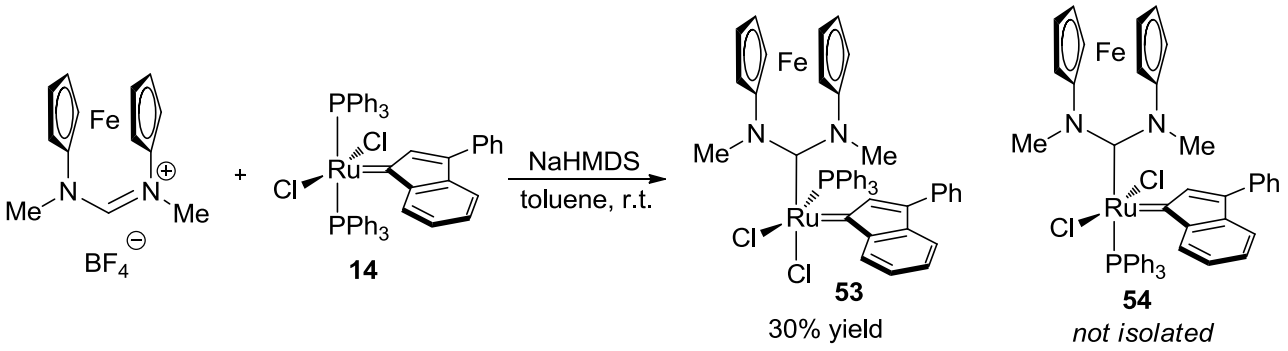
The concept of redox-switched ruthenium olefin metathesis catalysts, which is based on the different solubility of neutral and oxidized forms of the catalyst was reported by Plenio and Süßner.[88] They synthesized Grubbs-Hoveyda-type catalyst **51** with two redox-active ferrocene groups (Scheme 35).



Scheme 35. Ferrocenyl-tagged ruthenium complexes.

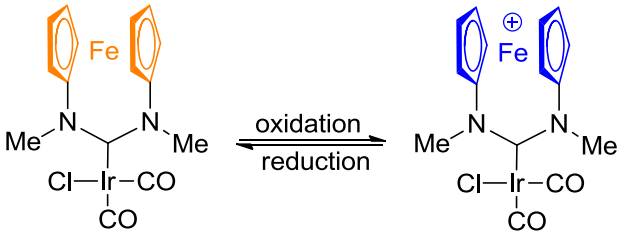
The neutral form **51** is highly soluble and active in toluene. On the other hand, the oxidized catalyst **52** is insoluble in toluene, and thus shows no activity in RCM. Addition of two equivalents of acetylferrocenium tetrafluoroborate (oxidizing agent) to **51** causes oxidation and precipitation from solution, thus stopping catalytic reaction. Addition of octamethylferrocene (reducing agent) restores catalyst to its neutral form and the RCM reaction proceeds to completion. Moreover, the catalyst can also be switched off and on several times after completion of the RCM reaction, allowing multiple recycling of the catalyst.

Christopher Bielawski and co-workers described the synthesis of redox-switchable complex **53** bearing redox-active *N*, *N*-dimethyldiaminocarbene[3]ferrocenophane (Scheme 36).[89] It is interesting that the reaction between NHC and indenylidene-type ruthenium precursor **14** resulted in formation of *cis*-dichloro complex **53** rather than expected catalyst **54** with *trans*-dichloro configuration.



Scheme 36. Redox-switched ruthenium complexes reported by Bielawski et al.

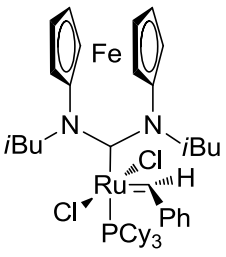
Complex **53** was studied in redox-controlled ROMP of *cis,cis*-1,5-cyclooctadiene. Oxidation of ferrocene center with DDQ over the course of polymerization reaction reduced the rate constant of the reaction (pre-oxidation: k_{obs} = 0.045 s^{-1}; post-oxidation: k_{obs} = 0.0012 s^{-1}). Subsequent reduction of the oxidized species with decamethylferrocene restored catalytic activity. The authors attributed this difference in catalytic activity to the relative donating ability of the redox-active ligand. The Tolman electronic parameters (TEP)[90,91] for both neutral and oxidized states of the NHC ligand were calculated using spectroelectrochemical FT-IR analysis of the respective iridium carbonyl complexes **55** and **56** (Scheme 37). In the neutral state the NHC ligand is characterized by lower value of TEP, and thus is more electron donating than its oxidized form.



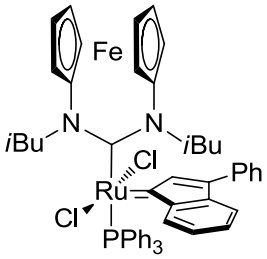
55 TEP = 2050 cm^{-1} **56** TEP = 2061 cm^{-1}

Scheme 37. Evaluation of the electronic properties of redox-active NHC ligand.

In addition, the authors attempted the synthesis of benzylidene-type **57** and indenylidene-type **58** catalysts (Scheme 38). The formation of these complexes was evidenced by diagnostic signals in the ^{1}H and ^{31}P NMR spectrums recorded for the crude reaction mixtures. However, it was not possible to isolate complex **57** in pure state. Catalyst **58** was isolated in quantities insufficient for further investigation.



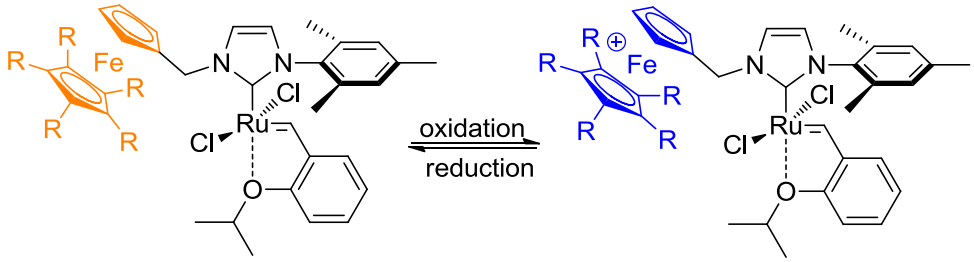
57
^{1}H NMR: 20.10 ppm (d, *J* = 6.3 Hz, 1H, Ru=CH)
^{31}P NMR: 28.5 ppm



58
^{1}H NMR: 8.63 ppm (d, *J* = 7.2 Hz, 1H)
^{31}P NMR: 30.4 ppm

Scheme 38. Attempted synthesis of benzylidene- and indenylidene-type catalysts.

In the same year Bielawski group reported the synthesis of other redox-active NHC ligand and its ruthenium complexes for redox-controlled ROMP and RCM reactions (Scheme 39).[92]



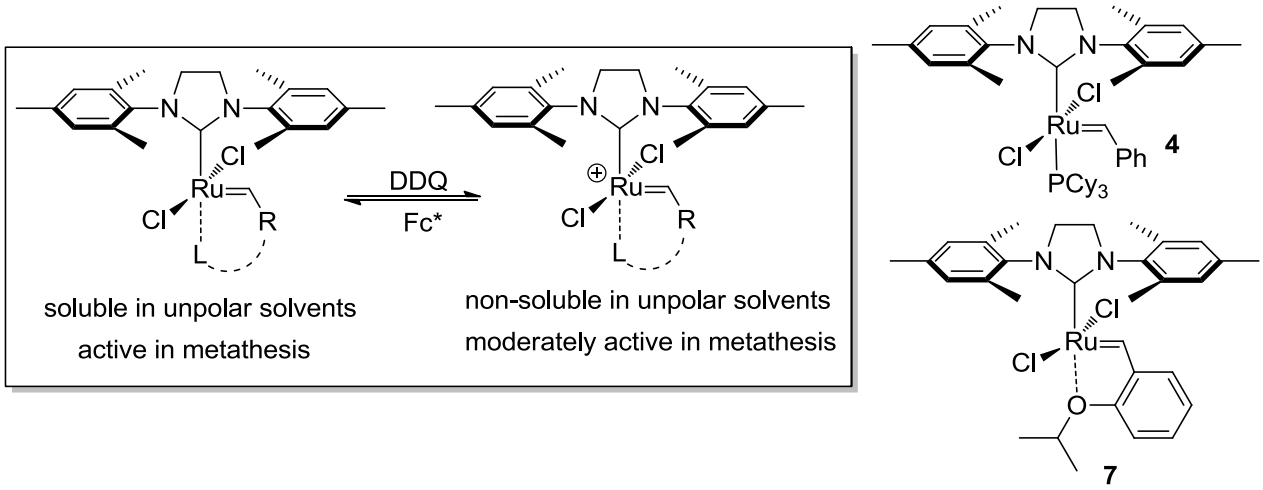
59a: R = H, **59b:** R = Me

60a: R = H, **60b:** R = Me

Scheme 39. Redox-switched ruthenium catalysts reported by Bielawski et al.

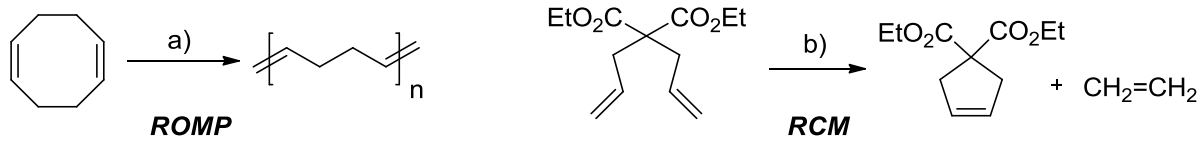
Complexes **59a,b** are active in RCM reaction of DEDAM. By adding $[FcCOCH_3][BF_4]$ as an oxidant over the course of RCM reaction, complexes are switched between neutral and oxidized states which exhibit different catalytic activity. In oxidized state the catalytic activity of **59a** is partially reduced and it can be restored to some extend (ca. 13%) upon reduction by decamethylferrocene. In contrast to **59a**, the activity of complex **59b** is almost completely restored (ca. 94%) after full redox-switching cycle. Reduced catalytic activity of oxidized complexes **60a,b** was attributed to the diminished electron-donating ability of the oxidized ligand.

Recently, Bielawski with co-workers have found that Grubbs 2nd generation catalyst **4** and Hoveyda 2nd generation catalyst **7** display reversible ruthenium-centered oxidations via a series of electrochemical measurements (Scheme 40).[93] These catalysts can be switched between two different states of activity in RCM and ROMP, primarily through changes in catalyst solubility.



Scheme 40. Metal-centered oxidation of ruthenium complexes.

As summarized in Scheme 41, two metathesis reactions were studied: the ROMP of *cis-cis*-1,5-cyclooctadiene and the RCM of diethyl diallylmalonate.



a) 0.003 mol% [Ru], [COD] = 0.5 M, C_6D_6 b) 1 mol% [Ru], [DEDAM] = 0.1 M, CD_2Cl_2.

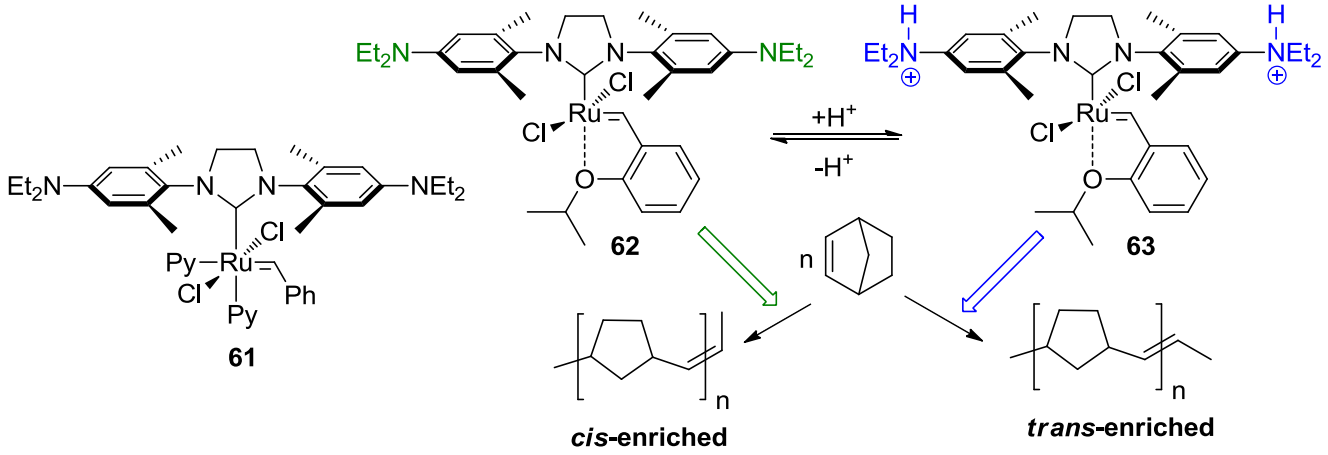
Scheme 41. Metathesis reactions studied using **4** and **7**.

In general, the addition of oxidants to the reaction mixture significantly reduced catalytic activity, which was surmised due to the precipitation of an oxidized derivative of the catalyst. The subsequent addition of decamethylferrocene restores the catalytic activity of the aforementioned complexes.

1.6.3. pH-Responsive Ruthenium Catalysts

The pH-responsive olefin metathesis catalysts represent a family of ruthenium-based complexes containing functional groups (e.g., amino, imino) that are able to be protonated and, hence, to alter the activity of catalysts by change in electronic effect.

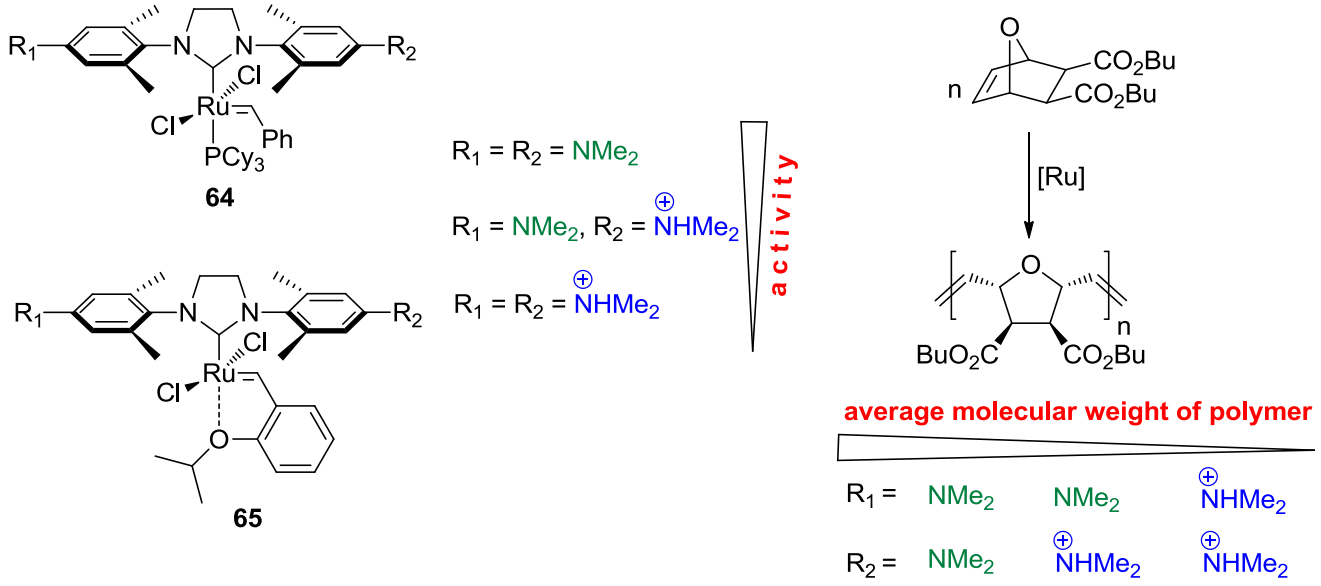
Plenio and co-workers prepared modified Grubbs 3rd generation **61** and Hoveyda 2nd generation **62** catalysts bearing NHC ligand substituted with two –NEt_2 groups (Scheme 42).[94] The electron donation of this NHC in the respective ruthenium complexes can be modulated by protonation of the amino group (formation of complex **63**). It was found that the change in the electron donation of the NHC ligand upon protonation leads to a significant change in the double- bond geometry (from *E/Z* ratio = 0.78 to *E/Z* = 1.04) and in the microstructure of polynorbornene prepared via ROMP. The *E/Z* ratio of the resulting polynorbornene can be tuned by addition of acid and protonation of the living catalyst attached to the polymer chain during the course of polymerization reaction.



Scheme 42. pH-Responsive ruthenium catalysts reported by Plenio et al.

Complex related to **62** with two redox-active ferrocene units instead of –NEt_2 groups was also prepared and tested in redox-switched ROMP reaction of norbornene. However, it turned out to be not suitable for this purpose, because both reduced and oxidized forms of this catalyst gave polymers with nearly the same *E/Z* ratio.

Schanz and co-workers utilized similar complexes **64** and **65** for controlled ROMP reaction of *exo*-7-oxanorbornene monomer (Scheme 43).[95] The catalytic activity of studied complexes in ROMP was gradually reduced upon gradual protonation of the -NMe_2 groups due to a significant change in electron-donating ability of NHC ligand (-NMe_2 – strong electron donor, -$^+NHMe_2$ – strong electron acceptor). The average molecular weights of the produced polymers were gradually reduced with the addition of acid, thus allowing partial control over the polymerization process.

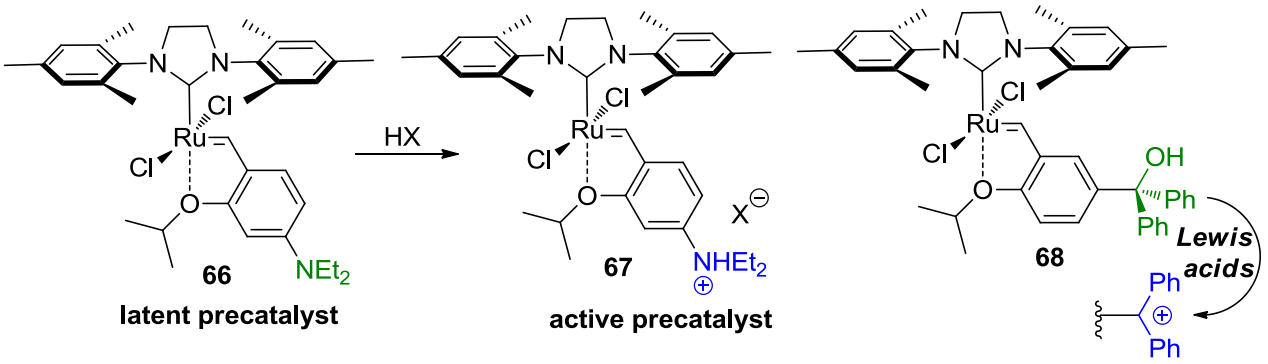


Scheme 43. pH-Responsive ruthenium catalysts reported by Plenio, Schanz et al.

In addition, Schanz and co-workers suggested protocol that allows efficient removal of catalyst **65** ($R_1 = R_2 = NMe_2$) from RCM reaction mixtures by acid addition. The protonated dicationic species ($R_1 = R_2 = {}^+NHMe_2$) exhibit low solubility in the organic solvents (toluene, ethyl acetate) and can be separated from the reaction medium by simple filtration.[96]

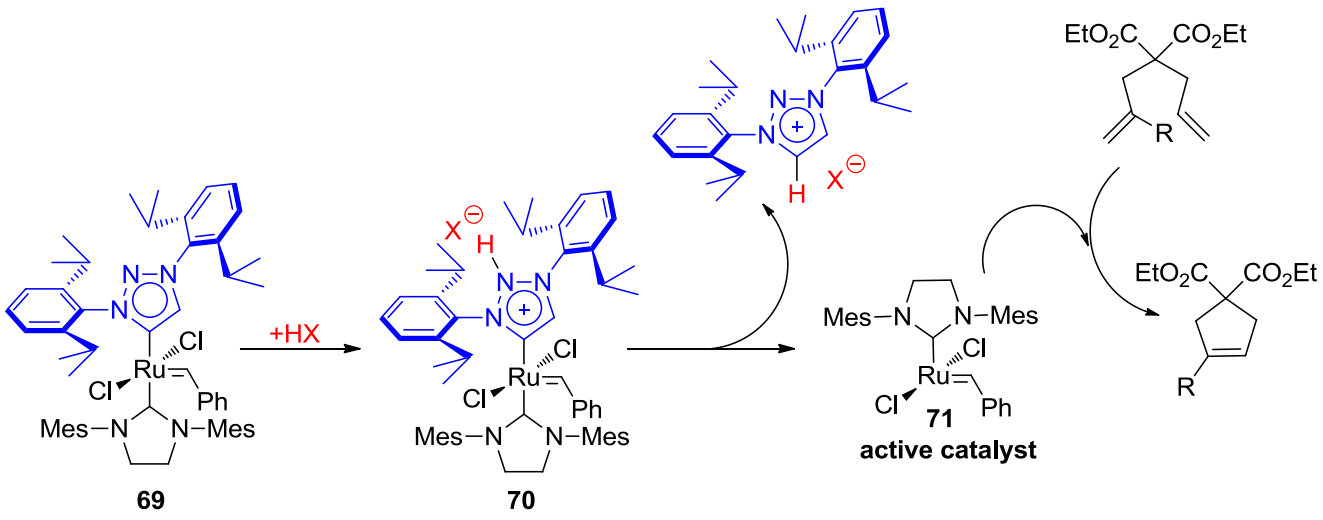
In 2006, Grela and co-workers discovered Hoveyda-type catalyst **66** with -NEt_2 group at chelating benzylidene ligand (Scheme 44).[97] The presence of electron-donating group results in slow catalyst activation, and as a result very low activity in metathesis of benchmark substrates. Protonation of -NEt_2 group (formation of **67**) dramatically increases the initiation rate by weakening the iPrO→Ru interaction. Catalyst **68** bearing -$C(OH)Ph_2$ substituent shows similar activity to that of regular Hoveyda 2nd generation catalyst **7**. Nonetheless, its activity can be even increased in the presence of a

weak Lewis acid which converts the neutral -C(OH)Ph_2 substituent to electron withdrawing carbocation.



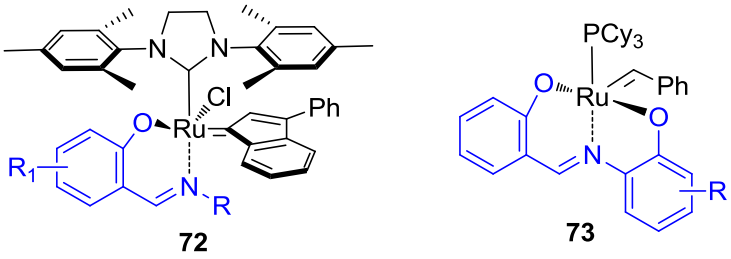
Scheme 44. Switchable catalysts reported by Grela et al.

Grubbs et al. have prepared complex **69** containing SIMes ligand and mesoionic 1,2,3-triazole carbene (MIC) (Scheme 45).[98] This complex is inactive in ring-closing metathesis at room temperature, however, addition of Brønsted acid results in protonolysis of the Ru-MIC bond to generate an active catalyst **71**.



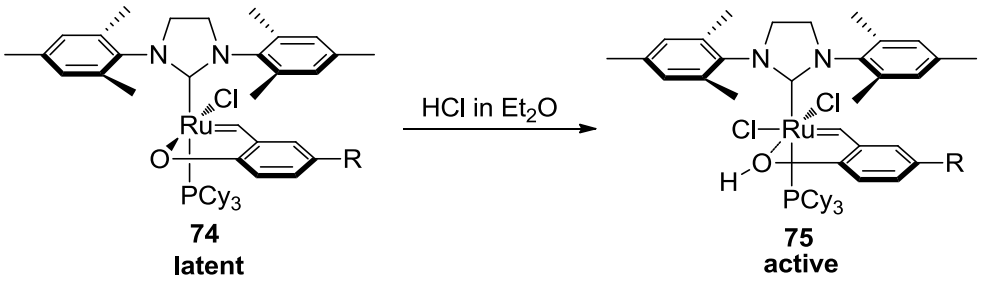
Scheme 45. Proposed mechanism for initiation of **69**.

There are several indenylidene-type **72**[99] and benzylidene-type **73**[100] complexes described in the literature which are latent at room temperature due to the presence of Schiff base ligands strongly bound to ruthenium (Scheme 46). Addition of HCl to these catalysts leads to decoordination of salicylaldimine ligands and subsequent generation of the catalytically active species.



Scheme 46. Ruthenium catalysts bearing salicylaldimine ligands.

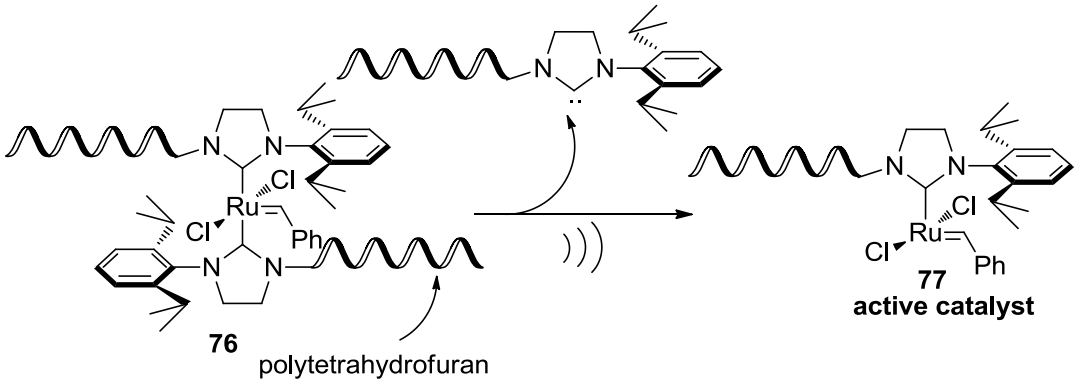
Recently, Pietraszuk and co-workers have developed aryloxybenzylidene ruthenium chelates **74** that are inactive in their dormant forms and display a dramatic increase in initiation rate after addition of a solution of HCl in ether (Scheme 47).[101] The proposed mechanism of activation involves protonation of the phenoxides and the formation of catalytically active complexes **75** which are closely related to Grubbs 2nd generation catalyst **4**.



Scheme 47. Activation of aryloxybenzylidene ruthenium chelates.

1.6.4. Mechanical Activation of Ruthenium Catalyst

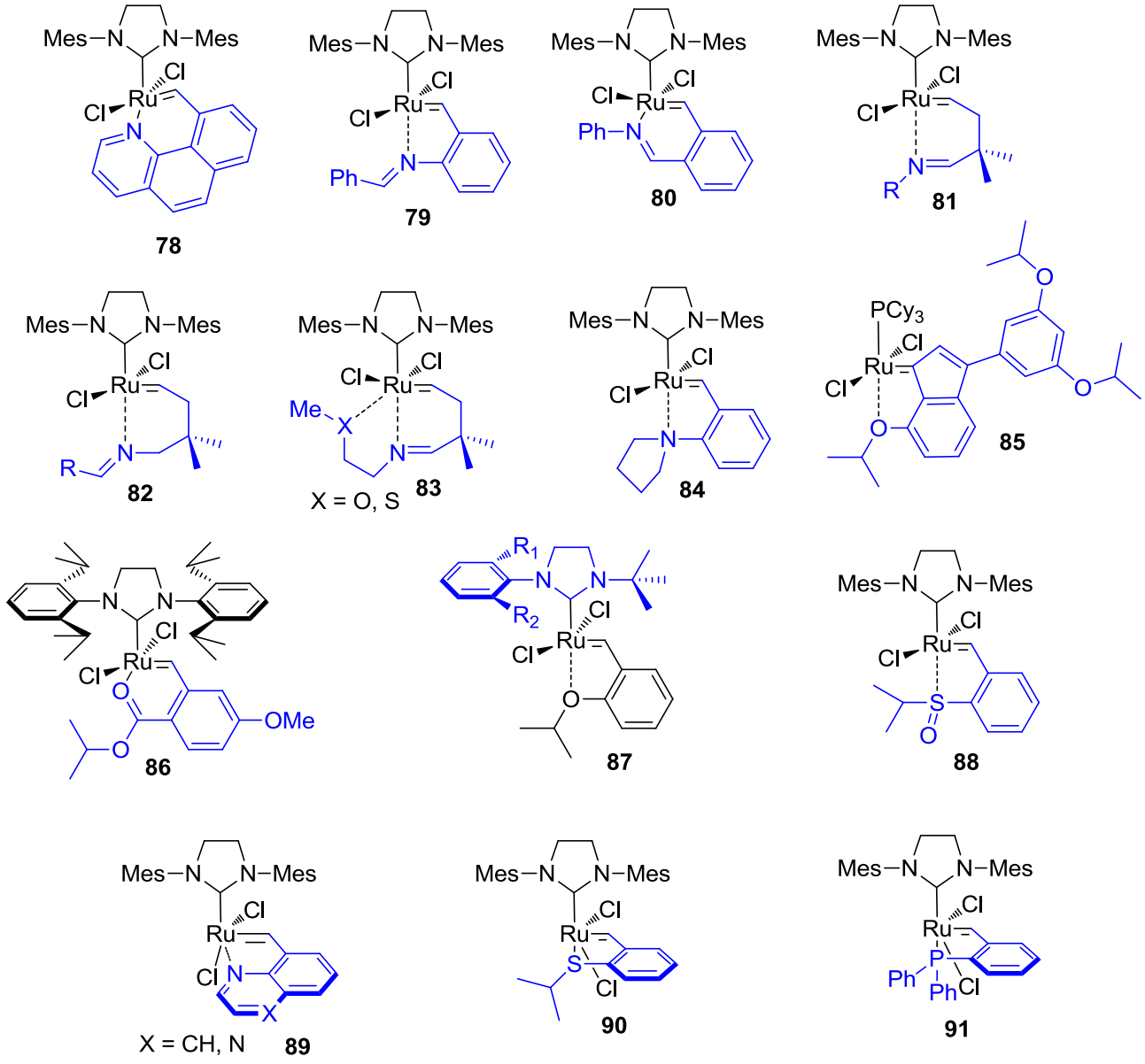
Sijbesma and Jakobs described latent ruthenium catalyst **76** bearing two NHC ligands substituted with polytetrahydrofuran chains (Scheme 48).[102] This catalyst is inactive at room temperature, because of strong NHC–Ru bonds which dissociate only at elevated temperatures. Mechanochemical scission of **76** under ultrasound irradiation results in cleavage of the NHC-Ru bond due to accumulation of stress in polymer chain. The efficiency of initiation depends on the length of the polymer chain. The authors noted that lower molecular weight polymer chains led to lower activity, and an analogue complex containing short butyl chains was not activated at all.



Scheme 48. Scission of **76** under ultrasound.

1.6.5. Thermal Activation of Ruthenium Catalysts

There are many ruthenium-based catalysts that are inactive or exhibit low activity in olefin metathesis at ambient temperature, but when heated become significantly more active. Most of these complexes either contain chelating ligands that are strongly bound to ruthenium or exist as inactive *cis*-dichloro isomers. Some representative latent complexes **78**,[103] **79**,[104] **80**,[104] **81**,[105] **82**,[105] **83**,[105] **84**,[106] **85**,[107] **86**,[108] **87**,[109] **88**,[110] **89**,[111] **90**,[112] **91**[113] are summarized in Scheme 49.



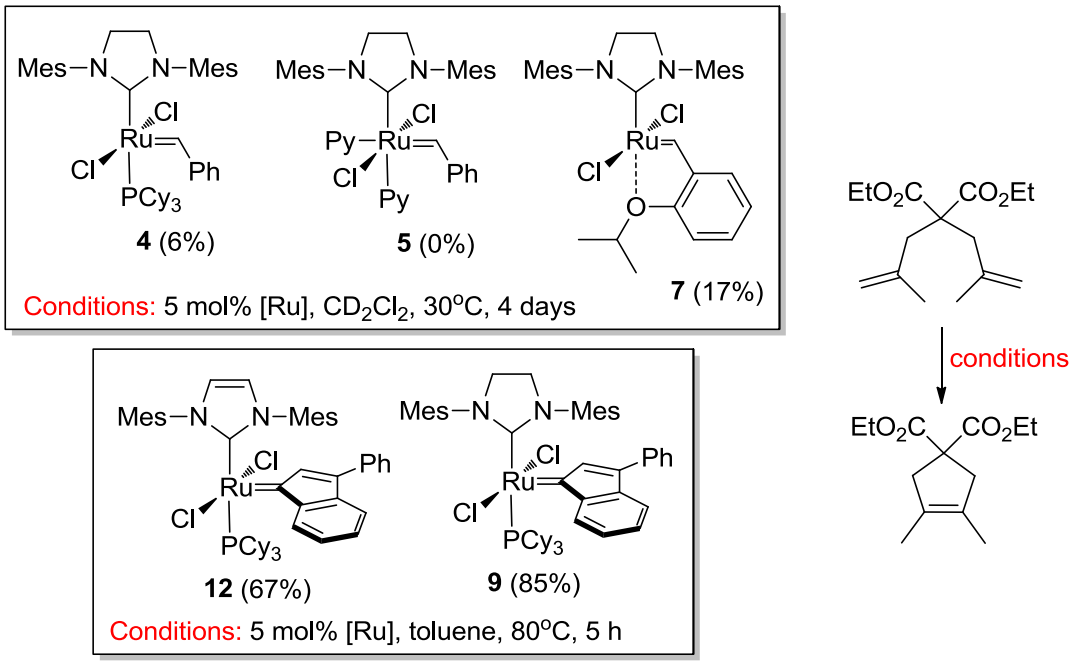
Scheme 49. Thermally switchable latent ruthenium olefin metathesis catalysts.

1.7. Ruthenium-Based Catalysts for Ring-Closing Metathesis of Hindered Olefins

The synthesis of hindered tetrasubstituted olefins by olefin metathesis remains a significant challenge. Normally, ring-closing metathesis of such olefins requires elevated temperatures, high catalyst loading,

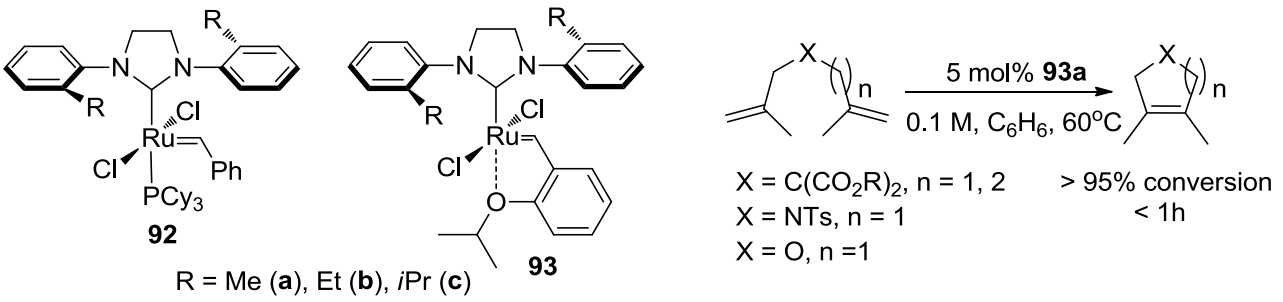
and extended reaction times. The conventional catalysts such as Grubbs 2nd generation **4** and Hoveyda 2nd generation **7** exhibit low activity in RCM of sterically demanding substrates.[114] In RCM of diethyl dimethallylmalonate these catalysts gave only 6% and 17% conversion at high catalyst loading (5 mol%) after 4 days at 30°C, while Grubbs 3rd generation catalyst **5** appeared to be completely inactive under the same reaction conditions (Scheme 50).

In 2007, Clavier and Nolan described indenylidene-type ruthenium complexes **9** and **12** which were more active than benzylidene analogues (Scheme 50).[115] These stable catalysts allowed the reaction to proceed at higher temperature (80°C), however, relatively high catalyst loading (5 mol%) was still required to reach good conversions.



Scheme 50. Activity of conventional ruthenium catalysts in RCM of diethyl dimethallylmalonate.

In 2008, Grubbs and co-workers improved the catalytic activity of ruthenium complexes by reducing the steric bulk of the NHC ligands (Scheme 51).[116] Complexes **92a** and **93a** bearing small methyl substituent at *ortho* positions of the *N*-aryl rings showed higher activity in RCM reactions of model hindered olefins than their ethyl and isopropyl substituted analogues. Under optimized conditions catalyst **93a** afforded different tetrasubstituted olefins in high yields within one hour.



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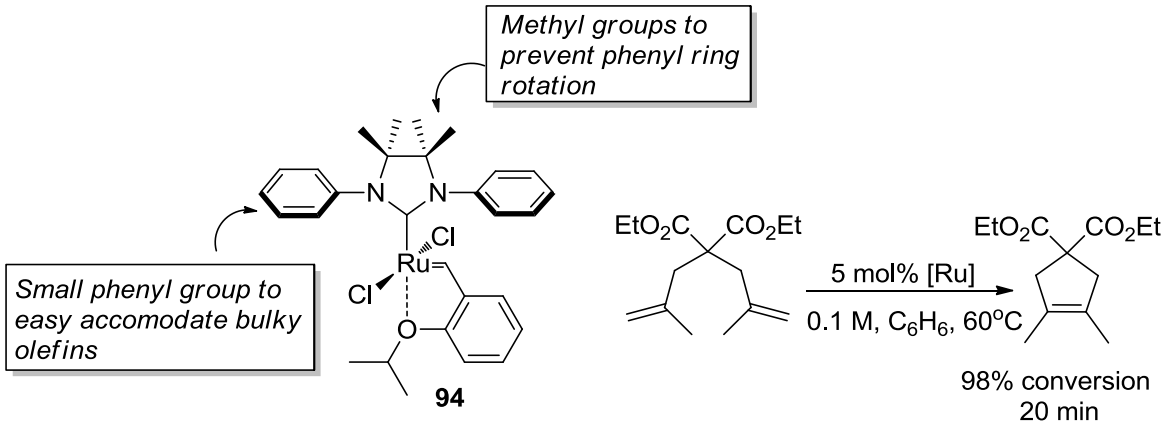
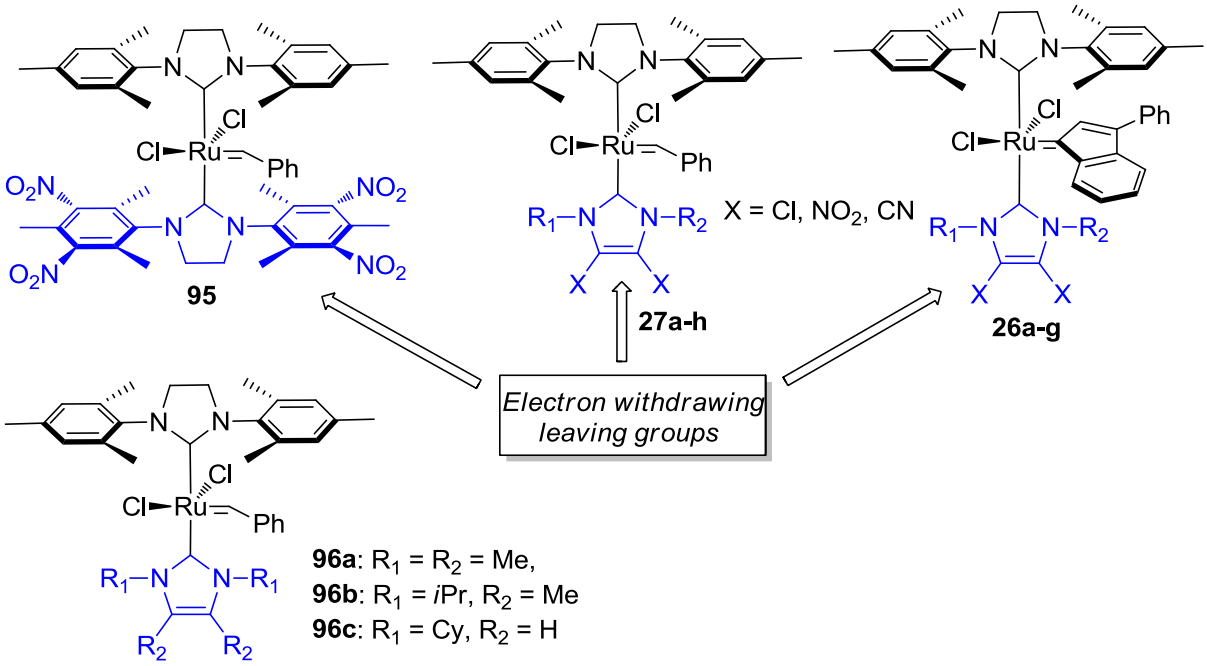
Scheme 51. Ruthenium complexes with a sterically reduced NHC ligands for RCM of hindered olefins.

In the same year Grubbs et al. offered a concept, according to which an *N*-phenyl-substituted NHC ligand has to be resistant to decomposition through C-H activation (Scheme 52).[117] Complex **94** turned out to be even more active in RCM reaction of DEDAM than aforementioned catalyst **93a**.



Scheme 52. Hoveyda-type catalyst with *N*-phenyl-substituted NHC ligand for RCM of hindered olefins.

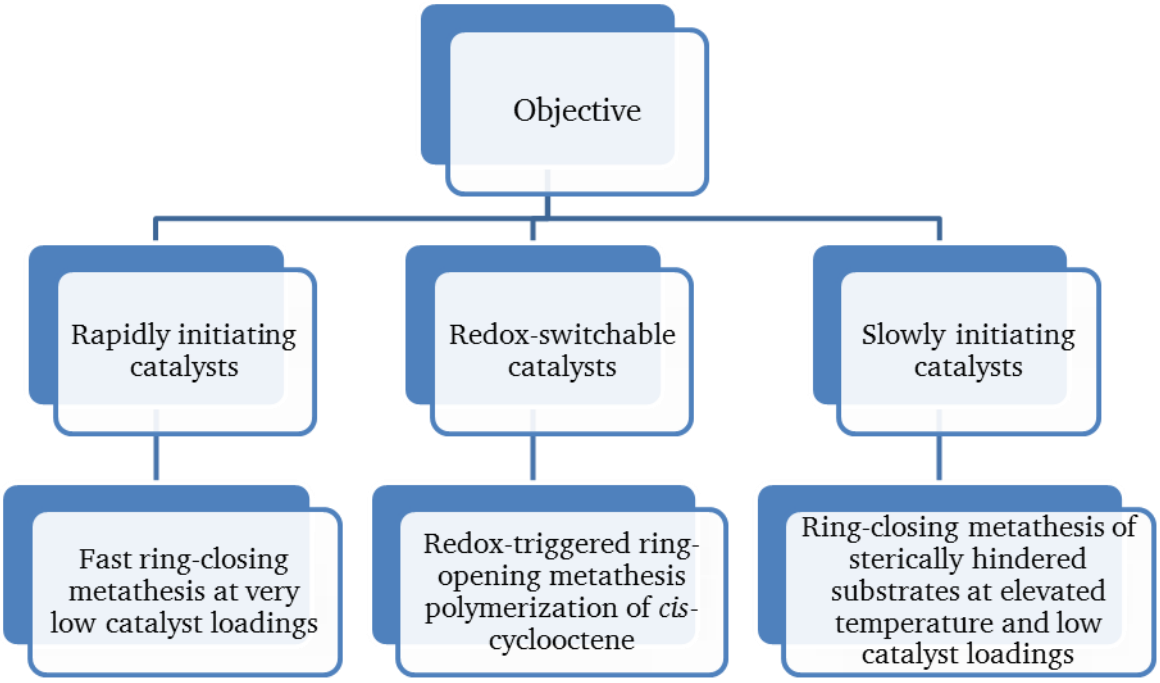
Some of the aforementioned complexes are suitable for RCM reactions of hindered substrates under mild reaction conditions. However, the need to use high catalytic loading prompted the scientific community to develop new catalysts. Plenio and co-workers reported a new types of ruthenium complex **26a-g**,[71] **27a-h**[70] and **95**[118] with mixed NHC ligands, one of them being electron-rich, the other one being electron-deficient (Scheme 53). The latter ligand should be released from ruthenium to generate the catalytically active species. These complexes display high stability in solution at elevated temperatures and excellent activities in RCM reactions leading to tetrasubstituted olefins. Number of cyclic products derived from hindered olefins were prepared in excellent yields using only 0.1-1 mol% of the respective catalyst. In 2010, Nolan and co-workers reported structurally related complexes **96a-c** which required higher temperature (110°C) to be activated (Scheme 53).[119]



Scheme 53. Bis-NHC-ruthenium complexes for RCM of hindered olefins.

2. Scope of the dissertation

This dissertation covers the synthesis of new ruthenium-based catalysts and their application in specific olefin metathesis transformations which are outlined in Scheme 54.



Scheme 54. Scope of the dissertation.

Ring-closing metathesis of sterically demanding diolefinic substrates is a difficult reaction and requires development of new catalysts with improved stability at elevated temperatures. The most efficient ruthenium-based catalysts for RCM of challenging substrates were prepared in our group. These slowly initiating catalysts contain two NHC ligand one of which is electron-withdrawing and acts as leaving group. Chapter 3.1 describes the synthesis of similar catalysts bearing new hexahydro-*s*-indacene based NHC ligand instead of traditional SIMes carbene. The structure of this ligand was properly designed in order to get catalysts which are less prone to decomposition via C-H activation. The synthesized complexes were tested in RCM reactions of various hindered olefins and were shown to be very efficient catalysts.

Rapidly initiating catalysts provide good substrate conversion within a short time or at low temperatures. Extremely fast ruthenium catalysts, such as Grubbs 3rd generation or Piers-type complexes, are useful for the synthesis of low-dispersity polymers by ring-opening metathesis polymerization, however, these catalysts have been rarely employed in ring-closing reactions due to their low stability under the reaction conditions. On the other hand, Hoveyda 2nd generation and Grela complexes initiate slower, possess higher stability and have found widespread application in ring-

closing metathesis. Nonetheless, relatively high loading of these catalysts is required to reach high conversions within a short period of time. That is why the development of new ruthenium catalysts which initiate faster than traditional Hoveyda-type complexes, but remain stable enough under the reaction condition is very relevant to catalysis. In chapters 3.2 and 3.3, the high-yield and scalable synthesis of new rapidly initiating *N*-Hoveyda and *O*-Hoveyda-type complexes is described. These catalysts appear to be very active in ring-closing metathesis reactions at catalyst loadings as low as 15-200 ppm.

Chapter 3.4 presents our contribution to switchable catalysts for olefin metathesis. Switchable catalysts are of great interest to polymer chemists since they allow control over polymerization reactions. For example, such catalysts can be mixed with the desired monomer, providing homogeneous mixture which can then be injected into a mold prior to polymerization. Redox-switched complexes that can be activated by oxidation of the redox-active unit at room temperature and mild conditions seems to be best suited. We prepared eight ruthenium complexes containing ferrocene-based redox-switches and studied their catalytic behavior in ring-opening metathesis polymerization of *cis*-cyclooctene. Two of eight complexes were found to be suitable for redox-controlled ROMP reactions employing chemical, as well as electrochemical, stimuli.

The synthesis of the respective metal complexes is the initial step of any research related to catalysis. Most of the known ruthenium-based catalysts for olefin metathesis contain NHC ligands. The transfer of *N*-heterocyclic carbene to ruthenium is often a crucial synthetic step. Chapter 3.5 highlights the use of 2-(pentafluorophenyl)imidazolidines as NHC-transfer reagents. Special attention is given to the application of 2-(pentafluorophenyl)imidazolidines in the synthesis of Hoveyda-type and indenylidene-type ruthenium complexes which are widely used in catalysis.

3. Cumulative part of the dissertation

Only part of the supporting information is included in the printed version of this dissertation and the full experimental details are contained in the electronic versions of the respective manuscripts.

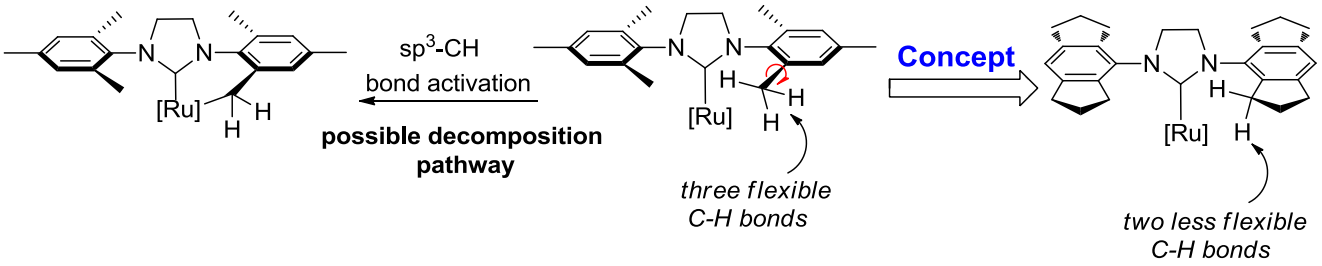
3.1. A hexahydro-*s*-indacene based NHC ligand for olefin metathesis catalysts

The content of this chapter has already been published:

Roman D. Savka, Herbert Plenio, *"A hexahydro-s-indacene based NHC ligand for olefin metathesis catalysts", Journal of Organometallic Chemistry* **2012**, *710,* 68-74.

Catalytically active species are highly reactive complexes which are able to participate in decomposition reactions other than the desired catalytic transformation. Therefore, the life time of the active species is an important factor determining its performance in catalysis.

N-Heterocyclic carbenes were shown to improve activity and stability of ruthenium metathesis catalysts. Nonetheless, *N*-heterocyclic carbenes can also take part in catalyst decomposition. One of the possible ways of decomposition involves sp^3-CH activation reaction (Scheme 55). The chances for undesired C-H activation are decreased by lowering the number of available C-H bonds and by restricting the conformational flexibility of these units. Consequently, the objective of this work was to prepare NHC ligand with two *N*-hexahydro-*s*-indacenyl units in which conformational mobility of the CH_2-groups in the annelated five-membered rings is significantly reduced (Scheme 55).

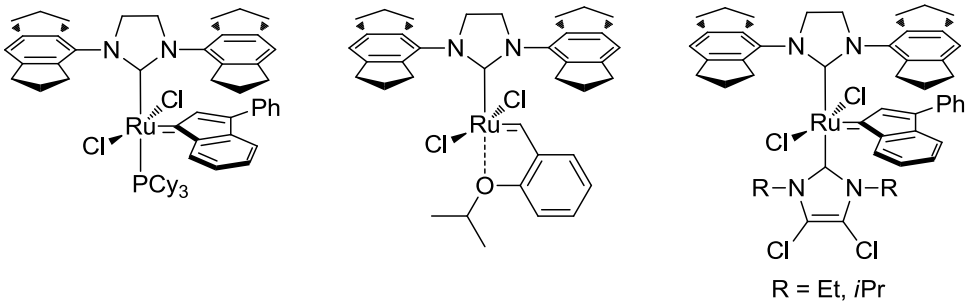


Scheme 55. Rational design of NHC ligand with reduced ability to participate in decomposition reactions.

- Lowering the number of available sp^3-CH-bonds
- Restricting the conformational flexibility of sp^3-CH-bonds

In this chapter, the synthesis of a new hexahydro-*s*-indacene based NHC ligand and its Ag, Ir and Ru complexes is described. The electronic properties of this NHC are evaluated by IR spectroscopy and cyclic voltammetry. The buried volume for the new NHC is calculated based on X-ray structure of (NHC)Ir(CO_2)Cl complex. Both electronic and steric parameters are shown to be similar to those of the SIMes ligand.

Finally, a few ruthenium-based catalysts bearing hexahydro-*s*-indacene based NHC ligand are described (Scheme 56) and their catalytic activity in ring-closing metathesis of various sterically hindered olefins is tested. The catalytic activity of the bis-NHC complexes is comparable to the best complexes with SIMes ligands. The activity of indenylidene and Hoveyda-type complexes is higher with respect to their relatives with SIMes ligand.



Scheme 56. Ruthenium-based complexes containing a hexahydro-*s*-indacene based NHC ligand.

The restricted mobility in the ortho-alkyl substituents results in stabilization of the less stable indenylidene and Hoveyda-type complexes, thus making them suitable catalysts for the synthesis of tetrasubstituted olefins.

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A hexahydro-*s*-indacene based NHC ligand for olefin metathesis catalysts

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ABSTRACT

The reaction of amino hexahydro-*s*-indacene with glyoxal, reduction of the diimine to the diamine and cyclization with $HC(OEt)_3$ yields the new 1,3-bis(1,2,3,5,6,7-hexahydro-*s*-indacen-4-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride **3**· HCl with conformationally restricted alkyl groups ortho to the heterocyclic substituent. Reaction of **3**· HCl with Ag_2O gave the respective silver NHC complex (yield 78%), which was used to synthesize the respective (**3**)IrCl(cod) (yield 86%), whose reaction with CO gave (**3**)$IrCl(CO)_2$ **6** (yield 98%). The Grubbs II type complex [(**3**)$RuCl_2(PCy_3)$(3-phenyl-indenylid-1-ene)] was synthesized (yield 68%) and converted into [(**3**)$RuCl_2$(py)(3-phenyl-indenylid-1-ene)] (yield 78%) in pyridine solvent. With this complex the respective Grubbs–Hoveyda species (yield 68%) and two bisNHC complexes [(**3**)(NHC_{ewg})$RuCl_2$(3-phenyl-indenylid-1-ene)] (yield 87%, 89%) were obtained. The stereoelectronic properties of the new NHC ligand were determined employing IR spectroscopy, cyclic voltammetry and buried-volume analysis based on the crystal structure of complex **6**. The activity of the ruthenium complexes in RCM reactions of sterically hindered substrates was tested.

1. Introduction

Next to the intrinsic activity of a given catalyst in a catalytic transformation, the life time of the active species is a very important factor determining its performance in catalysis. Catalytically active species are highly reactive complexes, which obviously are also able to participate in (decomposition) reactions other than the desired catalytic transformation. In order to improve the life time of a catalyst, it is important to better understand potential decomposition pathways. For ruthenium-based olefin metathesis catalysts such unwanted degradation reactions were studied [1,2]. Initially, ruthenium methylidene species were identified as straightforward entries to decomposition reactions [3]. More detailed studies on Grubbs II type species showed, that such reactions can also be induced by the phosphine ligands and some of the respective degraded dimeric complexes were isolated and characterized [4]. Alternative pathways involve the formation of Ru–H complexes [5]. *N*-heterocyclic carbenes can also take part in catalyst decomposition and the *N*-phenyl ring in such ligands was shown to undergo sp^2-CH activation reactions [6–9]. Since sp^2-CH is more reactive than sp^3-CH, more stable catalysts are generated when the two ortho-hydrogen groups in phenyl rings are replaced by two alkyl groups like in a *N*-mesityl or *N*-xylyl substituent. Nonetheless, even such CH-bonds can be activated during olefin metathesis [10,11] and the respective decomposition products have been isolated [4]. The rate of CH-activation of an *N*-aryl group in the *N*-heterocyclic carbene bonded to ruthenium should depend on the orientation of the respective CH bond with respect to the ruthenium. In order to impede a favorable (with respect to the unwanted CH-activation) spatial arrangement of the CH –bond relative to ruthenium, Grubbs et al. tested the effect of sterically demanding substituents at the C3/C4 atom of the imidazolidine ring of the NHC ligand, which hinder the rotation around the N–C(aryl) bond [12]. The increased catalytic activity of such complexes in RCM reactions leading to tetrasubstituted olefins was attributed to the hindered access to decomposition pathways [13]. Alternatively, the chances for undesired CH-activation might be decreased by simply lowering the number of available CH-bonds and by restricting the conformational flexibility of these units.

We thus decided to synthesize an NHC ligand with two *N*-hexahydro-*s*-indacenyl units. Obviously, the conformational mobility of the CH_2-groups in the annelated five-membered rings is significantly reduced, as compared to the methyl groups in the 1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene (SIMes) ligand, which might decrease the likelihood of the undesired CH-activation. This in turn could lead to catalysts with improved performance. We wish to report here on the synthesis of a new imidazolinium salt featuring hexahydro-*s*-indacene units, the synthesis of Ag, Ir and Ru complexes with the new NHC

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ligand, its stereoelectronic properties and an investigation of the catalytic behavior of the respective Grubbs type olefin metathesis catalysts.

2. Results and discussion

2.1. Synthesis of NHC ligand and metal complexes

The synthesis of the amino hexahydro-*s*-indacene (Scheme 1) was done starting from indane, following a literature procedure with a few minor modifications [14]. The hexahydro-*s*-indacene imidazolinium salt **3**· HCl was prepared in 48% overall yield following the standard three step route (Scheme 1) via reaction of the respective aniline with glyoxal to the diimine **1**, $LiAlH_4$ reduction to the diamine **2** and cyclization with triethylorthoformate **3**· HCl [15].

The silver complex **4** with NHC **3**, which should be useful as an NHC transfer reagent [16], was synthesized in the reaction of **3**· HCl with Ag_2O (Scheme 2). Based on the mass spectra, complex **4** probably has the $[Ag(\mathbf{3})_2][AgCl_2]$ structure [17]. Complex **4** was used for the synthesis of the respective (**3**)IrCl(cod) **5** from $[Ir(\mu\text{-}Cl)(cod)]_2$. Bubbling CO into a CH_2Cl_2 solution of **5** leads to the formation of (**3**)$IrCl(CO)_2$ **6** in nearly quantitative yield.

$[RuCl_2(PCy_3)_2$(3-phenyl-indenylid-1-ene)] [18] and its reaction with NHC **3** led to complex **7** (Scheme 3) in 68% yield. Complex **7** serves as an entry to the synthesis of other Grubbs type ruthenium complexes, which should be useful as precatalysts for olefin metathesis reactions. Replacing the PCy_3 ligand in **7** with an excess of pyridine provides the monopyridine complex **8** in 78% yield [19]. Reaction of **8** with 2-isopropoxystyrene leads to the respective Grubbs–Hoveyda type complex **9** in 68% yield as reported by Slugovc et al. for related complexes [20,21]. The pyridine ligand can be replaced by a weakly electron-donating NHC_{ewg} ligand, producing the respective bisNHC complexes **10** or **11** in almost 90% yield [22,23]. The ^1H NMR spectra of complexes **7**, **8**, **10** and **11** are very complex, since the four annelated five-membered rings give rise to four different sets of signals.

2.2. Crystal structure analysis of iridium complex *6*

The structure of (**3**)$IrCl(CO)_2$ was determined to evaluate the steric bulk of ligand **3**. The geometry around iridium is very close to a perfect square-planar coordination. These and other geometric parameters are comparable to those of related (NHC)$IrCl(CO)_2$ complexes [24–26]. Based on the crystal structure data the buried-volume [27] the NHC **3** was calculated to be 31%, which is virtually the same as that of SIMes (30%) [28] (Fig. 1).

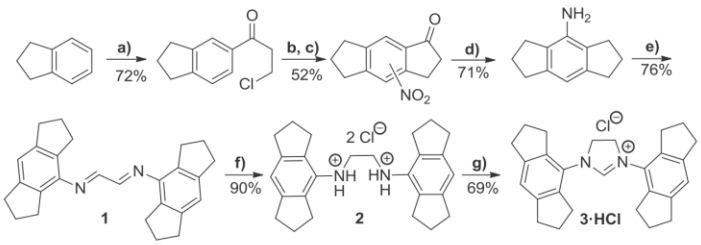
2.3. Evaluation of the electronic properties of NHC *3* by IR and cyclic voltammetry

The eight alkyl substituents of NHC **3** should lead to a ligand slightly more electron-donating ligand than with SIMes. The IR spectrum of **6** displays symmetric and asymmetric carbonyl stretches at 1979, 2066 cm^{-1} and a TEP = 2053.5 cm^{-1} was calculated [29]. This is slightly more donating than the respective SIMes ligand, but weaker than an NHC derived from SIMes, in which the two 4-methyl groups are replaced by 4-NEt_2 [15,30,31]. The Ir(I/II) redox potential of complex **5** is $E = +0.729$ V (separation of anodic and cathodic redox potential $\Delta E_{1/2} = 78$ mV) and thus nearly the same as that of the respective (SIMes)IrCl(cod) complex ($E = +0.735$ V). Due to the higher signal dispersion of the redox potential, the determination of electron donation is more precise than with IR [31]. The redox potentials of complexes **10** and **11** are $E = +0.515$ V ($\Delta E_{1/2} = 75$ mV) and $E = +0.527$ V ($\Delta E_{1/2} = 72$ mV), which is slightly more cathodic (ca. 20 mV) than the redox potentials of the analogous SIMes complexes [32]. The redox potential for the Grubbs–Hoveyda type complex is $E = +0.820$ V ($\Delta E_{1/2} = 69$ mV), which again is slightly more cathodic than the 0.85 V for the Grubbs–Hoveyda complex with the SIMes ligand [21,33]. In conclusion, the various data measured confirm that NHC **3** is a slightly stronger donor than SIMes.

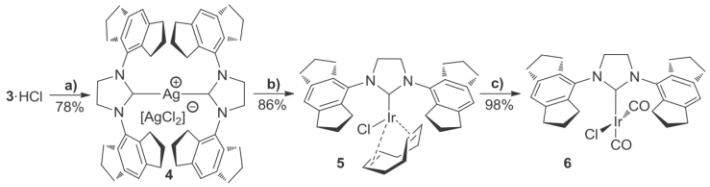
2.4. Screening of the catalytic activity of ruthenium complexes *7*, *9*, *10* and *11* in RCM reactions with sterically demanding olefins

The activity of the complexes in various sterically demanding ring closing metathesis reactions was tested. For several of those reactions, the bisNHC species **10** and **11** are more active than Grubbs–Hoveyda type complex **9** and the Grubbs II type complex **7**. At the respective optimum temperatures of 80 °C, 0.5 mol% of complexes **7** or **9** are required to obtain yields in excess of 80% for most substrates. At 100 °C only 0.2 mol% of complexes **10** or **11** are sufficient to obtain comparable yields. However, the difference in reactivity between the different precatalysts – especially concerning the performance of the Grubbs II complexes - is smaller than observed before [23]. One could argue that this is the expected result, since all of the precatalysts mentioned here finally (that is following activation), lead to the same catalytically active species. However, it is well known in the literature, that different precatalysts show distinctly different reactivity patterns, despite the fact that the same active species is formed following precatalyst activation [34]. This also applies to the bisNHC complexes, since it was shown for related (NHC)$(NHC_{ewg})RuCl_2$(3-phenyl-indenylid-1-ene) complexes, that precatalyst activation leads to the dissociation of the electron deficient NHC_{ewg} ligand [22].

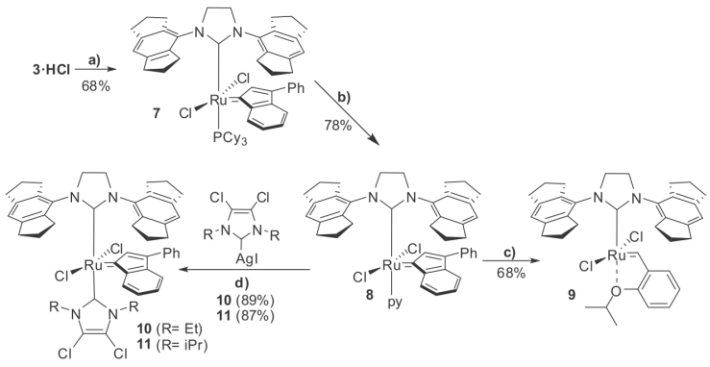
Compared to other catalysts employed for the synthesis of tetrasubstituted olefins via RCM reactions, the complexes **10** and



Scheme 1. Reagents and conditions: a) 3-chloropropionyl chloride, $AlCl_3$, CH_2Cl_2, −10 °C to rt then 2 N HCl, −10 °C; b) conc. H_2SO_4, 55–60 °C; c) HNO_3, H_2SO_4, 0 °C; d) H_2, 20% $Pd(OH)_2$ on carbon (50% water), $MeSO_3H$, MeOH, 1 atm, rt; e) aq. glyoxal, HCOOH, EtOH, rt; f) $LiAlH_4$, THF, 0 °C to rt then aq. HCl, 0 °C; g) $HC(OEt)_3$, HCOOH, 120 °C.



Scheme 2. Reagents and conditions: a) Ag_2O, CH_2Cl_2, 40 °C; b) $[Ir(\mu\text{-}Cl)cod]_2$, CH_2Cl_2, 45 °C; c) CO, CH_2Cl_2, RT, 1 atm.



Scheme 3. Reagents and conditions: a) KO*t*Bu, THF, rt then $[RuCl_2(PCy_3)_2(3\text{-phenyl-indenylid-1-ene})]$, toluene, 70 °C; b) pyridine, rt; c) 2-isopropoxystyrene, toluene, 60 °C; d) $AgI(NHC_{ewg})$ toluene, 60 °C.

11 reported here are amongst the most active systems for such reactions. Complexes **10** and **11** compare favorably with a few of the recently published catalyst complexes [19,35–38], but are on the other hand not significantly better than the most active catalysts [12,22,39,40]. Nonetheless it has to be conceded that the concept of this work (i.e. impeding CH-activation by restricted mobility) did not lead to significant improvements in catalytic activity for the bisNHC complexes. On the other hand, significantly improved activities for the related Grubbs–Hoveyda and Grubbs II species with the hexahydro-*s*-indacene based NHC ligand **3** compared to the related complexes with the SIMes ligand were observed. For several reactions (Table 1, entries 3, 5 and 6) the performance of **7** and **9** is nearly as good as that of **10** or **11** – or even slightly superior. This was not observed before [22,23,32]. A possible explanation for this is unusual leveling of the catalytic activities between the complexes **7**, **8**, **10** and **11** is a stabilization of the active species with hexahydro-*s*-indacene based NHC ligand relative to SIMes [41].

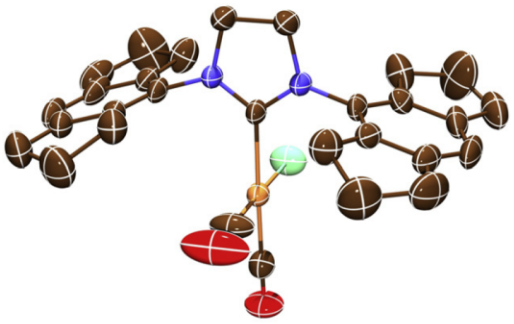


Fig. 1. Crystal structure of Ir complex **6** (ORTEP 50% probability). Important bond length [pm] and angles [o]. Ir–CO 184.7(10), 188.9(7), Ir–Cl 232.9(2), Ir–C(NHC) 208.1(6), Cl–Ir–CO 178.4(3), C(NHC)–Ir–CO 175.8(3).

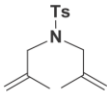
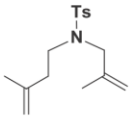
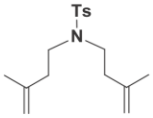
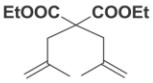
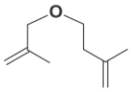
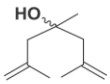
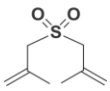
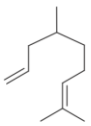
2.5. Kinetics of precatalyst activation

The UV/Vis spectrum of complex **9** is characterized by a strong absorbance at 378 nm. Upon precatalyst activation with an olefin this band looses intensity and is thus an excellent handle to determine the rate of the initiation reaction k_{obs} according to recently reported procedures [21,42]. Based on an exponential fit of the absorbance-time curve the k_{obs} for precatalyst activation of the Grubbs–Hoveyda type complex **9** with butyl vinyl ether was determined (Fig. 2). The $k_{obs} = 0.043\ s^{-1}$ is between that of the standard SIMes Grubbs–Hoveyda complex ($k_{obs} = 0.031\ s^{-1}$) and of the SIMes Grela complex ($k_{obs} = 0.060\ s^{-1}$) under the same reaction conditions [21].

3. Summary and conclusions

The synthesis of a new hexahydro-*s*-indacene based NHC ligand **3** and of several new transition metal complexes with Ag, Ir and Ru with this NHC ligand are reported. The stereoelectronic properties of the new ligand **3** were determined and found to be close to those of the SIMes ligand. The catalytic behavior of Grubbs II (complex **7**), Grubbs–Hoveyda (complex **9**) and bisNHC (complexes **10**, **11**) type complexes with the new NHC ligand in ring closing metathesis reactions of sterically demanding substrates was investigated. The catalytic activity of the bisNHC complexes **10** and **11** is very good and comparable to the best complexes with the standard SIMes ligand. However, a significant increase in the activity of the respective complexes **7** and **9** with

Table 1
Screening of the catalysts in ring closing metathesis of sterically demanding olefins.

Entry	Substrate	Complex	[Ru] mol%	T (°C)	Convers. %
1		**7**	0.5	80	83
		9	0.5	80	81
		10	0.2	100	85
		11	0.2	100	73
2		**7**	0.5	80	99
		7	0.2	80	77
		9	0.5	80	99
		9	0.2	80	84
		10	0.5	100	99
		10	0.2	100	97
		11	0.5	100	93
3		**7**	0.5	80	89
		9	0.5	80	98
		10	0.5	100	91
		11	0.5	100	94
4		**7**	0.5	80	32
		9	0.5	80	35
		10	0.5	100	65
		11	0.5	100	44
5		**7**	0.5	80	68
		9	0.5	80	71
		10	0.5	100	80
		10	0.2	100	37
		11	0.5	100	52
6		**7**	0.5	80	81
		9	0.5	80	99
		9	0.2	80	53
		10	0.5	100	95
		10	0.2	100	54
		11	0.5	100	95
7		**7**	0.5	80	72
		9	0.5	80	87
		10	0.5	100	99
		10	0.2	100	60
		11	0.2	100	51
8		**7**	0.2	80	97
		7	0.025	80	68
		9	0.2	80	99
		9	0.025	80	72
		10	0.025	100	99
		10	0.01	100	67
		11	0.2	100	99
		11	0.025	100	75

Conditions: solvent toluene, [substrate] = 0.02 mol/L, reaction time = 24 h; Ru complexes were added as a stock solution (3 mmol/L in toluene). Conversions determined by GC.

respect to their relatives with SIMes ligand was observed. In conclusion, the concept of restricted mobility in the ortho, ortho-alkyl substituents does not result in more active catalysts, but it leads to a stabilization of the less stable complexes of the Grubbs II and the Grubbs–Hoveyda type. For many RCM substrates a leveling of the catalytic activities of **7**, **9**, **10** and **11** is observed, which seems to be due to the improved design of the hexahydro-*s*-indacene based NHC ligand **3**.

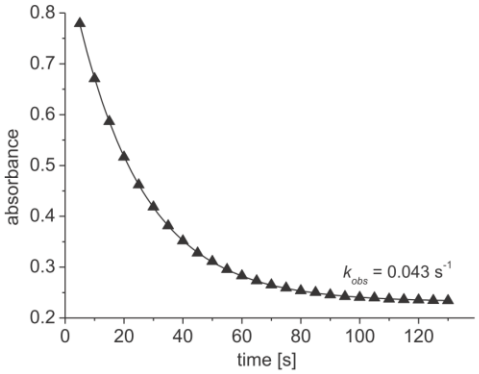


Fig. 2. Absorbance-time curves for Grubbs–Hoveyda complex **9** (initial [Ru] = 10^{-4} M) (at 378 nm) at butyl vinyl ether concentration of 0.8 mol/L and T = 30 °C in toluene solvent.

4. Experimental section

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification unless otherwise noted. Solvents were dried by passing over Al_2O_3 and/or by storing over molecular sieves. Tetrahydrofuran was dried under sodium and distilled under argon atmosphere. Dichloromethane and pyridine were degassed by freeze-pump-thaw cycles technique. Column chromatography was performed using silica 60 (0.063–0.20 mesh ASTM). TLC was performed by using Fluka silica 60 F254 (0.2 mm) on alumina plates. NMR spectra were recorded on Bruker DRX500 and Bruker DRX300. The chemical shifts (δ) are given in ppm relative to TMS, coupling constants are (J) in Hz. MS spectra were recorded on a Finnigan MAT95 spectrometer. GC experiments were run on a Clarus 500 GC with autosampler and FID detector. Column: Varian CP-Sil 8 CB (l = 15 m, diam. = 0.25 mm, dF = 1.0 μm), N_2 (flow: 17 cm/s; split 1:50); Injector-temperature: 200 °C, detector temperature: 270 °C. Temperature program: isotherm 60 °C for 5 min, heating to 300 °C with 25 °C/min, isotherm for 5 min. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as counter electrode. The pseudo reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of octamethylferrocene (ΔE = −0.010 mV (CH_2Cl_2)). NBu_4PF_6 (0.1 mol/L) was used as supporting electrolyte. UV/Vis spectra were recorded on a Zeiss Specord S10 spectrometer. 3-Chloro-1-indan-5-yl-propan-1-one, isomeric nitro-substituted 3,5,6,7-tetrahydro-*2H*-*s*-indacen-1-ones and 1,2,3,5,6,7-hexahydro-*s*-indacen-4-yl-amine were prepared according to a modified reported procedure [14]. The data for the crystal structure was solved, refined and processed [43] using the SHELX program package [44]. The data were deposited with the Cambridge Structural Database under CCDC 865892; a summary of the crystal data can be found in the supporting information.

4.1. 1,2,3,5,6,7-Hexahydro-s-indacen-4-yl-amine

The mixture of nitro compounds (15.6 g, 71.7 mmol) was dissolved in methanol (160 mL) with 20% palladium hydroxide on carbon (50% water wet. 3.89 g) and methanesulfonic acid (5.12 mL, 78.9 mmol). The mixture was hydrogenated at 1 atm for 24 h. The

catalyst was removed by filtration and washed with methanol. The methanol filtrate was diluted with water (780 mL) and the pH was adjusted to pH 10.6 with 2 N NaOH. The resulting slurry was filtered and the crude solid was recrystallized from methanol/water (9:1) with heating to give colorless crystals of the amine (8.8 g, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.64 (s, 1H, ArH), 3.40 (br.s, 2H, NH_2), 2.88 (t, J = 7.3 Hz, 4H, CH_2), 2.70 (t, J = 7.3 Hz, 4H, CH_2), 2.19–2.06 (m, 4H, CH_2). Spectrum identical to that reported literature [14].

4.1.1. (N,N',E,N,N',E)-N,N'-(ethane-1,2-diylidene)bis(1,2,3,5,6,7-hexahydro-s-indacen-4-yl-amine)

1,2,3,5,6,7-Hexahydro-*s*-indacen-4-yl-amine (8.2 g, 47 mmol) was dissolved in ethanol (90 mL), treated with aqueous glyoxal solution (2.69 mL, 23.5 mmol) and three drops of formic acid. The reaction mixture was stirred over night. The yellow solid was filtered off, washed with cold methanol and dried in vacuo (6.6 g, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (s, 2H, NCH), 7.00 (s, 2H, H_{Ar}), 3.06–2.73 (m, 16H, CH_2), 2.09 (qi, J = 7.3 Hz, 8H, $CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.43, 144.42, 143.86, 132.93, 118.47, 33.10, 30.75, 26.13. HRMS (EI): *m/z* calcd for $C_{26}H_{28}N_2$ 368.2253, found 368.2253.

4.1.2. N,N'-Bis(1,2,3,5,6,7-hexahydro-s-indacen-4-yl)ethane-1,2-diaminium chloride

(*N,N',E,N,N',E*)-*N,N'*-(Ethane-1,2-diylidene)bis(1,2,3,5,6,7-hexahydro-*s*-indacen-4-yl-amine) (3.23 g, 8.8 mmol) was placed in a Schlenk flask and dissolved in anhydrous tetrahydrofuran (80 mL) under an atmosphere of nitrogen. The solution was cooled to 0 °C and $LiAlH_4$ powder (0.70 g, 18.4 mmol) was added in small portions. The reaction mixture was stirred 30 min at 0 °C and then over night at room temperature. The reaction mixture was poured carefully into an excess of an ice/conc. HCl mixture. The off-white precipitate was collected by filtration, washed several times with cold water and dried in vacuo (3.5 g, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (s, 2H, H_{Ar}), 3.55 (s, 4H, NCH_2CH_2N), 2.92 (t, J = 7.2 Hz, 8H, CH_2), 2.79 (t, J = 7.3 Hz, 8H, CH_2), 2.11–1.87 (m, 8H, $CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.80 (arom. C–H), 132.94, 131.63, 118.01, 45.03 (N–C–C–N), 32.23, 30.18, 25.32. HRMS (EI): *m/z* calcd for $C_{26}H_{32}N_2$ (M-2HCl) 372.2566, found 372.2531.

4.1.3. 1,3-Bis(1,2,3,5,6,7-hexahydro-s-indacen-4-yl)-4,5-dihydro-1H-imidazol-3-ium chloride

N,N'-Bis-(1,2,3,5,6,7-hexahydro-s-indacen-4-yl)ethane-1,2-diaminium chloride (2.97 g, 8.0 mmol) was suspended in $HC(OEt_3)_3$ (42 mL), 3 drops of formic acid were added and the reaction mixture was stirred at 120 °C over night. The off-white precipitate was filtered off, washed several times with diethyl ether and dried in vacuo (1.9 g, 69% yield). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.30 (s, 1H, NCHN), 7.23 (s, 2H, H_{Ar}), 4.49 (s, 4H, NCH_2CH_2N), 2.99 (t, J = 7.1 Hz, 8H, CH_2), 2.89 (t, J = 7.2 Hz, 8H, CH_2), 2.09 (qv, J = 7.2 Hz, 8H, $CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.70 (N–C–N), 144.84, 137.53, 128.21, 121.42, 50.88 (N–C–C–N), 32.36, 29.62, 25.32. HRMS (EI): *m/z* calcd for $C_{27}H_{31}N_2$ 383.2488, found 383.2475.

4.2. Synthesis of [(3)$_2$Ag][AgCl$_2$]

The Schlenk flask containing bis(1,2,3,5,6,7-hexahydro-*s*-indacen-4-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (0.12 g, 0.28 mmol) and Ag_2O (0.032 g, 0.14 mmol) was evacuated and back-filled with nitrogen three times. Methylene chloride (6 mL) was added via syringe. The reaction mixture was stirred over night at 40 °C, cooled to room temperature and filtered through celite. The filtrate was concentrated to one-half its volume and pentane (20 mL) was added. The precipitate was filtered off and washed several times with pentane to afford the product as off-white microcrystalline solid (0.117 g, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (s, 4H, H_{Ar}), 4.03 (s, 8H, NCH_2CH_2N), 3.08–2.82 (m, 24H, CH_2), 2.85–2.68 (m, 8H, CH_2), 2.25–2.01 (m, 16H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ 205.14 (d, $J_{C\text{-}Ag}$ = 241.5 Hz), 205.00 (d, $J_{C\text{-}Ag}$ = 241.4 Hz), 145.60, 145.30, 138.98, 132.85, 121.30 (arom. C–H), 51.08 (N–C–C–N), 33.03, 30.67, 25.79. MS (ESI) calcd for $C_{54}H_{62}AgN_4$ (M+2H–$AgCl_2$) 873.4, found 873.5.

4.3. Synthesis of [(3)IrCl(cod)] **5**

The Schlenk flask containing [(3)$_2$Ag][$AgCl_2$] **4** (0.040 g, 0.038 mmol) and [Ir(μ-Cl)(cod)]$_2$ (0.026 g, 0.038 mmol) was evacuated and back-filled with nitrogen three times. Methylene chloride (2 mL) was added via syringe and the reaction mixture was stirred at 45 °C for 1 h. After this, the solvent was removed in vacuo and residue purified by column chromatography (silica, CH_2Cl_2) affording the desired complex as yellow powder (0.047 g, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (s, 2H, H_{Ar}), 4.17–4.08 (m, 2H), 4.00–3.83 (m, 5H), 3.06–2.73 (m, 13H), 2.70–2.57 (m, 2H), 2.28–2.07 (m, 6H), 2.08–1.95 (m, 2H), 1.68–1.46 (m, 4H), 1.38–1.29 (m, 2H), 1.30–1.19 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 206.45 (C–Ir), 145.22, 143.65, 142.07, 138.88, 134.08, 120.52 (arom. C–H), 83.83, 51.93 (N–C–C–N), 51.60 (N–C–C–N), 33.52, 33.33, 33.11, 31.89, 31.35, 29.87, 28.93, 26.48, 26.34. HRMS (EI): *m/z* calcd for $C_{35}H_{42}ClIrN_2$ 718.2662, found 718.2595.

4.4. Synthesis of [(3)IrCl(CO)$_2$] **6**

[(3)IrCl(cod)] **5** (0.020 g, 0.028 mmol) was dissolved in dichloromethane (5 mL) and CO was bubbled through this solution for 10 min. The solvent was evaporated in vacuo and the residue washed with pentane to obtain the product as yellow powder (0.018 g, 98% yield).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (s, 2H, H_{Ar}), 4.05 (s, 4H, NCH_2CH_2N), 3.32 (br. s, 4H, CH_2), 3.01–2.83 (m, 8H, CH_2), 2.79–2.67 (m, 4H, CH_2), 2.24–2.03 (m, 8H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.19 (C–Ir), 180.94 (CO), 168.80 (CO), 144.82, 140.05 (br), 132.38, 121.40 (arom. C–H), 51.69 (N–C–C–N), 33.17, 31.12, 26.08. HRMS (EI): *m/z* calcd for $C_{29}H_{30}ClN_2O_2Ir$ 666.1621, found 666.1577.

4.5. Synthesis of [(3)RuCl$_2$(PCy$_3$)(3-phenyl-indenylid-1-ene)] **7**

A Schlenk flask was charged with 1,3-bis(1,2,3,5,6,7-hexahydro-*s*-indacen-4-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (0.420 g, 1.00 mmol) and KO*t*Bu (0.124 g, 1.1 mmol) and THF (42 mL) added under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature for 1 h. After this time, the solvent was removed in vacuo and the residue was dissolved in toluene and transferred by cannula to another Schlenk flask containing [$RuCl_2(PCy_3)_2$(3-phenyl-indenylid-1-ene)] (0.513 g, 0.55 mmol). The reaction mixture was stirred for 4 h at 70 °C. The volatiles were removed in vacuo, and the remaining solid was purified by silica chromatography (cyclohexane/diethyl ether, 10:1 v/v) affording the desired ruthenium complex as a red solid (0.387 g, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (dd, J = 7.3, 0.8 Hz, 1H, H^{ind}), 7.67 (dd, J = 7.1, 1.5 Hz, 2H. H^{ind}), 7.47 (t, J = 7.4 Hz, 1H, H^{ind}), 7.36 (t, J = 7.6 Hz, 2H, H^{ind}), 7.23–7.14 (m, 3H, H^{ind}), 7.11 (dd, J = 6.9, 1.1 Hz, 1H, H^{ind}), 7.04 (s, 1H, arom. H^{NHC}), 6.66 (s, 1H, arom. H^{NHC}), 4.33–4.19 (m, 1H, H^{NHC}), 4.06–3.95 (m, 3H, H^{NHC} + 2 $H^{NCH_2CH_2N}$), 3.95–3.87 (m, 1H, $H^{NCH_2CH_2N}$), 3.79 (q, J = 9.7 Hz, 1H, $H^{NCH_2CH_2N}$), 3.05–2.85 (m, 5H, H^{NHC}), 2.82–2.73 (m, 1H, H^{NHC}), 2.71–2.62 (m, 1H, H^{NHC}), 2.62–2.45 (m, 2H, H^{NHC}), 2.41–2.28 (m, 2H, H^{NHC}), 2.28–2.16 (m, 2H, H^{NHC}), 2.16–2.02 (m, 6H), 1.83–1.71 (m, 1H, H^{NHC}), 1.72–1.35 (m, 16H), 1.36–1.19 (m, 4H), 1.16–0.91 (m, 14H), 0.89 (t, J = 7.1 Hz, 1H). ^{13}C

NMR (126 MHz, $CDCl_3$): δ 292.48, 215.87, 215.51, 145.10, 144.73, 144.70, 144.59, 144.49, 143.25, 143.05, 141.31, 141.04, 140.18, 138.23, 136.90, 135.96, 134.12, 132.27, 129.55, 128.67, 128.48, 127.36, 127.31, 126.76, 122.14, 121.19, 116.09, 52.28, 51.94, 33.39, 33.30, 33.20, 33.07, 32.35, 32.11, 31.83, 30.09, 29.78, 29.35, 28.96, 27.84, 27.77, 26.29, 25.95, 25.91, 25.27, 23.92, 22.33, 14.05. ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.46. MS (ESI) calcd for $C_{60}H_{74}ClN_2PRu$ (M+2H−Cl) 991.4, found 991.4; calcd for $C_{60}H_{73}N_2PRu$ (M − 2Cl) 954.3, found 954.4. Anal. calcd for $C_{60}H_{72}Cl_2N_2PRu$, C, 70.29; H, 7.18; N, 2.73, found C, 70.26, H, 7.25; N, 2.83.

4.6. Synthesis of [(3)$RuCl_2$(py)(3-phenyl-indenylid-1-ene)] **8**

[(**3**)$RuCl_2(PCy_3)$(3-phenyl-indenylid-1-ene)] (0.513 g, 0.500 mmol) was weighed into a Schlenk flask and pyridine (3.5 mL) added by syringe under an atmosphere of nitrogen. The resulting solution was stirred at room temperature for 1 h. Next, pentane (20 mL) was added and the reaction was left stirring for 15 min. The resulting suspension was then cooled to −40 °C. The precipitate was filtered off and washed with cold pentane to give the desired complex as an orange solid (0.321 g, 78% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, J = 7.2 Hz, 1H, H^{ind}), 7.92 (d, J = 3.8 Hz, 2H, o-H^{Py}), 7.71 (d, J = 7.2 Hz, 2H, H^{ind}), 7.53 (t, J = 6.8 Hz, 1H, p-H^{Py}), 7.46 (t, J = 6.9 Hz, 1H, H^{ind}), 7.38 (t, J = 7.1 Hz, 2H, H^{ind}), 7.27–7.16 (m, 2H, H^{ind}), 7.10 (d, J = 6.8 Hz, 1H, H^{ind}), 7.07–6.95 (m, 3H, m-H^{Py} + H^{ind}), 6.57 (s, 1H, arom. H^{NHC}), 6.33 (s, 1H, arom. H^{NHC}), 4.39–4.28 (m, 1H), 4.28–4.20 (m, 1H, $H^{NCH_2CH_2N}$), 4.20–4.05 (m, 2H, $H^{NCH_2CH_2N}$), 3.97–3.79 (m, 2H, H^{NHC} + H^{NCHCHN}), 3.41–3.27 (m, 1H, H^{NHC}), 3.11–2.90 (m, 5H, H^{NHC}), 2.91–2.81 (m, 1H, H^{NHC}), 2.81–2.69 (m, 2H, H^{NHC}), 2.63–2.52 (m, 1H, H^{NHC}), 2.51–2.40 (m, 1H, H^{NHC}), 2.36–2.24 (m, 3H, H^{NHC}), 2.23–2.08 (m, 3H, H^{NHC}), 2.03–1.86 (m, 2H, H^{NHC}), 1.70–1.55 (m, 2H, H^{NHC}), 1.35–1.20 (m, 1H, H^{NHC}). ^{13}C NMR (126 MHz, $CDCl_3$): δ 302.02, 212.42, 151.86, 145.10, 144.75, 144.30, 144.00, 142.89, 141.65, 140.97, 140.90, 140.63, 140.01, 139.16, 136.61, 133.31, 131.95, 129.13, 129.08, 128.54, 127.79, 127.60, 126.81, 123.88, 121.96, 121.88, 116.52, 52.36, 50.74, 33.19, 32.78, 32.34, 32.22, 30.46, 29.86, 26.22, 25.93, 25.49, 24.88. The attempted determination of mass spectra with complex **8** was unsuccessful, due to instability of this complex.

4.7. Synthesis of Hoveyda-Grubbs type complex **9**

[(**3**)(py)$RuCl_2$(3-phenyl-indenylid-1-ene)] **8** (0.10 g, 0.12 mmol) was dissolved in toluene (5 mL) and 1-ethenyl-2-(1-methylethoxy) benzene (24 μL, 0.16 mmol) was added under an atmosphere of argon. The reaction mixture was stirred for 4 h at 60 °C and then cooled to room temperature. The solvent was removed in vacuo and the remaining solid purified by column chromatography (silica, CH_2Cl_2), affording the product as a green powder (0.058 g, 68% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 16.58 (s, 1H, Ru=C-H), 7.54–7.44 (m, 1H), 7.29 (s, 2H, arom. H^{NHC}), 6.96 (dd, J = 7.5, 1.5 Hz, 1H), 6.91–6.77 (m, 2H), 4.91 (sep, 1H, $CH(CH_3)_2$), 4.18 (s, 4H, NCH_2CH_2N), 3.54 (br. s, 4H, CH_2), 2.97 (t, J = 7.3 Hz, 8H, CH_2), 2.89–2.71 (m, 4H, CH_2), 2.30–1.97 (m, 8H, CH_2), 1.32 (d, J = 6.1 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 296.98, 210.61, 152.35, 145.50, 144.95, 142.67, 129.46, 122.41, 121.22, 112.97, 74.95, 51.84, 33.18, 31.20, 25.86, 21.36. HRMS (EI): m/z calcd for $C_{37}H_{42}Cl_2N_2ORu$ 702.1709, found 702.1718.

4.8. Synthesis of [(3)(NHC_{ewg})$RuCl_2$(3-phenyl-indenylid-1-ene)] **10** and **11**

To [(**3**)(py)$RuCl_2$(3-phenyl-indenylid-1-ene)] (0.10 g, 0.12 mmol) and the appropriate silver complex **4** (0.17 mmol) were added 10 mL of toluene under an atmosphere of argon. The reaction mixture was heated to 60 °C. After 30 min, the solvent was evaporated in vacuo and the crude product purified by column chromatography (silica, cyclohexane/ethyl acetate, 2:1, v/v). The obtained product was washed with cold pentane (−10 °C) to provide complexes **10** and **11** as microcrystalline red solids.

4.9. [(3)(NHC-Et_2)$RuCl_2$(3-phenyl-indenylid-1-ene)] **10**

0.101 g, 89% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.71 (dd, J = 7.7, 1.0 Hz, 1H, H^{ind}), 7.63 (dd, J = 8.2, 1.1 Hz, 2H, H^{ind}), 7.44–7.40 (m, 1H, H^{ind}), 7.31 (t, J = 7.6 Hz, 2H, H^{ind}), 7.21–7.15 (m, 2H, H^{ind}), 7.10–7.06 (m, 2H, H^{ind}), 6.81 (s, 1H, arom. H^{NHC}), 6.53 (s, arom. 1H, H^{NHC}), 4.24–4.15 (m, 1H, H^{NHC}), 4.03–3.89 (m, 3H, $H^{NCH_2CH_2N}$), 3.74–3.64 (m, 3H, $H^{NCH_2CH_2N}$ + HNHC + $CH_aH_bCH_3$), 3.47 (dq, J = 13.7, 6.8 Hz, 1H, $CH_aH_bCH_3$), 3.34–3.22 (m, 1H, H^{NHC}), 3.16–3.01 (m, 2H, CH_2CH_3), 2.97–2.83 (m, 4H, H^{NHC}), 2.83–2.70 (m, 2H, H^{NHC}), 2.70–2.53 (m, 2H, H^{NHC}), 2.52–2.40 (m, 1H, H^{NHC}), 2.37–2.25 (m, 1H, H^{NHC}), 2.24–2.08 (m, 4H, H^{NHC}), 2.08–1.95 (m, 2H, H^{NHC}), 1.84–1.65 (m, 2H, H^{NHC}), 1.59–1.48 (m, 2H, H^{NHC}), 1.30–1.20 (m, 1H, H^{NHC}), 1.16 (t, J = 6.9 Hz, 3H, $CH_aH_bCH_3$), 0.42 (t, J = 7.1 Hz, 3H, CH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 295.04, 218.15, 183.55, 145.35, 145.04, 144.84, 144.49, 143.68, 143.48, 140.97, 140.84, 140.29, 137.24, 136.90, 134.46, 132.82, 129.09, 128.94, 128.84, 128.35, 127.71, 127.09, 121.92, 121.86, 117.55, 116.47, 116.20, 52.30, 51.75, 44.72, 43.46, 33.35, 32.77, 32.39, 32.15, 32.00, 30.48, 29.82, 26.01, 25.85, 25.61, 24.56, 17.03, 15.11, 1.16. MS (ESI) calcd for $C_{49}H_{50}Cl_3N_4Ru$ (M − Cl) 901.2, found 901.4.

4.10. [(3)(NHC-iPr_2)$RuCl_2$(3-phenyl-indenylid-1-ene)] **11**

0.102 g, 87% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.69 (d, J = 7.5 Hz, 1H, H^{ind}), 7.62 (d, J = 7.2 Hz, 2H, H^{ind}), 7.42 (t, J = 7.3 Hz, 1H, H^{ind}), 7.31 (t, J = 7.6 Hz, 2H, H^{ind}), 7.21–7.15 (m, 2H, H^{ind}), 7.13–7.06 (m, 2H, H^{ind}), 6.82 (s, 1H, arom. H^{NHC}), 6.58 (s, 1H, arom. H^{NHC}), 4.91 (sep, 1H, $CH_a(CH_3)_b(CH_3)_c$), 4.36–4.24 (m, 1H), 3.92–3.81 (m, 3H, $H^{NCH_2CH_2N}$), 3.80–3.70 (m, 1H, H^{NHC}), 3.69–3.57 (m, 2H, $CH_d(CH_3)_e(CH_3)_f$ + $H^{NCH_2CH_2N}$), 3.31–3.18 (m, 1H), 2.91 (dt, J = 14.2, 7.4 Hz, 4H), 2.83–2.68 (m, 2H), 2.69–2.54 (m, 2H), 2.52–2.39 (m, 1H), 2.38–2.25 (m, 1H), 2.24–1.96 (m, 6H), 1.83–1.73 (m, 1H), 1.73–1.62 (m, 1H), 1.58–1.46 (m, 2H), 1.43 (d, J = 6.7 Hz, 3H, $CH_a(CH_3)_b(CH_3)_c$), 1.26–1.18 (m, 1H), 1.00 (d, J = 6.9 Hz, 3H, $CH_a(CH_3)_b(CH_3)_c$), 0.87 (d, J = 6.9 Hz, 3H, $CH_d(CH_3)_e(CH_3)_f$), 0.26 (d, J = 7.0 Hz, 3H, $CH_d(CH_3)_e(CH_3)_f$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 296.86, 217.12, 184.57, 165.50, 145.71, 145.01, 144.93, 144.61, 143.63, 143.55, 142.97, 141.23, 140.41, 137.52, 137.16, 136.80, 134.68, 133.55, 129.18, 129.05, 128.85, 128.64, 128.49, 127.77, 127.16, 122.09, 121.93, 117.03, 116.39, 115.64, 56.67, 53.38, 52.24, 52.05, 33.42, 33.35, 32.69, 32.41, 32.05, 31.80, 30.40, 29.86, 25.82, 25.61, 25.51, 24.31, 22.28, 21.82, 21.73, 19.30, 1.28. MS (ESI) calcd for $C_{51}H_{54}Cl_2N_4Ru$ (M − 2Cl) 894.3, found 894.4. Anal. Calcd for $C_{51}H_{54}Cl_4N_4Ru$ C, 63.42; H, 5.64; N, 5.80, found C, 63.31; H, 5.83; N, 5.44.

4.11. General protocol for RCM catalyst screening

Reactions were carried out in sealed 25 mL Schlenk tubes under an atmosphere of argon at 80 °C or 100 °C. To a 25 mL Schlenk tube was added substrate (0.04–0.08 mmol) dissolved in dry toluene under an atmosphere of argon. This solution was heated to the designated temperature and the appropriate amount of the pre-catalyst from a stock solution ([Ru] = 3.0 mmol/L) in toluene was added (substrate concentration in solution is 0.02 mol/L). For the determination of substrate conversion, samples were taken after the specified times under a stream of argon. The samples were injected into GC vials containing 150 μL of a 25% (v/v) ethyl vinyl

ether solution in toluene and analyzed by GC. A final sample was taken after 24 h.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2012.03.015.

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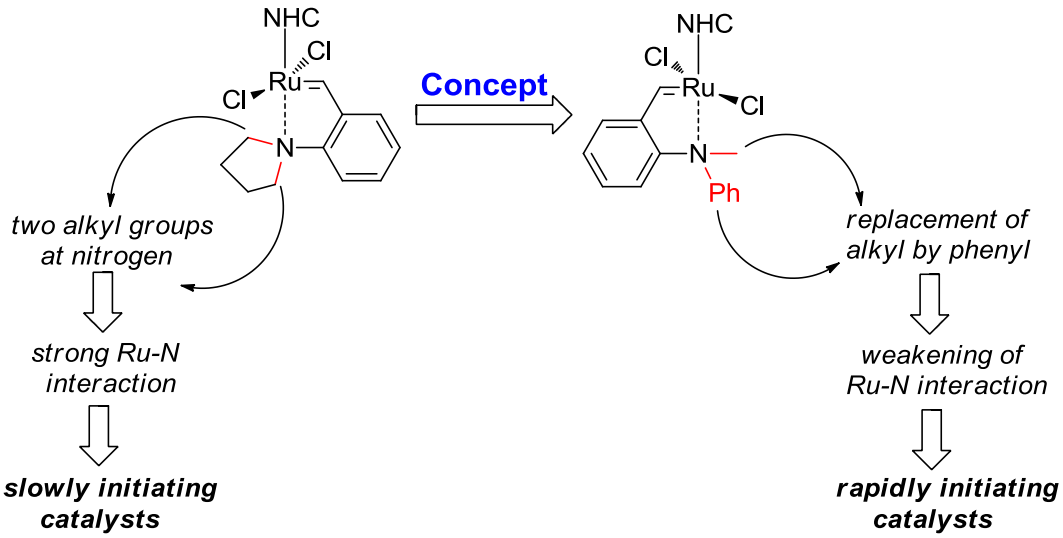
3.2. Fast Olefin Metathesis at Low Catalyst Loading

The content of this chapter has already been published:

Lars H. Peeck, Roman D. Savka, Herbert Plenio, *"Fast Olefin Metathesis at Low Catalyst Loading"*, *Chemistry – A European Journal* **2012**, *18*, 12845–12853.

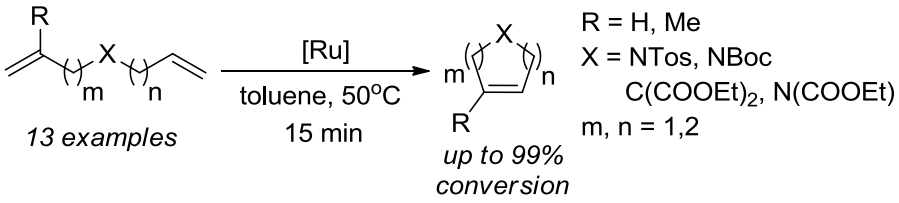
In this chapter, the synthesis and catalytic activity of a rapidly initiating *N*-Hoveyda-type complexes are discussed. Ruthenium complexes with $(alkyl)_2N$-derived styrene ligand are known to be latent due to the strong Ru-N interaction and slow initiation. The replacement of a single alkyl substituent by a phenyl group leads to a pronounced weakening of the Ru-N interaction, and consequently to a significant increase in the initiation rate of the catalysts (Scheme 57).



Scheme 57. The basic concept of the project.

From the synthetic point of view, rapidly initiating Hoveyda-type complexes are hardly available. The procedures reported in the literature usually afford such complexes in low yield. In this chapter, an improved scalable procedure that enables the preparation of such fast catalysts in high yields is proposed.

The presented complexes are characterized by fast catalyst activation, which translates into their high efficiency in RCM reactions of sterically unhindered olefins. The catalytic activity of the synthesized complexes is tested in RCM reactions of 13 different diolefinic substrates (Scheme 58).



Scheme 58. Tested ring-closing metathesis reactions.

Catalyst loadings of 15-150 ppm are sufficient for the conversion of a wide range of substrates into the respective cyclic RCM products. Based on the results of the screenings *N*-Hoveyda-type complexes reported here outperform other known catalysts in RCM reactions.

My estimated contribution to this work is 50%.

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Fast Olefin Metathesis at Low Catalyst Loading

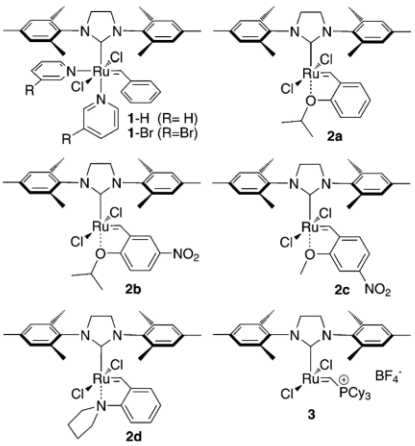
Lars H. Peeck, Roman D. Savka, and Herbert Plenio*[a]

Abstract: Reactions of the Grubbs 3rd generation complexes [$RuCl_2$(NHC)(Ind)(Py)] (N-heterocyclic carbene (NHC) = 1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene (SIMes), 1,3-bis(2,6-diisopropylphenylimidazolin)-2-ylidene (SIPr), or 1,3-bis(2,6-diisopropylphenylimidazol)-2-ylidene (IPr); Ind = 3-phenylindenylid-1-ene, Py = pyridine) with 2-ethenyl-*N*-alkylaniline (alkyl = Me, Et) result in the formation of the new *N*-Grubbs–Hoveyda-type complexes **5** (NHC = SIMes, alkyl = Me), **6** (SIMes, Et), **7** (IPr, Me), **8** (SIPr, Me), and **9** (SIPr, Et) with N-chelating benzylidene ligands in yields of 50–75%. Compared to their respective, conventional, *O*-Grubbs–Hoveyda complexes, the new complexes are characterized by fast catalyst activation, which translates into fast and efficient ring-closing metathesis (RCM) reactivity. Catalyst loadings of 15–150 ppm (0.0015–0.015 mol%) are sufficient for the conversion of a wide range of diolefinic substrates into the respective RCM products after 15 min at 50°C in toluene; compounds **8** and **9** are the most catalytically active complexes. The use of complex **8** in RCM reactions enables the formation of N-protected 2,5-dihydropyrroles with turnover numbers (TONs) of up to 58000 and turnover frequencies (TOFs) of up to 232000 h^{-1}; the use of the N-protected 1,2,3,6-tetrahydropyridines proceeds with TONs of up to 37000 and TOFs of up to 147000 h^{-1}; and the use of the N-protected 2,3,6,7-tetrahydroazepines proceeds with TONs of up to 19000 and TOFs of up to 76000 h^{-1}, with yields for these reactions ranging from 83–92%.

Keywords: alkenes · metathesis · precatalyst activation · ring-closing reactions · ruthenium

Introduction

The rate at which precatalysts[1] for olefin metathesis reactions are activated[2] has a strong influence on the rate of substrate conversion.[3] Slowly initiating precatalysts (latent complexes)[4] lead to slow reactions or require high temperatures, and appear to be useful for ring-closing metathesis (RCM) reactions of sterically hindered substrates.[5] More rapidly initiating complexes provide good substrate conversion within a short time or at low temperatures.[6] Extremely fast precatalysts, such as the Grubbs 3rd generation (**1**-Br in Scheme 1)[7] or Piers-type (**3** in Scheme 1) complexes, are also known.[8] These complexes are indispensable tools for the synthesis of low-dispersity polymers by ring-opening metathesis polymerization (ROMP), which requires a faster rate of initiation than the rate of chain growth.[9] On the other hand, the Grubbs 3rd generation complexes have rarely been employed in reactions other than ROMP[10], probably due to their low stability under the reaction conditions.[11] Complexes that are closely related to **1** (for example, those containing an indenylidene instead of a benzylidene ligand) also display a modest performance in RCM and enyne metathesis.[12] From a synthetic point of view, there should be an optimum rate of precatalyst activation



Scheme 1. Grubbs 3rd generation complexes (**1**), *O*-Grubbs–Hoveyda complexes (**2a**, **2b**, **2c**), *N*-Grubbs–Hoveyda complex (**2d**), and Piers complex with a SIMes-type NHC ligand (**3**).

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that lies somewhere between the extremes of latent and extremely fast precatalysts. Slowly initiating precatalysts can lead to impractical, slow, initiation-rate-limited metathesis conversions, whereas very quickly initiating complexes tend to be labile and may also generate the active species too rapidly. Compared with **1**, the initiation rates of the stable Grubbs–Hoveyda-type complexes[13] are much slower, but can be somewhat improved by replacing a hydrogen (**2a** in Scheme 1) with a 5-NO_2 (complex **2b**)[6] or a 3-phenyl group.[13a,14] Even-faster initiating complexes are obtained when the isopropoxy group is replaced by a smaller methoxy group (**2c** in Scheme 1).[2e] Closely related complexes that have an amine ligand (**2d** in Scheme 1) instead of the ether oxygen donor were first reported by Slugovc et al.[15] and the Grela group.[3b,16] These precatalysts are characterized by very slowly initiating reactions and are employed as latent catalysts for ROMP reactions.[4b,15,17]

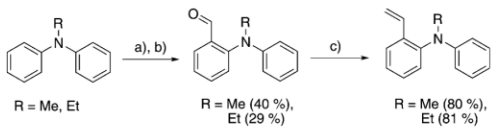
A structural peculiarity of these complexes (and of related complexes that contain thioether[18] and sulfoxide donor atoms) is the formation of *cis*-dichloro complexes during synthesis under kinetic control;[3b] however, the *cis* arrangement appears to be thermodynamically preferred by the thioether complexes.[19] The geometric *cis* or *trans* preferences appear to be based on the stronger σ-donor capacity of sulfur and nitrogen compared with that of an ether oxygen,[19a] as well as on solvent polarity and steric effects.[20]

Relative to $PhNMe_2$, the basicity of the nitrogen atom is reduced by more than four orders of magnitude when a single methyl substituent is replaced by a phenyl group in Ph_2NMe.[21] We anticipated that such a marked change at the donor atom in the benzylidene amine of a Grubbs–Hoveyda-type complex should lead to a pronounced weakening of the Ru–N interaction, and consequently to a significant increase in the initiation rate of the precatalyst. This may be useful for sterically unhindered olefin metathesis reactions, and we were hoping that more-rapidly initiating precatalysts should lead to faster olefin metathesis reactions, as long as the respective precatalysts are sufficiently stable. This does not appear to be the case for complex **1**, thus it was our aim to synthesize ruthenium complexes with a Ph_2N(alkyl)-derived styrene ligand and to study their behavior in olefin metathesis reactions.

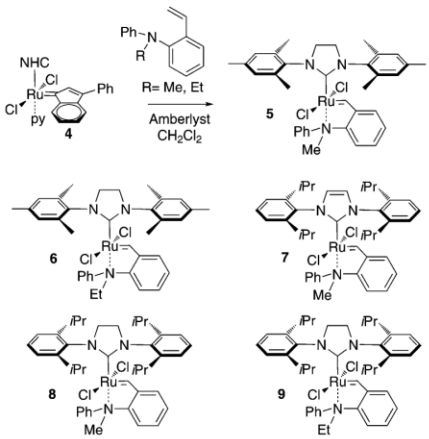
Results and Discussion

Synthesis of ligands and ruthenium complexes: The *ortho*-vinyl-substituted alkyldiphenylamines were prepared by directed *ortho*-metalation[22] of $RNPh_2$ (R = Me, Et) with *n*BuLi. The reaction of the respective lithium salts with dimethylformamide gave the respective aldehydes, which were then converted into the 2-vinyl-substituted amines by employing the Wittig reagent (Scheme 2).

The vinylated alkyldiarylamines were treated with the respective Grubbs 3rd generation complexes [$RuCl_2$(NHC)(Ind)(Py)] (N-heterocyclic carbene (NHC) = 1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene (SIMes), 1,3-bis(2,6-diisopropylphenylimidazol)-2-ylidene (IPr), 1,3-bis(2,6-diisopropylphenylimidazolin)-2-ylidene (SIPr); Ind = 3-phenylindenylid-1-ene, Py = pyridine). Initially, the formation of the desired complexes was not observed and only the stilbenes resulting from the cross-metathesis reaction of the styrenes were isolated. The desired *N*-Grubbs–Hoveyda-type complexes **5**, **6**, **7**, **8**, and **9** (Scheme 3) were formed in modest yields of 10–36% when using substoichiometric amounts of the styrenes at elevated temperatures.



Scheme 2. a) *n*BuLi, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), cyclohexane, 60 °C; b) DMF, THF, −78 °C to RT, then NH_4Cl, H_2O; c) $MePPh_3I$, KO*t*Bu, THF, −10 °C to RT.



Scheme 3. Synthesis of ruthenium complexes **5** (yield 30%, with acidic resin 70%), **6** (yield 10%, with acid resin 50%), **7** (yield 34%, with acidic resin 68%), **8** (yield 36%, with acidic resin 75%), and **9** (yield 27%, with acidic resin 60%).

The reason for the modest yields could be the reluctant substitution of pyridine by the weak nitrogen donor (alkyldiarylamine). To facilitate the formation of the desired complexes, we decided to efficiently remove the pyridine by in situ protonation with a protic ion-exchange resin (Amberlyst). Due to the pronounced difference in their Brønsted basicities, the protonation of pyridine is preferred to the protonation of the respective alkyldiarylamines. A related approach was first used by Verpoort et al. in the synthesis of various *O*-Grubbs–Hoveyda type complexes in excellent yields, by removing PCy_3 with a protic resin as the respective phosphonium salt.[23] When the synthesis of the new ruthenium complexes was carried out in the presence of Amberlyst resin in CH_2Cl_2 at 40 °C by using stoichiometric

amounts of the alkyldiarylamines, the desired complexes were obtained in much better yields (see Scheme 3). All complexes (except for **6**) are stable in the solid state and solutions of each could be exposed to an ambient atmosphere for 24 h without appreciable decomposition.

By employing the optimized reaction conditions, the synthesis of complexes **5**, **6**, **7**, **8**, and **9** was straightforward. However, in the absence of a protic resin when using toluene as the solvent, the reaction of 2-ethenyl-*N*-methyl-*N*-phenylaniline with [$RuCl_2$(SIMes)(Ind)(Py)] can result in the formation of two isomeric species. When the reaction was carried out at a low reaction temperature (below 75 °C in toluene) a mixture of two isomers was formed. The characteristic resonance of the benzylidene proton of the *trans* complex is located at $\delta = 17.00$ ppm (see below for the X-ray crystal structure of complex **5**). The other isomer could not be isolated from *trans*-**5**, but is characterized by a ^{1}H NMR resonance at $\delta = 17.23$ ppm. Based on literature precedent and the ^{1}H NMR shift of the benzylidene proton, this is most likely to be the *cis*-isomer of **5**.[19b] This *cis*/*trans* ratio critically depends on the reaction temperature and at lower temperatures the *cis* isomer is primarily formed, for example, at 65 °C the *cis*/*trans* ratio is 1.7, and at 60 °C the *cis*/*trans* ratio is 4.0.

Preliminary tests revealed that the catalytic activity of pure *trans*-**5** is excellent (Figure 1), and at a 0.1 mol% loading of complex *trans*-**5**, the room temperature reaction of diethyl diallyl malonate (DEDAM) leads to the quantitative formation of the desired cyclic product within about 10 min. A mixture of isomers, when primarily composed of *cis*-**5**, is less active. We therefore concluded that either *cis*-**5** is less active, or the time needed for *cis*-**5** to convert into *trans*-**5** is limiting the catalytic turnover. Based on literature precedent, the latter explanation is more likely.[24] Consequently, in the later catalytic and initiation studies pure *trans*-**5** is employed (which will be denoted as **5**).

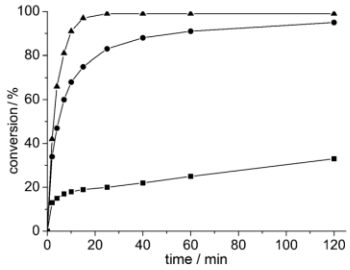


Figure 1. Conversion–time curves for the room temperature (293 K) RCM reaction of DEDAM (0.1 mol L^{-1}) with [Ru] (0.1 mol%) in toluene by using *trans*-**5** and mixtures of *trans*-**5** and *cis*-**5**. ■: *trans*/*cis* = 0.25; ●: *trans*/*cis* = 0.59; ▲: *trans*-**5**.

Redox potentials: We have previously shown that the redox potentials of ruthenium in Grubbs-type complexes are an excellent indicator to evaluate the donor capacity of the ligands coordinated to this metal.[2e,5b,25] Consequently, the redox potentials in CH_2Cl_2 of the complexes reported herein were determined (**5**: $E = 0.806$ V, $E_a - E_c = 74$ mV; **7**: $E = 0.757$ V, $E_a - E_c = 76$ mV; **8**: $E = 0.827$ V, $E_a - E_c = 79$ mV; and **9**: $E = 0.813$ V, $E_a - E_c = 90$ mV). The redox potentials for the complexes with a saturated NHC backbone (**5**, **8**, and **9**) are comparable to and only slightly less anodic than those of the respective *O*-Grubbs–Hoveyda complexes (**2a**: $E = 0.84$ V).[2e] This underlines the modest donor capacity of the diarylamino nitrogen atom. The redox potentials for the three complexes with saturated NHC ligands (**5**, **8**, and **9**) are fairly similar, whereas complex **7**, with an unsaturated IPr backbone, can be oxidized more easily. This is unexpected, as normally the donor abilities of saturated and unsaturated NHC ligands are fairly similar.[26]

X-ray crystal structure of complex 5: With a view to the rapid initiation reactions of complex **5**, the most interesting structural parameter appeared to be the Ru–N separation. Single crystals of **5** were obtained by evaporating a solution in cyclohexane in an open beaker, which also provided convincing evidence for the excellent stability of **5** (see Figure 2). However, at 234.7(4) pm the Ru–N separation is unspectacular. In closely related complexes in which the phenyl group in **5** is replaced by an alkyl group, the Ru–N separation averages 232 pm (based on three complexes with 232.1, 232.0, 231.9 pm).[3b] Such small structural changes can hardly account for the massive difference in the initiation rates of the diarylalkylamino complex **5** compared with the aryldialkylamino complexes. On the other hand, these separations are much longer than the Ru–O bond length in complex **2a** (226.1 pm).[13b] The nitrogen coordinated to the ruthenium atom is nearly tetrahedral (the sum of the three C-N-C angles is 334°, which is not much smaller than the 328.4° for a tetrahedron).

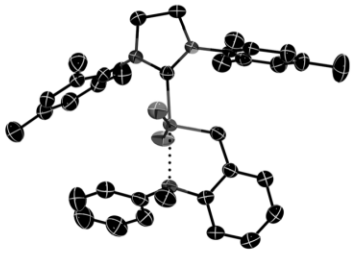


Figure 2. ORTEP diagram for the crystal structure of complex **5**. Important bond lengths [pm] and angles [°]: Ru–N 234.7(4), Ru–CHAr 182.6(5), Ru–C(NHC) 201.4(5), Ru–Cl 234.0(1), 235.0(1); Cl-Ru-Cl 162.58(6), N-Ru-C(NHC) 175.53(15).

Evaluation of the catalytic activity of complexes 2a, 2b, 4a, 5, 6, 7, 8, and 9: To gauge the performance of the new complexes **5**, **7**, **8**, and **9**, and the benchmark precatalysts **2a** and **2b**, were tested in the RCM reaction of diallyl-*N*-tosylamide

at 0 °C in toluene (Figures 3 and 4). Excellent substrate conversion is observed for all of the new complexes, which catalyze RCM reactions faster than the benchmark catalysts; between 75 (complex **5**) and 96 % (complex **9**) of the substrate is converted to product within 40 min and at 1000 ppm [Ru]. In the series of reactions involving SIMes-based complexes **2a** and **2b**, faster initiation rates appears to translate into faster catalysis at low temperatures. However, the nature of the active species is also important: the SIPr based complexes **8** and **9** show higher activities than the SIMes complexes. The ability of complex **5** to rapidly catalyze RCM reactions is also apparent for DEDAM reactions (Figure 5). With the use of this precatalyst, full substrate conversion is achieved within about 10 min, whereas precatalysts **2a** and **2b** need a much longer reaction time to achieve full conversion.

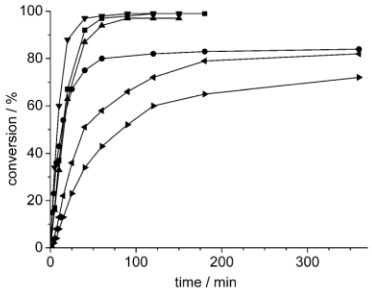


Figure 3. RCM of diallyl-*N*-tosylamide (0.1 mol L^{-1}) at 0 °C in toluene with the *trans* complexes **2b**, **5**, and **7**–**9** (0.1 mol %; 1000 ppm). ■: Complex 8; ●: complex **5**; ▲: complex **7**; ▼: Complex **9**; ◀: complex **3**; ▶: complex **2**.

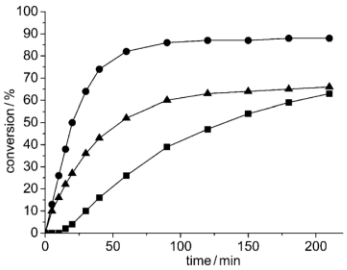


Figure 4. RCM of diallyl-*N*-tosylamide (0.1 mol L^{-1}) at 0 °C in toluene with the *trans* complexes **2a**, **5**, and **9** (0.025 mol %; 250 ppm). ■: Complex **2a**; ●: complex **9**; ▲: complex **5**.

These initial experiments demonstrate that one advantage of the newly synthesized complexes is the short time required for the RCM transformations. Furthermore, we note a strong influence of temperature on the catalyst performance. To obtain a yield of about 84 % in the RCM of diallyl-*N*-tosylamide at 0 °C requires 1000 ppm of complex **5** and a reaction time of 120 min. At 50 °C, the same yield is obtained within 15 min by using only 25 ppm of complex **5** (Table 1). This pronounced difference in RCM reactivity indicates that the rate of the catalytic transformation increases more rapidly with temperature than does the decomposition rate of the active species.

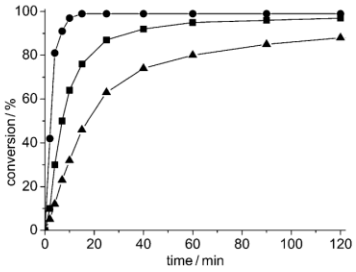
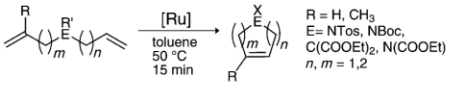


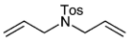
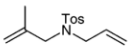
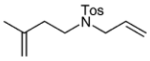
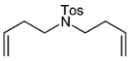
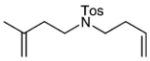
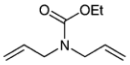
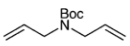
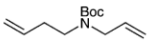
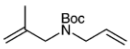
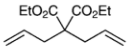
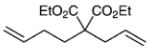
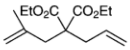
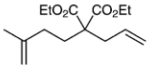
Figure 5. RCM reaction of DEDAM (0.1 mol L^{-1}) at 20 °C in toluene with the complexes **2a**, **2b**, and **5** (1000 ppm). ■: Complex **2b**; ●: complex **5**; ▲: complex **2a**.

To optimize the performance of the different ruthenium complexes, the temperature for the RCM reaction of diallyl-*N*-tosylamide and complex **5** in toluene was systematically varied between 0 °C and 60 °C. An increase in the reaction temperature to 50 °C led to an increase in the catalytic efficiency. Next, complexes **5**, **6**, **7**, **8**, and **9** were systematically tested in a number of ring-closing metathesis reactions at this temperature. The results of the extensive screening studies are summarized in Table 1. Complex **7** is less efficient than the other complexes and was therefore only studied in a few transformations. For many reactions, the benchmark complexes **2a** and **2b** and the Grubbs 3rd generation type complex **4a** were employed under the same reaction conditions. Complex **4a** was tested in four RCM reactions (Table 1, entries 1, 7, 9, and 13) and turned out to be less active than the newly synthesized complexes. The data in Table 1 also show that precatalysts **2a** and **2b** perform quite well under our optimized reaction conditions. For several substrates (Table 1, entries 1, 3, 4, 6, and 7), the catalytic performance is close to that of complex **5**, and for other substrates (Table 1, entries 2, 5, and 8–12), complex **5** is clearly more effective than both **2a** and **2b**. For most metathesis transformations (Table 1, entries 1, 3–5, 7–10, and 14), the SIPr complexes **8** and **9** are even more efficient than complex **5**.

Apart from the very modest catalyst loading, the short reactions times required for this transformation are notable; all of the reactions that involve the new complexes studied herein are complete in less than 15 min. Dorta et al.[27] also demonstrated very fast RCM reactions at low catalyst loadings by performing the reactions in the neat substrate, or in highly concentrated solutions, and by employing a Grubbs–Hoveyda-type complex with a specialized NHC ligand. The latter approach is extremely useful but may be limited to liquid or highly soluble substrates, the RCM reactions of which lead to five or six-membered rings. The much lower effective molarities with other substrates that result in the

Table 1. Screening of different catalysts for the ring closing metathesis reactions.



	Substrate[a]	[Ru][b] [ppm]	Conversion[c] [%] 2a	2b	4a	5	6	7	8	9
1		50	–	–	–	98 (94)	–	–	–	–
		25	70	61	60	84	71	55	98	97
		15	–	–	–	–	–	–	87	76
2		150	–	–	–	99 (95)	–	–	–	–
		50	39	83	–	93	45	40	81	72
3		200	–	–	–	96 (94)	–	–	–	–
		150	76	80	–	90	–	–	96	98
4		200	–	–	–	93 (89)	–	–	–	–
		100	67	76	–	82	–	71	93	–
		50	–	–	–	–	–	–	83	82
5		100	–	–	–	95 (91)	–	–	–	–
		50	28	55	–	91	–	–	92	95
6		100	–	–	–	97 (93)	–	–	–	–
		50	75	51	–	89	44	45	77	81
7		50	–	–	–	98 (95)	–	–	–	–
		25	77	68	37	87	66	65	91	93
		15	–	–	–	–	–	–	78	83
8		100	–	–	–	99(93)	–	–	–	–
		50	60	67	–	79	–	–	99	–
		25	–	–	–	–	–	–	92	87
9		300	53	61	34	85	–	–	98	–
		150	–	–	–	–	–	51	85	86
10		200	29	65	–	84	67	72	97	91
		100	–	–	–	58	–	–	68	74
11		200	84	82	–	–	–	–	86	–
		100	62	65	–	–	–	–	79	77
12		100	–	–	–	95 (91)	–	–	–	–
		50	36	15	–	58	–	–	54	–
13		100	–	–	–	98	–	–	–	–
		50	26	35	8	59	–	–	–	–

[a] [substrate] = 0.5 M. [b] 100 ppm [Ru] corresponds to 0.01 mol% catalyst loading. [c] Conversions determined by GC, averaged over two runs; yields of isolated products are reported in parentheses.

formation of seven-membered rings could easily lead to the undesired formation of acyclic diene metathesis (ADMET) polymers.[28] Other examples of olefin metathesis reactions with a low catalyst-loading that involve the use of robotic equipment in a glove box have been reported by Nolan, Slugovc et al.[29] and Grubbs et al.[30] Pederson, Grubbs et al. have recently evaluated several ruthenium complexes in the synthesis of five-, six-, and seven-membered N-heterocycles. In their work, 500 ppm of the Ru complex was used for the full conversion of substrates (Table 1, entries 7–9) during a reaction time of 8 h;[31] for entry 7, this leads to a TON of 2000 and a TOF of 310 h^{-1}. We are reporting here that the synthesis of the respective heterocycles in less than 15 min requires only 15–150 ppm of the newly synthesized *N*-Grubbs–Hoveyda complexes.

In conclusion, the formation of N-protected 2,5-dihydropyrroles by using complex **8** (Table 1, entry 1) proceeds with a TON of 58000 (yield 87%) and a TOF of 232000 h^{-1}. The formation of N-protected 1,2,3,6-tetrahydropyridines by using complex **8** (Table 1, entry 8) proceeds with a TON of 37000 (92% yield) and a TOF of 147000 h^{-1}. The respective N-protected 2,3,6,7-tetrahydroazepines (Table 1, entry 5) require a catalyst loading of 50 ppm (0.005 mol%), resulting in a TON of 19000 (95% yield) and a TOF of 76000 h^{-1}. This is a very significant improvement with respect to the literature data.[29] For the various DEDAM type substrates (Table 1, entries 10–12), the catalyst loadings and yields reported herein are comparable to those reported by Nolan, Slugovc et al., although the time required for such transformations by using complex **5** is much shorter.

The reactions described herein were carried out by using standard Schlenk techniques. However, the use of purified toluene and of purified reactants is very important in order to minimize the decomposition of the sensitive, catalytically active species. To learn more about the nature of potential impurities, we tested the effect of water on the substrate conversion. A small amount of water was deliberately added to the toluene solvent prior to the RCM conversion to establish a water content of about 100 ppm.[32] The RCM of the diallyl-*N*-tosylamide was performed in this "wet" toluene with a 25 ppm loading of **5**, and the product was obtained in 71% yield (instead of 84%, see Table 1, entry 1). We therefore concluded that the water concentration only has a weak influence on the RCM reaction. It is likely that the limiting factor for RCM reactions is the presence of other trace impurities in the solvent (sulfur-containing compounds, such as methyl thiophene, are potential candidates[33]) or in the RCM substrates.

Precatalyst activation: The new ruthenium complexes display a strong absorbance at around 370 nm, which probably results from a ligand–metal charge transfer (LMCT),[34] and provides an excellent UV/Vis spectroscopic handle for kinetic studies. The reactions of the ruthenium complexes with butyl vinyl ether (BuVE) could serve as a reasonable model for the initiation reactions with RCM substrates. After the addition of BuVE to a solution of complex **5** in toluene, the time dependent UV/Vis spectra at 30 °C were recorded and the respective absorbance–time curves at around 370 nm were fitted with an exponential function according to the method reported previously.[2e,5a] Complex **5** is characterized by very fast precatalyst activation (k_{obs} = 0.2 s^{-1} at [BuVE] = 0.1 mol L^{-1}). This step is about 30 times faster than the reaction that uses reference complex **2a** (k_{obs} = 0.006 s^{-1}), and is about 15 times faster than the reaction that uses **2b** (k_{obs} = 0.013 s^{-1}).[35] Complex **6** is even faster; it is in fact too fast to obtain accurate data by using conventional cuvette-based UV/Vis spectroscopy at 30 °C. Even at [BuVE] = 0.1 mol L^{-1} the initiation reaction is finished in less than 10 s. This fast reaction time may explain the faster RCM reactions observed with **5** compared with complexes **2a** and **2b**. This also confirms that the diarylami-

no-based ligands in the *N*-Grubbs–Hoveyda complexes presented herein lead to a pronounced acceleration of precatalyst activation.

The rates of the BuVE (0.1 mol L^{-1}) reactions when using the more bulky complexes **8** and **9** were also determined under the same reaction conditions. Based on the evaluation of the 370 nm absorbance peak, the SIPr ruthenium complexes show a much slower precatalyst activation; the initiation rates for complexes **7**, **8**, and **9** are k_{obs} = 0.0080, 0.0025, and 0.0072 s^{-1}, respectively. The slower initiation rate for the SIPr-based complexes compared with the SIMes complex **5** was unexpected. Therefore the SIPr-based *O*-Grubbs–Hoveyda complex **10** (same as complex **2a**, but with an SIPr ligand instead of the SIMes ligand in complex **2a**) was also investigated.[36] Activation of this complex is even slower, and at [BuVE] = 0.1 mol L^{-1} a k_{obs} = 0.00044 s^{-1} was determined; complex **10** initiates the reaction almost six times more slowly than complex **8**, and almost sixteen times more slowly than complex **9**. The slow rates determined for the SIPr-based complexes (compared with SIMes complexes) appear to be in contrast to the fast and efficient olefin metathesis reactivity observed for complex **10**. The rapid substrate conversion of complex **10** was also confirmed for several ADMET polymerization reactions of α,ω-dienes, as the initial polymerization rate was found to be higher than that of complex **2a**.[36] Considering the very fast rate of catalyst initiation for the SIMes complexes **5** and **6** reported herein, it is also possible to consider a second initiation step that becomes rate limiting when the first initiation step is very fast.[37]

Conclusion

The reactions of the Grubbs 3rd generation type complexes [$RuCl_2$(NHC)(Ind)(py)] (NHC = SIMes, SIPr, or IPr) with 2-ethenyl-*N*-alkyl-*N*-phenylaniline (alkyl = Me, Et) result in the efficient formation of new *N*-Grubbs–Hoveyda-type complexes **5**–**9** in yields of 50–75%. These complexes combine a fast precatalyst initiation and high stability with excellent activity in various ring-closing metathesis reactions. Low precatalyst loadings of 15–300 ppm are sufficient for the conversion of a range of RCM substrates into the respective cyclic olefins in reaction times of less than 15 min. For most reactions, the SIPr complexes **8** and **9** are the most efficient precatalysts, especially for the synthesis of N-heterocycles: 15–25 ppm (0.0015–0.0025 mol%) of complex **8** are sufficient for the formation of N-protected 2,5-dihydropyrroles (TOF of up to 232000 h^{-1}) and N-protected 1,2,3,6-tetrahydropyridines (TOF of up to 147000 h^{-1}) in yields of around 90%; the synthesis of the respective N-protected 2,3,6,7-tetrahydroazepines with **8** requires a catalyst loading of 50 ppm (0.005 mol%, 95% yield, TOF of up to 76000 h^{-1}).

The initiation rates of the SIPr based complexes **8** and **9** are much slower than those of the related SIMes-based complexes **5** and **6**.

The new alkylidene ligand 2-(*N,N*-methyphenyl)aminobenzylidene (L) will be useful in a large number of [$RuCl_2$(NHC)(L)] complexes with different NHC ligands and should lead to a new family of rapidly initiating, but stable, ruthenium precatalysts. As already demonstrated by numerous research groups for the *O*-Grubbs–Hoveyda complex **2a**, additional modifications at the N substituents of the new *N*-Grubbs–Hoveyda complexes can enable fine-tuning of the catalytic activity to obtain tailored catalysts for specific olefin metathesis transformations.

Experimental Section

General experimental: All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. All reactions involving ruthenium complexes were performed under an atmosphere of argon. CH_2Cl_2 (99.5%) and pentane (99%) were obtained from Grüssing GmbH, toluene from Sigma–Aldrich (lab. reagent grade, 99.3%, Lot.: STBB5057). These solvents were dried and degassed by using a column purification system described by Grubbs et al.[38] In this system, the solvents are sparged and pressurized with argon (0.1–1 bar), successive passed through one column filled with activated alumina and then a second column, either filled with a supported copper catalyst (toluene, pentane) or, again, activated alumina (CH_2Cl_2). Toluene was additionally dried over CaH_2 and distilled onto molecular sieves (4 Å). RCM substrates were purified by column chromatography using distilled mixtures of pentane and diethyl ether. Diethyl diallyl malonate was purified by distillation. Cyclohexane, *n*-hexane, pyridine, and dimethylformamide were heated at reflux over calcium hydride and distilled under an argon atmosphere. Tetrahydrofuran was dried under sodium and distilled under an argon atmosphere. All solvents were stored over molecular sieves (4 Å). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX300 spectrometer. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (^1H, ^{13}C NMR = 0.0 ppm) or the residual peak of $CHCl_3$ (^1H NMR = 7.26, ^{13}C NMR = 77.16 ppm).[39] Abbreviations for NMR data: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad signal, Ar = aromatic protons. UV/Vis spectrophotometric data were acquired on an Analytik Jena SPECORD S 600 UV/Vis spectrophotometer. Thin layer chromatography (TLC) was performed by using silica 60 F 254 (0.2 mm) on aluminum plates. Preparative chromatography was done on Merck silica 60 (0.063–0.02 mesh), but complexes **6**–**9** were purified by column chromatography on granular silica (60 Å pore size, 40–63 μm, 230–400 mesh) from Roth AG. GC experiments were run on a Clarus 500 GC with an autosampler and FID detector [column: Varian CP-Sil 8 CB (l = 15 m, d_i = 0.25 mm, d_F = 1.0 Lm), N_2 (flow: 17 cm s^{-1}; split 1:50); injector temperature: 270 °C, detector temperature: 350 °C]. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as a counter electrode. The pseudoreference electrode was a Ag wire. Potentials were calibrated internally against the formal potential of ferrocene ($E_{1/2}$ = +0.46 V (CH_2Cl_2)). NBu_4PF_6 (0.1 mol L^{-1}) was used as a supporting electrolyte.

Preparation of catalyst stock solution: c = 0.75 mmol L^{-1}: The ruthenium complex (4.0×10^{-6} mol) was weighed into a Schlenk tube (10 mL). The tube was evacuated, backfilled with nitrogen, and then dried toluene (5.34 mL) was added under a stream of argon. The Schlenk tube was kept in an ultrasonic bath for 1 min for complete dissolution of the precatalyst.

Catalyst Screening: All reactions were carried out in sealed Schlenk tubes (10 mL) under an atmosphere of argon at 0, 20, or 50 °C. In a Schlenk tube (10 mL), the substrate (0.2–0.6 mmol) was dissolved in dry toluene under an atmosphere of argon. This solution was either cooled to 0 °C or heated to 20 or 50 °C, and the catalyst (0.0015–0.1 mol%; 15–

1000 ppm) from a stock solution in toluene (0.75 mmol L^{-1}) was added (for screenings carried out at 0 °C, the stock solution was precooled to 0 °C). The substrate concentration was defined as $C(S)=n(S)/(V(S)+V(\text{toluene})+V(\text{stock sol.}))$. For the determination of substrate conversion, samples (50 μL, substrate conc. 0.1 M or 10 μL, substrate conc. 0.5 M) were taken after the specified times under a stream of argon and injected into GC vials containing a 25% (v/v) ethyl vinyl ether solution in toluene (250 μL). The conversions were determined by GC. The products were isolated by column chromatography (silica) using mixtures of pentane/diethyl ether as the eluent.

Synthesis of 2-[methyl(phenyl)amino]benzaldehyde and 2-[ethyl(phenyl)amino]benzaldehyde: {2-[Methyl(phenyl)amino]phenyl}lithium and {2-[ethyl(phenyl)amino]phenyl}lithium were generated in situ according to a modified procedure reported for [2-(NMe_2)phenyl]lithium.[40] Ph_2NMe or Ph_2NEt (5.46 mmol), TMEDA (122 μL, 0.82 mmol), and anhydrous cyclohexane (2.8 mL) were added to a dry Schlenk tube under a nitrogen atmosphere to reach a 2 M concentration of the respective anilines. Next, a solution of *n*BuLi in *n*-hexane (2.5 M, 2.18 mL, 5.46 mmol) was added by syringe to the vigorously stirred mixture at RT. The solution was warmed to 60 °C and stirring was continued for 90 min (for *N*-methyl-*N*-phenylaniline) or for 5 h (for *N*-ethyl-*N*-phenylaniline). Then the mixture was allowed to cool to room temperature and the volatile compounds were removed in vacuo. Dry tetrahydrofuran (5 mL) was added under an atmosphere of nitrogen and the resulting orange solution was cooled to −78 °C. Next, dry dimethylformamide (844 μL, 10.9 mmol) was added dropwise with vigorous stirring. The now colorless solution was allowed to warm to room temperature, stirred for 60 min, and then poured into a half-saturated solution of ammonium chloride (200 mL). The product was extracted with diethyl ether (3×100 mL). The organic phases were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed in vacuo and the residue was purified by column chromatography (cyclohexane/diethyl ether, 10:1 v/v).

2-[Methyl(phenyl)amino]benzaldehyde: 2-[Methyl(phenyl)amino]benzaldehyde[41] was obtained as a yellow oil (461 mg, 40% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=10.16$ (d, $J=0.8$ Hz, 1H; C*H*O), 7.96 (dd, $J=7.8$, 1.7 Hz, 1H), 7.65 (ddd, $J=8.0$, 7.3, 1.7 Hz, 1H), 7.36 (tt, $J=7.5$, 1.0 Hz, 1H), 7.30–7.18 (m, 3H), 6.84 (tt, $J=7.5$, 1.0 Hz; 1H), 6.78–6.72 (m, 2H), 3.38 ppm (s, 3H; NCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=191.35$, 152.10, 150.19, 135.89, 132.89, 129.37, 129.05, 127.82, 126.11, 119.27, 115.30, 41.63, 29.82 ppm.

2-[Ethyl(phenyl)amino]benzaldehyde: 2-[Ethyl(phenyl)amino]benzaldehyde was obtained as a yellow oil that crystallized upon cooling (357 mg, 29% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=10.14$ (d, $J=0.8$ Hz, 1H; C*H*O), 7.96 (dd, $J=7.8$, 1.7 Hz, 1H), 7.65 (ddd, $J=8.0$, 7.4, 1.7 Hz, 1H), 7.36 (tt, $J=7.5$, 1.0 Hz, 1H), 7.27 (dd, $J=8.1$, 0.9 Hz, 1H), 7.21–7.16 (m, 2H), 6.79 (tt, $J=7.4$, 1.0 Hz, 1H), 6.71–6.67 (m, 2H), 3.81 (q, $J=7.1$ Hz, 2H; NCH_2CH$_3$), 1.26 ppm (t, $J=7.1$ Hz, 3H; NCH$_2$CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=191.63$, 150.57, 149.39, 135.85, 133.74, 129.47, 129.26, 129.04, 126.34, 118.84, 115.28, 47.93, 12.83 ppm; HRMS (EI): *m/z* calcd for $C_{15}H_{15}NO$: 225.1154 $[M]^+$; found: 225.1144.

Synthesis of 2-ethenyl-*N*-methyl-*N*-phenylaniline and 2-ethenyl-*N*-ethyl-*N*-phenylaniline: A Schlenk flask containing methyltriphenylphosphonium iodide (525 mg, 1.30 mmol) was evacuated and back-filled with argon three times. Tetrahydrofuran (10 mL) was added by syringe and the formed suspension was cooled to −10 °C. KO*t*Bu (140 mg, 1.25 mmol) was added in portions to the stirred mixture under a stream of argon, and stirring was continued at −10 °C for 20 min. Next, a solution of 2-[methyl(phenyl)amino]benzaldehyde (230 mg, 1.09 mmol) or 2-[ethyl(phenyl)amino]benzaldehyde (246 mg, 1.09 mmol) in tetrahydrofuran (2 mL) was added. The mixture was allowed to warm to room temperature, stirred overnight, and was poured into water (200 mL). The product was extracted with diethyl ether (3×100 mL). The organic phases were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed in vacuo and the residue was purified by column chromatography (cyclohexane/0.5% NEt_3).

2-Ethenyl-N-methyl-N-phenylaniline: 2-Ethenyl-*N*-methyl-*N*-phenylaniline was obtained as a colorless liquid (184 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.67$ (dd, $J=7.7$, 1.7 Hz, 1H), 7.31 (td, $J=7.5$, 1.8 Hz, 1H), 7.29–7.25 (m, 1H), 7.21–7.13 (m, 3H), 6.79 (dd, $J=17.7$, 11.0 Hz, 1H), 6.73 (tt, $J=7.3$, 1.0 Hz, 1H), 6.62–6.58 (m, 2H), 5.74 (dd, $J=17.7$, 1.3 Hz, 1H), 5.22 (dd, $J=11.0$, 1.3 Hz, 1H), 3.21 ppm (s, 3H; NCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=149.57$, 146.41, 136.35, 133.23, 129.48, 129.05, 128.64, 126.66, 126.54, 117.38, 115.26, 113.58, 39.82 ppm; HRMS (EI): *m/z* calcd for $C_{15}H_{15}N$: 209.1205 $[M]^+$; found: 209.1177.

2-Ethenyl-N-ethyl-N-phenylaniline: 2-Ethenyl-*N*-ethyl-*N*-phenylaniline was obtained as a colorless liquid (197 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.71$–7.65 (m, 1H), 7.36–7.24 (m, 2H), 7.19–7.11 (m, 3H), 6.78 (dd, $J=17.7$, 11.0 Hz, 1H), 6.68 (tt, $J=7.4$, 1.0 Hz, 1H), 6.58–6.52 (m, 2H), 5.72 (dd, $J=17.7$, 1.3 Hz, 1H), 5.20 (dd, $J=11.0$, 1.3 Hz, 1H), 3.64 (q, $J=7.1$ Hz, 2H; NCH_2CH$_3$), 1.20 ppm (t, $J=7.1$ Hz, 3H; NCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=148.69$, 144.42, 137.08, 133.40, 130.29, 129.36, 129.15, 126.83, 126.56, 116.90, 115.20, 113.32, 46.19, 12.60 ppm; HRMS (EI): *m/z* calcd for $C_{16}H_{17}N$: 223.1361 $[M]^+$; found: 223.1341.

Synthesis of [$RuCl_2$(IPr)(PCy_3)(Ind)]: [$RuCl_2$(IPr)(PCy_3)(Ind)] is a known compound,[42] but was prepared according to a modified procedure: A Schlenk flask containing 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium chloride (485 mg, 1.14 mmol) was evacuated and back-filled with argon three times. *n*-Hexane (40 mL) and a solution of sodium tamylate in tetrahydrofuran (2.5 M, 456 μL, 1.14 mmol) were added to the flask under an atmosphere of argon. The mixture was allowed to stir at RT for 90 min, then [$RuCl_2(PCy_3)_2$(Ind)] (523 mg, 0.566 mmol) was added as a solid. The mixture was stirred overnight at 50 °C. Next, the volatiles were removed in vacuo and the residue was passed through a short column of silica (cyclohexane/diethyl ether, 10:1 v/v). After evaporation of the volatile compounds, *n*-hexane (5 mL) was added to the remaining solid, and the mixture was sonicated and kept in the fridge at −35 °C for 2 h. After filtration, washing with cold methanol (5 mL), and drying in vacuo, the product was obtained as a bright-red powder (362 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.85$ (d, $J=6.9$ Hz, 1H), 7.67–7.59 (m, 2H), 7.56–7.38 (m, 4H), 7.34 (t, $J=7.5$ Hz, 2H), 7.25–7.05 (m, 3H), 7.01 (s, 1H), 6.98–6.87 (m, 3H), 6.73 (d, $J=7.3$ Hz, 1H), 6.62 (d, $J=7.6$ Hz, 1H), 3.77 (sep, $J=6.6$ Hz, 1H; CH(CH$_3$)$_2$), 3.47 (sep, $J=6.6$ Hz, 1H; CH(CH$_3$)$_2$), 3.06 (sep, $J=6.6$ Hz, 1H; CH(CH$_3$)$_2$), 2.78 (sep, $J=6.6$ Hz, 1H; CH(CH$_3$)$_2$), 2.06 (q, $J=11.1$ Hz, 3H), 1.78–1.64 (m, 3H), 1.63–0.89 (m, 45H), 0.75 (d, $J=6.7$ Hz, 3H; CH(CH_3)$_2$), 0.61 ppm (d, $J=6.6$ Hz, 3H; CH(CH_3)$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta=24.46$ ppm.

[$RuCl_2$(IPr)(py)(Ind)]: A Schlenk tube containing [$RuCl_2$(IPr)(PCy_3)(Ind)] (352 mg, 0.34 mmol) was evacuated and back-filled with argon three times. Pyridine (2 mL) was added by syringe under an atmosphere of argon. The resulting solution was stirred at room temperature for 1 h and concentrated to half of its volume. Next, pentane (20 mL) was added and the reaction was left stirring for 15 min. The resulting suspension was then cooled to −40 °C. The precipitate was filtered off, washed with cold pentane, and dried in vacuo to give the desired complex as a brownish solid (251 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.98$ (d, $J=7.0$ Hz, 1H), 7.91 (dd, $J=6.4$, 1.3 Hz, 2H), 7.65 (dd, $J=8.2$, 1.0 Hz, 2H), 7.61–7.52 (m, 2H), 7.52–7.38 (m, 3H), 7.34 (t, $J=7.7$ Hz, 2H), 7.31 (br, 1H), 7.20 (td, $J=7.5$, 1.0 Hz, 1H), 7.08 (d, $J=7.1$ Hz, 1H), 6.99–6.83 (m, 5H), 6.74 (d, $J=6.5$ Hz, 1H), 6.67 (t, $J=7.5$ Hz, 1H), 5.95 (s, 1H; NCH), 4.24–4.10 (m, 1H; CH(CH$_3$)$_2$), 3.11–2.92 (m, 2H; CH(CH$_3$)$_2$), 2.62–2.46 (m, 1H; CH(CH$_3$)$_2$), 1.53 (br, 6H; CH(CH_3)$_2$), 1.45 (d, $J=4.8$ Hz, 3H; CH(CH_3)$_2$), 1.24–1.13 (m, 9H; CH(CH_3)$_2$), 0.68 (d, $J=5.4$ Hz, 3H; CH(CH_3)$_2$), 0.50 ppm (d, $J=5.0$ Hz, 3H; CH(CH_3)$_2$); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=300.85$, 181.29, 152.91, 149.17, 148.99, 146.83, 146.69, 141.82, 141.29, 140.58, 139.61, 136.92, 136.54, 135.91, 135.05, 131.12, 130.57, 129.39, 129.27, 128.60, 127.92, 127.36, 126.64, 126.24, 125.79, 123.97, 123.71, 123.41, 117.18, 30.14, 29.28, 28.53, 27.59, 27.27, 27.16, 26.59, 25.78, 23.50, 23.02, 22.57, 20.84 ppm; MS (ESI): *m/z* calcd for $C_{42}H_{46}N_2Ru$: 679.5 $[M-H-2Cl-Py]^+$; found: 679.3.

General procedure for the synthesis of complexes 5–9: A flame-dried Schlenk tube containing [$RuCl_2$(NHC)(Ind)(py)] (0.13 mmol) was evacuated and back-filled with argon three times. Methylene chloride (2 mL), 2-ethenyl-*N*-methylaniline (32.0 μL, 0.16 mmol) or 2-ethenyl-*N*-ethylaniline (36.2 μL, 0.16 mmol) and Amberlyst resin (dry form, 137 mg,

4.70 mmol $H^+ g^{-1}$) were added under an atmosphere of argon. The mixture was stirred at 40 °C for 30 min (for NHC = SIMes) or 60 min (for NHC = IPr, SIPr) and then filtered to separate the resin. The filtrate was evaporated in vacuo and the remaining solid was purified as follows:

Complex 5: The solid was dissolved in a minimal amount of methylene chloride, then pentane (15 mL) was added under vigorous stirring and the resulting suspension was cooled to −35 °C. The precipitated product was collected by filtration, washed with cold pentane, and dried in vacuo (61.5 mg, 70 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 17.00 (s, 1H; RuC*H*), 7.59 (td, J = 8.0, 1.5 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H; *o*-Ar*H*), 7.19 (td, J = 7.5 Hz, 1.0 Hz, 1H; *m*-ArH), 7.13–6.88 (m, 8H; Ar*H*), 6.80–6.70 (m, 2H; Ar*H*), 4.07 (s, 4H; NCH_2CH_2N), 2.91 (s, 3H; NCH_3), 2.79–1.70 ppm (m, 18H; *o*-ArCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 299.2, 210.3, 208.5, 155.8, 151.4, 146.5, 139.2, 138.9, 138.6, 129.5, 129.4, 129.3, 127.9, 127.4, 126.9, 123.5, 122.0, 121.1, 53.8, 51.7, 21.3, 19.5 ppm; elemental analysis calcd (%) for $C_{35}H_{39}Cl_2N_3Ru$: C 62.40, H 5.84, N 6.24; found: C 62.53, H 5.95, N 5.96.

Complexes 6, 7, 8, and 9: The solid was purified by column chromatography (ethyl acetate/cyclohexane, 1:5 v/v for **6**; cyclohexane/acetone, 5:1 v/v for **7**; ethyl acetate/cyclohexane, 1:4 v/v for **8**; and pentane/diethyl ether, 8:1 v/v for **9**). The complexes were treated with pentane (5 mL) and the resulting suspension was cooled to −35 °C. The products were collected by filtration, washed with cold pentane, and dried in vacuo: complex **6** (45 mg, 50 % yield), complex **7** (67 mg, 68 % yield), complex **8** (74 mg, 75 % yield), and complex **9** (60 mg, 60 % yield).

Complex ***6***: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 16.93 (s, 1H; RuC*H*), 7.53 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.17 (t, J = 7.3 Hz, 1H), 7.12–7.01 (m, 5H), 7.01–6.88 (m, 5H), 4.05 (s, 4H; NCH_2CH_2N), 3.69–3.49 (m, 1H; $NCH_aH_bCH_3$), 2.95–2.75 (m, 1H; $NCH_aH_bCH_3$), 2.68–2.09 (m, 18H; ArCH_3), 0.55 ppm (t, J = 6.8 Hz, 3H; NCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 300.60, 300.47, 210.53, 196.57, 157.83, 148.00, 143.93, 139.14 (br), 138.68 (br), 138.52, 129.56, 129.30, 128.68, 127.60, 127.02, 123.24, 121.31, 121.01, 56.77, 51.66, 21.31, 19.55 (br), 11.24 ppm; HRMS (EI): *m/z* calcd for $C_{36}H_{40}N_3ClRu$: 651.1950 $[M-HCl]^+$; found: 651.1909.

Complex ***7***: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.86 (s, 1H; RuC*H*), 7.58 (t, J = 7.7 Hz, 2H), 7.51 (td, J = 7.9, 1.5 Hz, 1H), 7.38 (dd, J = 7.8, 1.3 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.15 (td, J = 7.6, 1.0 Hz, 1H), 7.09–7.04 (m, 4H), 6.96–6.91 (m, 2H), 6.87–6.83 (m, 2H), 3.12–3.00 (m, 4H; $CH(CH_3)_2$), 2.91 (s, 3H; NCH_3), 1.21 (d, J = 6.0 Hz, 6H; $CH(CH_3)_2$), 1.11 (d, J = 6.9 Hz, 6H; $CH(CH_3)_2$), 1.07 (d, J = 6.9 Hz, 6H; $CH(CH_3)_2$), 1.04 ppm (d, J = 6.7 Hz, 6H; $CH(CH_3)_2$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 288.97. 288.93, 177.81, 155.43, 150.81, 148.39, 148.24, 148.00, 136.41, 130.31, 128.84, 127.40, 126.19, 125.80, 124.01, 123.88, 123.44, 121.20, 120.77, 53.15, 28.87, 28.77, 26.67, 26.41, 23.17, 23.00 ppm; HRMS (EI): *m/z* calcd for $C_{41}H_{49}N_3Cl_2Ru$: 755.2338 $[M]^+$; found: 755.2291.

Complex ***8***: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 16.74 (s, 1H; RuC*H*), 7.58–7.46 (m, 3H), 7.40–7.28 (m, 4H), 7.22–7.03 (m, 4H), 6.98–6.77 (m, 4H), 4.18–4.00 (m, 4H; NCH_2CH_2N), 3.69–3.51 (m, 4H; $CH(CH_3)_2$), 2.94 (s, 3H; NCH_3), 1.23 (d, J = 6.7 Hz, 18H; $CH(CH_3)_2$), 1.05 ppm (d, J = 6.2 Hz, 6H; $CH(CH_3)_2$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 291.20, 212.03, 154.85, 150.86, 149.29, 148.85, 148.62, 129.56, 128.61, 128.04, 127.30, 125.97, 124.59, 124.31 (br), 123.31, 121.27, 121.17, 54.59, 52.53, 28.70, 26.62, 23.95 ppm; HRMS (EI): *m/z* calcd for $C_{41}H_{51}N_3Cl_2Ru$: 757.2495 $[M]^+$; found: 757.2537.

Complex ***9***: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 16.69 (s, 1H; RuC*H*), 7.62–7.28 (m, 6H), 7.25 (d, J = 7.7 Hz, 2H), 7.14–7.00 (m, 5H), 6.96–6.88 (m, 1H), 6.83 (dd, J = 7.6, 1.3 Hz, 1H), 4.27–3.14 (br, 4H; NCH_2CH_2N + dq, J = 13.8, 6.9 Hz, 1H; $NCH_aH_bCH_3$ + m, 4H; $CH(CH_3)_2$), 2.84 (dq, J = 13.8, 6.9 Hz, 1H; $NCH_aH_bCH_3$), 1.93–0.56 (br, 24H; $CH(CH_3)_2$), 0.43 ppm (t, J = 7.0 Hz, 3H; $NCH_aH_bCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 293.24, 293.15, 212.14, 156.93, 148.95 (br), 147.52, 144.76, 129.54, 127.99, 127.65, 127.58, 126.81, 124.62 (br), 123.20, 121.51, 120.79, 56.24, 54.48 (br), 28.72, 26.82 (br), 23.74 (br), 10.97, 8.41 ppm; HRMS (EI): *m/z* calcd for $C_{42}H_{53}N_3Cl_2Ru$: 771.2651 $[M]^+$; found: 771.2588.

Synthesis of complex 5 in the absence of protic resin: $[RuCl_2(SIMes)(Ind)(Py)]$ (200 mg, 0.27 mmol) was added to a solution of 2-(*N*-methyl-*N*-phenyl)aminostyrene (70 mg, 0.32 mmol) in toluene (2.5 mL) and the mixture was stirred for 120 min at 75 °C (at lower temperatures a mixture of *cis*-**5** and *trans*-**5** was obtained). The mixture was concentrated in vacuo and purified by column chromatography (cyclohexane/acetone, 7:1 v/v + 0.5 % NEt_3). The obtained product was recrystallized from cyclohexane to yield the desired complex as a green, microcrystalline solid (52 mg, 30 %). R_f = 0.15 (cyclohexane/acetone, 7:1 v/v + 0.5 % NEt_3).

X-ray crystal structure analysis of complex *trans*-5: The crystal structure was solved and refined by using the SHELX package.[43] A brief summary of crystal data and structure refinement, and bond lengths, angles, and coordinates can be found in the Supporting Information. CCDC-872791 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information

Fast Olefin Metathesis at Low Catalyst Loading

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General conditions for the UV/Vis experiments

All experiments were carried out in quartz cuvettes 110-QS with a path length of 10.00 mm. The temperature (30 °C or 0 °C) was adjusted using a thermostat and controlled with a thermometer.

The following general procedure was applied in all experiments with BuVE (butyl vinyl ether): $1.00 \cdot 10^{-5}$ mol of precatalyst was dissolved in abs. toluene (50 mL) to give a $2.00 \cdot 10^{-4}$ M solution. 1500 µL of this stock solution were filled in a cuvette and an additional amount of toluene was added. This amount was calculated such that, after the addition of substrate, the precatalyst concentration is $1.00 \cdot 10^{-4}$ M. The cuvette was then placed in the spectrometer and was allowed to adjust to the respective temperature. The measurement was started in the moment of the addition of the corresponding amount of preheated (same temperature as inside the cuvette) substrate. During the measurement the cuvette was closed with a PTFE stopper (not gas tight).

To determine k_{obs}, the initiation process of the precatalyst was monitored by recording UV/Vis spectra to follow the spectral changes with time. The precatalyst's LMCT band absorbance – time traces were fitted with an exponential function.

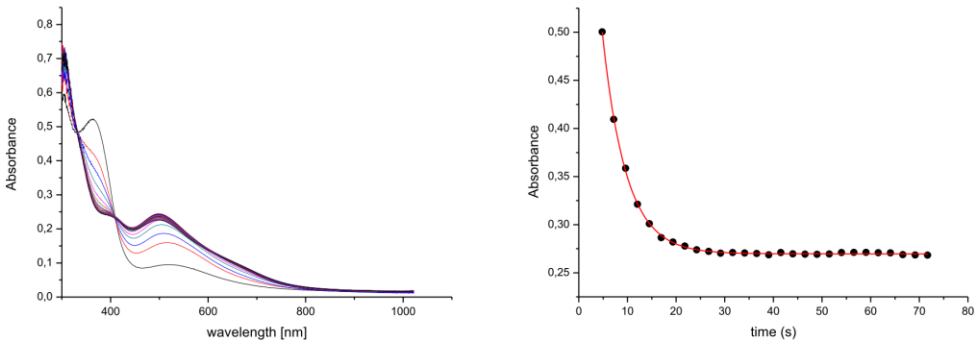


Fig. SI-1: Left: UV/Vis traces of complex **5** ($1.00 \cdot 10^{-4}$ M) with reaction with BuVE (0.1 M). Right: Corresponding absorbance – time curves at 366 nm. The data are fitted using (y = A1·exp(-x/t1) + y0) and (k_{obs} = 1/t1).

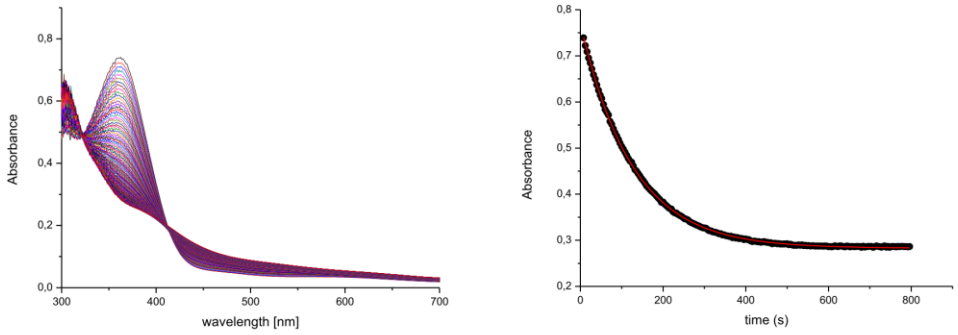


Fig. SI-2: Left: UV/Vis traces of complex **7** ($1.00 \cdot 10^{-4}$ M) with reaction with BuVE (0.1 M). Right: Corresponding absorbance – time curves at 362 nm. The data are fitted using (y = A1·exp(-x/t1) + y0) and (k_{obs} = 1/t1).

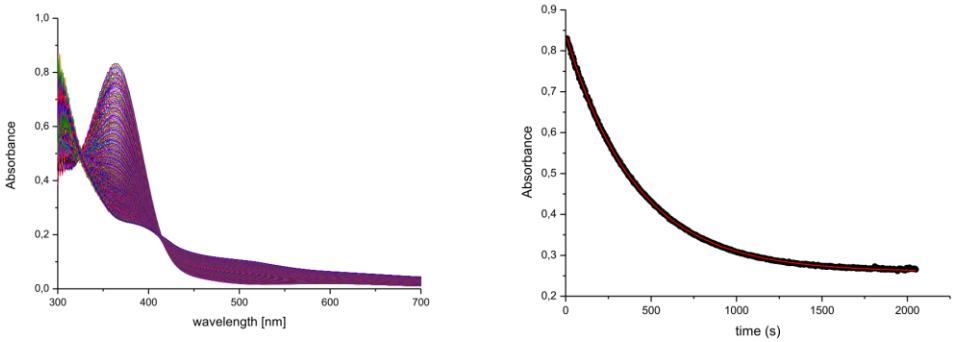


Fig. SI-3: Left: UV/Vis traces of complex **8** ($1.00 \cdot 10^{-4}$ M) with reaction with BuVE (0.1 M). Right: Corresponding absorbance – time curves at 364 nm. The data are fitted using (y = A1·exp(-x/t1) + y0) and (k_{obs} = 1/t1).

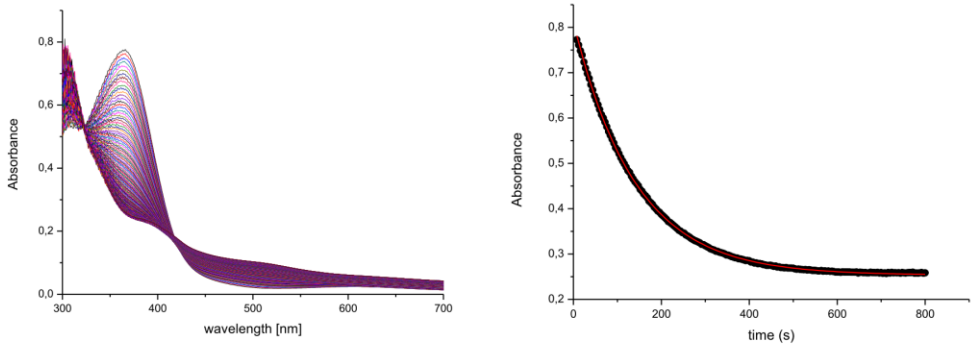


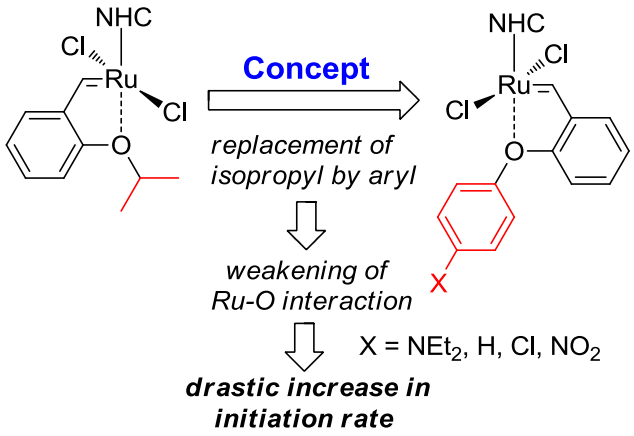
Fig. SI-4: Left: UV/Vis traces of complex **9** ($1.00 \cdot 10^{-4}$ M) with reaction with BuVE (0.1 M). Right: Corresponding absorbance – time curves at 365 nm. The data are fitted using (y = A1·exp(-x/t1) + y0) and (k_{obs} = 1/t1).

3.3. Fast Olefin Metathesis: Synthesis of 2-Aryloxy-Substituted Hoveyda-Type Complexes and Application in Ring-Closing Metathesis

The content of this chapter has already been published:

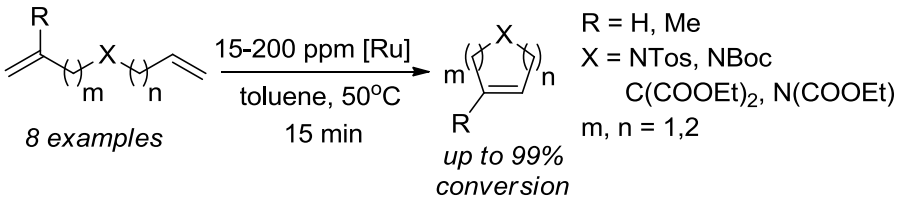
Pavlo Kos, Roman Savka, Herbert Plenio, *"Fast Olefin Metathesis: Synthesis of 2-Aryloxy-Substituted Hoveyda-Type Complexes and Application in Ring-Closing Metathesis", Advanced Synthesis & Catalysis* **2013**, *355*, 439–447.

This chapter deals with the synthesis and catalytic activity of a rapidly initiating 2-aryloxy-substituted Hoveyda-type complexes. The objective of this work was to replace an sp^3-carbon by an sp^2-carbon in a phenyl groups in order to decrease oxygen donation (Scheme 59). This resulted in faster initiation rate due to the weakening of the Ru-O interaction in such complexes.



Scheme 59. The basic concept of the project.

The efficiency of the eight newly synthesized ruthenium complexes was demonstrated by an extensive screening for eight different RCM substrates (Scheme 60). Catalyst loadings of between 15–200 ppm are sufficient for the formation of >90% yield of the respective cyclic products. Complex with NHC = SIMes and X = H and the respective SIPr-analogues with X = H, NEt_2 appear to be the most efficient catalysts. In general, complexes bearing SIPr ligands initiate slower than those with SIMes carbene providing higher final conversion of the respective cyclic olefin at low temperature.



Scheme 60. Tested ring-closing metathesis reactions.

My estimated contribution to this work is 40%.

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Fast Olefin Metathesis: Synthesis of 2-Aryloxy-Substituted Hoveyda-Type Complexes and Application in Ring-Closing Metathesis

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Abstract: Four 1-(4-R-phenoxy)-2-ethenylbenzenes (R = NMe_2, H, Cl, NO_2) **4a**, **4b**, **4c** and **4d** were reacted with the ruthenium complexes [$RuCl_2$(NHC)(3-phenylindenylidene)(py)] in the presence of a protic resin to result in the formation of the respective Hoveyda-type complexes **5a–d** {NHC = SIMes [1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene]} and **6a–d** {NHC = SIPr [1,3-bis(2,6-diisopropylphenylimidazolin)-2-ylidene]} in 66–84% yield. The lower steric bulk and the decreased donation of the diaryl ether oxygen atoms in complexes **5** and **6** led to rapidly initiating precatalysts. The Ru(II/III) redox potentials of complexes **6** were determined (**6a–d:** $\Delta E = 0.89$–1.08 V). In the crystal structure of **5b** two independent molecules were observed in the unit cell, displaying Ru–O distances of 226.6(4) and 230.5(3) pm. The catalytic performance of complexes **5** and **6** in various ring-closing metathesis (RCM) reactions was studied. Catalyst loadings of between 15–200 ppm are sufficient for the formation of >90% yield of the respective cyclic products. Complex **6b** catalyzes the formation of *N*-protected 2,5-dihydropyrroles with up to TON 64,000 and TOF 256,000 h^{-1}, of the *N*-protected 1,2,3,6- tetrahydropyridines with up to TON 18,200 and TOF 73,000 h^{-1} and of the *N*-protected 2,3,6,7-tetrahydroazepines with up to TON 8,100 and TOF 32,000 h^{-1} with yields ranging between 77 and 96%.

Keywords: cyclic voltammetry; olefin metathesis; ring-closing metathesis; ruthenium

Introduction

Progress in olefin metathesis depends on the continuous evolution of catalyst complexes.[1] As a consequence of the development of numerous efficient ruthenium- and molybdenum-based complexes, olefin metathesis has been firmly established as a powerful synthetic tool in organic synthesis and polymer chemistry.[2] Especially Hoveyda-type complexes combine excellent stability with high activity in various olefin metathesis reactions and have been modified extensively to optimize their catalytic performance.[3] Typically, such complexes are characterized by a 2-isopropoxy group at the benzylidene ligand, whose oxygen atom also binds to ruthenium in a chelating manner.[4] The behavior of such complexes in various olefin metathesis transformations has been modified extensively by introducing various electron-withdrawing or electron-donating groups at the 4- and 5-positions of the six-membered ring. These modifications are often based on the assumption that a decrease in the electron density of the oxygen donor leads to a faster dissociation of the ruthenium-oxygen bond, while electron-rich oxygen groups appear to be more tightly bound to ruthenium.[4f,g,5] This is a useful model in a dissociative scenario for catalyst activation, but it was also shown later that electron-withdrawing substituents also led to enhanced precatalyst activation *via* an interchange activation pathway which is aided by an electron-deficient ruthenium.[6] The initiation of such precatalysts occurs simultaneously along two mechanistic pathways and finally leads to faster precatalyst activation.[6b,7] Based on a significant contribution of an interchange pathway, this mechanistic model also explains why using the small 2-methoxy group leads to significantly faster initiation rates than with the 2-isopropoxy substituted complexes.[6b,8]

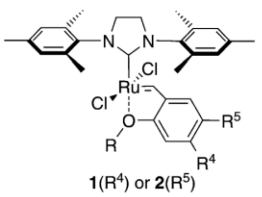
Despite the large number of modified Hoveyda-type complexes,[4b] many of which were introduced by the Grela group,[9] 2-phenoxy-substituted complexes have not been reported. Replacing an sp^3-carbon by

an sp^2-carbon in a phenyl groups leads to a decrease in the oxygen donation. This should weaken the Ru···O interaction in such complexes and result in faster initiation rates. Obviously such rapidly initiating complexes offer the potential for fast and efficient olefin metathesis reactions. We want to present here the synthesis and the characterization of new 2-phenoxy-substituted Hoveyda-type complexes as well as studies probing the catalytic activity of these complexes in various ring-closing metathesis (RCM) reactions.[10]

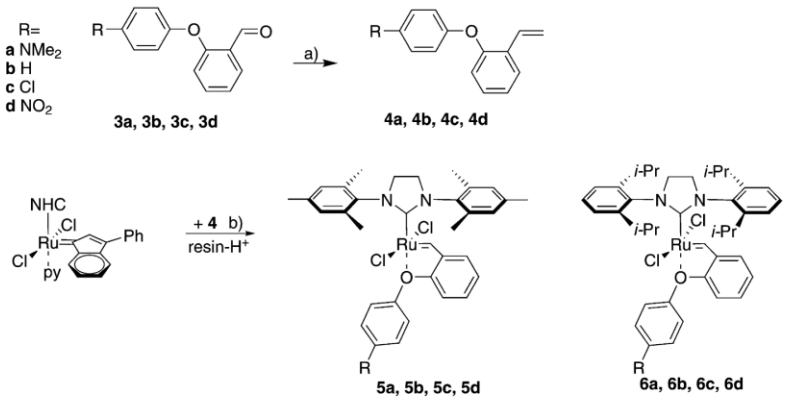
Results and Discussion

Synthesis of 2-Aryloxy Hoveyda Complexes

The new ruthenium complexes **5** and **6** were synthesized according to Scheme 2. The nucleophilic substitution of 2-fluorobenzaldehyde with various 4-substituted phenols (R = Cl, H, NMe_2) furnishes the unsymmetrical diaryl ethers **3** according to a literature procedure.[11] For the synthesis of the nitro-substituted **3d** a slightly different approach was taken, by reacting 1-fluoro-4-nitrobenzene with 2-hydroxybenzaldehyde. Next, the aldehydes were converted into the respective vinyl-substituted ethers employing the Wittig reagent in yields of 77–84%. The synthesis of the new ruthenium complexes was achieved in 69–84% yield in the presence of Amberlyst resin at 40 °C using $[RuCl_2(NHC)(3\text{-phenylindenylidene})(py)]$ (NHC = SIMes, SIPr)[12] and a slight excess (1.1 equiv.) of the respective diaryl ethers **4**. For the most electron-deficient and least stable complex **5d** the best yields are obtained when the synthesis of this complex is carried out in THF solvent at 0 °C. The removal of the pyridine ligand from the reaction equilibrium by protonation with the protic resin (Amberlyst) is essential for the synthesis of the new complexes reported here – without the acidic resin the respective complexes **5** and **6** are only formed in poor yields or not at all. The same strategy was recently used successfully for the synthesis of related *N*-Hoveyda complexes.[13] However, the idea of using the protic resin for the efficient synthesis of Hoveyda-type complexes is based on a related approach introduced by Verpoort and Monsaert.[14] These authors reported on the facile synthesis of 2-O-*i*-Pr-substituted Hoveyda complexes from Grubbs I and II complexes in >90% yield *via* protonation of PCy_3 and removal as the respective phosphonium salt. An important advantage of the complexes **5** and **6** reported here is their simple and high-yielding synthesis, which will facilitate synthesis of such complexes in multi-gram amounts.



Scheme 1. *O*-Hoveyda type complexes, complex **1**(H) with R = O-*i*-Pr, R^4, R^5 = H.



Scheme 2. Synthesis of diaryl ethers **4** (**a**: R = NMe_2, **b**: H, **c**: Cl, **d**: NO_2) and of the new complexes **5** and **6**. *Reagents and conditions:* (**3a**, **b**, **c** are known compounds, while **3d** was synthesized from 1-fluoro-4-nitrobenzene and 2-hydroxybenzaldehyde in 70% yield; a) vinylation of aldehydes: $[MePPh_3]^+I^-$, KO-*t*-Bu, THF, 0 °C→room temperature, overnight, yields: 77–84%; b) synthesis of **5a–c** and **6a–d**: protic resin (Amberlyst), CH_2Cl_2, 40 °C, 30–60 min, yields: 71% (**5a**), 81% (**5b**), 69% (**5c**) and 73% (**6a**), 84% (**6b**), 75% (**6c**), 66% (**6d**); synthesis of complex **5d**: protic resin (Amberlyst), THF, 0 °C, 30 min, yield: 75%.

X-Ray Crystal Structure of Complex 5b

The crystal structure of a 2-phenoxy-substituted complex was determined, in order to learn whether the presence of the poorly donating diaryl ether oxygen atom results in longer ruthenium-oxygen distances than in the respective 2-isopropoxy complexes. In the solid state two independent molecules of **5b** are observed, which differ with respect to the orientation of the OPh group relative to the rest of the molecule. In the rotamer displayed (Figure 1), the plane of the C_6H_5 unit is nearly orthogonal (angle 82°) to the plane of the 1,2-substituted benzene ring, while in the second molecule the corresponding angle amounts to 60°. Other small changes of the geometric parameters are also seen, notably the Ru–O bond differs by nearly 4 pm [226.4(4) or 230.5(3) pm] in the two isomers. The shorter distance is close to the Ru–O distance observed in the standard Hoveyda complex (226.1 ppm)[15] with an 2-isopropoxy instead of the 2-phenoxy group. The significant variability of the Ru–O distances in the two molecules of **5b** is caused by packing effects, and indicates that the energy potential curve for Ru–O bond is shallow and thus sensitive to small perturbations.

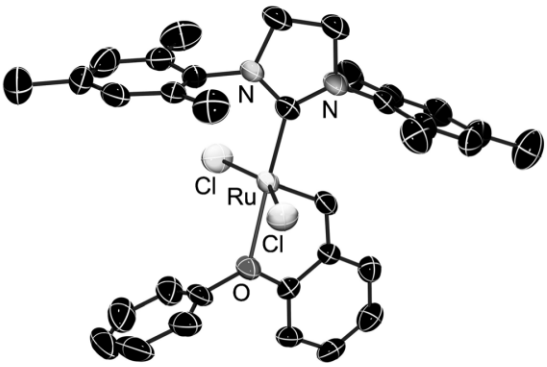


Figure 1. ORTEP (50% probability) of complex **5b**, only one of the two independent molecules in the crystal is displayed. Important bond lengths (pm) and angles (°) (first number(s) given correspond to rotamer 1 followed by the respective data for rotamer 2): Ru–O 226.6(4), 230.5(3); Ru–C(NHC) 198.4(5), 197.0(6); Ru=CHR 182.1(5), 180.9(5), Ru–Cl 230.7(2), 232.3(2), 232.1(2), 234.0(2); Cl–Ru–Cl 153.71(6), 158.31(6) (data deposited as CCDC 908389. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif).

Redox Potentials

The cyclic voltammetry-derived Ru(II/III) redox potentials provide useful information concerning the donor ability of the ligands coordinated to the metal.[16] In the series of complexes **5** and **6** reported here, the substituents in the 4-position are modulated from strongly electron-donating (**a**: NMe_2) to strongly electron-withdrawing (**d**: NO_2). The redox potentials of the eight complexes **5a–d** and **6a–d** were determined in CH_2Cl_2 (Table 1). The SIPr **6** complexes are characterized by a quasi-reversible electrochemistry. The redox potentials of the rapidly initiating SIMes complexes could not be determined with good precision, due to the lack of sufficient reversibility in the cyclic voltammograms. A comparison of the redox potentials of the different complexes **5** and **6** with those of the 2-isopropoxy-substituted complexes **1** and **2** reveals that the substituents R^4 and R^5 (Scheme 1) in the latter complexes have a much stronger influence on the redox potential than the R group in the complexes reported here. Especially the 4-substituent R^4 (*trans* to the benzylidene carbon in complexes **1**) has a pronounced effect on the redox potential, which ranges from 0.46 V for **1** ($R^4 = NEt_2$) to 1.04 V for **1** ($R^4 = NO_2$).[6b] This corresponds to a redox potential spread of 580 mV. In contrast, within the series of complexes **6** only a modest 190 mV shift is found between $R = NEt_2$ and NO_2. This underlines our previous hypothesis that the electronic communication between ruthenium and the substituents mainly occurs *via* the Ru=CHR unit and only to a lesser degree *via* the Ru–O interaction.[6b]

Table 1. Redox potentials [V] and peak separations $E_a - E_c$ [mV] of complexes **5a–d** and **6a–d**.[a]

R =	Redox potentials [V], ($E_a - E_c$) [mV] **5**	**6**
a NMe_2	0.87(110)[b]	0.886(97)
b H	0.941(83)	0.977(92)
c Cl	0.99(170)[b]	1.013(92)
d NO_2	1.07(180)[b]	1.075(91)

[a] Solvent: CH_2Cl_2, scan rate: 100 mVs^{-1}, supporting electrolyte 0.1 M NBu_4PF_6, potentials *vs* Fc/Fc^+ $E_{1/2} = +0.460$ V.

[b] Insufficient electrochemical reversibility.

Precatalyst Activation of Complexes 5 and 6

Due to the electron-deficient nature of the diphenyl oxygen, both complexes **5** and **6** are characterized by weak ruthenium-oxygen interactions. Consequently, in the presence of excess olefin this bond is broken rapidly, as evidenced by a correspondingly rapid decrease in the absorbance of the LMCT band (Figure 2),[17] which is normally observed between 360–400 nm for such complexes. This dissociation reaction requires less than 20 sec in **5d**, even at a very low concentra-

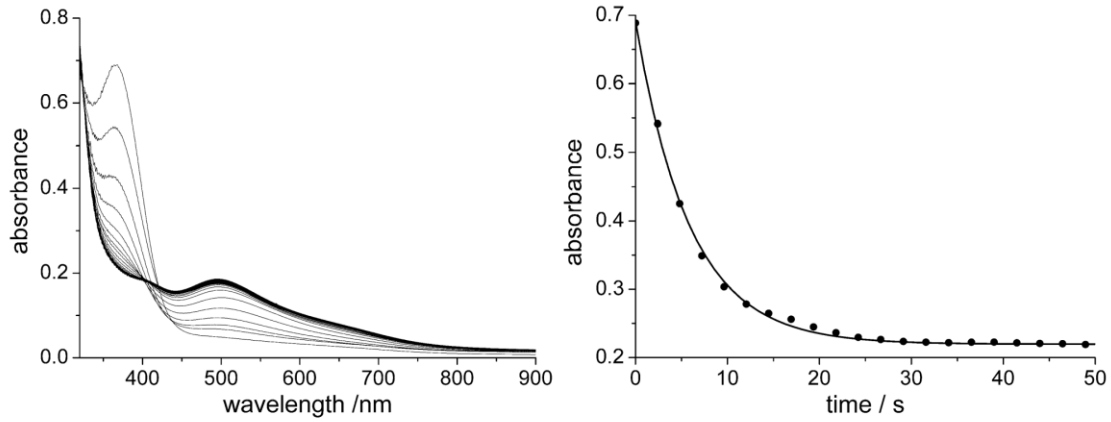


Figure 2. *Left:* UV/Vis traces of complex **5d** ($1.0 \cdot 10^{-4}$ mol·L^{-1}) during reaction with BuVE (0.01 M) in toluene at $T = 30$ °C. *Right:* corresponding absorbance-time trace at 370 nm. The data are fitted using [$y = A1 \cdot \exp(-x/t_1) + y_0$].

tion of butyl vinyl ether (0.01 mol·L^{-1}) and at a temperature slightly above ambient (30 °C). The new complexes appear to be the fastest initiating Hoveyda-type complexes, which should be also useful in ROMP reactions. However, the SiMes complexes **5** initiate *circa* 10 times faster than the SiPr complexes **6**. Following RCM transformation, this absorbance fails to recover intensity and consequently the UV/Vis spectra provide no evidence for a significant return of the 2-phenoxystyrene following the olefin metathesis transformation.[18] Other than that, the kinetics of the new complexes **5** and **6** reveal more details than those of the 2-isopropoxy-substituted complex **1**. Due to the very fast loss of the benzylidene ligand additional steps are observed in the UV/Vis spectra. A pronounced feature is the absorbance at 510 nm, which builds up with the same rate as the loss of intensity of the 370 nm band, but decays with a different rate. We are currently working on a detailed kinetic and mechanistic analysis of such complexes.

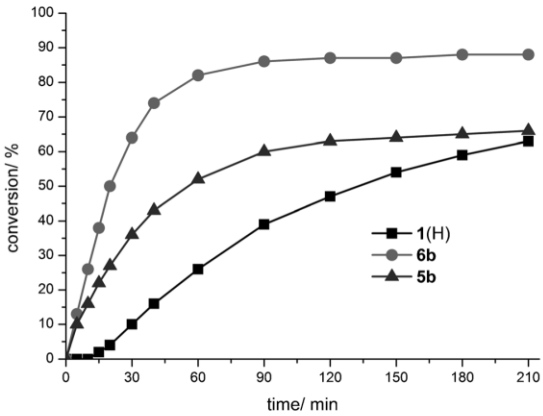


Figure 3. RCM reaction of *N,N*-diallyltosylamide (0.1 mol·L^{-1}) at 0 °C in toluene with complexes **1**(H), **5b** and **6b** (0.025 mol%; 250 ppm).

Evaluation of the Catalytic Activity of Complexes 5 and 6 in RCM

The new complexes **5** and **6** are characterized by rapid precatalyst initiation, which enables efficient RCM reactions at low reaction temperatures. To demonstrate this, the conversion-time curves for the RCM reaction of diallyl-*N*-tosylamide catalyzed by complexes **5b** and **6b** were determined at 0 °C and plotted together with the respective curves for complex **1**(H) (Figure 3). The faster precatalyst activation of complexes **5b** and **6b** compared to **1**(H) is evidenced by the faster initial transformation of substrate diallyl-*N*-tosylamide into the respective RCM product. Notably, within 60 min at 0 °C a conversion of 80% is observed at only 250 ppm (0.025 mol%) of **6b**. After 120 min the reactions almost reach the final conversion for complexes **5b** and **6b**, while it takes longer for the less rapidly initiating complex **1**(H). It was, however, unexpected to see no performance difference between **5b** and **6b** in the initial stage of the RCM reaction, since it is known that SIMes-based complexes initiate faster than those with SIPr.[13] To test this, another conversion-time curve with shorter sampling intervals (Figure 4) was recorded. With this more detailed view, at least during the first 6 min, the faster initiating complex **5b** produces more product. Obviously, the lower initiation efficiency is rapidly offset by the higher catalytic performance of complex **6b**.

In order to demonstrate the efficiency of the newly synthesized ruthenium complexes an extensive screen-

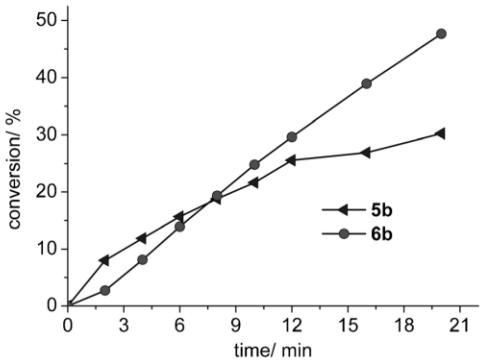


Figure 4. RCM reaction of *N,N*-diallyl-tosylamide (0.1 mol·L^{-1}) at 0 °C in toluene with complexes **5b** and **6b** (0.025 mol%; 250 ppm)

ing was done for eight different RCM substrates and the eight newly synthesized complexes **5** and **6** (Table 2). In general, the complexes reported here provide excellent substrate conversions within less than 15 min of reaction time at low catalyst loadings of between 15–100 ppm (0.0015–0.01 mol%) at 50 °C in toluene as solvent. Over the years diethyl diallylmalonate (DEDAM) has become something like a benchmark substrate for RCM reactions.[19] The comparison of the yields reported for complexes **5** and **6** with previous data observed for this substrate underline the excellent performance of the complexes reported here. Four out of the eight new complexes (**5c**, **6a**, **6b**, **6c**) give more than 80% conversion for DEDAM at 100 ppm (0.01 mol%) of catalyst loading, which is a considerably lower catalyst loading than described recently in the Grela galaxy benchmark paper.[19a] Recently other examples of olefin metathesis reactions employing low catalyst loading were reported. Nolan, Slugovc et al.[20] described the high activity of complexes based on the SIPr ligand, whose performance is comparable to that of the complexes **6** reported here. Grubbs et al. demonstrated excellent activities in RCM reactions of DEDAM using robotic equipment in a glove box.[21] On the other hand, the synthesis of various five-, six- and seven-membered N-heterocycles was reported by Pederson, Grubbs et al.; however, in their work 500 ppm of Ru complex were used for the full conversion of nitrogen-containing substrates leading to the respective heterocycles during 8 h reaction time.[22] For BocN(diallyl)$_2$ (Table 2, entry 5) this leads to TON 2,000 and TOF 310 h^{-1}, while the same reaction employing complex

Table 2. Screening of catalysts in ring-closing metathesis reactions.

Substrate	cat [ppm][a]	1	5a	5b	5c	5d	6a	6b	6c	6d
		Conversion[b] [%]								
EtOOC COOEt	200	29	90	92		83		99		
	100		52	75	80	49	88	80	82	54
	50							37		
	200							86		
EtO_2C CO_2Et	100		42	98	94	40	89	64	66	51
	50	36		78	51			33		
COOEt N	100				73		95	89		
	50	75		79	54		80	77	73	
Tos N	25	70	83	90	73	83	99		81	99
	15			74	64		91	96	78	92
Boc N	50			91		80		98		
	25	77	64	86	70	41	86	92		76
Boc N	100			93						
	50	60	71	60		54	89	91		83
Tos N	200		92	92		77	99	99		98
	100							81		
Tos N	50	39		61			90	72		84

[a] 100 ppm correspond to 0.01 mol%.
[b] [substrate] = 0.5 M, conversions determined by GC, average of two runs.

6b takes place with TON 64,000 and TOF 256,000 h^{-1}. The efficiency of the complexes **5** and **6** reported here is close to the excellent activities recently demonstrated for N-Hoveyda complexes with diarylamino ligands.[13] As observed before, for RCM reactions leading to disubstituted olefins, the SIPr-based complexes are more powerful catalysts, while for the synthesis of trisubstituted olefins the SIMes complexes tend to perform better. We note that the use of purified reaction solvent (toluene) and especially of the purified substrates is an essential requirement for the observation of excellent catalytic activities and for avoiding premature catalyst decomposition.

In conclusion, the formation of *N*-protected 2,5-dihydropyrroles with complex **6b** proceeds with TON of 64,000 (yield 87%) and TOF 256,000 h^{-1}, of the *N*-protected 1,2,3,6-tetrahydropyridines with TON 18,200 (92% yield) and TOF 73.000 h^{-1} and of the respective *N*-protected 2,3,6,7-tetrahydroazepines in TON 8,100 (95% yield) and TOF 32,000 h^{-1} with yields ranging between 77–96% for the various substrates.

Conclusions

The reactions of [$RuCl_2$(NHC)(3-phenylindeneylidene)(py)] (NHC = SIMes, SIPr) with 1-ethenyl-2-phenoxybenzenes (with EWG/EDG groups R *para* to ethenyl) gave eight new Hoveyda-type complexes in yields between 66–84%. This synthesis critically relies on the efficient removal of pyridine as the respective pyridinium salt using the acidic Amberlyst resin. The new complexes feature the excellent stability of Hoveyda-type complexes, but undergo full precatalyst activation within a few seconds. The fast precatalyst initiation translates into rapid olefin metathesis reactions – even at low reaction temperatures. The catalytic activity in various RCM reactions was probed and the new complexes found to be highly efficient; only 15–100 ppm (0.0015–0.01 mol%) are needed to reach >90% conversion within less than 15 min of reaction time for a variety of RCM reactions.

Experimental Section

General Experimental Details

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. All reactions involving ruthenium complexes were performed under an atmosphere of argon. CH_2Cl_2 (99.5%) and pentane (99%) were obtained from Grüssing GmbH, Toluene from Sigma–Aldrich (Lab. Reagent grade, 99.3%). These solvents were dried and degassed by using a column purification system as described by Grubbs et al.[23] In this system, the solvents are sparged and pressurized with argon (0.1–1 bar), followed by successive passages through a column filled with activated alumina and a second column, either filled with a supported copper catalyst (pentane) or again activated alumina (toluene, CH_2Cl_2). Dimethylformamide was refluxed over calcium hydride and distilled under an argon atmosphere. Tetrahydrofuran was dried with sodium and distilled under an argon atmosphere. Toluene was additionally dried over CaH_2 and distilled onto molecular sieves (4 Å). All solvents were stored over molecular sieves (4 Å). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX300 spectrometer. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (^1H, ^{13}C NMR = 0.0 ppm) or the residual peak of $CHCl_3$ (^1H NMR = 7.26 ppm, ^{13}C NMR = 77.16 ppm). Abbreviations for NMR data: s = singlet; d = doublet; t = triplet; q = quartet; sep = septet; m = multiplet; bs = broad signal. Preparative chromatography was performed using Merck silica 60 (0.063–0.02 mesh). GC experiments were run on a Clarus 500 GC with autosampler and FID detector; column: Varian CP-Sil 8 CB (l = 15 m, di = 0.25 mm), N_2 (flow: 17 cm s^{-1}; split 1:50); injector temperature: 270 °C, detector temperature: 350 °C. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as counter electrode. The pseudo reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of ferrocene [$E_{1/2}$ = + 0.46 V (CH_2Cl_2)]. NBu_4PF_6 (0.1 mol/L) was used as supporting electrolyte.

General Procedure for the Synthesis of 2-(Aryloxy)benzaldehydes (3a–d)

2-(Aryloxy)benzaldehydes **(3a-c)** were synthesized following a literature procedure[11] with modifications. Into a dry Schlenk flask under argon atmosphere were added the corresponding phenol (17.7 mmol), 2-fluorobenzaldehyde (2.0 g, 16.1 mmol), potassium carbonate (5.6 g, 40.3 mmol) and anhydrous DMF (40 mL) at room temperature. The mixture was warmed in a sealed flask to 170 °C and stirred at this temperature for 2 h **(3b, 3c)** or at 150 °C for 1.5 h **(3a)**. Then the mixture was allowed to cool to room temperature and was treated with water (200 mL) and the product was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with NaOH (1 M, 50 mL), brine (150 mL), dried over anhydrous $MgSO_4$ and evaporated under vacuum. The residue was purified by column chromatography [cyclohexane/ethyl acetate 10:1, v/v for **(3b, 3c)**] or used in the next reaction without purification **(3a)**.

2-[4-(Dimethylamino)phenoxy]benzaldehyde **(3a)** was obtained as a white solid; yield: 3.07 g (79%). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.59 (d, J = 0.8 Hz, 1 H), 7.90 (dd, J = 7.8, 1.8 Hz, 1 H), 7.44 (ddd, J = 8.5, 7.3, 1.8 Hz, 1 H), 7.12–7.05 (m, 1 H), 7.03–6.97 (m, 2 H), 6.84–6.74 (m, 3 H), 2.96 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.85, 161.75, 148.14, 145.47, 135.76, 128.33, 126.05, 122.23, 121.25, 116.90, 114.18, 41.34.

2-Phenoxybenzaldehyde **(3b)** was obtained as a yellow oil; yield: 2.52 g (79%). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.52 (d, J = 0.8 Hz, 1 H), 7.94 (dd, J = 7.8, 1.8 Hz, 1 H), 7.51

(ddd, $J=8.4$, 7.3, 1.8 Hz, 1H), 7.43–7.35 (m, 2H), 7.22–7.15 (m, 2H), 7.10–7.04 (m, 2H), 6.90 (dd, $J=8.4$, 0.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.45, 160.10, 156.53, 135.85, 130.22, 128.55, 127.03, 124.44, 123.44, 119.51, 118.60.

2-(4-Chlorophenoxy)benzaldehyde **(3c)** was obtained as a yellow solid; yield: 3.07 g (82%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=10.48$ (d, $J=0.7$ Hz, 1H), 7.94 (dd, $J=7.8$, 1.8 Hz, 1H), 7.53 (ddd, $J=8.4$, 7.3, 1.8 Hz, 1H), 7.37–7.33 (m, 2H), 7.24–7.19 (m, 1H), 7.03–6.99 (m, 2H), 6.89 (dd, $J=8.4$, 0.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=189.14$, 159.62, 155.20, 135.95, 130.26, 129.65, 128.85, 127.13, 123.91, 120.72, 118.60.

2-(4-Nitrophenoxy)benzaldehyde **(3d):** Into a dry Schlenk flask under an argon atmosphere were added 1-fluoro-4-nitrobenzene (2.0 g, 14.2 mmol), salicylic aldehyde (2.1 g, 17.0 mmol), potassium carbonate (4.9 g, 35.5 mmol) and anhydrous DMF (40 mL). The mixture was warmed in a sealed flask to 100 °C and stirred at this temperature overnight. Then the mixture was allowed to cool to room temperature, treated with water (200 mL) and the product was extracted with diethyl ether (3×50 mL). Combined organic layers were washed with NaOH (1M in water, 50 mL) and brine (150 mL), dried over anhydrous $MgSO_4$ and evaporated under vacuo. Residue was purified by column chromatography (cyclohexane/ethyl acetate 4:1, v/v) to afford **3d** as a yellow solid; yield: 2.40 g (69%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=10.34$ (d, $J=0.7$ Hz, 1H), 8.28–8.23 (m, 2H), 8.00 (dd, $J=7.8$, 1.8 Hz, 1H), 7.66 (dd, $J=8.3$, 7.4, 1.8 Hz, 1H), 7.41–7.35 (m, 1H), 7.13–7.06 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=188.36$, 162.64, 157.14, 143.61, 136.26, 129.71, 128.14, 126.31, 125.85, 120.93, 117.87; HR-MS: $m/z=$ 243.0531, calcd. for $C_{13}H_9NO_4$: 243.0542; analysis calcd. for $C_{13}H_9NO_4$ (243.05): C 64.18, H 3.73, N 5.76; found: C 64.23, H 3.72, N 5.88.

General Procedure for the Synthesis of 1-Phenoxy-2-vinylbenzenes (4a–d)

A Schlenk flask containing methyltriphenylphosphonium iodide (3.0 g, 7.42 mmol) was evacuated and back-filled with argon three times. Anhydrous tetrahydrofuran (50 mL) was added by syringe and the formed suspension was cooled to −10 °C. KO-*t*-Bu (902 mg, 8.04 mmol) was added in portions to the stirred mixture under a stream of argon, and stirring continued at −10 °C for 20 min. Next, the 2-(aryloxy)benzaldehyde (**3a–d**) (6.18 mmol) was added. The mixture was allowed to warm to room temperature, stirred overnight and poured into water (500 mL). The product was extracted with diethyl ether (3×100 mL). The organic phases were combined, washed with brine and dried over magnesium sulfate. The solvent was removed under vacuum and the residue was purified by column chromatography (cyclohexane/ethyl acetate 20:1, v/v).

N,N-Dimethyl-4-(2-vinylphenoxy)aniline **(4a)** was obtained as a colorless solid; yield: 1.18 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.58$ (dd, $J=7.7$, 1.8 Hz, 1H), 7.20–7.01 (m, 3H), 6.96–6.89 (m, 2H), 6.80 (dd, $J=8.2$, 1.2 Hz, 1H), 6.76 (d, $J=9.0$ Hz, 2H), 5.82 (dd, $J=17.7$, 1.4 Hz, 1H), 5.30 (dd, $J=11.1$, 1.4 Hz, 1H), 2.93 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=155.69$, 147.37, 131.49, 128.89, 128.66, 126.61, 122.78, 120.11, 117.92, 115.02, 114.34, 41.51; HR-MS: $m/z=239.1310$, calcd. for $C_{16}H_{17}NO$: 239.1304; analysis calcd. for $C_{16}H_{17}NO$ (239.13): C 80.30, H 7.16, N 5.85; found C 79.88, H 7.11, N 5.83.

1-Phenoxy-2-vinylbenzene **(4b)** was obtained as a colorless solid; yield: 0.99 g (82%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=$ 7.62 (dd, $J=7.8$, 1.7 Hz, 1H), 7.34–7.30 (m, 2H), 7.24 (dd, 1H), 7.16–7.13 (m, 1H), 7.07 (tt, $J=7.6$, 1.1 Hz, 1H), 7.01 (dd, $J=17.7$, 11.1 Hz, 1H), 6.97–6.94 (m, 2H), 6.92 (dd, $J=$ 8.1, 1.1 Hz, 1H), 5.81 (dd, $J=17.7$, 1.3 Hz, 1H), 5.29 (dd, $J=$ 11.1, 1.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=158.05$, 153.75, 131.12, 129.97, 129.83, 129.14, 126.77, 124.21, 122.81, 120.23, 117.91, 115.51; analysis calcd. for $C_{14}H_{12}O$ (196.09): C 85.68, H 6.16; found C 85.49, H 6.11.

1-(4-Chlorophenoxy)-2-vinylbenzene **(4c)** was obtained as a colorless liquid; yield: 1.20 g (84%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.60$ (dd, $J=7.7$, 1.8 Hz, 1H), 7.28–7.20 (m, 3H), 7.18–7.12 (m, 1H), 6.99–6.87 (m, 2H), 6.87–6.82 (m, 2H), 5.78 (dd, $J=17.7$, 1.3 Hz, 1H), 5.27 (dd, $J=$ 11.1, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=156.76$, 153.32, 130.85, 130.07, 129.79, 129.26, 127.77, 126.93, 124.66, 120.33, 118.97, 115.86; HR-MS: $m/z=230.04815$, calcd. for $C_{14}H_{11}ClO$: 230.0494; analysis calcd. for $C_{14}H_{11}ClO$ (230.69): C 72.89, H 4.81; found C 72.82, H 4.92.

1-(4-Nitrophenoxy)-2-vinylbenzene **(4d)** was obtained as a yellow solid; yield: 1.15 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.22$–8.16 (m, 2H), 7.68–7.64 (m, 2H), 7.38–7.24 (m, 2H), 7.04–7.00 (m, 1H), 6.97–6.91 (m, 1H), 6.79 (dd, $J=$ 17.7, 11.1 Hz, 1H), 5.79 (dd, $J=17.7$, 1.1 Hz, 1H), 5.29 (dd, $J=11.1$, 1.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 163.61, 151.47, 142.67, 130.74, 130.20, 129.65, 127.31, 126.21, 126.14, 121.73, 116.81, 116.51; HR-MS: $m/z=241.0714$, calcd. for $C_{14}H_{11}NO_3$: 241.0739; analysis calcd. for $C_{14}H_{11}NO_3$ (241.25): C 69.70, H 4.60, N 5.81; found C 69.93, H 4.68, N 5.69.

General Procedure for the Synthesis of Complexes (5a–d, 6a–d)

Complexes **(5a–c, 6a–d):** A flame-dried Schlenk tube containing [$RuCl_2$(SIMes)(3-phenylindeneylidene)(py)] (200 mg, 0.27 mmol) or [$RuCl_2$(SIPr)(3-phenylindeneylidene)(py)] (200 mg, 0.24 mmol) was evacuated and back-filled with argon three times. Methylene chloride (4 mL), the respective 1-alkoxy-2-vinylbenzene [0.30 mmol for complexes **(5a–c)** or 0.26 mmol for complexes **(6a-d)**] and Amberlyst resin [275 mg for complexes **(5a–c)** or 250 mg for complexes **(6a–d)**, dry form, 4.70 mmol H^+/g] were added under an atmosphere of argon. The mixture was stirred at 40 °C for 30 min for complexes **(5a–c)** or 60 min for complexes **(6b–d)** or at room temperature for 1 h for complex **(6a)** and then filtered, to separate the resin. The filtrate was evaporated under vacuum and the remaining solid was treated with pentane (10 mL) and the resulting suspension was kept in an ultrasonic bath for 1 min. The solid residue was filtered, washed with methanol (5 mL) and pentane (10 mL) and dried under vacuum.

Complex **(5a)** was obtained as a green solid; yield: 135 mg (71%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=16.71$ (s, 1H), 7.37 (t, $J=7.5$ Hz, 1H), 7.13 (d, $J=8.3$ Hz, 2H), 7.03 (s, 4H), 6.98 (d, $J=7.3$ Hz, 1H), 6.90 (t, $J=7.3$ Hz, 1H), 6.61 (d, $J=8.0$ Hz, 3H), 4.15 (s, 4H), 2.93 (s, 6H), 2.47 (s, 12H), 2.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=292.65$, 210.50, 154.24, 143.89, 138.79, 136.22, 129.54, 129.46, 128.74,

127.69, 123.66, 122.90, 122.53, 113.86, 113.13, 51.81, 41.20, 21.24, 19.43; HR-MS: m/z = 703.1661, calcd. for $C_{36}H_{41}N_3O_4Cl_2Ru$: 703.16809.

***Complex* (5b)** was obtained as a green solid; yield: 142 mg (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 16.71 (d, J = 0.9 Hz, 1H), 7.44–7.36 (m, 1H), 7.25–7.14 (m, 5H), 7.03 (s, 4H), 7.00 (d, J = 1.8 Hz, 1H), 6.94 (td, J = 7.5, 0.8 Hz, 1H), 6.66 (d, J = 8.3 Hz, 1H), 4.16 (s, 4H), 2.46 (s, 12H), 2.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 292.53, 210.04, 153.24, 153.04, 144.21, 138.85, 136.03, 129.52, 129.44, 126.03, 124.21, 122.82, 122.08, 51.79, 21.22, 19.44; HR-MS: m/z = 660.1239, calcd. for $C_{34}H_{36}N_2OCl_2Ru$: 660.1253.

***Complex* (5c)** was obtained as a green solid; yield: 129 mg (69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.70 (s, 1H), 7.42 (t, J = 7.1 Hz, 1H), 7.24–7.18 (m, 4H), 7.06–6.94 (m, 6H), 6.65 (d, J = 8.1 Hz, 1H), 4.16 (s, 4H), 2.45 (s, 12H), 2.38 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 292.09, 209.55, 152.61, 151.71, 144.10, 138.98, 138.83, 135.94, 131.40, 129.55, 124.60, 123.43, 122.96, 114.00, 51.80, 21.23, 19.41; HR-MS: m/z = 694.0845, calcd. for $C_{34}H_{35}N_2OCl_3Ru$: 694.0820.

***Complex* (5d):** A flame-dried Schlenk tube containing [$RuCl_2$(SIMes)(3-phenylindeneylidene)(py)] (200 mg, 0.27 mmol) was evacuated and back-filled with argon three times. Tetrahydrofuran (5 mL) was added and resulting suspension was cooled to 0 °C. Then 1-(4-nitrophenoxy)-2-vinylbenzene (65.7 mg, 0.27 mmol) and Amberlyst resin (275 mg, dry form, 4.70 mmol H^+/g) were added and the mixture was stirred at 0 °C for 30 min, filtered and evaporated under vacuum. The solid residue was washed with methanol (5 mL), pentane (10 mL) and dried under vacuum to afford **5d** as a green solid; yield: 141 mg (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.69 (s, 1H), 8.12 (d, J = 7.2 Hz, 2H), 7.49 (s, 1H), 7.35 (d, J = 7.4 Hz, 2H), 7.04 (s, 6H), 6.79 (d, J = 7.3 Hz, 1H), 4.18 (s, 4H), 2.43 (s, 12H), 2.40 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 291.42, 208.52, 158.38, 150.86, 145.17, 144.58, 139.16, 138.94, 129.59, 129.46, 125.78, 125.30, 123.47, 121.80, 114.94, 51.79, 21.28, 19.43; MS (EI): m/z = 705 [M^+] (HR-MS could not be obtained).

***Complex* (6a)** was obtained as a green solid; yield: 139 mg (73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.59 (s, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 7.6 Hz, 5H), 7.22 (d, J = 8.1 Hz, 2H), 6.95–6.83 (m, 2H), 6.64–6.52 (m, 3H), 4.13 (s, 4H), 3.64 (sep., J = 6.2 Hz, 4H), 2.92 (s, 6H), 1.27 (d, J = 6.7 Hz, 12H), 1.19 (d, J = 6.4 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 287.86, 213.42, 148.85, 142.88, 137.25, 129.67, 129.33, 124.67, 123.74, 123.46, 121.94, 113.73, 113.04, 54.77, 41.10, 28.70, 26.49, 24.07; HR-MS: m/z = 787.2600, calcd. for $C_{42}H_{53}N_3OCl_2Ru$: 787.2567; analysis calcd. for $C_{42}H_{53}N_3OCl_2Ru$ (787.88): C 64.03, H 6.78, N 5.33; found C 64.56, H 6.96, N 5.12.

***Complex* (6b)** was obtained as a green solid; yield: 151 mg (84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.59 (d, J = 0.5 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.39–7.24 (m, 9H), 7.23–7.18 (m, 1H), 6.95 (dd, J = 7.6, 1.6 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.56 (d, J = 8.3 Hz, 1H), 4.14 (s, 4H), 3.63 (sep, J = 6.7 Hz, 4H), 1.27 (d, J = 6.9 Hz, 12H), 1.17 (d, J = 6.6 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 287.38, 212.79, 154.03, 153.04, 148.87, 143.08, 137.11, 129.74, 129.50, 129.33, 126.46, 124.66, 123.93, 123.16, 122.19, 113.85, 54.76, 28.71, 26.51, 23.97; HR-MS: m/z = 744.2178, calcd. for $C_{40}H_{48}N_2OCl_2Ru$: 744.2185.

***Complex* (6c)** was obtained as a green solid; yield: 141 mg (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.57 (s, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.39–7.35 (m, 1H), 7.34–7.29 (m, 6H), 7.26–7.23 (m, 2H), 7.00–6.88 (m, 2H), 6.55 (d, J = 8.3 Hz, 1H), 4.15 (s, 4H), 3.61 (sep, J = 6.8 Hz, 4H), 1.27 (d, J = 6.9 Hz, 12H), 1.18 (d, J = 6.6 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 286.85, 212.24, 153.61, 151.49, 148.85, 142.93, 137.00, 131.91, 129.82, 129.62, 129.37, 124.69, 124.51, 124.32, 122.34, 113.69, 54.76, 28.73, 26.49, 23.97; HR-MS: m/z = 778.1784, calcd. for $C_{40}H_{47}N_2OCl_3Ru$: 778.17584; analysis calcd. for $C_{40}H_{47}N_2OCl_3Ru$ (778.80): C 61.63, H 6.08, N 3.60; found: C 61.19, H 6.16, N 3.68.

***Complex* (6d)** was obtained as a green solid; yield: 125 mg (66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.55 (s, 1H), 8.18–8.14 (m, 2H), 7.53–7.47 (m, 4H), 7.45–7.40 (m, 1H), 7.33 (d, J = 7.7 Hz, 4H), 7.00–6.98 (m, 2H), 6.63 (d, J = 8.3 Hz, 1H), 4.16 (s, 4H), 3.57 (sep, J = 6.7 Hz, 4H), 1.27 (d, J = 6.9 Hz, 12H), 1.17 (d, J = 6.6 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 285.70, 211.08, 157.97, 152.17, 148.89, 145.60, 143.22, 136.77, 129.97, 129.39, 126.16, 125.35, 124.71, 123.29, 122.80, 116.78, 114.27, 54.77, 28.79, 26.51, 23.89; HR-MS: m/z = 789.2029, calcd. for $C_{40}H_{74}N_3O_3Cl_2Ru$: 789.2032.

Preparation of Catalyst Stock Solution

The ruthenium complex (c = 0.75 mmol L^{-1}: $4.0 \cdot 10^{-6}$ mol) was weighed into a 10 mL Schlenk tube. The tube was evacuated, backfilled with argon and 5.34 mL of dried toluene were added under a stream of argon. The Schlenk tube was kept in an ultrasonic bath for 1 min for complete dissolution of the precatalyst.

Catalyst Screening

All reactions were carried out in sealed 10-mL Schlenk tubes under an atmosphere of argon at 50 °C. In a 10-mL Schlenk tube, substrate (0.2–0.6 mmol) was dissolved in dry toluene under an atmosphere of argon. This solution was either ice-cooled to 0 °C or heated to 50 °C and catalyst (0.0015–0.025 mol%) (15–250 ppm) from a stock solution (0.75 mmol L^{-1}) in toluene was added (for screenings carried out at 0 °C, the stock solution was precooled to 0 °C). The substrate concentration was defined as c(S) = n(S)/[V(S) + V(toluene) + V(stock solution)]. For the determination of substrate conversion, samples (10 μL, substrate conc. 0.5 M) were taken after the specified times under a stream of argon and injected into GC vials containing 250 μL of a 25% (v/v) ethyl vinyl ether solution in toluene. The conversions were determined by GC.

Supporting Information

Full experimental details including NMR spectra, cyclic voltammograms, mass spectra and crystal structure data are contained in the Supporting Information.

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Advanced Synthesis & Catalysis

Supporting Information

Supporting Information

Fast olefin metathesis:

Synthesis of 2-aryloxy-substituted Hoveyda type complexes

and application in ring-closing metathesis

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General conditions for the UV/Vis experiments

All experiments were carried out in quartz cuvettes 110-QS with a path length of 10.00 mm. The temperature (30 °C) was adjusted using a thermostat and controlled with a thermometer. Butyl vinyl ether (BuVE) was used as substrates for measurements.

The following general procedure was applied in all experiments with BuVE: $1.00 \cdot 10^{-5}$ mol of precatalyst was dissolved in abs. toluene (50 mL) to give a $2.00 \cdot 10^{-4}$ M solution. Stock solution of BuVE (0.1 M) was prepared by dissolving of $2 \cdot 10^{3}$ mol of BuVE in abs toluene (20 mL). 1500 µL of stock solution of precatalyst were filled in a cuvette and an additional amount of toluene was added. This amount was calculated such that, after the addition of stock solution of substrate, the precatalyst concentration is $1.00 \cdot 10^{-4}$ M. The cuvette was then placed in the spectrometer and was allowed to adjust to the respective temperature. The measurement was started in the moment of the addition of the corresponding amount of preheated (same temperature as inside the cuvette) stock solution of substrate. During the measurement the cuvette was closed with a PTFE stopper (not gas tight).

Reaction of precatalysts with BuVE

To determine k_{obs}, the initiation process of the precatalyst was monitored by recording UV/Vis spectra to follow the spectral changes with time. The precatalyst's LMCT band absorbance – time traces were fitted with an exponential function.

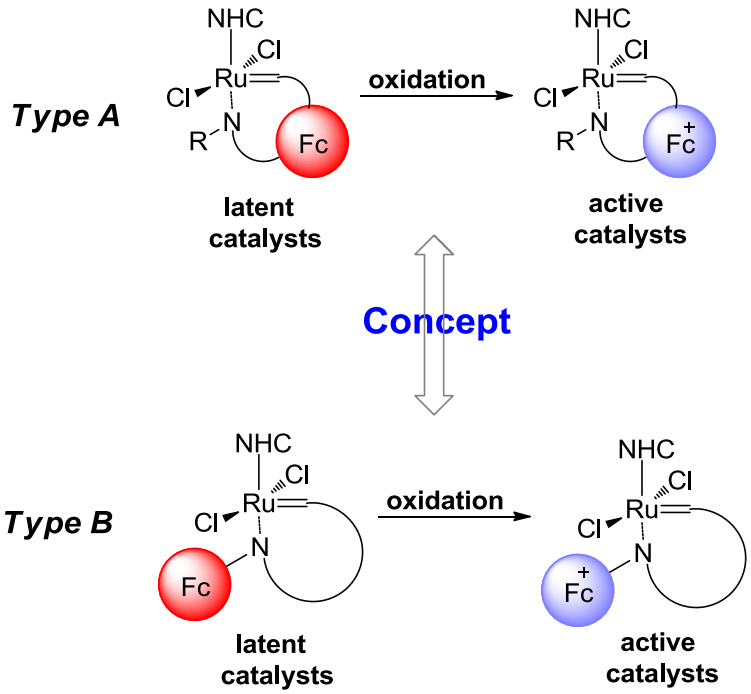
3.4. Oxidation-triggered Ring-opening Metathesis Polymerization

The content of this chapter has already been published:

Roman Savka, Sabine Foro, Markus Gallei, Matthias Rehahn, Herbert Plenio, *"Oxidation-triggered Ring-opening Metathesis Polymerization" Chemistry – A European Journal* **2013**, *19*, 10655–10662.

Spatial and temporal control over polymerization reactions can be achieved by using switchable catalysts. Switchable catalysts require physical or chemical stimuli to convert a catalytically inactive species into an active one.

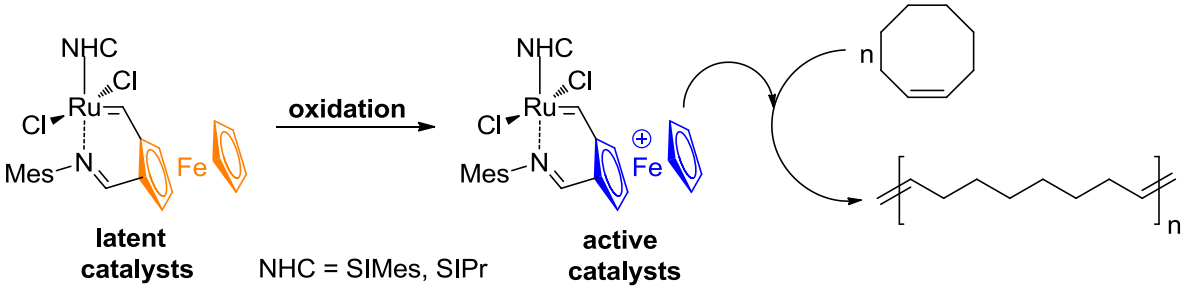
In this chapter the synthesis of oxidation-activated ruthenium-based catalysts for ROMP reaction of *cis*-cyclooctene is described. The synthesized complexes contain nitrogen donor and redox-active ferrocene group (Scheme 61). The redox-active unit is either directly attached to the nitrogen donor (Scheme 61, **Type B**) or in conjugation with ruthenium center (Scheme 61, **Type A**). The oxidation of the ferrocene group changes the donor ability of the nitrogen, and thus affects the initiation rate of the respective catalyst.



Scheme 61. The basic concept of the project.

- Oxidation of redox-active unit turns the catalyst on, to enable ROMP.
- Ferrocene as redox-active tag ⟹ easy to oxidize under mild conditions.

Two of the eight complexes were found to be latent catalysts for ROMP reactions in the reduced state, but are able to polymerize *cis*-cyclooctene following chemical or electrochemical oxidation of the ferrocenyl group (Scheme 62, Figure 3).



Scheme 62. ROMP reaction of *cis*-cyclooctene catalyzed by oxidized complexes.

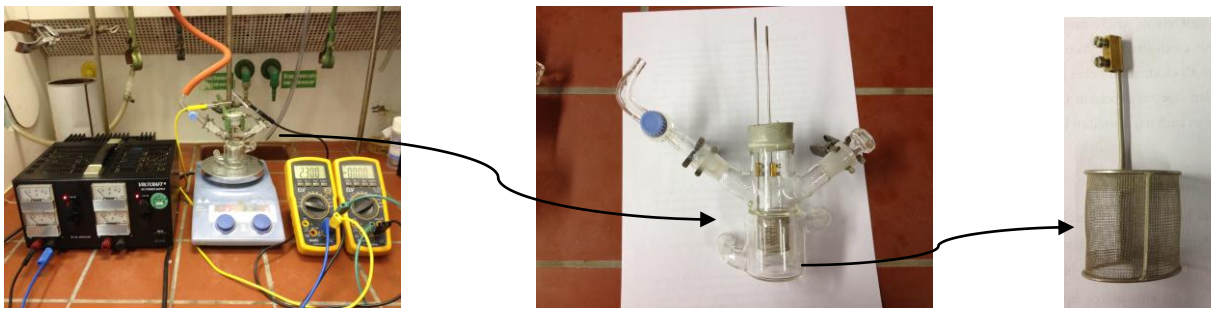


Figure 3. Electrochemical setup (left), electrochemical cell (middle) and platinum mesh anode (right).

My estimated contribution to this work is 90%.

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Oxidation-Triggered Ring-Opening Metathesis Polymerization

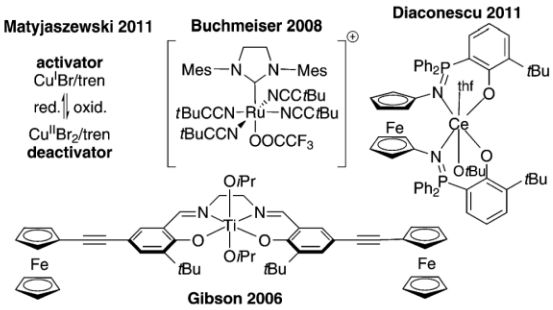
Roman Savka,[a] Sabine Foro,[c] Markus Gallei,[b] Matthias Rehahn,[b] and Herbert Plenio*[a]

Abstract: Eight new *N*-Hoveyda-type complexes were synthesized in yields of 67–92% through reaction of [$RuCl_2$-(NHC)(Ind)(py)] (NHC = 1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene (SIMes) or 1,3-bis(2,6-diisopropylphenylimidazolin)-2-ylidene (SIPr), Ind = 3-phenylindenylid-1-ene, py = pyridine) with various 1- or 1,2-substituted ferrocene compounds with vinyl and amine or imine substituents. The redox potentials of the respective complexes were determined; in all complexes an iron-centered oxidation reaction occurs at potentials close to $E = +0.5$ V. The crystal structures of the reduced and of the respective oxidized Hoveyda-type complexes were determined and show that the oxidation of the ferrocene unit has little effect on the ruthenium environment. Two of the eight new complexes were found to be switchable catalysts, in that the reduced form is inactive in the ring-opening metathesis polymerization of *cis*-cyclooctene (COE), whereas the oxidized complexes produce polyCOE. The other complexes are not switchable catalysts and are either inactive or active in both reduced and oxidized states.

Keywords: iron · olefin metathesis · oxidation · polymerization · ring-opening metathesis polymerization · ruthenium

Introduction

Latent or switchable catalysts require physical or chemical stimuli to convert a catalytically inactive species into an active one.[1] This principle has been put to good use in polymer chemistry since it allows spatial and temporal control over polymerization reactions.[2,3] Various stimuli, such as light-induced catalyst activation, have been employed in ring-opening polymerization[4] and ring-opening metathesis polymerization (ROMP) reactions (Scheme 1).[5] Buchmeiser et al. reported a ROMP catalyst that is activated upon irradiation with UV light.[6] Later, Grubbs et al. described an alternative approach using a pH-responsive catalyst that, in combination with a photo acid, also turns out to be a photosensitive ROMP catalyst.[7] The same group reported a different pH-sensitive catalyst in which an NHC ligand bound to ruthenium is decomposed by protons resulting in catalyst activation.[8] Slugovc et al. reported on pyridine/chloride-induced ROMP reactions.[9]



Scheme 1. Light- or redox-switchable polymerization catalysts (tren = tris[2-(dimethylamino)ethyl]amine).

The modulation of ligand donor ability by the protonation of basic groups attached to a ligand enables control over the stereochemistry of ROMP polymers because the electron density at the catalytic site has been shown to have an influence on the *E*/*Z* ratio of polynorbornenes.[10] Alternatively, activation of olefin metathesis catalysts is also possible by utilizing ultrasound-induced shear forces.[11] Recently, Matyjaszewski et al. demonstrated redox-controlled atom-transfer radical polymerization (ATRP) by electrochemically shuttling between a deactivated Cu^{2+} and an activated Cu^{+} state.[12] Ferrocene-based redox switches[13] attached to a catalytically active complex modulate the electron donation of

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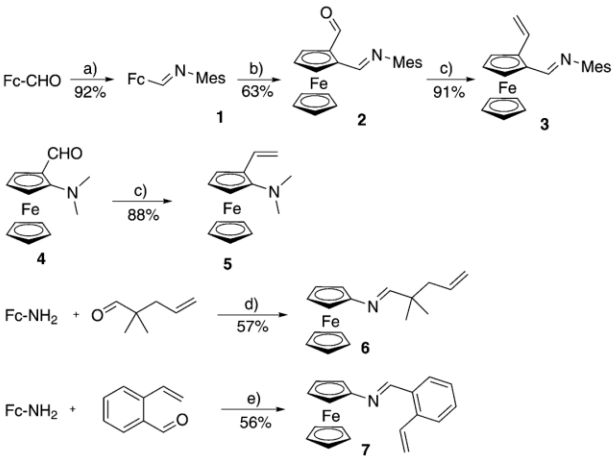
the respective ligand, which then oscillates between a high- and low-activity polymerization catalyst state.[14] In another example, ring-closing metathesis reactions were controlled through a redox-switched solubility change since the oxidation of a ferrocene-tagged olefin metathesis catalyst led to the precipitation of the salt from the nonpolar solvent, followed by redissolution upon reduction of the catalyst.[15]

Herein, we demonstrate oxidation-activated catalysts for ROMP reactions employing chemical, as well as electrochemical, stimuli.

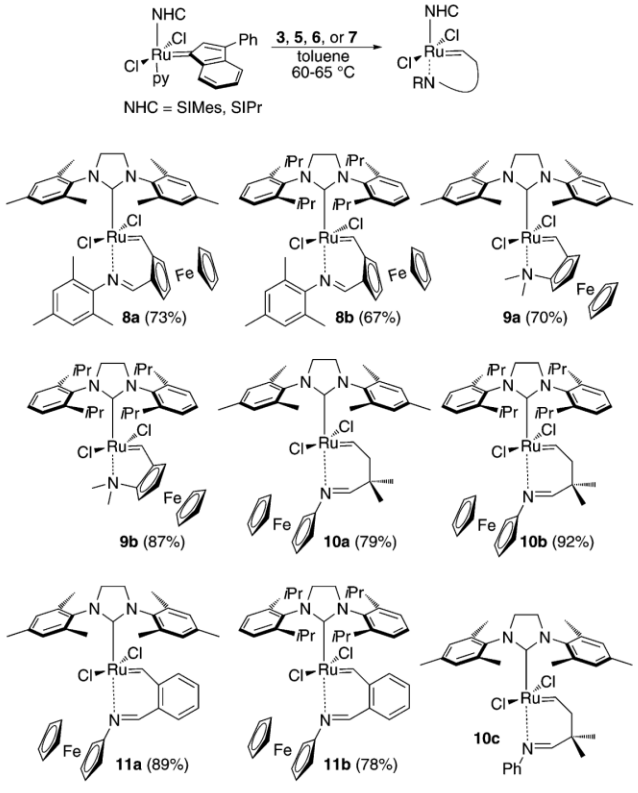
Results and Discussion

Synthesis of ligands and Hoveyda-type ruthenium complexes: The synthesis of new ferrocene-containing ligands is described in Scheme 2. The bidentate ligands are characterized by a nitrogen donor and a vinyl group bonded to a ferrocene group. The nitrogen donor is either directly attached to the ferrocene unit (**5**, **6**, and **7**) or in conjugation with the electrochemically active group (**3**) to allow a large change in the donor ability of this nitrogen donor upon oxidation of the ferrocene unit.[16] The vinyl group is required for the formation of a carbene complex with a suitable ruthenium precursor complex.

The reactions of the new ligands, **3**, **5**, **6**, and **7**, with the commercially available [$RuCl_2$-(NHC)(Ind)(py)] (Ind = 3-phenylindenylid-1-ene; py = pyridine; NHC = 1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene (SIMes) or 1,3-bis(2,6-diisopropylphenylimidazolin)-2-ylidene (SIPr)) result in the facile formation of the respective Hoveyda-type complexes in yields of 67–92% (Scheme 3). All complexes were characterized by NMR spectroscopy and mass spectrometry. Complexes with organometallic fragments in the benzylidene ligand are rare, although recently a Hoveyda-type complex with a {$Cr(CO)_3$} unit was reported.[17] Complexes, closely related to **8**, **9**, **10**, and **11**, with phenyl or 1,2-benzenediyl groups instead of ferrocenyl groups, have been reported in the literature before and several were shown to be latent catalysts in ROMP or ring-closing metathesis (RCM) reactions.[18]

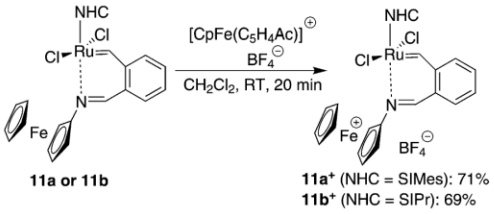


Scheme 2. Synthesis of ferrocenyl-based ligands (Fc = ferrocenyl; Mes = mesityl). Reagents and conditions: a) 2,4,6-trimethylaniline, TsOH (Ts = tosyl), toluene, reflux, overnight; b) *n*BuLi, THF, −78 °C, 1 h then DMF, −78 °C to RT; c) $MePPh_3I$, KO*t*Bu, THF, −10 °C to RT, overnight; d) molecular sieves, CH_2Cl_2, RT; e) molecular sieves, toluene, 100 °C.



Scheme 3. Synthesis of the new ferrocenyl-substituted Hoveyda complexes **8a**, **8b**, **9a**, **9b**, **10a**, **10b**, **11a**, and **11b** (yields given in brackets), and the structure of the known complex **10c**.

The complexes **8**–**11** can be oxidized, thereby converting an electron-donating ferrocene into an electron-withdrawing ferrocenium unit. To better understand the properties of the oxidized species, complexes **11a** and **11b** were reacted with acetyl ferrocenium BF_4^- to afford **11a**$^+$ and **11b**$^+$ in good yields (Scheme 4). The oxidized complexes are stable spe-



Scheme 4. Synthesis of oxidized ferrocenyl-substituted Hoveyda complexes.

cies and single crystals of **11a**$^+$ were obtained without special precautions. The NMR signals of the paramagnetic complexes **11a**$^+$ and **11b**$^+$ are broadened (especially for the protons close to the paramagnetic iron), but nonetheless the benzylidene proton can be identified at $\delta = 16.2$ (**11a**$^+$) and 16.9 ppm (**11b**$^+$), which corresponds to a nearly 2 ppm shift of this resonance in comparison with the neutral complexes **11a** and **11b**. The identification of the oxidized complexes is based on high-resolution mass spectra and a crystal structure analysis of **11a**$^+$.

Determination of redox potentials: The redox potentials for the eight new complexes, **8**–**11**, were determined (Table 1).

Table 1. Redox potentials of complexes **8**–**11**.[a]

Complex	Redox potential [V] ($E_a - E_c$ [mV])
8a	0.518 (64)
8b	0.513 (64)
9a	0.483 (96)
9b	0.511 (78)
10a	0.496 (81)
10b	0.482 (68)
11a	0.501 (72)
11b	0.485 (62)
10c	0.783 (–)[b]

[a] Solvent: CH_2Cl_2, scan rate: 100 mV s^{-1}, supporting electrolyte: 0.1 M NBu_4PF_6, potentials versus $FcMe_8$: $E_{1/2} = -0.01$ V. [b] Oxidation potential only, irreversible oxidation.

For all complexes a single reversible redox event is observed and all potentials are located in a narrow range of 0.48–0.52 V. This is not surprising for the structurally closely related complexes **10a**, **10b**, **11a**, and **11b**, but is unexpected for the four complexes **8a**, **8b**, **9a** and **9b**. In principle, two redox reactions have to be considered in such complexes: the oxidation of $Ru^{II/III}$ and of $Fe^{II/III}$. The similarity of the redox potentials in the series of complexes studied raised the question of whether the observed redox events are iron or ruthenium centered. On comparing the redox potentials of iron in nitrogen-substituted ferrocenes (typically close to $E = 0.0$ V)[19] with those of ruthenium in Grubbs–Hoveyda-type complexes ($E = +0.45$–$+1.1$ V)[20] the redox potentials observed in the Hoveyda-type complexes **8**–**11** appear to be closer to the $Ru^{II/III}$ potentials than to the typical $Fe^{II/III}$ potentials. However, it is known that, upon coordination of metal ions to donor atoms located in the vicinity to the ferrocene unit, the $Fe^{II/III}$ redox potentials can be shifted anodically by several hundred millivolts.[21] To firmly assign the iron- or ruthenium-centered nature of the oxidation reaction, the redox potential of the closely related and known[18c] complex **10c**, in which the ferrocenyl group is replaced by a phenyl group, was determined. Based on the oxidation curve, the $Ru^{II/III}$ redox potential for complex **10c** was estimated as approximately 0.75 V.[22] This is clearly higher than the $Fe^{II/III}$ redox potentials reported for complexes **8**–**11**, but is a typical $Ru^{II/III}$ value for such complexes.[20a] Based on this experiment, the redox potentials reported in Table 1 correspond to $Fe^{II/III}$.

X-ray crystal structure analysis of ferrocenyl-substituted Hoveyda-type complexes: The crystal structures[23] of complexes **8a**, **11a**, and of the oxidized complex **11a**$^+$ were determined (Figures 1, 2, and 3). Selected bond lengths and

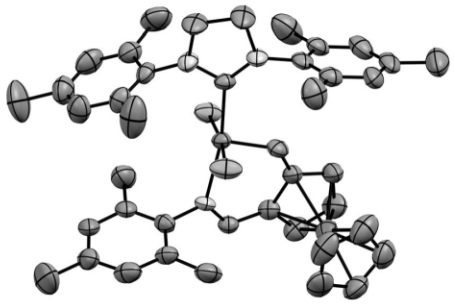


Figure 1. X-ray crystal structure of complex **8a**. Selected bond lengths [pm] and angles [°]: Ru=CH 181.3(1), Ru–C(NHC) 202.6(11), Ru–Cl 237.0(3), 237.8(3), Ru–N 217.6(8), Fe–C average 203.1; Cl-Ru-Cl 173.1(3), N-Ru-C(NHC) 168.8(3). CCDC-916243 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

angles are summarized in the legend of the respective figures. In all complexes studied, ruthenium displays a nearly square-pyramidal coordination geometry, which is typical for such complexes.[24] Complex **8a** crystallizes as a racemic mixture of the two planar chiral isomers. In the crystal of **8a**, the two chloro ligands are located *trans* to each other; there is no evidence (NOESY NMR spectroscopy) that a different structure (*cis*-chloro) occurs in solution. On com-

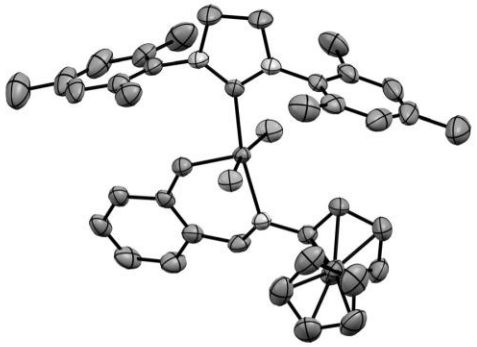


Figure 2. X-ray crystal structure of complex **11a**. Selected bond lengths [pm] and angles [°]: Ru=CH 182.6(3), Ru–C(NHC) 207.0(3), Ru–Cl 237.1(1), 237.5(1), Ru–N 213.1(3), Fe–C average 204.6; Cl-Ru-Cl 168.2(3), N-Ru-C(NHC) 170.1(1). CCDC-916235 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

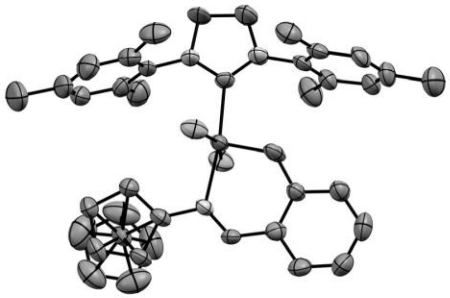
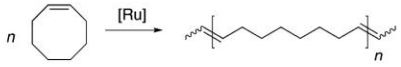


Figure 3. X-ray crystal structure of oxidized complex $\mathbf{11a}^+$ (cation only, BF_4^- omitted). Selected bond lengths [pm] and angles [°]: Ru=CH 182.8(8), Ru–C(NHC) 206.6(7), Ru–Cl 235.6(3), 233.1(3), Ru–N 213.2(6), Fe–C average 207.5; Cl-Ru-Cl 161.5(1), N-Ru-C(NHC) 170.8(1). CCDC-916218 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

paring the bond parameters of **8a** to those of the related complex by Slugovc et al.,[18a] which has a 1,2-phenylendiyl group instead of the ferrocene group, only two significant differences are found: the Ru–N bond in **8a** is almost 10 pm longer, and the Ru=CH bond in **8a** is approximately 5 pm shorter. The crystal structures of **11a** and $\mathbf{11a}^+$ were of particular interest in order to determine whether oxidation leads to characteristic changes in the structure of the oxidized complex compared to the neutral species (**11a**). On comparing the geometric parameters around ruthenium, only minor changes are seen; the iron-centered oxidation appears to have little influence. The Fe–C bond lengths in $\mathbf{11a}^+$ show modest elongation (**11a** Fe–C average = 204.6 pm and $\mathbf{11a}^+$ Fe–C average = 207.5 pm), which is indicative of iron-centered oxidation of the bimetallic complexes. The eclipsed orientation of the two cyclopentadienyl rings in $\mathbf{11a}^+$ is as normal as the staggered orientation of those rings in the neutral complex **11a**.[25] These structural changes reconfirm the iron-centered nature of the electrochemical redox processes.

Redox-switched ring-opening metathesis polymerization: The five complexes **8a**, **9a**, **9b**, **10a**, and **11a** were evaluated in the ROMP of *cis*-cyclooctene, which is a popular monomer in ROMP reactions (Scheme 5).[26] To be useful as



Scheme 5. ROMP reaction of *cis*-cyclooctene.

switched catalysts, the complexes need to be latent catalysts in the reduced state and display sufficient polymerization activity in the oxidized state.

Complexes **9a** and **10a** were found to rapidly polymerize *cis*-cyclooctene at room temperature and cannot be considered to be latent. The respective SIPr-based complexes **9b** and **10b** initiate the reaction more slowly, but still show significant ROMP activity with *cis*-cyclooctene under the same reaction conditions and thus are not suitable for switched ROMP reactions (Figure 4). The nonlatent behavior of com-

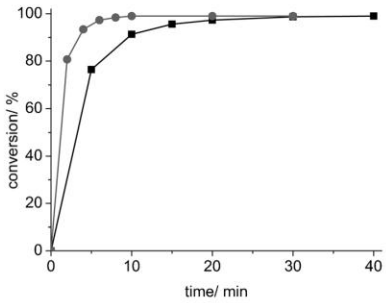


Figure 4. Conversion–time data for the ROMP reaction of *cis*-cyclooctene (0.2 mol L^{-1}) at 20 °C in toluene/CH_2Cl_2 with complexes **9a** (●; 0.1 mol %) and **10a** (■; 0.1 mol %).

plex **10a** is closely related to that of **10c** (Ph instead of Fc), which displays room temperature activity in the ROMP of dicyclopentadiene.[18c] The nonlatency of complexes **9** reconfirms the previous observation that five-membered-ring Hoveyda-type chelates initiate reactions much faster than six-membered-ring chelates.[18a] In this vain, complex **11a** shows negligible ROMP activity at room temperature; unfortunately the same holds true for the oxidized complex $\mathbf{11a}^+$. This is in line with the behavior of the related com-

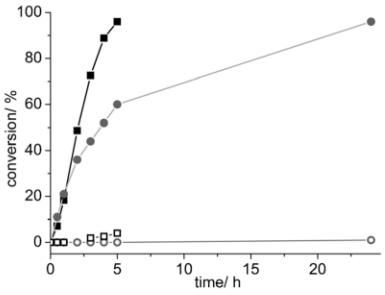


Figure 5. Conversion–time data for the ROMP reaction of *cis*-cyclooctene (0.2 mol L^{-1}) at 20 °C in toluene/CH_2Cl_2 (12:1) with the complexes **8a** (■,□; 0.1 mol %) and **8b** (●,○; 0.2 mol %) with (■,●) or without (□,○) added oxidizer (acetylferrocenium tetrafluoroborate).

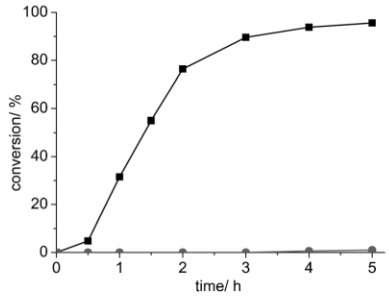


Figure 6. Conversion–time data for the ROMP reaction of *cis*-cyclooctene (0.2 mol L^{-1}) at 20 °C in CH_2Cl_2 with the complex **8a** (●; 0.1 mol %) and electrochemically oxidized **8a** (■; 0.1 mol %).

plex with Ph instead of Fc, which was previously found to be a very reluctant ROMP catalyst.[18a]

In contrast, complexes **8a** and **8b** appear to be useful in redox-switched ROMP (Figure 5). The reaction of *cis*-cyclooctene with **8a** gives only 4 % conversion after 5 h. Adding an oxidizer (acetylferrocenium tetrafluoroborate) to complex **8a** immediately generates **8a**$^+$, which is a much more active catalyst in ROMP reactions. Even better results are obtained with the more slowly initiating complex **8b** in the same reaction; with **8b**, after 24 h, less than 1 % of the monomer is consumed, whereas **8b**$^+$ converts 96 % of the monomer into a polymer during the same period of time (Figure 5).

We do not know with certainty, why complexes **11** are inactive following oxidation and why complexes **8** are switchable catalysts. The main difference between the two complexes is that the oxidation of the ferrocene unit in complexes **11** has a smaller influence on the electron density at the ruthenium atom than in complexes **8**. This becomes apparent when comparing the redox potentials of related Hoveyda-type complexes bearing substituents on the 2-OPh or on the 1,2-benzenediyl unit.[20b,c] In complexes **8**, oxidation of the ferrocene unit acts on the nitrogen donor and on the ruthenium. In complexes **11**, the oxidation of the ferrocenyl unit weakens nitrogen donation, but has little influence on the ruthenium atom. It is known that weak donors *trans* to the NHC ligand and electron deficiency at the ruthenium center both enhance precatalyst activation.[20b] Both of these effects are active in complexes **8**$^+$ and this likely contributes to their better switchability in comparison with **11**.

Next, we were interested in whether the ROMP activity can also be switched electrochemically. Analogous experiments by using complex **8a** were done in CH_2Cl_2 as the solvent and in the presence of a supporting electrolyte, Bu_4NPF_6 (Figure 6). Again, complex **8a** was found to be a latent catalyst and, over 5 h, only about 1 % of the monomer underwent a ROMP reaction. In the next experiment, a solution of complex **8a** with *cis*-cyclooctene in CH_2Cl_2 was oxidized electrochemically on a platinum mesh electrode. A constant current of 1 mA was applied to the cell until 0.385 C of charge had been passed through the solution. The electrochemical oxidation of **8a** generates a catalytically active species that converts 95 % of the monomer into a polymer over the following 5 h. To make sure that the polymerization of the monomer is induced by oxidation of the ruthenium complex, the experiment was repeated in the absence of ruthenium complex **8a**, under otherwise identical conditions. Polymerization of *cis*-cyclooctene was not observed. This clearly shows that the oxidation of precatalyst **8a** to form **8a**$^+$ is responsible for the redox-switched catalysis.

The molar masses of the polycyclooctene (polyCOE) compounds produced with complexes **9a** and **10a** were determined by using size-exclusion chromatography (SEC) against polystyrene standards (Table 1). Unfortunately, the polymer obtained from the switchable catalysts **8a** and **8b** was insoluble in THF[27] and SEC data could not be obtained.[28] This insolubility of polyCOE in various solvents is not uncommon and has been reported previously.[29] Nonetheless, the question remains, whether the insolubility of polyCOE is due to very long polymer chains or whether an unknown (oxidation-induced) process leads to significant cross-linking. To clarify this, the oxidation-triggered polymerization of **8b** was repeated for a much higher ratio of COE/Ru (100:1) to obtain shorter polymer chains. The polymer formed in this experiment is soluble and (according to NMR spectroscopy) is a normal linear polyCOE. SEC data (Figure SI42 in the Supporting Information) reveal the formation of a polymer with $M_n = 88000\ g\,mol^{-1}$ and $M_w = 129000\ g\,mol^{-1}$, indicative of a relatively low initiation efficiency of the switched catalyst. The insolubility of the ("switched") polymer at COE/Ru = 1000 appears to be due to the length of the (linear) polymer chains.

The ^1H NMR spectra of the various polyCOE compounds obtained (or the $CDCl_3$ soluble fraction) display two peaks, at $\delta = 5.34$ and 5.38 ppm, which can be integrated to provide the *trans*/*cis* ratio (data are listed in Table 2). This parameter depends very much on catalyst design and has an influence on T_m.

Table 2. Data for polyCOE synthesis obtained with complexes **8a**, **9a**, and **10a**.

Catalyst	Ratio COE/Ru	M_n [g mol^{-1}][c]	PDI	*trans*/*cis* ratio[e]	Time	Conversion [%]
8a^{+}[a]	1000	–[d]	–	3.2:1	5 h	96
8a^{+}[b]	1000	–[d]	–	3.1:1	5 h	95
8b^{+}[a]	500	–[d]	–	2.8:1[f]	24 h	96
9a	1000	55760	1.16	4.3:1	10 min	99
10a	1000	66990	1.22	4.3:1	30 min	99

[a] Chemical oxidation. [b] Electrochemical oxidation. [c] Solvent: THF. [d] Insoluble in THF. [e] Determined by NMR spectroscopy in $CDCl_3$. [f] Same ratio observed for the soluble polyCOE obtained at COE/Ru = 100.

Conclusion

Eight new Hoveyda-type complexes with ferrocenyl substituents were synthesized. Two of these complexes (**8a** and **8b**) were found to be latent catalysts for ROMP reactions in the reduced state, but are able to polymerize *cis*-cyclooctene following chemical or electrochemical oxidation of the ferrocenyl group. The oxidative stimulus by using mild chemical oxidizers is orthogonal to most organic functional groups. The electrochemical initiation of the polymerization through electrodes adjusted to an oxidative potential is unprecedented for ROMP reactions and could enable microstructure control of the polymerization process. Furthermore, control over the cross-linking process, might provide access to thermally triggered shape-memory polymers.

Experimental Section

Synthesis of complexes 8a and 8b: A Schlenk flask containing [$RuCl_2$(SIMes)(Ind)(py)] (200 mg, 0.26 mmol) or [$RuCl_2$(SIPr)(Ind)(py)] (216 mg, 0.26 mmol) was evacuated and back-filled with nitrogen three times. Next, a stock solution of **3** (0.1 M, 3.1 mL) in dry and degassed toluene was added under an atmosphere of nitrogen. The resulting solution was heated for 1.5 h at 65 °C. The volatile compounds were removed in vacuo and the residue purified by column chromatography (cyclohexane/acetone/NEt_3, 100:20:1 v/v/v). After evaporation of the volatile compounds, *n*-pentane (5 mL) was added to the remaining solid, and the mixture was sonicated and kept in a fridge at −35 °C for 2 h. The precipitate was collected by filtration and dried in vacuo.

*Complex **8a***: Complex **8a** was obtained as a brown-orange powder (156 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 17.45 (s, 1H; Ru=C*H*), 8.06 (s, 1H; N=C*H*), 7.12 (s, 1H; aromatic H^{SIMes}), 7.01 (s, 1H; aromatic H^{SIMes}), 6.84 (s, 1H; aromatic H^{SIMes}), 6.75 (s, 1H; aromatic H^{SIMes}), 6.56 (s, 2H; aromatic H^{Mes}), 4.80–4.77 (m, 1H; H^{Fc}), 4.47 (t, J = 2.5 Hz, 1H; H^{Fc}), 4.40–4.37 (m, 1H; H^{Fc}), 4.16 (s, 5H; H^{Fc}), 4.09–4.02 (m, 2H; NCH_2), 3.91–3.84 (m, 2H; NCH_2), 2.68 (s, 3H; *o*-Me^{SIMes}), 2.50 (s, 3H; *o*-Me^{SIMes}), 2.45 (s, 3H; *p*-Me), 2.27 (s, 3H; *p*-Me), 2.18 (s, 3H; *o*-Me^{SIMes}), 2.15 (s, 3H; *p*-Me), 1.99 (s, 3H; *o*-Me^{SIMes}), 1.87 (s, 3H; *o*-Me^{Mes}), 1.81 ppm (s, 3H; *o*-Me^{Mes}); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 314.13, 217.03, 169.40, 146.80, 139.30, 139.17, 138.75, 138.71, 138.62, 138.13, 137.92, 134.76, 134.46, 132.01, 129.51, 129.14, 128.62, 99.30, 76.65, 75.15, 72.77, 70.22, 65.00, 51.92, 50.98, 21.39, 21.23, 20.90, 20.76, 20.35, 20.03, 19.19, 18.33 ppm; HRMS (EI): *m*/*z* calcd for $C_{42}H_{47}N_3Cl_2FeRu$: 821.1531 $[M]^+$; found: 821.1511. Single crystals of **8a** were obtained by slow evaporation of CH_2Cl_2/cyclohexane at ambient temperature under air.

*Complex **8b***: Complex **8b** was obtained as a brown powder (158 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 17.49 (s, 1H; Ru=C*H*), 8.12 (s, 1H; N=C*H*), 7.63 (t, J = 7.7 Hz, 1H; aromatic *p*-H^{SIPr}), 7.52 (d, J = 7.1 Hz, 1H; aromatic *m*-H^{SIPr}), 7.43–7.37 (m, 2H; aromatic H^{SIPr}), 7.16 (t, J = 7.8 Hz, 2H; aromatic H^{SIPr}), 6.65 (s, 2H; aromatic H^{Mes}), 4.81–4.79 (m, 1H; H^{Fc}), 4.47 (t, J = 2.6 Hz, 1H; H^{Fc}), 4.44–4.36 (m, 1H; NCH_xH_y), 4.34–4.32 (m, 1H; H^{Fc}), 4.23–4.10 (m, 8H; 5H^{Fc}, 2C*H*(Me)$_2$, NCH_xCH_y), 4.09–3.97 (m, 2H; NCH_2), 3.05 (sep, J = 6.8 Hz, 1H; C*H*(Me)$_2$), 3.00 (sep, J = 6.8 Hz, 1H; C*H*(Me)$_2$), 2.22 (s, 3H; *p*-Me^{Mes}), 1.93 (s, 3H; *o*-Me^{Mes}), 1.75 (s, 3H; *o*-Me^{Mes}), 1.38 (d, J = 7.0 Hz, 3H; Me^{iPr}), 1.36 (d, J = 6.6 Hz, 3H; Me^{iPr}), 1.32 (d, J = 6.5 Hz, 3H; Me^{iPr}), 1.17 (d, J = 6.9 Hz, 3H; Me^{iPr}), 1.14 (d, J = 6.8 Hz, 3H; Me^{iPr}), 1.09 (d, J = 6.8 Hz, 3H; Me^{iPr}), 0.92 (d, J = 6.6 Hz, 3H; Me^{iPr}), 0.58 ppm (d, J = 6.5 Hz, 3H; Me^{iPr}); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 309.77, 220.16, 169.42, 150.34, 149.55, 149.18, 148.62, 147.32, 138.69, 135.23, 134.90, 132.47, 130.42, 129.83, 129.18, 129.08, 128.47, 124.83, 124.41, 123.75, 97.38, 76.53, 75.47, 72.71, 70.27, 66.43, 55.09, 53.66, 29.54, 28.72, 28.41, 28.23, 28.02, 27.05, 26.38, 26.34, 24.59, 23.90, 22.72, 22.36, 21.16, 20.97, 20.72 ppm; HRMS (EI): *m*/*z* calcd for $C_{48}H_{59}N_3Cl_2FeRu$: 905.2470 $[M]^+$; found: 905.2472.

Synthesis of complexes 9a and 9b: A Schlenk flask containing [$RuCl_2$(SIMes)(Ind)(py)] (200 mg, 0.26 mmol) or [$RuCl_2$(SIPr)(Ind)(py)] (216 mg, 0.26 mmol) was evacuated and back-filled with nitrogen three times. Toluene (3 mL) and **5** (75 µL, 0.29 mmol) were added under an atmosphere of nitrogen and the resulting mixture was heated for 1.5 h at 65 °C. After evaporation of the volatile compounds, methanol (5 mL) was added to the remaining solid, and the mixture sonicated and kept in the fridge at −35 °C for 2 h. The precipitate was collected by filtration, washed with cold methanol, and dried in vacuo.

*Complex **9a***: Complex **9a** was obtained as a pink powder (131 mg, 70% yield). ^{1}H NMR (500 MHz, C_6D_6): δ = 16.43 (d, J = 0.8 Hz, 1H), 6.94 (s, 2H), 6.91 (s, 2H), 4.26 (s, 5H), 4.02–4.00 (m, 1H), 3.86 (t, J = 2.6 Hz, 1H), 3.74 (dd, J = 2.7, 1.1 Hz, 1H), 3.45 (s, 4H), 2.68 (s, 9H), 2.64 (s, 9H), 2.19 ppm (s, 6H); ^{13}C NMR (126 MHz, C_6D_6): δ = 291.81, 212.61, 129.79, 129.67, 115.15, 101.18, 69.91, 68.87, 61.11, 57.58, 51.72, 21.15, 19.99 ppm (brs); HRMS (EI): *m*/*z* calcd for $C_{34}H_{41}N_3Cl_2FeRu$: 719.1061 $[M]^+$; found: 719.1056.

*Complex **9b***: Complex **9b** was obtained as a pink powder (182 mg, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 16.45 (d, J = 0.8 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.39–7.27 (m, 4H), 4.50 (dt, J = 2.5, 0.8 Hz, 1H), 4.23 (t, J = 2.7 Hz, 1H), 4.20 (s, 5H), 4.09 (s, 4H), 3.80 (dd, J = 2.6, 1.1 Hz, 1H), 3.75 (sep, J = 6.8 Hz, 4H), 2.80 (brs, 3H), 2.63 (brs, 3H), 1.40 (d, J = 6.6 Hz, 6H), 1.28 ppm (t, J = 6.9 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 294.43, 214.13, 148.65, 137.78, 129.32, 124.43, 124.35, 114.01, 100.96, 69.82, 69.17, 62.09, 57.33, 54.72, 53.65 (brs), 28.70, 28.59, 26.65, 26.56, 24.38, 24.19 ppm; HRMS (EI): *m*/*z* calcd for $C_{40}H_{53}N_3Cl_2FeRu$: 803.2000 $[M]^+$; found: 803.1999.

Synthesis of complexes 10a and 10b: A Schlenk flask containing [$RuCl_2$(SIMes)(Ind)(py)] (200 mg, 0.26 mmol) or [$RuCl_2$(SIPr)(Ind)(py)] (216 mg, 0.26 mmol) was evacuated and back-filled with nitrogen three times. Next, a solution of **6** (92 mg, 0.31 mmol) in dry and degassed toluene (3 mL) was added under an atmosphere of nitrogen. The resulting mixture was heated for 1 h at 60 °C. After evaporation of the volatile compounds, methanol (10 mL) was added to the remaining solid, and the mixture was sonicated. The precipitate was collected by filtration, washed with methanol, and dried in vacuo.

*Complex **10a***: Complex **10a** was obtained as a brownish powder (156 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 18.72 (t, J = 5.2 Hz, 1H), 8.08 (s, 1H), 7.03 (s, 4H), 4.04 (s, 9H), 3.92 (t, J = 1.9 Hz, 2H), 3.90 (t, J = 1.9 Hz, 2H), 2.96 (d, J = 5.2 Hz, 2H), 2.71–2.23 (m, 18H), 1.05 ppm (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 343.65, 218.31, 173.29, 140.10, 138.39, 129.57, 103.11, 70.29, 66.40, 63.74, 51.59 (brs), 42.10, 26.85, 21.39, 20.28 (brs), 18.42 ppm (brs); HRMS (EI): *m*/*z* calcd for $C_{37}H_{45}N_3Cl_2FeRu$: 759.1374 $[M]^+$; found: 759.1414.

*Complex **10b***: Complex **10b** was obtained as a brownish powder (202 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 18.80 (t, J = 4.8 Hz, 1H), 8.21 (s, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.32 (d, J = 7.7 Hz, 4H), 4.10 (s, 4H), 3.97 (d, J = 2.9 Hz, 7H), 3.88 (t, J = 1.9 Hz, 2H), 3.60 (d, J = 12.6 Hz, 4H), 2.70 (d, J = 4.8 Hz, 2H), 1.22 (d, J = 6.8 Hz, 24H),

1.02 ppm (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=220.03, 175.24, 165.53, 149.33 (brs), 129.32, 124.55, 104.13, 70.14, 66.70, 64.80, 63.00, 54.43, 41.31, 28.77, 26.71, 26.63, 23.64 ppm; HRMS (EI): *m*/*z* calcd for $C_{43}H_{57}N_3Cl_2FeRu$: 843.2313 $[M]^+$; found: 843.2331.

Synthesis of complexes 11a and 11b: A Schlenk flask containing [$RuCl_2$-(SIMes)(Ind)(py)] (200 mg, 0.26 mmol) or [$RuCl_2$(SIPr)(Ind)(py)] (216 mg,0. 26 mmol) was evacuated and back-filled with nitrogen three times. A stock solution of **7** (3.1 mL, 0.1 M) in dry and degassed toluene was added under an atmosphere of nitrogen. The resulting mixture was heated for 1 h at 60 °C. After evaporation of the volatile compounds, methanol (5 mL) was added to the remaining solid, the mixture was sonicated and cooled to −40 °C. The precipitate was collected by filtration, washed with methanol, and dried in vacuo.

*Complex **11a***: Complex **11a** was obtained as a dark-green powder (180 mg, 89 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ=18.65 (s, 1H), 9.10 (s, 1H), 7.67 (td, *J*=7.5, 1.3 Hz, 1H), 7.50 (d, *J*=7.5 Hz, 1H), 7.45 (td, *J*=7.5, 1.3 Hz, 1H), 7.15 (s, 4H), 6.71 (d, *J*=7.7 Hz, 1H), 4.21 (t, *J*=1.9 Hz, 2H), 4.20 (s, 5H), 4.14 (s, 4H), 4.07 (t, *J*=1.9 Hz, 2H), 2.74–2.31 ppm (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=310.84, 310.75, 214.52, 164.58, 150.13, 141.62, 140.43 (brs), 138.72 (brs), 134.65, 133.06, 129.81, 128.56, 127.92 (brs), 127.07, 126.37 (brs), 123.62, 104.04, 70.68, 67.24, 64.72, 53.57, 52.46 (brs), 51.07 (brs), 21.46, 20.53 (brs), 18.53 ppm (brs); HRMS (EI): *m*/*z* calcd for $C_{39}H_{41}N_3Cl_2FeRu$: 779.1061 $[M]^+$; found: 779.1072. Single crystals of **11a** were obtained by slow evaporation of CH_2Cl_2/cyclohexane at ambient temperature under air.

*Complex **11b***: Complex **11b** was obtained as a dark-green powder (175 mg, 78 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ=18.65 (s, 1H), 9.16 (s, 1H), 7.64 (td, *J*=7.5, 1.3 Hz, 1H), 7.60 (brs, 2H), 7.50–7.45 (m, 2H), 7.43 (d, *J*=7.8 Hz, 4H), 6.62 (d, *J*=7.7 Hz, 1H), 4.30 (t, *J*=1.9 Hz, 2H), 4.19 (brs, 4H), 4.10 (s, 5H), 4.05 (t, *J*=1.9 Hz, 2H), 3.86–3.45 (brm, 4H), 1.45–1.20 (brm, 18H), 1.02 ppm (brs, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=303.56, 215.75, 164.64, 139.23, 133.87, 132.39, 128.34, 128.00, 127.19, 126.77, 125.55, 123.76 (brs), 123.39, 104.04, 69.27, 67.52, 66.12, 65.95, 64.41, 28.42–25.57 ppm (several broad signals); HRMS (EI): *m*/*z* calcd for $C_{45}H_{53}N_3Cl_2FeRu$: 863.2000 $[M]^+$; found: 863.2000.

Synthesis of oxidized complexes 11a$^+$ and 11b$^+$; A Schlenk flask containing complex **11a** (40 mg, 0.051 mmol) or **11b** (44 mg, 0.051 mmol) and acetylferrocenium tetrafluoroborate (13.9 mg, 0.051 mmol) was evacuated and back-filled with nitrogen three times. CH_2Cl_2 (2 mL) was added under an atmosphere of nitrogen and the resulting solution was stirred for 20 min at room temperature. The solution was filtered and the filtrate was concentrated in vacuo. Next, diethyl ether (50 mL) was added and the precipitate was collected by filtration. The precipitate was washed with diethyl ether and toluene and dried in vacuo.

*Complex **11a**$^+$*: Paramagnetic complex **11a**$^+$ was obtained as a brownish powder (31 mg, 71 % yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ=16.21 ppm (s, 1H; Ru=C*H*); HRMS (EI): *m*/*z* calcd for $C_{39}H_{41}N_3Cl_2FeRu$: 779.1061 $[M-BF_4]^+$; found: 779.1060. Single crystals of **11a**$^+$ were obtained by slow evaporation of CH_2Cl_2/benzene at ambient temperature under air.

*Complex **11b**$^+$*: Paramagnetic complex **11b**$^+$ was obtained as a brown powder (33 mg, 69 % yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ=16.86 ppm (s, 1H; Ru=C*H*); HRMS (EI): *m*/*z* calcd for $C_{45}H_{53}N_3Cl_2FeRu$: 863.2000 $[M-BF_4]^+$; found: 863.1959.

General procedure for the ROMP reaction of *cis*-cyclooctene by utilizing the oxidized complexes: A Schlenk tube (10 mL) charged with complexes **8**, **9**, **10**, or **11** (0.0025 mmol) and acetylferrocenium tetrafluoroborate (0.8 mg, 0.0025 mmol) was evacuated and back-filled with argon three times. CH_2Cl_2 (500 μL) was added under a stream of argon and the mixture was stirred for 10 min at room temperature. Next, a stock solution of *cis*-cyclooctene in toluene (6.0 mL (corresponding to a catalyst loading of 0.10 mol %) or 3.0 mL (catalyst loading of 0.2 mol %)) was added to the mixture. For the determination of substrate conversion, samples (60 μL) were taken after the specified times under a stream of argon and injected into vials containing ethyl vinyl ether (50 μL) and methanol (500 μL). The mixture was filtered through a clean pad of cotton to remove the insoluble polymer and the solution was analyzed by GC. The same procedure was applied for polymerization reactions utilizing complexes **8a**, **8b**, **9a**, **10a**, and **11a**.

General procedure for the ROMP reaction of *cis*-cyclooctene utilizing oxidized complex 8a and electrolysis at constant current: A three-necked electrochemical cell equipped with a magnetic stirring bar, argon inlet, platinum mesh anode, and silver spiral cathode was evacuated and back-filled with argon three times. Next, a stock solution of *cis*-cyclooctene in CH_2Cl_2 (20 mL) and complex **8a** (3.3 mg, 4.0 μmol) dissolved in CH_2Cl_2 (300 μL) were added under a stream of argon. A constant current of 1 mA was applied to the cell until 0.385 C of charge had been passed through the solution (*t*=385 s). For the determination of substrate conversion, samples (60 μL) were taken after the specified times under a stream of argon and injected into vials containing ethyl vinyl ether (50 μL) and methanol (500 μL). The mixture was filtered through a clean pad of cotton to remove insoluble polymer and the solution analyzed by GC.

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Supporting Information

Oxidation-Triggered Ring-Opening Metathesis Polymerization

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Supporting Information

Oxidation-triggered Ring-opening Metathesis Polymerization

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General experimental: All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. All reactions involving ruthenium complexes were performed under an atmosphere of argon. CH_2Cl_2 (99.5%) were obtained from Grüssing GmbH, toluene from Sigma–Aldrich (lab reagent grade, 99.3%). The solvents were dried by passing through a column filled with activated alumina and a second column; either filled with a supported copper catalyst (toluene) or, again, activated alumina (CH_2Cl_2). Toluene was additionally dried over CaH_2 and distilled onto molecular sieves (4 Å) under an atmosphere of argon. Dimethylformamide was heated at reflux over calcium hydride, distilled under reduced pressure and degassed using freeze-pump-thaw technique. Tetrahydrofuran was dried under sodium and distilled under an argon atmosphere. All solvents were stored over molecular sieves (4 Å). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC300 or a DRX500 spectrometer. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (^1H, ^{13}C NMR = 0.0 ppm) or the residual peak of chloroform (^1H NMR=7.26, ^{13}C NMR = 77.16 ppm), benzene (^1H NMR = 7.16, ^{13}C NMR = 128.06 ppm) or methylene chloride (^1H NMR = 5.32, ^{13}C NMR = 53.84 ppm). [1] Abbreviations for NMR: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad signal. Thin layer chromatography (tlc) was performed by using silica 60 F 254 (0.2 mm) on aluminum plates. Preparative chromatography was done on Merck silica 60 (0.063–0.02 mesh). GC experiments were run on a Clarus 500 GC with an autosampler and FID detector [column: Varian CP-Sil 8 CB (l=15 m, d_i=0.25 mm, d_F=1.0 Lm, N_2-flow: 17 cms^{-1}; split 1:50), injector temperature: 270°C, detector temperature: 350°C]. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as a counter electrode. The pseudoreference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of octamethylferrocene ($E_{1/2}$ = -0.01 V (CH_2Cl_2)) NBu_4PF_6 (0.1 mol L^{-1}) was used as a supporting electrolyte. Molecular weights were determined by using SEC performed with THF as the mobile phase (flow rate 1 mL min^{-1}) on a SDV column set from PSS (SDV 10^3, SDV 10^5, SDV 10^6) at 30 °C with a Waters 410 RI-detector. Calibration was carried out using PS standards (from Polymer Standard Service, Mainz). Acetylferrocenium tetrafluoroborate,[2] Fc-NH_2,[3] ferrocene **4**,[4] and 2-vinylbenzaldehyde[5] were prepared according to literature procedures. X-ray crystal structure data were solved and refined using the SHELX program package.[6]

Preparation of 0.2 M stock solutions of *cis*-cyclooctene. *Solution in toluene*: a standard stock solution was prepared by dissolving of *cis*-cyclooctene (524.7 µL, 4.00 mmol) and mesitylene (554.5 µL, 4.00 mmol) in dry toluene (20.0 mL) under an atmosphere of argon.
Solution in methylene chloride: a standard stock solution was prepared by dissolving of *cis*-cyclooctene (1312 µL, 10.0 mmol), mesitylene (1386 µL, 10.0 mmol) and Bu_4NPF_6 (1.93 g, 5.00 mmol) in dry CH_2Cl_2 (50.0 mL) under an atmosphere of argon.

Synthesis of 1 (modified synthesis)[7]: Ferrocenecarbaldehyde (2.0 g, 9.3 mmol) was dissolved in toluene (150 mL) in a 250 mL round bottom flask. 2,4,6-Trimethylaniline (1.51 mL, 10.8 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added. The resulting solution was refluxed in a Dean–Stark apparatus overnight. After cooling to room temperature the toluene solution was treated with saturated solution of $NaHCO_3$, the organic layer was separated, dried over magnesium sulfate and concentrated *in vacuo*. The pure product was obtained by crystallization from pentane at -40°C.

1 was obtained as orange-red crystals (2.77 g, 90% yield). ^1H NMR (500 MHz, $CDCl_3$): δ= 8.07 (s, 1H, CH=N), 6.88 (s, 2H, C_6H_2), 4.81 (s, 2H, C_5H_4), 4.49 (s, 2H, C_5H_4), 4.27 (s, 5H, C_5H_5), 2.28 (s, 3H, Me), 2.17 (s,

6H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 163.22, 149.33, 132.66, 128.81, 127.05, 81.02, 71.01, 69.26, 68.85, 20.87, 18.50.

Synthesis of 2: To a stirred solution of **1** (1.22 g, 3.7 mmol) in dry THF (10 mL) under nitrogen atmosphere at -78°C *n*BuLi (2.5 M in hexane, 1.17 mL, 4.4 mmol) was added dropwise. The mixture was stirred for 1h at this temperature, observing the formation of red precipitate. Next, dry dimethylformamide (569 µL, 7.4 mmol) was added dropwise with vigorous stirring and the mixture slowly allowed to warm to room temperature. After stirring for 1 h at room temperature the mixture was poured onto ice and the product was extracted with diethyl ether (3×100 mL). The combined organic phases, washed with brine, and dried over $MgSO_4$. The volatiles were removed *in vacuo* and the residue purified by column chromatography (cyclohexane/diethyl ether, 4:1 v/v + 10% NEt_3) affording the desired product as orange-red viscous oil (837 mg, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 10.45 (s, 1H), 8.52 (s, 1H), 6.89 (s, 2H), 5.30 (s, 1H), 5.10 – 5.06 (m, 1H), 4.84 (t, *J* = 2.4 Hz, 1H), 4.37 (s, 5H), 2.29 (s, 3H), 2.17 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6): δ== 92.89, 161.83, 149.88, 132.82, 129.30, 126.89, 83.01, 80.03, 73.81, 73.64, 73.32, 70.90, 20.95, 18.72. HRMS (EI): m/z calcd for $C_{21}H_{21}NOFe$: 359.0972 $[M]^+$; found: 359.0950.

Synthesis of 3 and 5: A Schlenk flask containing methyltriphenylphosphonium iodide (891 mg, 2.2 mmol) was evacuated and back-filled with nitrogen three times. THF (15 mL) was added by syringe and the formed suspension was cooled to -10°C. KO*t*Bu (247 mg, 2.2 mmol) was added in portions to the stirred mixture under a stream of nitrogen, and stirring was continued at -10°C for 20 min. Next, a solution of **2** (610 mg, 1.7 mmol) or **4** (437 mg, 1.7 mmol) in THF (10 mL) was added. The mixture was allowed to warm to room temperature, stirred overnight, and poured into water (200 mL). The product was extracted with diethyl ether (3×100 mL). The organic phases were combined, washed with brine, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography (cyclohexane/diethyl ether, 15:1 v/v + 1.5% NEt_3) for **3** and (cyclohexane/ diethyl ether, 5:1 v/v + 5% NEt_3) for **5**.

3 was obtained as orange-red viscous oil (552 mg, 91% yield). ^{1}H NMR (300 MHz, C_6D_6): δ= 8.06 (s, 1H), 6.99 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.84 (s, 2H), 5.38 (d, *J* = 17.5 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 4.83 – 4.78 (m, 1H), 4.56 – 4.49 (m, 1H), 4.24 – 4.17 (m, 1H), 4.01 (s, 5H), 2.23 (s, 3H), 2.18 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6): δ= 162.21, 150.41, 133.44, 132.35, 129.20, 126.81, 113.02, 84.99, 79.47, 70.67, 70.25, 68.43, 21.05, 18.82. HRMS (EI): m/z calcd for $C_{22}H_{23}NFe$: 357.1180 $[M]^+$; found: 357.1143.

5 was obtained as orange oil (382 mg, 88% yield).^{1}H NMR (300 MHz, $CDCl_3$): δ= 6.71 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.35 (dd, *J* = 17.5, 1.9 Hz, 1H), 5.09 (dd, *J* = 10.8, 1.9 Hz, 1H), 4.28 (ddd, *J* = 2.6, 1.5, 0.5 Hz, 1H), 4.12 (s, 5H), 4.04 – 3.99 (m, 2H), 2.61 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 133.56, 113.27, 111.31, 78.08, 69.66, 63.44, 62.49, 56.77, 45.60. HRMS (EI): m/z calcd for $C_{14}H_{17}NFe$: 255.0670 $[M]^+$; found: 255.0693.

Synthesis of 6: A Schlenk flask containing molecular sieves (4 Å, 700 mg) was evacuated and back-filled with nitrogen three times. Next, CH_2Cl_2 (10 mL), Fc-NH_2 (512 mg, 2.54 mmol) and 2,2-dimethyl-4-pentenal (346 µL, 2.54 mmol) were added under nitrogen atmosphere. The mixture was stirred at room temperature overnight. The molecular sieves were removed by filtration and the solution concentrated under vacuum. The residue was purified by column chromatography (cyclohexane/ diethyl ether, 5:1 v/v) to provide the desired imine as orange oil (427 mg, 57% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.94 (s, 1H), 5.91 – 5.74 (m, 1H), 5.12 – 5.09 (m, 1H), 5.08 – 5.04 (m, 1H), 4.41 (t, *J* = 2.0 Hz, 2H), 4.15 – 4.11 (m, 7H), 2.25 (t, *J* = 1.2 Hz, 1H), 2.23 (t, *J* = 1.2 Hz, 1H), 1.12 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 170.07,

134.79, 117.63, 105.97, 69.48, 66.58, 62.70, 44.96, 39.77, 24.78. HRMS (EI): m/z calcd for $C_{17}H_{21}NFe$: 295.1023 $[M]^+$; found: 295.0989.

Synthesis of 7: A Schlenk flask containing molecular sieves (4 Å, 700 mg) was evacuated and back-filled with nitrogen three times. Next, toluene (15 mL), Fc-NH_2 (300 mg, 1.49 mmol) and 2-vinylbenzaldehyde (189 µL, 1.49 mmol) were added under nitrogen atmosphere. The mixture was stirred at 100°C for 3 h. After cooling to room temperature, the sieves were removed by filtration and the solution concentrated under vacuum. The residue was purified by column chromatography (cyclohexane/ethyl acetate, 10:1 v/v). The crude product is a mixture of the desired product and starting material (ca. 40 mol%), which was used in the next step without additional purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.97 (s, 1H), 8.02 (dd, J = 7.7, 1.6 Hz, 1H), 7.62 – 7.18 (m, 7H, overlapping product signals with those of 2-vinylbenzaldehyde), 5.68 (dd, J = 11.3, 1.5 Hz, 1H), 5.47 (dd, J = 11.3, 1.5 Hz, 1H), 4.60 (t, J = 1.8 Hz, 2H), 4.27 (t, J = 11.3, 1.5 Hz, 2H), 4.20 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 156.22, 138.24, 134.15, , 133.51, 130.35, 128.11, 127.42, 127.15, 118.29, 105.83, 69.70, 67.46, 63.12. HRMS (EI): m/z calcd for $C_{19}H_{17}NFe$: 315.0710 $[M]^+$; found: 315.0683.

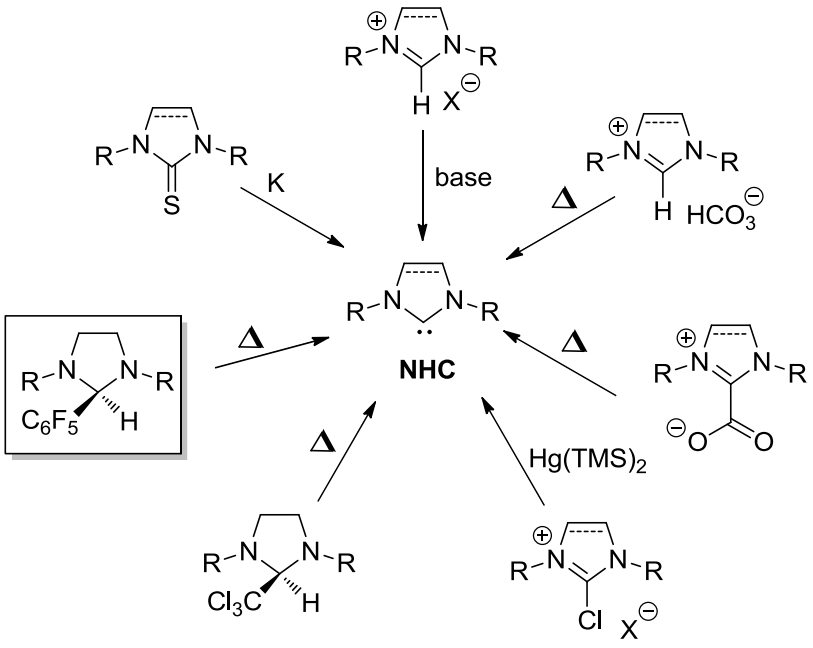
3.5. 2-(Pentafluorophenyl)imidazolidines

The content of this chapter has already been published:

Roman Savka, *"2-(Pentafluorophenyl)imidazolidines". Synlett* **2013,** *24*, 1735–1736.

N-Heterocyclic carbenes (NHCs) have become ubiquitous organocatalysts and ligands for transition-metal complexes. Several methods highlighted in Scheme 63 allow the formation of free NHCs. Among them 2-(pentafluorophenyl)imidazolidines appear to be very useful reagents.

This chapter highlights the applications of 2-(pentafluorophenyl)imidazolidines in the formation of free NHCs. The literature data concerning the synthesis of NHC-transition-metal complexes, including ruthenium-based olefin metathesis catalysts, from 2-(pentafluorophenyl)imidazolidines are discussed.



Scheme 63. Different methods for the formation of free NHCs.

SYNLETT
Spotlight 441

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

2-(Pentafluorophenyl)imidazolidines

Compiled by Roman Savka
Roman Savka was born in 1987 in Lviv, Ukraine. He received his M.Sc. degree in 2010 from Ivan Franko National University of Lviv. He is currently working toward his Ph.D. under the supervision of Prof. Dr. Herbert Plenio at the Technical University of Darmstadt, Germany. His research interests are focused on the synthesis of new N-heterocyclic carbenes and ruthenium complexes for olefin metathesis.

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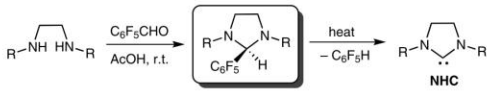
Introduction

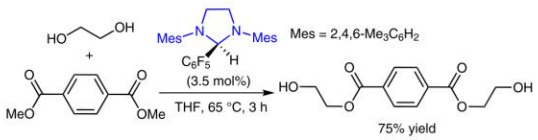
N-Heterocyclic carbenes (NHCs) have emerged as a unique class of organocatalysts and as ligands for transition metals.[1] The high reactivity of free NHCs, which makes these compounds very useful, translates into their sensitivity towards air and moisture. That is why NHCs are generally prepared in situ by deprotonation of azolium salts with strong non-nucleophilic bases [e.g., *t*-BuOK or $KN(SiMe_3)_2$]. The use of strong bases which are incompatible with many functional groups and the formation of typical byproducts (e.g., inorganic salts and alcohols) limit the scope of this method. An alternative approach to NHCs includes thermolysis of imidazolium-2-carboxylates, 2-(trichloromethyl)imidazolidines, silver–NHC complexes and other reagents. However, many of these reagents are poorly soluble. Moreover, they are commonly synthesized from NHCs. In 2004, Waymouth, Hedrick, and co-workers reported the synthesis of 2-(pentafluorophenyl)imidazolidines as useful and readily available NHC-transfer reagents (Scheme 1).[2] The advantages of pentafluorophenyl adducts are: (a) high stability in air; (b) good solubility in common organic solvents; (c) thermolysis generally occurs under mild heating; (d) the only byproduct of the thermolysis is pentafluorobenzene; (e) straightforward synthesis. 2-(Pentafluorophenyl)imidazolidines can be prepared from structurally diverse diamines and commercially available pentafluorobenzaldehyde (Scheme 1).



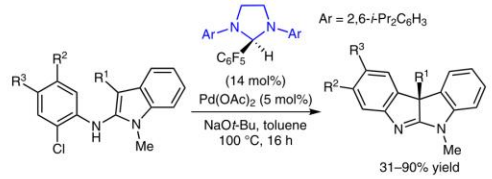
Scheme 1 Synthesis and thermolysis of 2-(pentafluorophenyl)imidazolidines[2,3]

Abstracts

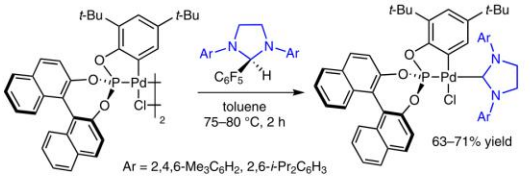
(A) Pentafluorophenyl adducts have been shown to be effective transesterification catalysts. Transesterification of dimethyl terephthalate with excess ethylene glycol to give bis(2-hydroxyethyl) terephthalate, an important precursor to poly(ethylene terephthalate), was investigated.[2]



(B) Previously unknown indoloindoles were prepared via a palladium-catalyzed dearomatization reaction.[4] The catalyst used was formed in situ from palladium acetate and the pentaflurobenzene adduct of the carbene ligand.



(C) The preparation of chiral palladacycles from BINOL-based palladium complexes and pentafluorophenyl adducts was described.[5] It was reported before that the reaction of free carbene, prepared from the respective imidazolinium salt, with related palladium complexes did not proceed cleanly and gave a mixture of compounds.[6] However, the same reaction with pentafluorophenyl adduct worked well to produce the desired product in 68% yield.



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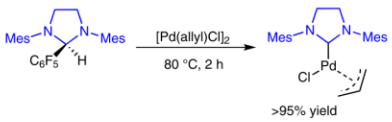
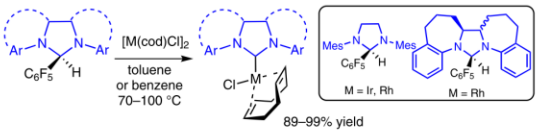
Advanced online publication: 19.07.2013
DOI: 10.1055/s-0033-1339476; Art ID: ST-2013-V0450-V

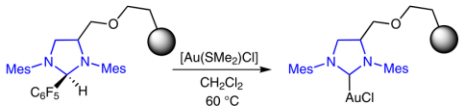
(D) Waymouth, Hedrick, and co-workers reported the synthesis of a palladium complex.[2] Treatment of $[Pd(allyl)Cl]_2$ with pentafluorophenyl adduct at 80 °C in toluene gave the desired product in more than 95% yield. Moreover, the authors reported that this reaction can be carried out in air without prior solvent purification.



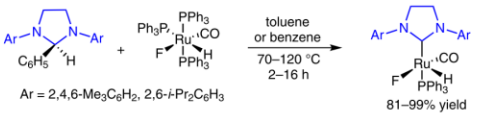
(E) Grubbs and co-workers used pentafluorophenyl adducts for the synthesis of iridium and rhodium complexes in excellent yield.[3,7] Pentafluorophenyl adducts were chosen as carbene precursors rather than the traditional imidazolinium salts in order to allow ligation onto metal fragments in the absence of a strong base.



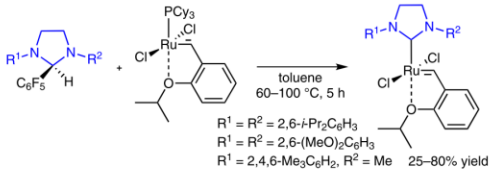
(F) Trapp and co-workers described the synthesis of gold and ruthenium catalysts using pentafluorophenyl adduct coated onto the inner surface of fused-silica capillaries.[8] The authors have mentioned that the advantage of using pentafluorophenyl adduct is that the bonded carbene can be thermally generated and immediately converted into the bonded catalysts.



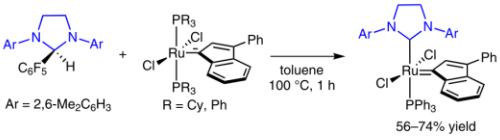
(G) The two new ruthenium complexes of the general formula Ru(NHC)$(PPh_3)F(CO)H$ were prepared from the respective pentafluorophenyl adducts and $Ru(PPh_3)_3F(CO)H$ complex.[9] The synthesized compounds were shown to be effective catalysts for hydrodefluorination of aromatic hydrocarbons.



(H) Grubbs–Hoveyda 2nd generation catalysts were prepared utilizing pentafluorophenyl adducts.[3] The complex containing a methoxy groups was obtained in 25% yield. However, other methods that were attempted to prepare this complex were unsuccessful, highlighting the utility of pentafluorophenyl adducts.



(I) Verpoort and co-workers reported a straightforward synthesis of ruthenium–indenylidene-type complexes by a ligand-exchange reaction.[10] The use of pentafluorophenyl adducts allowed to obtain the desired products in good yield without any chromatographic purification.



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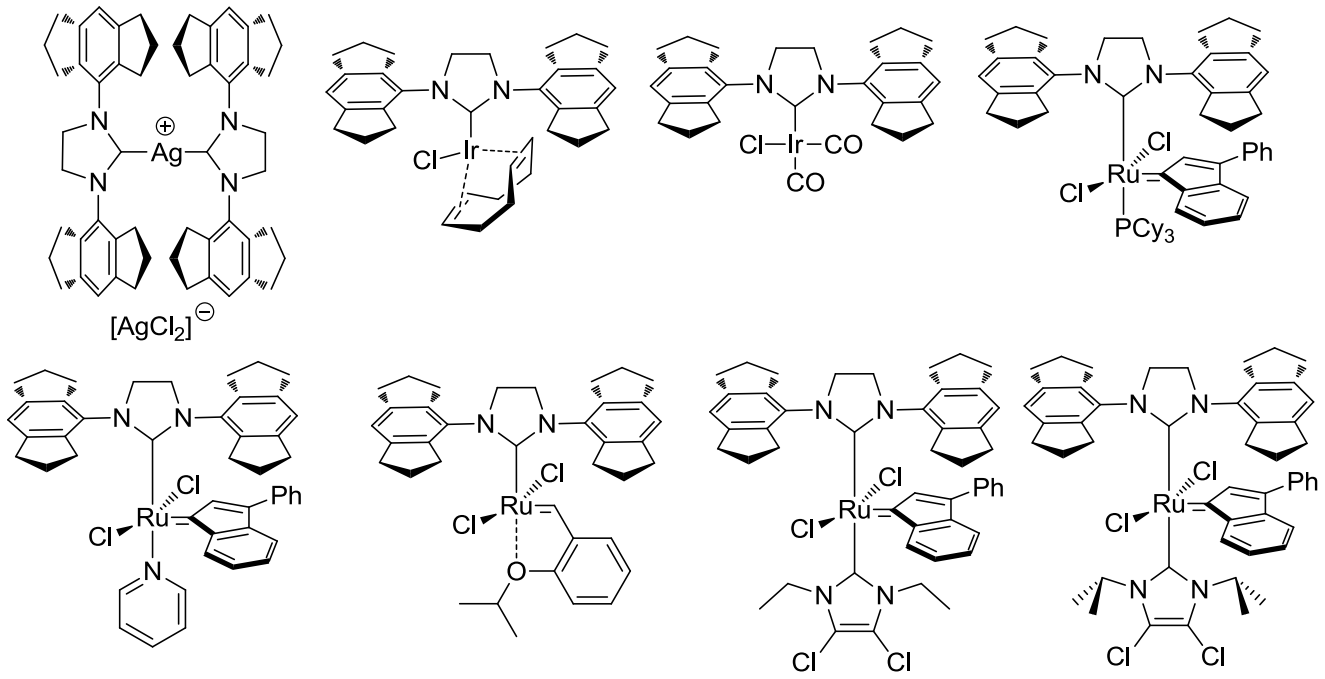
4. Summary and Conclusions

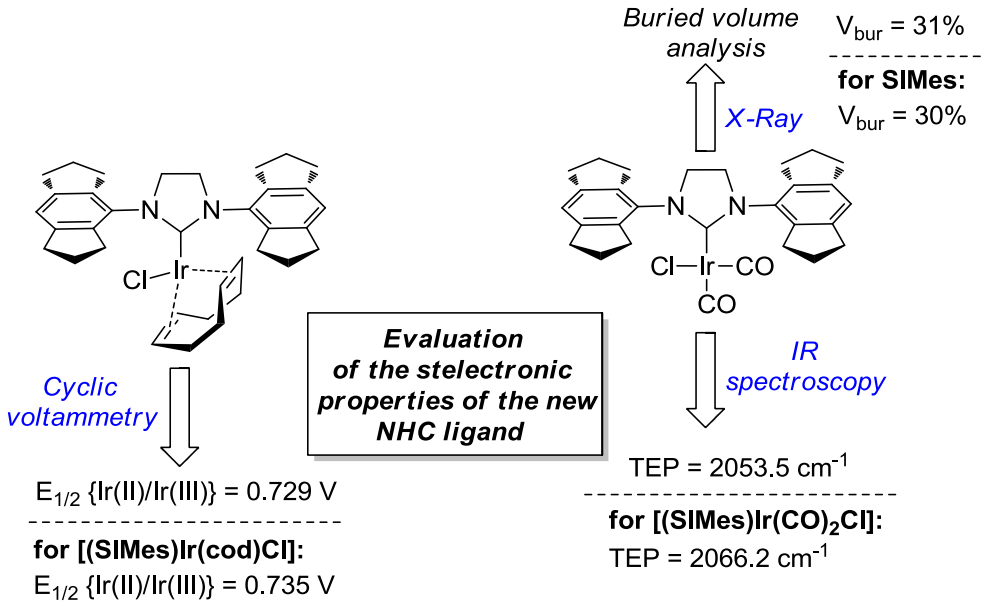
In the following paragraphs the most important aspects of my work will be presented as a short summary.

1. A new hexahydro-*s*-indacene based NHC ligand and transition metal complexes with Ag, Ir and Ru were prepared (Scheme 64).



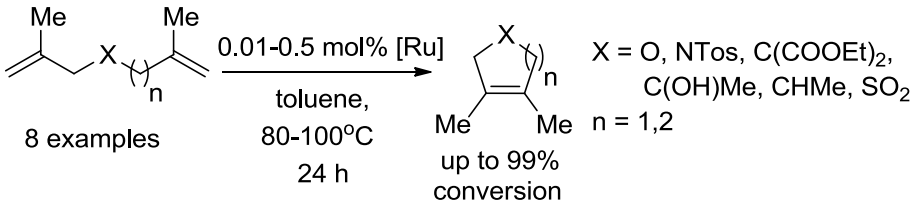
Scheme 64. Transition metal complexes containing hexahydro-*s*-indacene based NHC ligand.

2. The stereoelectronic properties of the new NHC ligand were determined and found to be similar to those of the SIMes ligand (Scheme 65).



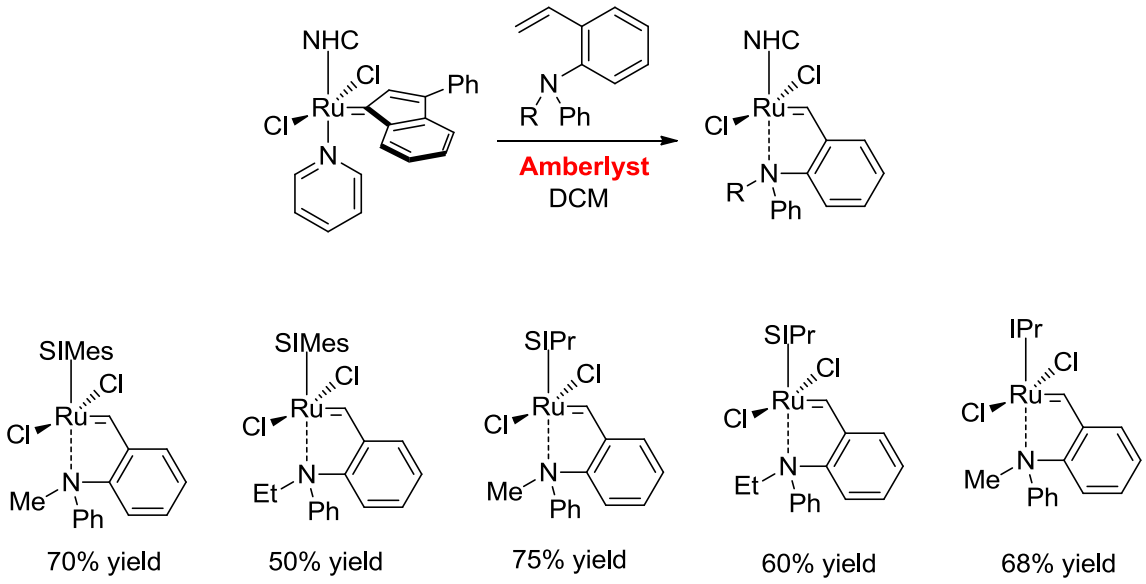
Scheme 65. Evaluation of the stereoelectronic properties of hexahydro-*s*-indacene based NHC ligand.

3. The catalytic behavior of ruthenium complexes with the new NHC ligand in ring-closing metathesis reactions of sterically demanding substrates was investigated (Scheme 66). The catalytic activity of the bisNHC complexes is very good and comparable to the best complexes with the standard SIMes ligand. However, an increase in the activity of the respective Hoveyda and indenylidene complexes with hexahydro-*s*-indacene based NHC ligand compared to their SIMes analogues was observed.



Scheme 66. RCM reactions of sterically demanding olefins studied in this work.

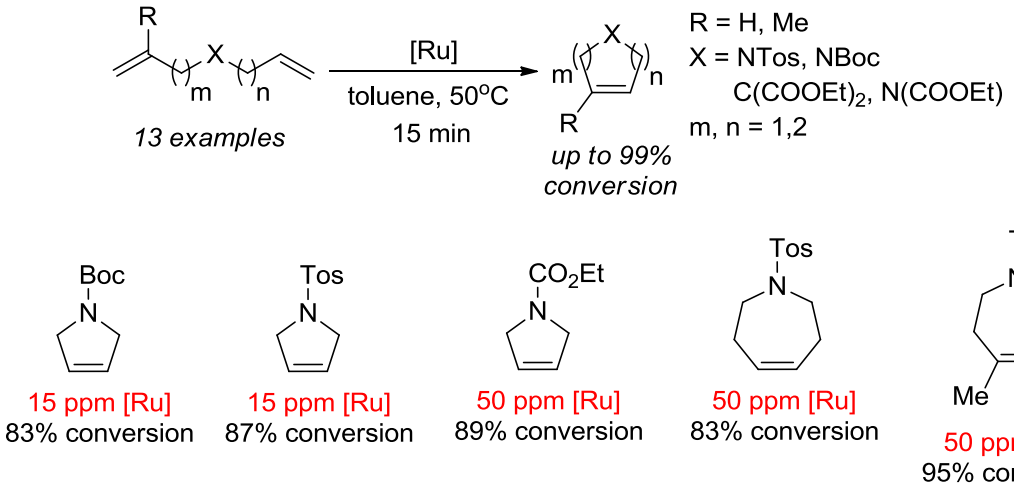
4. New *N*-Hoveyda-type complexes were obtained by the reaction of the Grubbs 3rd generation type complexes [$RuCl_2$(NHC)(Ind)(Py)] (NHC = SIMes, SIPr, IPr) with 2-ethenyl-*N*-alkyl-*N*-phenylaniline (alkyl = Me, Et) (Scheme 67). The new procedure, which is based on the use of acidic Amberlyst resin as pyridine scavenger, allows the formation of the desired complexes in 50-75% yield.



Scheme 67. Synthesis of new *N*-Hoveyda-type complexes.

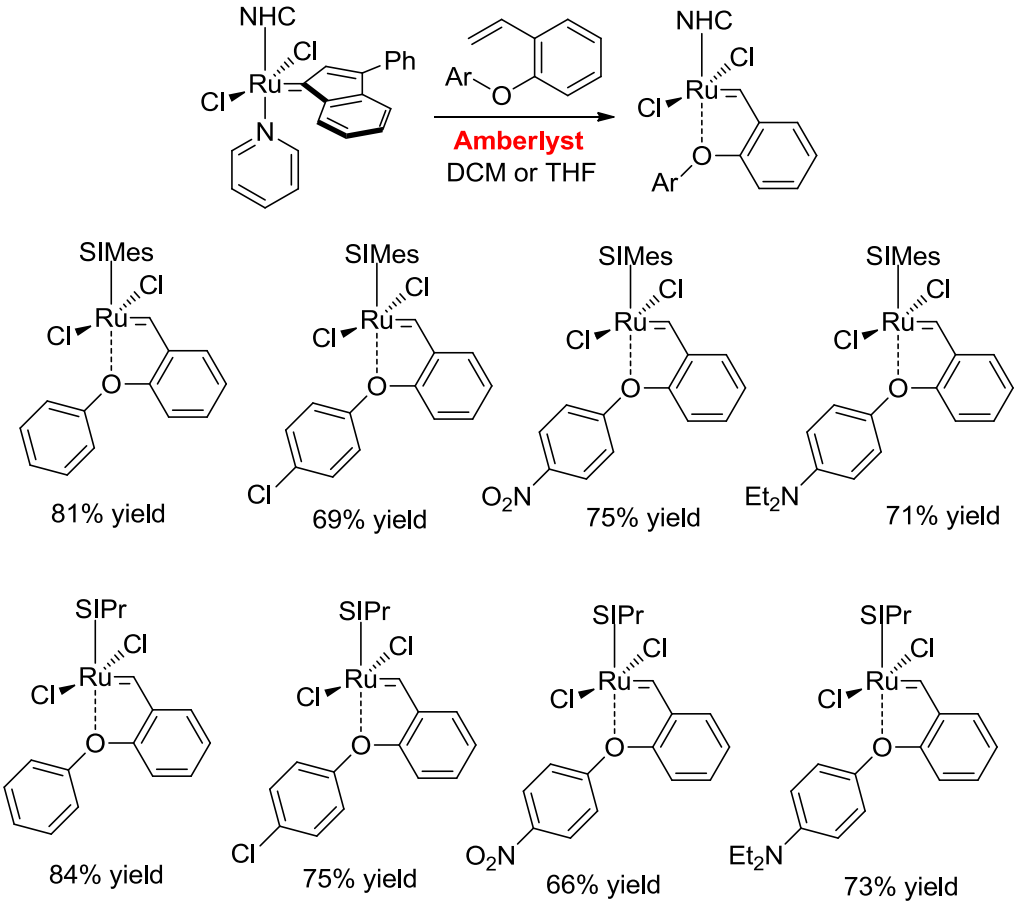
5. New *N*-Hoveyda-type complexes (Scheme 67) are characterized by very fast initiation rates. Low catalyst loadings of 15-300 ppm are sufficient for the conversion of a range of RCM substrates into the respective cyclic olefins in reaction times of less than 15 min (Scheme 68). The most active complex affords *N*-protected 2,5-dihydropyrroles (TOF of up to 232000 h^{-1}) and *N*-protected 1,2,3,6-tetrahydropyridines (TOF of up to 147000 h^{-1}) in yields of around 90%; the synthesis of the

respective *N*-protected 2,3,6,7-tetrahydroazepines requires a catalyst loading of 50 ppm (95% yield, TOF of up to 76000 h^{-1}).



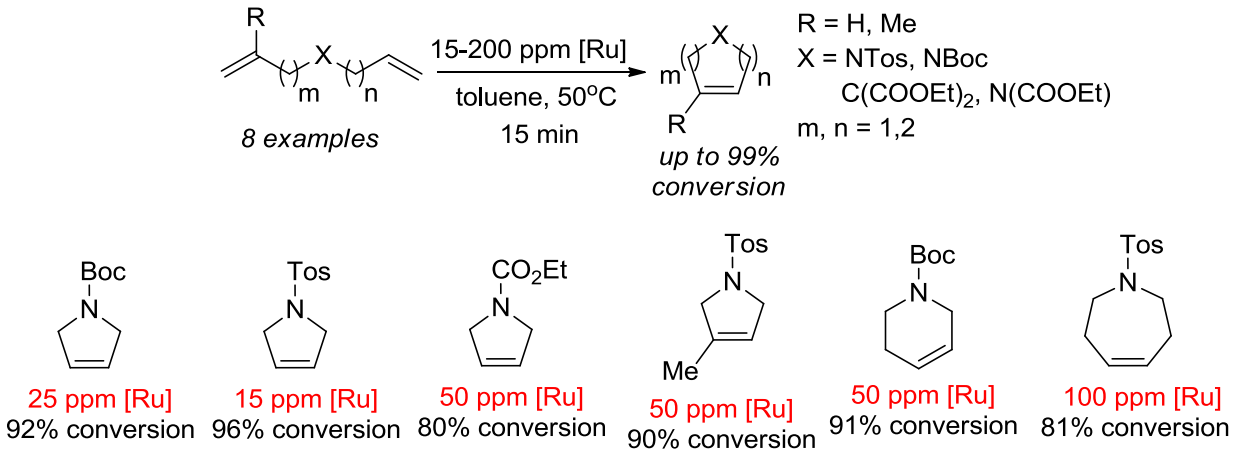
Scheme 68. Results for selected RCM reactions.

6. New 2-aryloxy-substituted Hoveyda-type complexes were synthesized in the reaction of the Grubbs 3rd generation type complexes [$RuCl_2$(NHC)(3-phenylindeneylidene)(Py)] (NHC = SIMes, SIPr) with 1-ethenyl-2-phenoxybenzenes (with EWG/EDG groups R *para* to oxygen) (Scheme 69). The use of Amberlyst resin enables the formation of the desired catalysts in yields between 66-84%.



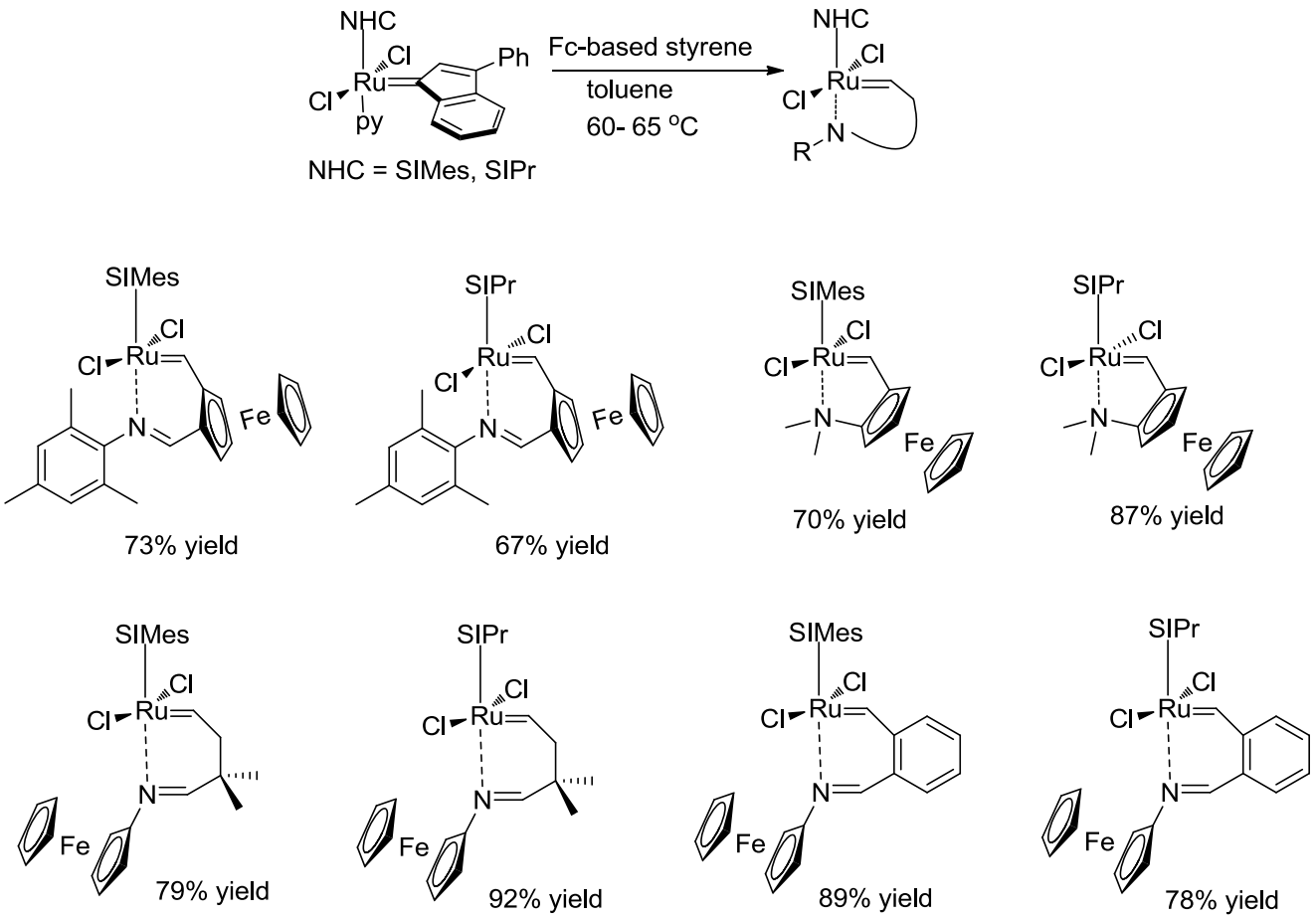
Scheme 69. Synthesis of *O*-Hoveyda-type complexes.

7. The fast initiation of 2-aryloxy-substituted Hoveyda-type complexes translates into rapid olefin metathesis reactions. The catalytic activity in various RCM reactions was probed and the new complexes found to be highly efficient. Catalyst loadings as low as 15-100 ppm are sufficient to reach >90% conversion within less than 15 min of reaction time for a variety of RCM substrates (Scheme 70).

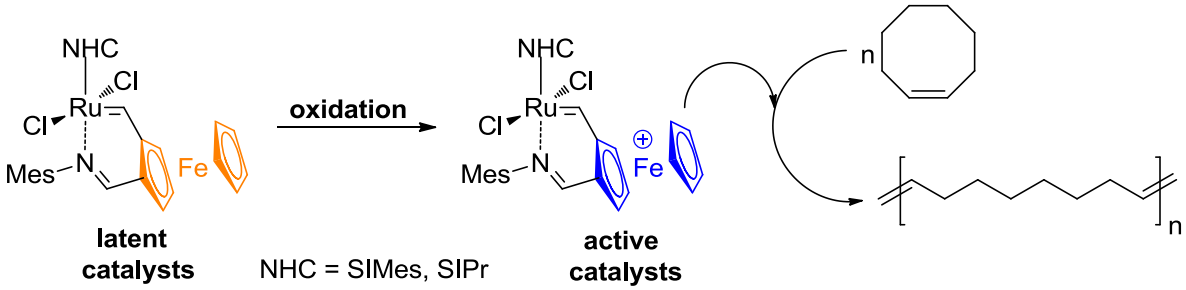


Scheme 70. . Results for selected RCM reactions.

8. Eight new Hoveyda-type complexes with ferrocenyl substituents were synthesized (Scheme 71). The redox potentials for the new complexes were determined. An iron-centered oxidation reaction occurs at potential close to E = +0.5 V, while the oxidation of ruthenium occurs at around E = +0.8 V. Two of these complexes were found to be latent catalysts for ROMP reactions in the reduced state, but are able to polymerize *cis*-cyclooctene following chemical or electrochemical oxidation of the ferrocenyl group (Scheme 62). The other complexes are not switchable catalysts and either inactive or active in both reduced and oxidized states.



Scheme 71. Synthesis of the new ferrocenyl-substituted Hoveyda complexes.



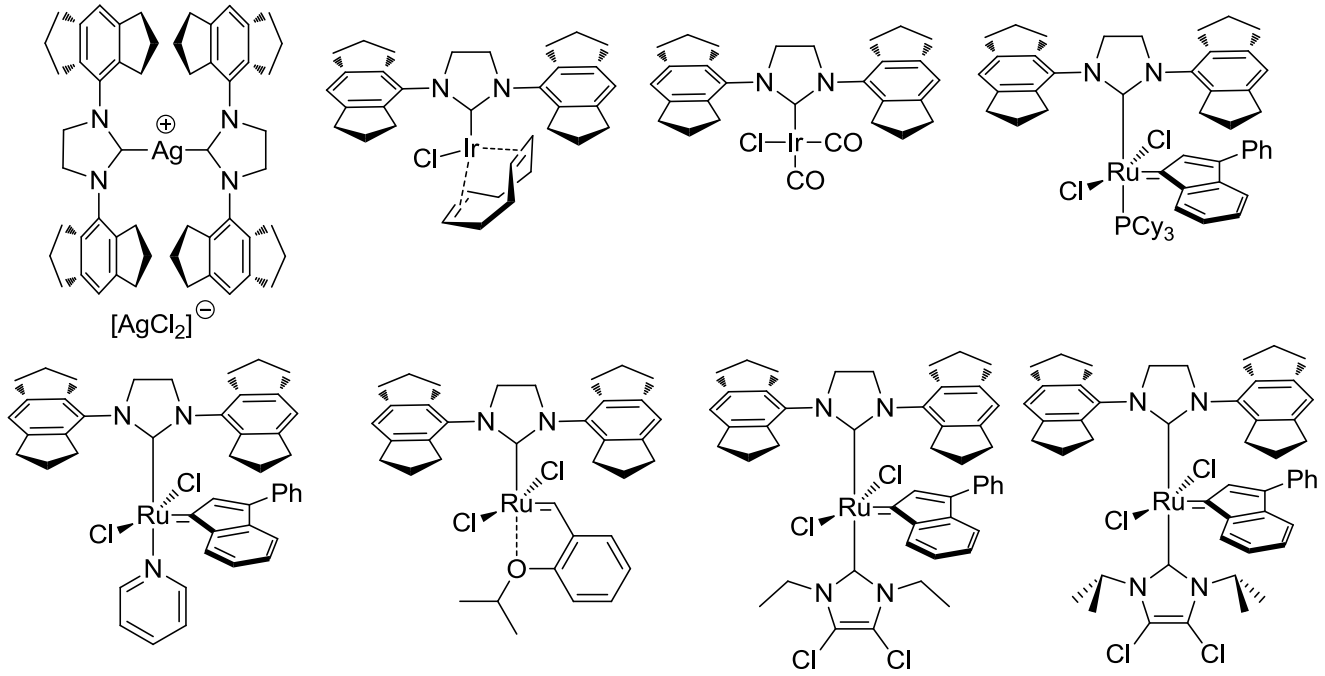
Scheme 62. ROMP reaction of *cis*-cyclooctene catalyzed by oxidized complexes.

9. The electrochemical initiation of ROMP reaction through electrodes was done for the first time and could enable microstructure control of the obtained polymers.

5. Zusammenfassung der Ergebnisse

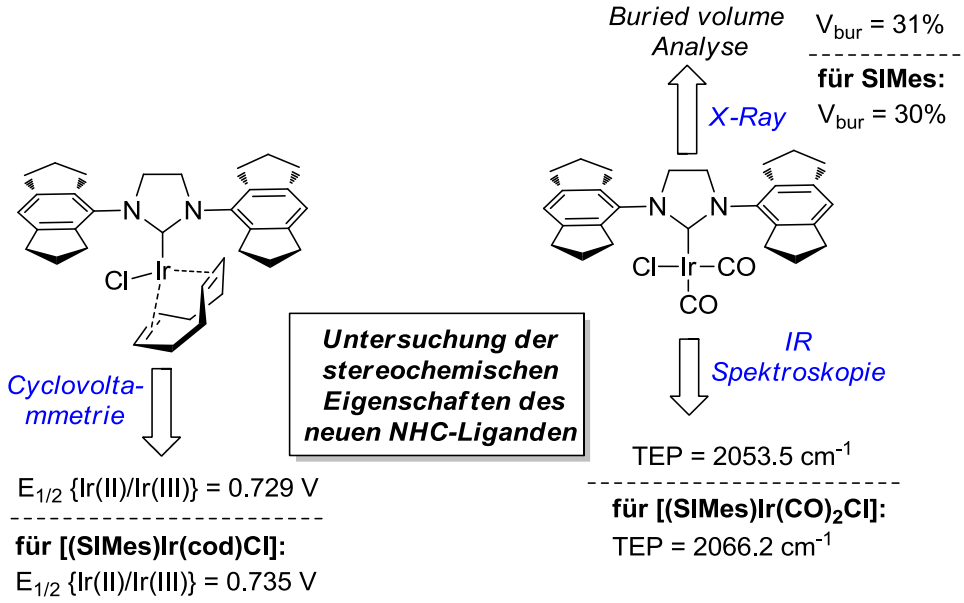
Im Folgenden sind die wichtigsten Aspekte meiner Arbeit kurz zusammengefasst.

1. Es wurden ein neuer Hexahydro-*s*-indacen-basierter NHC-Ligand, sowie die dazugehörigen Übergangsmetallkomplexe mit Ag, Ir und Ru dargestellt (Schema 64).



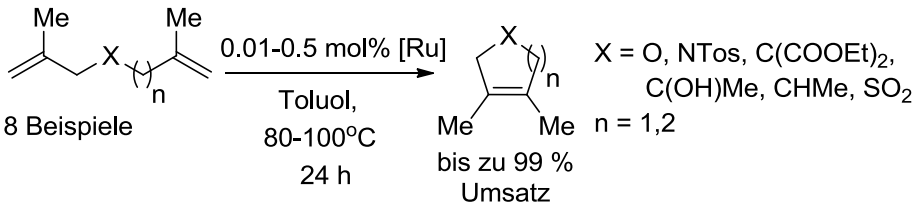
Schema 64. Übergangsmetallkomplexe mit Hexahydro-*s*-indacen-basierten NHC-Liganden.

2. Die stereochemischen Eigenschaften des neuen NHC-Liganden wurden untersucht. Die ermittelten Werte für „buried volume“, TEP sowie CV lassen sich mit denen des SIMes-Liganden vergleichen.



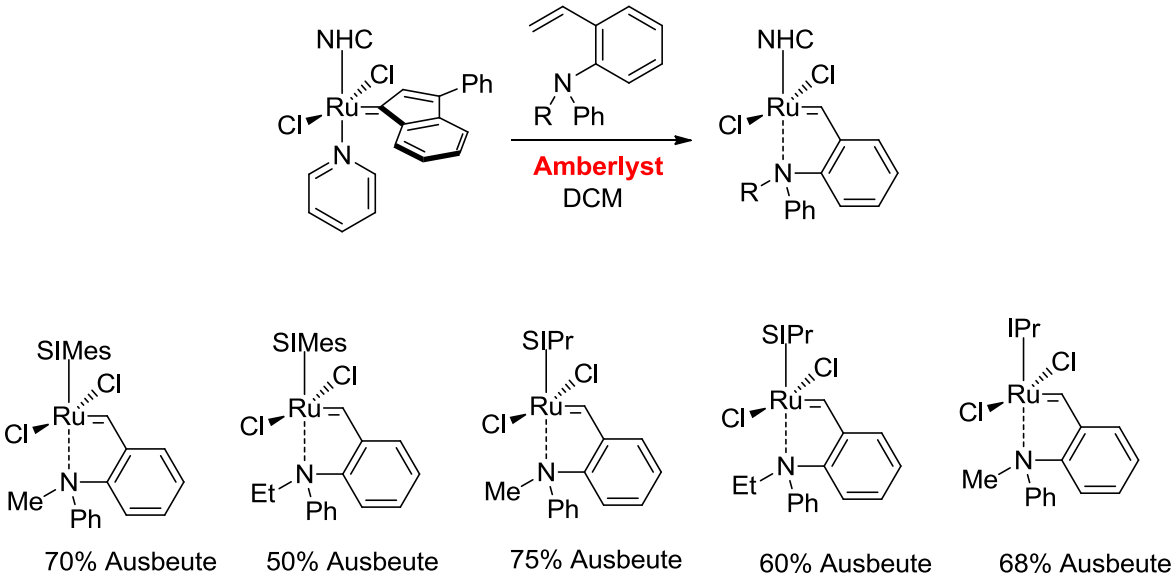
Schema 65. Untersuchung der stereochemischen Eigenschaften des Hexahydro-*s*-indacen-basierten NHC-Liganden.

3. Das katalytische Verhalten der Hexahydro-*s*-indacen–basierten Rutheniumkomplexe wurde mittels Ringschlussmetathese-Reaktion (RCM), unter Verwendung sterisch anspruchsvoller Substrate, untersucht (Schema 66). Der Bis-NHC-Komplex weist eine hohe katalytische Aktivität auf. Diese ist vergleichbar mit der Aktivität von SIMes-basierten Katalysatoren. Verglichen mit den entsprechenden SIMes-substituierten Komplexen, konnte eine signifikante Steigerung der Aktivität sowohl bei den Hoveyda- als auch bei den Indenyliden-Komplexen beobachtet werden.



Schema 66. Untersuchte RCM-Reaktionen mit sterisch anspruchsvollen Olefinen.

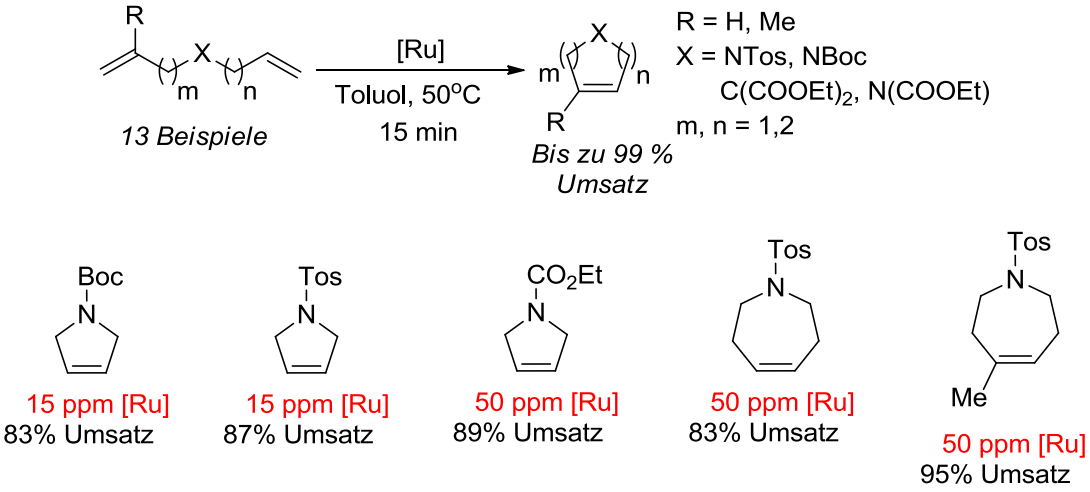
4. Neue Verbindungen der *N*-Hoveyda-Klasse wurden durch die Reaktion von Grubbs-Komplexen der dritten Generation [$RuCl_2$(NHC)(Ind)(Py)] (NHC = SIMes, SIPr, IPr) mit 2-Ethenyl-*N*-alkyl-*N*-phenylanilin (Alkyl = Me, Et) erhalten (Schema 67). Die neue Synthesevorschrift, welche auf der Verwendung von *Amberlyst®15* basiert, führt zur Bildung der gewünschten Komplexe in Ausbeuten von 50-75%.



Schema 67. Synthese neuer *N*-Hoveyda- Komplexe.

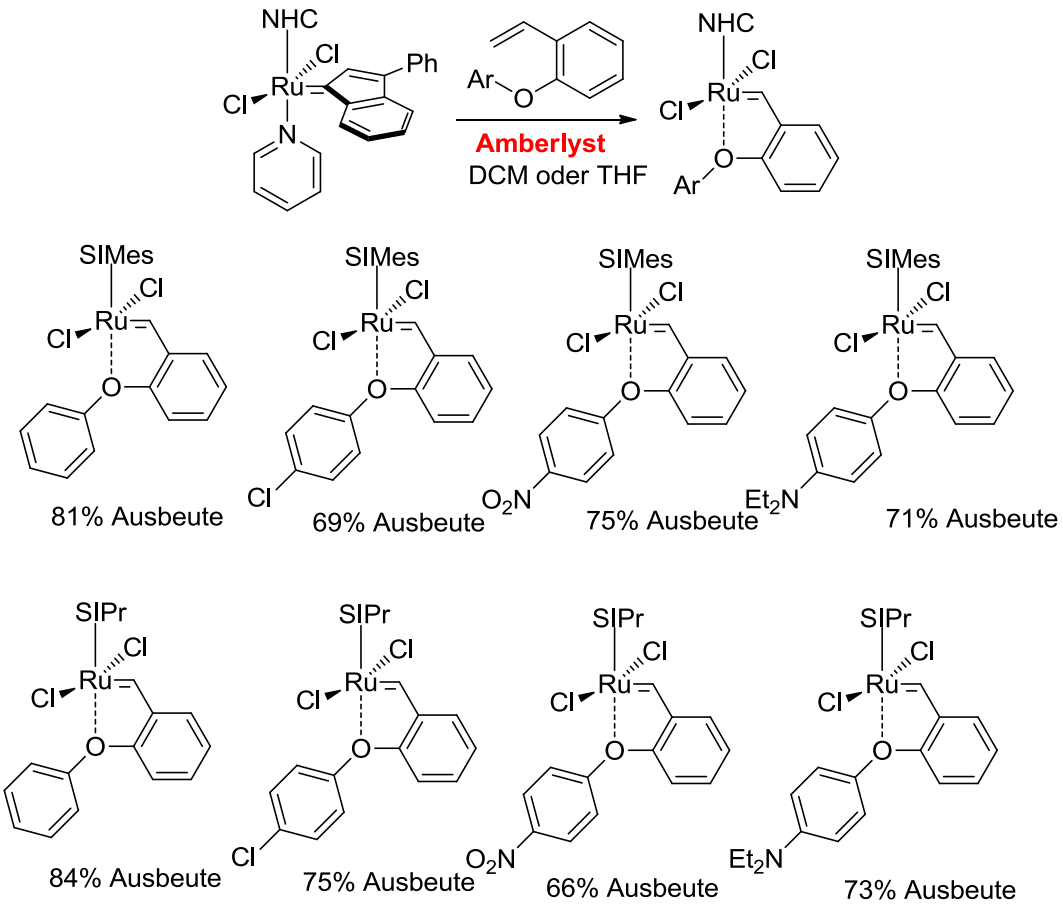
5. Charakteristisch für die neuen *N*-Hoveyda- Komplexe (Schema 67) ist eine sehr hohe Geschwindigkeit der Präkatalysatoraktivierung. Die Ru-Komplexe zeigen eine sehr hohe katalytische Aktivität und eine niedrige Katalysatorbeladung von 15-300 ppm ist für die Umsetzung eines breiten Spektrums an RCM Substraten ausreichend. Die entsprechenden cyclischen Olefine werden

in Reaktionszeiten von unter 15 Minuten gebildet (Schema 68). Der aktivste Komplex erlaubt die Bildung *N*-geschützter 2,5-Dihydropyrrole (TOF bis zu 232000 h^{-1}) und *N*-geschützter 1,2,3,6-tetrahydropyridine (TOF bis zu 147000 h^{-1}) in Ausbeuten von ca. 90%. Die Synthese der entsprechenden *N*-geschützten 2,3,6,7-Tetrahydroazepine gelingt mit einer Katalysatorbeladung von 50 ppm (95% Ausbeute, TOF bis zu 76000 h^{-1}).



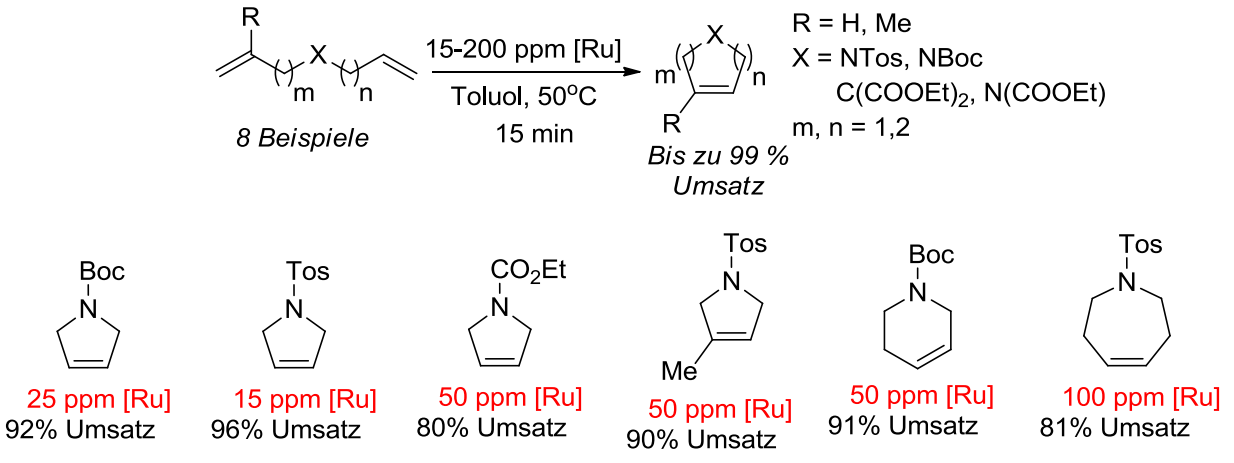
Schema 68. Ergebnisse ausgewählter RCM-Reaktionen.

6. Neue 2-Aryloxy-substituierte Hoveyda-Komplexe wurden durch eine Reaktion von Grubbs–Komplexen der dritten Generation [$RuCl_2$(NHC)(3-phenylindeneyliden)(Py)] (NHC = SIMes, SIPr) mit 1-Ethenyl-2-phenoxybenzenen (mit EWG/EDG Substituenten R *para* zum Sauerstoff) synthetisiert (Schema 69). Die Verwendung von *Amberlyst® 15* ermöglicht die Bildung der gewünschten Produkte in Ausbeuten zwischen 66-84%.



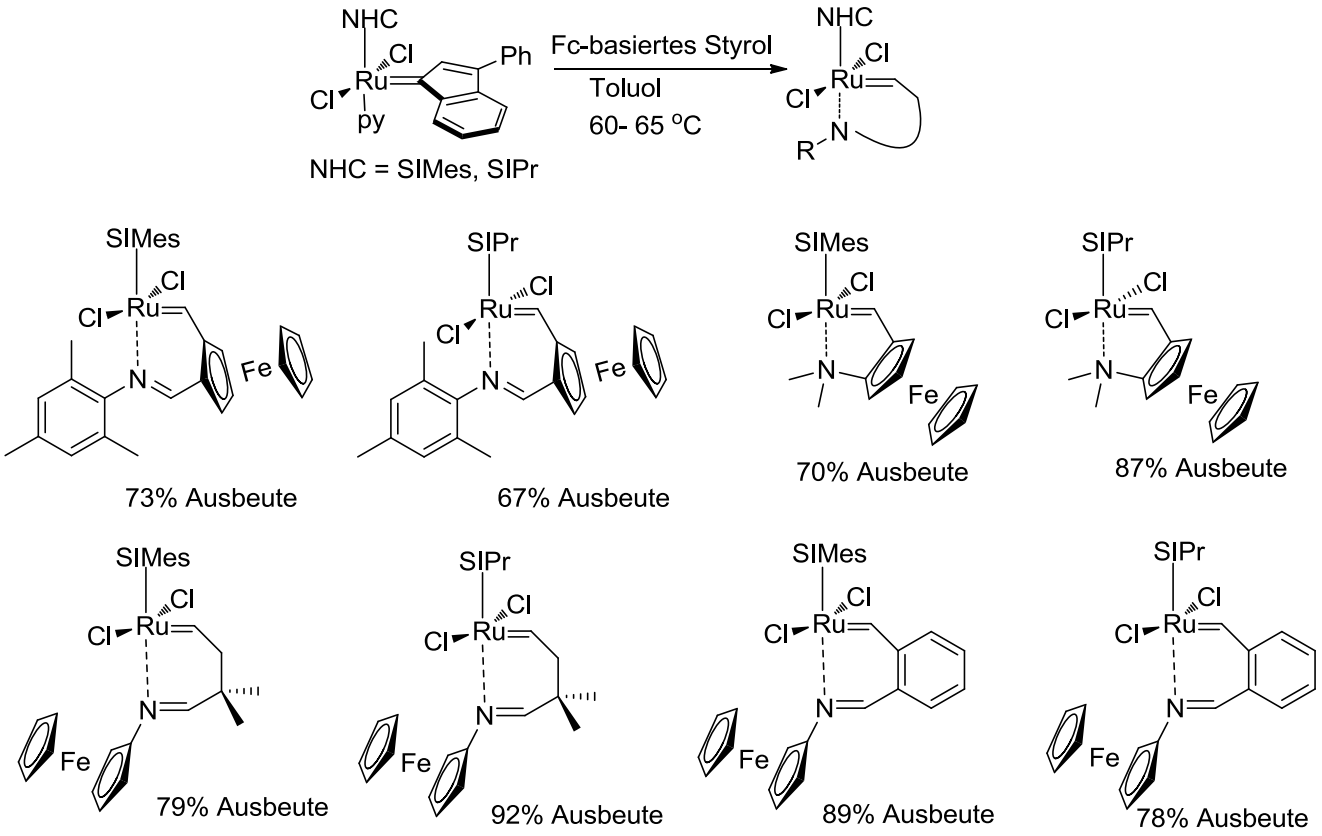
Schema 69. Synthese neuer *O*-Hoveyda-Komplexen.

7. Die schnelle Initiierung von 2-aryloxy-substituierten Hoveyda-Komplexen führt zu schnellen Olefinmetathesereaktionen. Die katalytische Aktivität wurde in zahlreichen RCM-Reaktionen untersucht und die neuen Komplexe als hoch effizient erkannt. Katalysatorbeladungen von lediglich 15-100 ppm sind ausreichend, um einen Umsatz > 90% in weniger als 15 min Reaktionszeit für eine Vielzahl von RCM-Substraten zu erreichen (Schema 70).

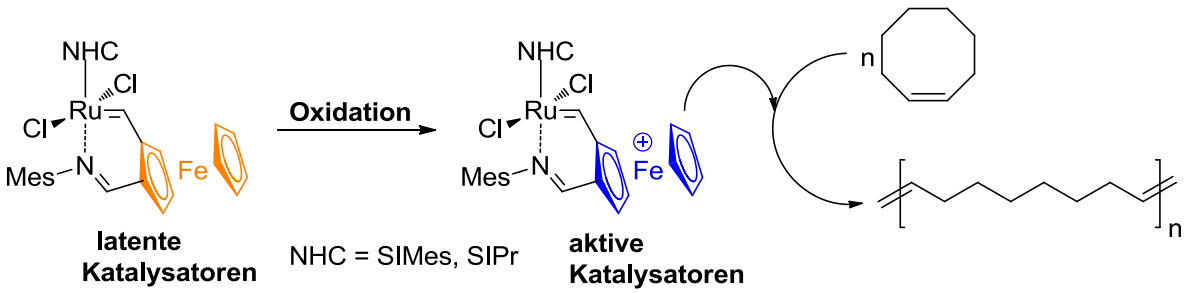


Schema 70. Untersuchte RCM-Reaktionen mit ausgewählten Ergebnissen.

8. Acht neue Hoveyda-Komplexe mit ferrocentragenden Substituenten wurden synthetisiert (Schema 71) und deren Redoxpotentiale bestimmt. Eine Oxidation des Eisenzentrums tritt bei einem Potential von etwa E = +0.5 V auf, wohingegen die Oxidation des Rutheniums bei einem Potential von ca. E = +0.8 V erfolgt. Zwei dieser Komplexe stellten im reduzierten Zustand latente Katalysatoren für ROMP Reaktionen dar. Durch chemische oder elektrochemische Oxidation der Ferroceneinheit am Katalysator konnte *cis*-Cycloocten polymerisiert werden (Schema 62). Die restlichen Verbindungen erwiesen sich nicht als latent, sondern stellten, sowohl im oxidierten als auch im reduzierten Zustand, entweder inaktive oder aktive Komplexe dar.



Schema 71. Synthese neuer ferrocensubstituierter Hoveyda-Komplexe.



Schema 62. ROMP-Reaktion von *cis*-Cycloocten, katalysiert durch oxidierte Komplexe.

9. Die elektrochemische Initiierung von ROMP-Reaktionen unter Verwendung von Elektroden wurde erstmals durchgeführt und erlaubt die Kontrolle der Mikrostruktur des gebildeten Polymers.

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Erklärung

Ich erkläre hiermit, dass ich meine Dissertation selbstständig und nur mit den angegebenen Hilfsmitteln angefertigt habe.

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Erklärung

Ich erkläre hiermit, noch keinen Promotionsversuch unternommen zu haben.

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