ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 117–124 117
DOI: 10.1021/om900857w

Latent Thermo-Switchable Olefin Metathesis Initiators Bearing a Pyridyl-Functionalized Chelating Carbene: Influence of the Leaving Group's Rigidity on the Catalyst's Performance

Anna Szadkowska,[†] Xaver Gstrein,[‡] Daniel Burtscher,[‡] Katarzyna Jarzembska,[§] Krzysztof Woźniak,[§] Christian Slugovc,*[,‡] and Karol Grela*[,†]

[†]*Institute of Organic Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland,* [‡]*Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology, Stremayrgasse 16 A 8010 Graz, Austria, and* [§]*Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*

Received October 2, 2009

The synthesis and characterization of two ruthenium complexes bearing chelating carbene ligands is described. Carbene precursors, 2-(2-vinylphenyl)pyridine and 10-vinylbenzo[*h*]quinoline, are applied to prepare (SPY-5-31)-dichloro-(κ^2(C,N)-N-2-(2-vinylbenzylidene)pyridine(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)ruthenium (**VIII**) and (SPY-5-31)-dichloro-(κ^2(C,N)-2-(benzo[*h*]quinolin-10-yl)methylidene)(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)-ruthenium (**IX**). Both catalysts/initiators are used to perform ring-closing metathesis (RCM) and ring-opening metathesis polymerizations (ROMP). RCM experiments reveal significant thermal stability of the catalysts under forcing reaction conditions such as boiling toluene for 48 h. Even challenging substrates such as diethylallyl(2-methylallyl)malonate are completely transformed with low catalyst loadings (0.1 mol % at 110 °C). The high thermal stability, i.e., latency, might be explained by a slow generation of the catalytically active methylidene species. This feature leads to high molecular weight polymers and a thermal switchability in ROMP. Initiation of polymerizations of several norbornene derivatives occurs at about 48 ± 5 °C in the case of initiator **VIII** and at 110 ± 9 °C in the case of **IX**. A substantial increase of the switching temperature in the following cases could be supported with higher rigidity of the chelating carbene moiety in **IX** when compared to **VIII**.

Introduction

A considerable amount of research has been done recently in the field of new catalysts/initiators for olefin metathesis reactions. Some discoveries in the development of catalysts, which commenced in the early 1990s, promoted applications of metals such as molybdenum and ruthenium (Figure 1) in olefin metathesis.[1−4] Especially ruthenium-based systems have found widespread applications in organic synthesis, particularly because of their extensive functional group tolerance. A lot of effort has been aimed at altering the alkylidene moieties connected to the ruthenium core and at using diverse types of anionic and neutral ligands. Recently, phosphine-free NHC-bearing ruthenium initiators have caused remarkable effects on catalytic activity and stability.[1−4] Nowadays, aspirations in the area of olefin metathesis are still directed toward reactivity improvements of more demanding substrates.

Systematic studies on the reactivity of phosphine-free NHC-Ru complexes have shown that the influence of steric hindrance is essential.[2] However, if the catalyst is overactive under the given conditions, it might be difficult or even impossible to impose a reasonable control over molecular properties in ROMP or to achieve complete conversions in RCM. This is because of fast catalyst degradation.[5−8] In some industrial setups of ROMP, for example RIM, it is required to store a mixture of a monomer and initiator before the metathesis process occurs.[7,8] The presence of a N→Ru,

*Corresponding authors. E-mail: klgrela@gmail.com (K.G.); slugovc@tugraz.at (C.S.).

(1) (a) The Nobel Prize in Chemistry for 2005, jointly awarded to Yves Chauvin, Robert H. Grubbs, and Richard R Schrock "for the development of the metathesis method in organic synthesis". For more reading, see: http://nobelprize.org/nobel_prizes/chemistry/laureates/2005/chemadv05.pdf. (b) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741. (c) Morgan, B. P.; Galdamez, G. A.; Gilliard, R. J.Jr.; Smith, R. C. *Dalton Trans.* **2009**, 2020.

(2) For selected reviews on olefin metathesis, see: (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (b) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003. (c) Connon, S. J.; Blechert, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900. (d) Astruc, D. *New J. Chem.* **2005**, *29*, 42.

(3) (a) Burtscher, D.; Grela, K. *Angew. Chem., Int. Ed.* **2008**, *121*, 450. (b) Guxłajski, Ł; Michrowska, A.; Narożnik, J.; Kaczmarska, Z.; Rupnicki, L.; Grela, K. *ChemSusChem* **2008**, *1*, 103.

(4) Śledź, P.; Mauduit, M.; Grela, K. *Chem. Soc. Rev.* **2008**, *37*, 2433.

(5) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.

(6) Dall'Asta, G.; Motroni, G. *Eur. Polym. J.* **1971**, *7*, 707.

(7) Askar, J. *J. Appl. Polym. Sci.* **1993**, *47*, 289.

(8) (a) For some industrial applications of ruthenium catalysts in ROMP olefin metathesis (especially RIM process), see: Mol, J. C. *J. Mol. Catal. A* **2004**, *213*, 39. (b) *Ring Opening Metathesis Polymerisation and Related Chemistry*; Khosravi, E., Szymańska-Buzar, T.., Eds.; Kluwer Academic Publishers: Dordrecht, 2002; p 105. (c) http://www.telene.com/.

Published on Web 12/14/2009

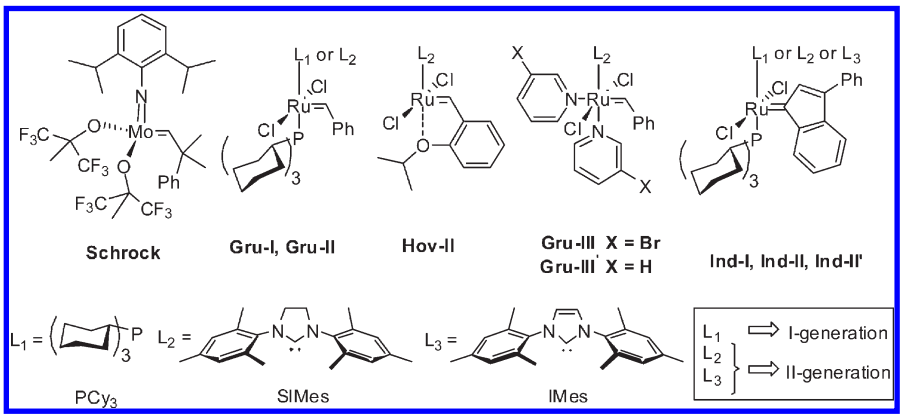


Figure 1. Selected catalysts for olefin metathesis.

O→Ru, or S→Ru chelate can favor the resting state of the precatalyst over its metathesis active form (Figure 2).[9−12] After the initiation event (controlled by temperature, light, or a chemical agent) and the first catalytic turnover, the loss of the donor group allows catalysis to proceed quickly.[10c,e−g] This switch in initiator structure from chelated to nonchelated form makes the above-mentioned strategy successful. It enables us not only to catalyze the metathesis reactions but also to perform them in a well-controlled manner.[10e,11−17] Potential applications of such catalysts are not limited to polymer chemistry only, but could also be used in multitransformation or multicomponent synthetic sequences involving a metathesis step at higher temperatures.

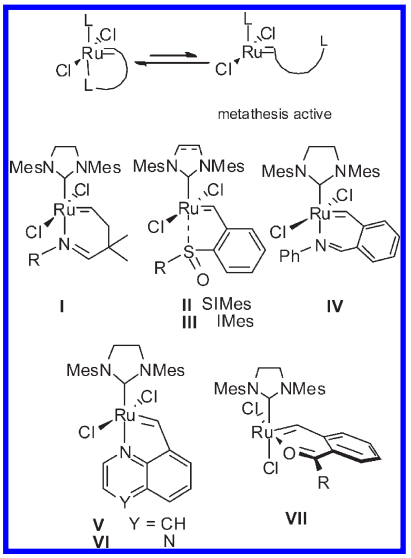


Figure 2. Some examples of latent ruthenium catalysts bearing N- O-, and S-chelating ligands.

The influence of the N→Ru chelation on the catalytic activity is still the subject of numerous investigations. In this contribution, we describe the effect of the rigidness of the N-chelating ligand on the catalytic performance of the formed ruthenium complex in RCM and ROMP. Our previous work described some catalysts containing imine-based N-chelating ligands as well as quinoline and quinoxaline ones. In general, these compounds possess quite a good stability and can potentially be applied at high temperatures. These results have encouraged us to conduct yet another design leading to another class of N→Ru chelated carbene complexes.[10f,13a,b] We have anticipated that using strongly chelating rigid ligands (10-benzo[*h*]quinoline and 2-phenylpyridine) would lead to initiators exhibiting favorable properties in the applications mentioned above.

(9) Usually, catalysts that are inert to a given olefinic substrate at room or slightly above room temperature are called "latent" or "dormant" initiators. Since the initiation rate depends not only on the catalyst but also on monomer structure, solvent, and temperature, these terms should be used with care.

(10) (a) Denk, K.; Fridgen, J.; Herrmann, W. A. *Adv. Synth. Catal.* **2002**, *344*, 666. (b) Jordaan, M.; Vosloo, H. C. M. *Adv. Synth. Catal.* **2007**, *349*, 184. (c) De Clercq, B.; Verpoort, F. *Adv. Synth. Catal.* **2002**, *344*, 639. (d) Chang, S.; Jones, L.II; Wang, C.; Henling, L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 3460. (e) van der Schaaf, P.; Kolly, R.; Kirner, H. J.; Rime, F.; Muhlebach, A.; Hafner, A. *J. Organomet. Chem.* **2000**, *606*, 65. (f) Slugovc, C.; Burtscher, D.; Stelzer, F.; Mereiter, K. *Organometallics* **2005**, *24*, 2255. (g) Burtscher, D.; Perner, B.; Mereiter, K.; Slugovc, C. *J. Organomet. Chem.* **2006**, *691*, 5423.

(11) (a) Szadkowska, A.; Grela, K. *Curr. Org. Chem.* **2008**, *12*, 1631. (b) Szadkowska, A.; Makal, A.; Kadyrov, R.; Woźniak, K.; Grela, K. *Organometallics* **2009**, *28*, 2693.

(12) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2004**, *23*, 5399.

(13) (a) Barbasiewicz, M.; Szadkowska, A.; Bujok, R.; Grela, K. *Organometallics* **2006**, *25*, 3599. (b) Gstrein, X.; Burtscher, D.; Szadkowska, A.; Barbasiewicz, M.; Stelzer, F.; Grela, K.; Slugovc, C. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3494. (c) Hejl, A.; Day, M. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 6149. (d) Slugovc, C.; Perner, B.; Stelzer, F.; Mereiter, K. *Organometallics* **2004**, *23*, 3622. (e) Gawin, R.; Makal, A.; Wozniak, K.; Mauduit, M.; Grela, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 7206.

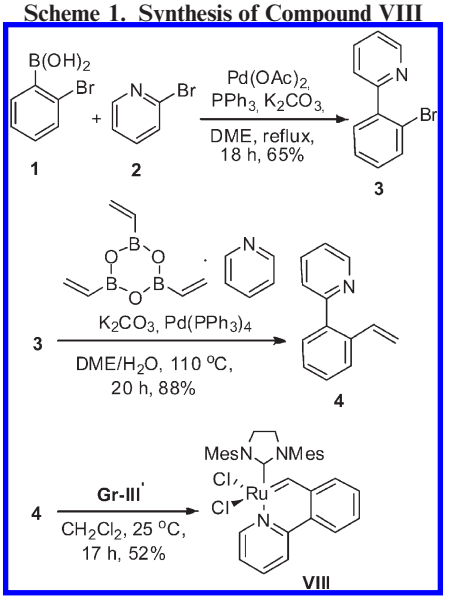
(14) Guławski, Ł.; Michrowska, A.; Bujok, R.; Grela, K. *J. Mol. Catal. A* **2006**, *254*, 118.

(15) (a) Kadyrov, R.; Rosiak, A.; Tarabocchia, J.; Szadkowska, A.; Bieniek, M.; Grela, K. New Concepts in Designing Ruthenium based Second Generation Olefin Metathesis Catalysts and their Application. In *Catalysis of Organic Reactions: Twenty-second Conference*; Prunier, M. L., Ed.; Chemical Industries Series, Vol. *123*; CRC Press, 2008; p 568; (b) Grela, K.; Szadkowska, A.; Barbasiewicz, M.; Kadyrow, R. (Degussa AG) *Neuartige schwefelhaltige Metathese Katalysatoren*, DE Patent Application 102007020694.3, 2007. (c) Ben-Asuly, A.; Tzur, E.; Diesendruck, C. E.; Sigalov, M.; Goldberg, I.; Lemcoff, N. G. *Organometallics* **2008**, *27*, 811. (d) Kost, T.; Sigalov, M.; Goldberg, I.; Ben-Asuly, A.; Lemcoff, N. G. *J. Organomet. Chem.* **2008**, *693*, 2200.

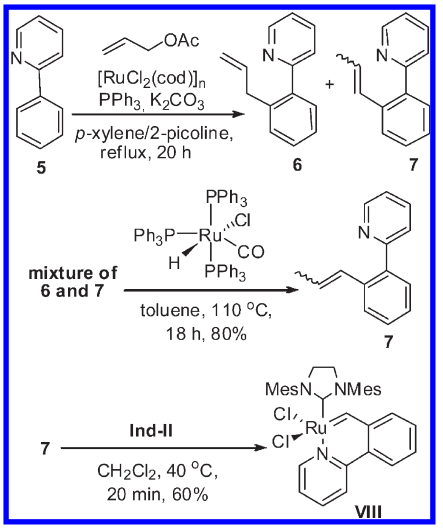
(16) (a) Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4038. (b) Michrowska, A.; Bujok, R.; Harutyunyan, S.; Sashuk, V.; Dolgonos, G.; Grela, K. *J. Am. Chem. Soc.* **2004**, *126*, 9318. (c) Barbasiewicz, M.; Szadkowska, A.; Makal, A.; Jarzembska, K.; Woźniak, K.; Grela, K. *Chem.—Eur. J.* **2008**, *14*, 9337.

(17) (a) Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 794. (b) Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2403. (c) Bieniek, M.; Bujok, R.; Cabaj, M.; Lugan, N.; Lavigne, G.; Arlt, D.; Grela, K. *J. Am. Chem. Soc.* **2006**, *128*, 13652. (d) Bieniek, M.; Bujok, R.; Stępkowska, H.; Jacobi, A.; Hagenkötter, R.; Arlt, D.; Jarzembska, K.; Woźniak, K.; Grela, K. *J. Organomet. Chem.* **2006**, *691*, 5289. (e) Michrowska, A.; Guławski, Ł.; Kaczmarska, Z.; Mennecke, K.; Kirschning, A.; Grela, K. *Green Chem.* **2006**, *8*, 685. (f) For an overview on Hoveyda−Grubbs catalysts, see: Michrowska, A.; Grela, K. *Pure Appl. Chem.* **2008**, *80*, 31.

Scheme 1. Synthesis of Compound VIII



Scheme 2. Alternative Synthesis of Ligand 7 and Complex VIII



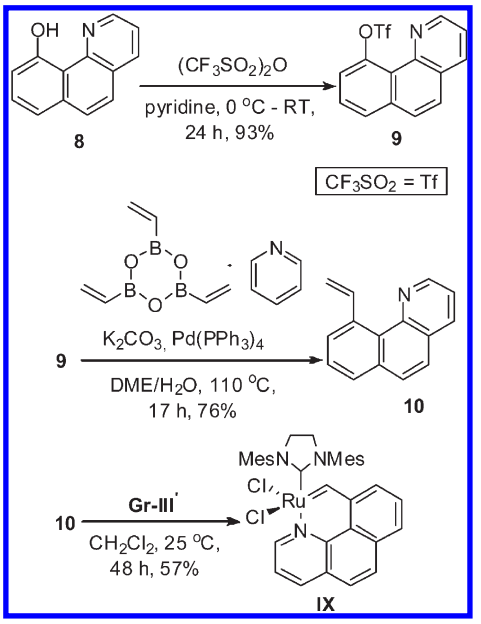
Results and Discussion

The preparation of the presented initiators was straightforward, based on well-known transformations. The synthesis of the designed precursor **4** consisted of a set of Suzuki−Miyaura cross-couplings, using a 2,4,6-trivinylcyclotriboroxane-pyridyne complex to introduce the vinyl group to the ligand precursor (Scheme 1). As shown in the same scheme, catalyst **5** was obtained by the carbene exchange reaction of $(H_2IMes)(pyridine)_2(Cl)_2Ru{=}CHPh$ (**Gr-III′**) with the vinyl derivative **4** described above. A mixture of 1 equiv of **Gr-III′** and 2 equiv of **4** was subjected to overnight stirring in CH_2Cl_2 at 25 °C, leading to formation of **VIII** as green microcrystals in 52% yield by precipitation upon addition of Et_2O.

Encouraged by the report on *ortho*-selective allylation of 2-pyridylarenes published by Inoue and co-workers, we tried an alternative ligand synthesis (Scheme 2).[18] In this case, the synthesis of **VIII** starts from inexpensive 2-phenylpyridine **5**, which is allylated using allyl acetate, in the presence of 5 mol % of dichloro(1,5-cyclooctadiene)ruthenium(II) to yield two isomeric products: **6** and **7**. Complexes **6** and **7** were formed in a ratio of 80:20, according to GC analysis. This isomeric mixture was not separated, but further isomerized, to **7** in pure form. This was achieved by using Krompiec $(PPh_3)_2ClRu(H)(CO)$ catalyst (2.5 mol %) in dry toluene.[19] This reaction proceeded smoothly to give 2-(2-prop-1-enyl)phenyl)pyridine (**7**) in 80% yield as the only product. Synthesis of the catalyst **VIII** employed the metathesis-ligand exchange reaction between **Ind-II** and **7** in the presence of CuCl, completed with the final 60% conversion into **VIII** in pure form (after chromatographic workup).

(18) Oi, S.; Tanaka, Y.; Inoue, Y. *Organometallics* **2006**, *25*, 4773.

Scheme 3. Synthesis of Ru-Initiator IX



Complex **VIII** was found to be perfectly air stable and was fully characterized by spectral techniques and by elemental analysis. The ^1H NMR for **VIII** was consistent with the expected C_s symmetric structure, and the benzylidene proton resonance signal appeared at 18.85 ppm. The ^{13}C NMR spectrum showed the carbene carbon at 314.7 ppm, while the NHC carbon gave a resonance at 216.5 ppm.

As the aim of the current work was to check whether decreasing the flexibility of the chelating carbene moiety might result in increased latency of the catalyst/initiator, the catalyst **IX** was prepared. In **IX**, more pronounced rigidity was introduced by using a more π-conjugated chelating carbene ligand (Scheme 3). In the first step of the synthesis of the ligand precursor, compound **9** was synthesized via esterification of 10-hydoxybenzo[*h*]quinoline (**8**) with triflic anhydride in pyridine.[20] Further, in the Suzuki−Miyaura cross-coupling reaction compound **10** was made,[21] which then was used to obtain the initiator **IX** via a carbene exchange with **Gr-III′** as the ruthenium source.

In general, the ^1H NMR spectrum of initiator **IX** was similar to the one observed for the catalyst **VIII** (C_s symmetry). The characteristic carbene proton appeared at 19.19 ppm. In the ^{13}C NMR spectrum, the carbene carbon

(19) Krompiec, S.; Kuznik, N.; Bieg, T.; Adamus, B.; Majnusz, J.; Grymel, M. *Pol. J. Chem.* **2000**, *74*, 1197.
(20) Stille, J. K.; Echavarren, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
(21) Kerins, F.; O Shea, D. F. *J. Org. Chem.* **2002**, *67*, 9681.

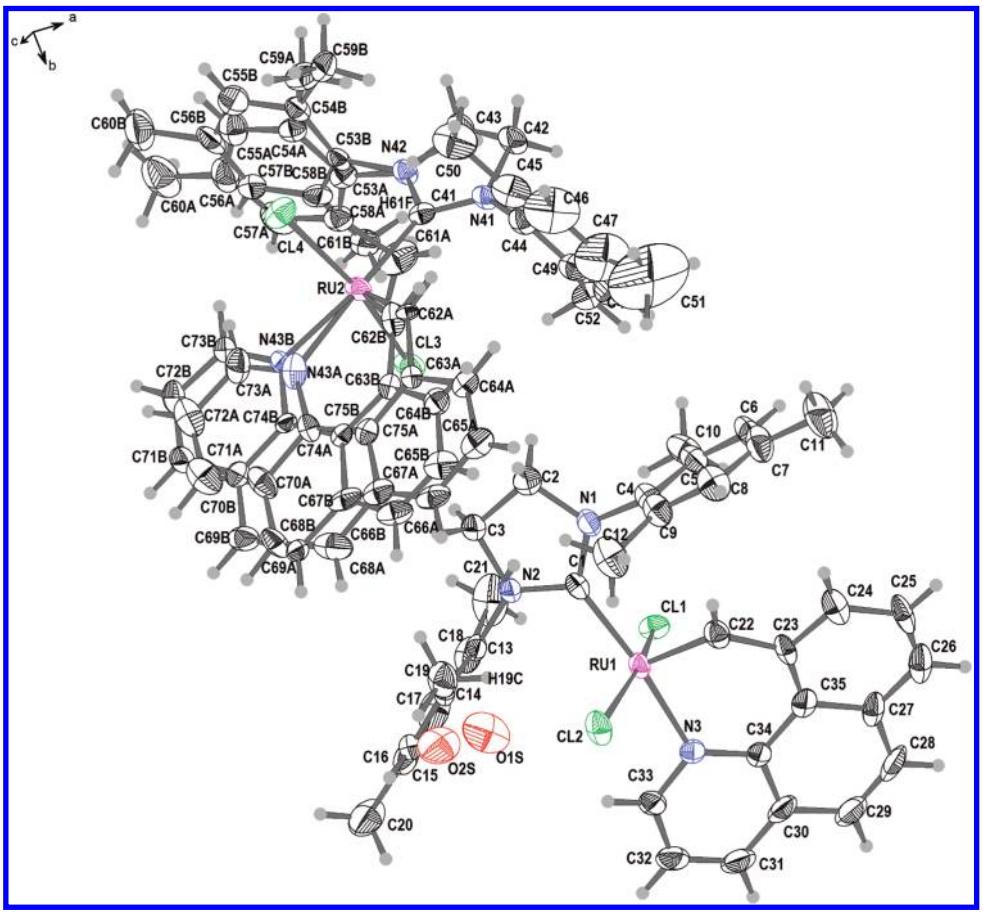


Figure 3. ORTEP drawing of two independent molecules of **IX** (the upper one disordered) represented by atomic displacement parameters drawn at the 50% probability level. Hydrogen atom labels are excluded for clarity.

appeared at 290.4 ppm and the NHC carbon was observed at 215.5 ppm.

Having in mind that the *trans*−*cis* isomerization process occurred in some previous N-chelating catalysts,[12] we tried to measure the kinetics of isomerization of the catalysts **VIII** and **IX** to their *cis*-dichloro counterparts. Monitoring ^{1}H NMR spectra of **VIII** or **IX** at 23 °C in CD_2Cl_2 for two months[13a,b] led us to conclude that no isomerization was taking place. It is worth noting that also no sign of decomposition of the compounds was observed. These results correlate very well with the observed high stability of complexes **VIII** and **IX** in the solid state.

To learn more about the structural peculiarities exhibited by **VIII** and **IX**, we focused on obtaining single-crystal X-ray crystallographic data for the complexes. Unfortunately, despite many trials of crystallization of **VIII**, single crystals suitable for X-ray measurement were not obtained. In the case of **IX**, a single crystal of acceptable quality was obtained by a slow diffusion of *n*-hexane into benzene solution. The crystal structure was successfully solved and refined and is shown in Figure 3. Other structural information for catalyst **IX** is given in Table 1.

Compound **IX** crystallized in the tetragonal $P4_2/n$ space group with two independent molecules in the asymmetric part of the unit cell, forming green needle-shaped crystals. Both ruthenium complex molecules occupy general positions, and there is one disordered water molecule (in the form of two halves) per two independent Ru moieties in the crystal structure. These disordered water molecules are located close to the $\bar{4}$ axes and thus form a regular, almost planar, octagon (see red dots in Figure 4). Among these two independent molecules of complex **IX**, one comprises atoms of very well determined positions while the other one exhibits a high degree of disorder in the ylidene group. In the case of the disordered ylidene fragment, one benzene ring takes two relatively well-defined positions in space, whereas the second benzene ring apparently (large ADP values) is trying to occupy two positions, although the resolution of the data is not good enough to distinguish them. The benzoquinoline

Table 1. Selected Bond Lengths (Å) and Angles (deg)

parameter	value
Ru(1)−C(22)	1.814(4)
Ru(1)−C(1)	2.039(4)
Ru(1)−N(3)	2.107(3)
Ru(1)−Cl(2)	2.339(1)
Ru(1)−Cl(1)	2.346(1)
Ru(2)−C(62B)/Ru(2)−C(62A)	1.661(18)/1.932(16)
Ru(2)−C(41)	2.039(4)
Ru(2)−N(43B)/Ru(2)−N(43A)	2.121(14)/2.117(16)
Ru(2)−Cl(4)	2.338(1)
Ru(2)−Cl(3)	2.358(1)
C(22)−Ru(1)−C(1)	99.42(18)
C(1)−Ru(1)−N(3)	171.24(15)
C(22)−Ru(1)−N(3)	88.82(17)
Cl(2)−Ru(1)−Cl(1)	160.36(4)
C(62B)−Ru(2)−C(41)/C(62A)−Ru(2)−C(41)	104.0(7)/95.7(5)
C(62B)−Ru(2)−N(43A)/C(62B)−Ru(2)−N(43B)	77.4(7)/90.4(7)
C(62A)−Ru(2)−N(43A)/C(62A)−Ru(2)−N(43B)	85.8(6)/98.8(6)
C(41)−Ru(2)−N(43A)/C(41)−Ru(2)−N(43B)	176.2(4)/165.5(4)
Cl(4)−Ru(2)−Cl(3)	160.28(5)

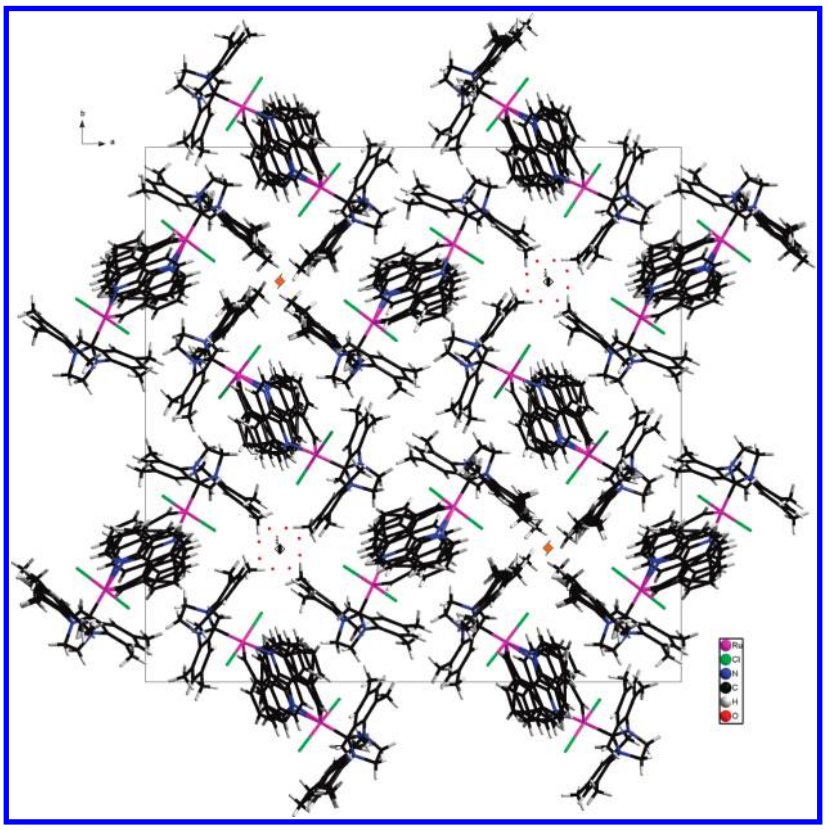


Figure 4. Projection of the unit cell contents along the *z*-axis. Water oxygen atoms are illustrated as red dots; red squares, 4_2 axis; black-striped squares, $\bar{4}$ axis.

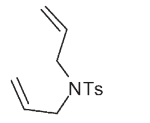
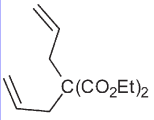
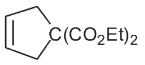
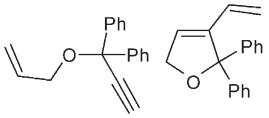
molecular fragment is also disordered and occupies two alternative positions in the crystal lattice. However, the bond lengths in the first molecule do not differ much from the corresponding parameters in the second molecule (there is only a slight difference in the length of the Ru−N bond: 2.107(3) and 2.121(14)/2.117(16) Å in the ordered and disordered moiety, respectively). Consequently, both ruthenium centers exhibit a deformed quadratic pyramid geometry with the carbene carbon atom occupying the top position and two chloro ligands in a *trans* arrangement (SPY-5-31 isomer) with very similar bond lengths and valence angles (Table 1). The base of the square pyramid is formed by the two above-mentioned chloro ligands, Cl(1) and Cl(2), the benzo[*h*]quinoline nitrogen N(3), and the C(1) atom of the H_2IMes ligand, while the carbene carbon atom, C(22), forms the apex. Molecules of complex **IX** are arranged in space in such a way that benzoquinoline ligands lie parallel one above another (alternating between the two independent molecules); see Figure 4. They are shifted relative to each other to compromise interactions between steric hindrance and stacking of the molecules. The ylidene ligands lie perpendicular to each other as a consequence of the presence of the 4-fold axis with benzene rings forming perpendicular planes to those defined by benzoquinoline ligands, as shown below. There are two different kinds of cavities around the 4-fold axes. The cavities associated with the $\bar{4}$ axis contain water molecules, as we have already mentioned, and the ones around the 4_2 axis are relatively smaller and empty; however they allow the ylidene fragments to pack most efficiently.

The basic layout of the two moieties (e.g., the Cl(1)−Cl(2) vector being essentially perpendicular to the dihydroimidazole main plane), as well as the bond lengths and angles (see Table 1), agrees well with related complexes studied in recent years.[12,13a] However, the compound stands out by being comparatively distorted in the chelating ring part. The C(22)−Ru−N(3) angle is equal to 88.82(17)°, whereas all other angles forming the chelating six-membered ring are larger than 120°. Furthermore, the chelating six-membered ring is highly distorted out of the plane. If one chooses a plane passing by C(22), C(23), C(35), and C(34), to the N(3) atoms, Ru lies slightly out of this plane, which corresponds to a slight bending of the benzo[*h*]quinoline moiety with respect to the Ru−N bond.

In order to establish a structure/reactivity relationship for the two complexes, three model RCM reactions were used. Catalysts **VIII** and **IX** were tested in ring-closing metathesis of *N*,*N*-diallyltosylamine (**S1**), RCM of diethyldiallyl malonate (**S2**), and cycloisomerization of enyne (**S3**) (Table 2). The course of each reaction was monitored by GC with *n*-dodecane or *n*-tetradecane as internal standard, measuring the increase in the amount of product with time. In all reactions tested, the initiator **IX** performed significantly slower, as compared to the catalyst **VIII** under identical conditions. Interestingly, the model reactions were far from completion, even after 24 h. No byproduct formation was detected, and it should be noted that after that time pure initiator was observed in both reaction mixtures.

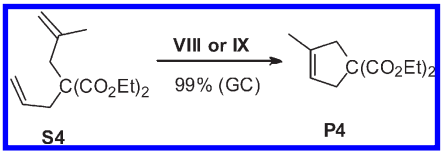
The activity of complexes **VIII** and **IX** was then tested at 80 °C, using diethylallyl(2-methylallyl)malonate (**S4**) as the more demanding model substrate. The 99% conversion according to GC analysis was obtained after 24 h for both of the catalysts tested (Scheme 4). This result proves that elevated temperatures are necessary for ring-closing metathesis when both **VIII** or **IX** are used as initiators.

Table 2. Catalytic Activity of VIII and IX in Test Reactions at Low Temperature[a]

substrate	product	catalysts		
		VIII	IX	
		3h 40% 24h 60%	3h 0% 24h 3%	
S1	P1			
		3h 0% 24h 10%	3h 0% 24h 0%	
S2	P2			
		3h 21% 24h 65%	3h 0% 24h 15%	
S3	P3			

[a] Conditions: 5 mol %, *c*[**S1**, **S2**, or **S3**] = 0.02 M, dichloromethane, 40 °C, 24 h; conversions according to GC.

Scheme 4. RCM of Diene S4[a]



[a] Conditions: *c*[**S4**] = 0.02 M, 5 mol % of **VIII** or **IX**, toluene, 80 °C, 24 h.

Having established the good application profile of **VIII** and **IX** at elevated temperatures, we decided to verify how the catalysts perform at lower loadings. It was found that complexes **VIII** and **IX** applied in RCM of substrate **S4** in low amount (0.1 mol %) resulted in conversions of 54% and 47%, respectively, after 24 h at 110 °C in toluene. In order to ascertain whether our latent catalysts were still active after this time, we extended the time of the reaction of ring closing of diethylallyl(2-methylallyl)malonate to 48 h. It appeared that both complexes **VIII** and **IX** performed remarkably well and reached a conversion of 99% after that time.

It should be noted that despite such extreme conditions (boiling toluene, 24−48 h), reaction solutions remained green, which is an indication that initiation of the catalyst was rather small and the stability of **VIII** and **IX** is high even in the presence of the substrate. Remarkable stability combined with high efficiency at the elevated temperatures is useful in metathesis of more demanding compounds, such as tri- or tetrasubstituted dienes and, at the same time, determine **VIII** and **IX** as thermo-switchable latent initiators in ROMP. To gain information on the latency of compounds **VIII** and **IX** in ROMP, we conducted model polymerizations utilizing (±)-*endo*,*exo*-5,6-bis(ethoxymethyl)bicyclo-[2.2.1]hept-2-ene (**M1**), (±)-*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (**M2**), and a mixture of 78% *endo*- and 22% *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ethyl ester (**M3**) (Figure 5). It can be expected

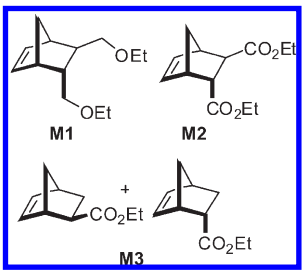


Figure 5. Monomers used in ROMP.

that in the case of the monomers **M1**−**M3** different rates of initiation and polymerization[22] should be observed as a consequence of different anchor groups.

As the first criterion, we monitored the performance of complexes **VIII** and **IX** as initiators for the polymerization of the monomers by ^{1}H NMR spectroscopy in solution. One equivalent of **VIII** or **IX** was added into a NMR tube and dissolved in $CDCl_3$ (0.5 mL) under an inert atmosphere of nitrogen. Monomer **M2** (20 equiv) dissolved in $CDCl_3$ (0.2 mL) was added, and the NMR tube was tightly closed with a rubber septum. ^{1}H NMR spectra were recorded immediately and, subsequently, every 2 days for 30 days, maintaining the temperature of 22 °C. In the case of **IX**, no polymerization was observed, whereas **VIII** promoted slow polymerization of **M2** under these conditions. After 20 days, a conversion of 55% was achieved. At that time, the initiator was consumed, as indicated by the disappearance of the characteristic NMR signals of **VIII**, and no further conversion was observed within another 8 days of monitoring. The observation might be explained by a moderate sensitivity presumably toward oxygen of the propagating species, since both ruthenium compounds are, even without exclusion of oxygen, perfectly stable in $CDCl_3$ solutions for more then 2 months.

Furthermore, polymerizations in solution were carried out. For this purpose, toluene was used as the solvent. The corresponding initiator (1 equiv) was dissolved in 3 mL of toluene and added to 300 equiv of the monomer under an inert atmosphere of argon. The reaction mixture was heated to 110 °C, stirred at this temperature for 5 h, and allowed to cool to room temperature. Then 50 μL of ethyl vinyl ether was added. Finally, precipitation of the polymer was achieved by slow addition of the reaction mixture to vigorously stirred methanol. The resulting white precipitates were sampled and dried in a vacuum, giving rise to yields of 27−96%. Also the remaining liquid was evaporated to dryness and the residue was dried *in vacuo* in order to quantify the amount of residual monomer.

Similarly, bulk polymerizations of **M1**−**M3** were performed using **VIII** and **IX** as the initiators. The corresponding complex (1.0 equiv) was dissolved in 50 μL of CH_2Cl_2 and added to the neat monomer (300 equiv) placed in a Schlenk tube. The reaction vessel was put into a preheated (110 °C) oil bath for 5 h and stirred continuously. After cooling the reaction mixture to room temperature, the residue was dissolved in CH_2Cl_2 and 50 μL of ethyl vinyl ether was added. Further workup was done as in the case of the solution polymerization. Yields and residual monomer contents of these trials are presented in Table 3. All polymers were characterized by ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopies, SEC (size exclusion chromatography), and DSC (differential scanning calorimetry). The spectroscopic methods (NMR and IR) revealed the occurrence of ROMP in all

(22) Slugovc, C.; Demel, S.; Riegler, S.; Hobisch, J.; Stelzer, F. *Macromol. Rapid Commun.* **2004**, *25*, 475.

Table 3. Yields of Polymers Obtained from Solution and Bulk Polymerization

polymer	solution[a] yield % (residual monomer %)	bulk[b] yield % (residual monomer %)
polyM1/VIII	91 (−) M_n = 1 180 000; PDI = 1.9	95 (< 3)[c] M_n = 2140000; PDI = 2.1
polyM2/VIII	81 (15) M_n = 1 230 000; PDI = 2.2	91 (−) M_n = 2 080 000; PDI = 2.6
polyM3/VIII	96 (−) M_n = 1 090 000; PDI = 2.4	87 (−) M_n = 2 010 000; PDI = 2.2
polyM1/IX	23 (68) M_n = 1 280 000; PDI = 2.3	95 (< 3)[c] M_n = 231 000; PDI = 2.1
polyM2/IX	27 (61) M_n = 1 310 000; PDI = 2.2	72 (14) M_n = 2 090 000; PDI = 1.9
polyM3/IX	89 (< 5) M_n = 1 470 000; PDI = 2.4	69 (12) M_n = 2 190 000; PDI = 2.3

[a] Reaction conditions: initiator:monomer = 1:300, solvent, toluene; 110 °C, 5 h. [b] Reaction conditions: initiator:monomer = 1:300, no solvent; 110 °C, 5 h. [c] Insoluble polymer.

cases under these conditions. No differences in the stereochemistry of the obtained polymers were observed while using the different initiators. SEC of the polymeric samples obtained from the solution polymerization in THF, relative to polystyrene standards, revealed molecular weights (M_n's) of > 1 000 000 g/mol in all cases. The M_n values for the polymers obtained from the bulk polymerization were even higher, exceeding 2 000 000 g/mol in all cases. Using an initiator providing fast and complete initiation, M_n's of about 50 000 g/mol could be expected.[23] Conclusively, initiation is considerably small for all initiator−monomer combinations under investigation and even lower when no solvent is applied. There are no significant differences in the M_n values of the polymers obtained with **VIII** and **IX**. Polydispersities of the polymers are reported for completeness; however, they do not add important information. They ranged from 1.9 to 2.6. The results on yield of polymers obtained from the solution and bulk polymerizations are presented in Table 3. M_n and PDI for each polymerization experiment can be found in the Supporting Material.

Further information on the course of the bulk polymerizations was obtained by means of monitoring the polymerization by DSC.[10f] The initiator (1 equiv) and the monomer (500 equiv) were filled into DSC pans, which were then placed into the apparatus. A heating ramp of 3 °C/min commenced at 20 °C. The reaction exotherm was read out as a function of temperature, thus allowing an easy and convenient characterization of the thermal switchability of newly synthesized initiators. The "switching temperature" for the initiators is characterized by the onset of the exothermic heat-flow. Figure 6 shows the corresponding graphs.

The polymerizations of **M1**−**M3** initiated by **VIII** were characterized by an onset of the exothermal heat flow in the range 46 ± 1 to 52 ± 1 °C, while polymerizations with **IX** commenced at distinctly higher temperatures. Onset temperatures in the range 104 ± 2 to 117 ± 2 °C were determined. This trend reassembles the results obtained from the catalytic activity of these complexes in RCM presented before.

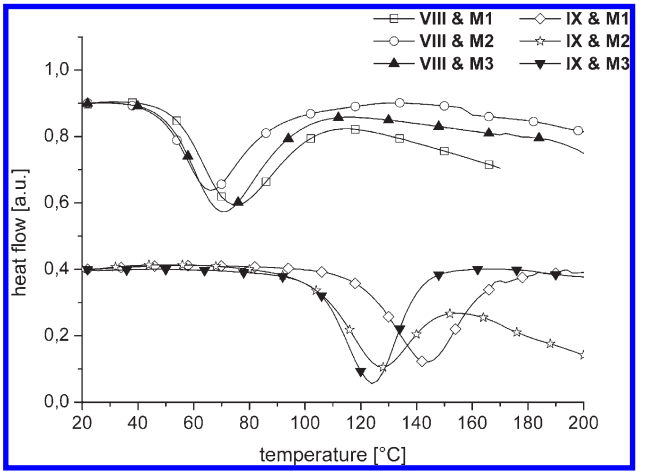


Figure 6. Course of polymerization of **M1**, **M2**, and **M3** initiated by **VIII** and **IX** (heating rate = 3 °C/min, initiator:monomer ratio = 1:500).

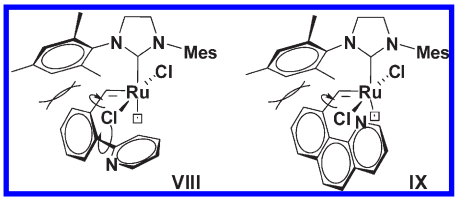


Figure 7. Proposed influence of the ligand rigidity on initiation of precatalysts **VIII** and **IX** via ligand decoordination.

Polymerizations of monomers **M2** and **M3** commenced at lower temperatures when compared to the experiments with monomer **M1**. This trend was more pronounced in the case of **IX** as the initiator. A similar observation was made before.[13b]

The results obtained in RCM and ROMP transformations showed a significantly increased latency of complex **IX** compared to **VIII**. The observed feature might be explained by the increased rigidity of the chelating carbene ligand of **IX**. For the generation of the 14-electron complex necessary for initiation, the N-donor atom has to dissociate from the ruthenium center.[24] This is easier to achieve in the complex **VIII** because of the possibility of free rotation of the aromatic rings in the 2-phenylpyridine moiety, whereas in **IX** the halide ligands and mesityl substituents impede the departure of the nitrogen atom from the vacant coordination site (Figure 7). Additionally, the increased aromatic character of the ruthenacycle might contribute to the pronounced latency of **IX**.[16c] As we previously reported, the initiation step of the Hoveyda−Grubbs-type catalysts remains dependent on the topology of the ligand core. The presence of a conjugated π-electron system within the chelating framework tends to stabilize the catalyst resting state, thereby retarding the initiation step.[16c]

Conclusions

In summary, we disclosed the syntheses of two new ruthenium complexes bearing chelating carbene ligands. Both complexes are stable at ambient conditions and exhibit catalytic activity at elevated temperatures. Remarkably,

(23) Burtscher, D.; Lexer, C.; Mereiter, K.; Winde, R.; Karch.; Slugovc, C. *J. Polym Sci. Part A: Polym. Chem.* **2008**, *46*, 4630.

(24) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *27*, 6543.

0.1 mol % of either of the introduced catalysts accomplished complete RCM of diethylallyl(2-methylallyl)malonate at 110 °C in less than 48 h. Although the reaction time is not particularly impressive, the results are good indications of the high temperature stability of the compounds under investigation. The latency of complex **IX**, containing the π-conjugated system, was more pronounced than that of the more "flexible" counterpart **VIII**, as revealed by determination of the "switching temperatures" for initiators **VIII** and **IX** in ROMP of several norbornene derivatives. Both dormant catalysts/initiators could be useful in a range of high-temperature applications.

Experimental Section[25]

General Syntheses of Catalysts. Synthesis of Catalyst VIII, SPY-5-31)-Dichloro-(κ^2(*C*,*N*)-*N*-2-(2-vinylbenzylidene)pyridine-(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)-ruthenium. To a solution of **4** (140 mg, 0.77 mmol) in CH_2Cl_2 (5 mL) was added $(H_2IMes)(pyridine)_2Cl_2Ru{=}CHPh$ (**Gru-III′**) (280 mg, 0.33 mmol), and the reaction mixture was stirred at 25 °C for 17 h. Afterward the mixture was evaporated to dryness and the residue was redissolved in CH_2Cl_2/Et_2O. Upon addition of *n*-heptane a green precipitate formed, which was separated by filtration, washed with heptanes, and dried under vacuum. Yield: 109 mg (52%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.45−2.49 (m, 18H), 4.15 (m, 4H), 6.65 (d, 1H), 7.10−7.16 (m, 4H), 7.55 (t, 1H), 7.57 (t, 1H), 7.60 (m, 2H), 7.74 (t, 1H), 7.97 (d, 1H), 8.14 (d, 1H), 16.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.4, 19.4, 21.0, 21.1, 26.0, 26.2, 26.7, 26.8, 31.4, 121.9, 122.1, 122.7, 126.3, 128.0, 128.2, 128.5, 128.7, 129.4, 130.0, 130.1, 130.2, 135.0, 136.7, 138.4, 140.4, 145.0, 148.2, 156.5, 216.5, 314.4. MS (FD/FI, *m*/*z*): calcd for $[M]^{+\bullet}$ ($C_{33}H_{35}N_3{}^{35}Cl_2{}^{102}Ru$) 646.1330; found 646.1346. IR (KBr): ν 3502, 2950, 2914, 2857, 2735, 1955, 1730, 1630, 1600, 1556, 1479, 1438, 1419, 1380, 1307, 1262, 1159, 1121, 1099, 1033, 950, 851, 789, 754, 735, 677, 641, 630, 579, 503, 474, 451, 420 cm^{-1}. Anal. Calcd for $C_{33}H_{35}N_3{}^{35}Cl_2{}^{102}Ru$: C, 61.29; N, 6.49; H, 5.61; Cl, 10.95. Found: C, 61.17; N, 6.42; H, 5.61; Cl, 11.06.

Alternative Synthesis of Catalyst VIII. A Schlenk tube equipped with a stirring bar was charged with ruthenium complex (**Ind-II**) (127 mg, 0.15 mmol) and CuCl (17.8 mg, 0.18 mmol). The tube was flushed with argon and charged with anhydrous methylene chloride (3.5 mL). Next, a solution of **7** (32 mg, 0.18 mmol) in methylene chloride (4 mL) was added under an argon atmosphere, and the resulting solution was stirred at 40 °C for 0.5 h. After this time, TLC indicated complete conversion of the substrate. The resulting mixture was concentrated *in vacuo*, the residue was redissolved in AcOEt, and the solution was passed through a Paster pipet containing a small amount of cotton and evaporated to dryness. The crude product was purified by column chromatography (using eluents cyclohexane/ethyl acetate, 10:1 to 1:1 v/v). After evaporation of the solvents, the resulting solid was collected and washed a few times with AcOEt and with cold *n*-pentane.

(25) For full experimental details and other information see the Supporting Information.

Synthesis of Catalyst IX, (SPY-5-31)-Dichloro-(κ^2(*C*,*N*)-2-(benzo[*h*]quinolin-10-yl)methylidene)(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)ruthenium . A Schlenk tube equipped with a stirring bar was charged with $(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh$ (**Gru-III′**) (622.0 mg, 0.733 mmol) and **10** (166.2 mg, 0.822 mmol). The tube was flushed with argon, and anhydrous CH_2Cl_2 (25 mL) was added. The purple reaction mixture was stirred at 25 °C for 48 h, whereupon the color changed to dark green. The volume of the solvent was reduced to about 5 mL, and upon addition of Et_2O (50 mL) a green precipitate formed, which was filtered off. The residue was washed with Et_2O (3 × 10 mL) and dried *in vacuo*. Yield: 282.1 mg (57%).

^{1}H NMR (δ, 20 °C, 500 MHz, $CDCl_3$): 19.19 (s, 1H, Ru=C*H*), 8.25 (d, $^3J_{HH}$ = 5.0 Hz, 1H, bq^2), 8.17 (d, $^3J_{HH}$ = 7.5 Hz,1H, bq^7), 8.07 (d, $^3J_{HH}$ = 8.0 Hz,1H, bq^4), 7.90 (d, 1H, bq^5), 7.64 (m, 2H, bq^{6,8}), 7.44 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, bq^3), 7.17 (s, 4H, Ph^{Mes3,5}), 7.10 (d, $^3J_{HH}$ = 7.5 Hz, 1H, bq^9), 4.20 (s, 4H, NCH_2), 2.55 (bs, 12H, CH_3), 2.50 (s, 6H, CH_3). ^{13}C NMR (δ, 20 °C, 125 MHz, $CDCl_3$): 290.4 (1C, Ru=*C*H), 215.5 (1C, N*C*N), 147.7 (1C, ^{bq2}), 146.0 (1C, bq^{10b}), 142.8, 139.4 (b), 138.8, 137.1, 136.1, 129.9, 129.8, 129.7, 128.6, 126.9, 124.9, 122.7, 121.6 (23C, bq^{3-10a}, Ph^{Mes1-6}), 51.7 (b, 2C, N*C*H$_2$), 21.4 (2C, *C*H$_3$), 19.5 (b, 4C, *C*H$_3$). MS (FD/FI, *m*/*z*): calcd for $[M]^{+\bullet}$ (C_{35} $H_{35}N_3{}^{35}Cl_2{}^{102}Ru$) 669.1252; found 669.1274. IR (KBr): ν 2951, 2916, 2855, 2737, 1739, 1622, 1607, 1581, 1516, 1481, 1431, 1419, 1402, 1379, 1336, 1314, 1292, 1261, 1213, 1185, 1170, 1135, 1034, 993, 976, 914, 882, 855, 839, 794, 759, 713, 643, 615, 578, 506, 458, 422, 411 cm^{-1}. Anal. Calcd for $C_{35}H_{35}N_3{}^{35}Cl_2{}^{102}Ru$: C, 62.82; N, 6.27; H, 5.27; Cl, 10.58. Found: C, 63.00; N, 6.12; H, 5.43; Cl, 10.47.

Acknowledgment. This work was supported by grant number N204157636, which was provided by the Polish Ministry of Science and Higher Education. K.G. and K.W. thank the Foundation for Polish Science for the "Mistrz" professorships. Single-crystal X-ray measurements were accomplished at the Structural Research Lab (SRL) of the Chemistry Department, Warsaw University, Poland. SRL has been established with financial support from European Regional Development Fund in the Sector Operational Program "Improvement of the Competitiveness of Enterprises, years 2004−2006" project no. WKP_ 1/1.4.3./1/2004 /72/72/165/2005/U. Parts of this work were supported by the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the K_{plus}-Program of the Austrian Ministry of Traffic, Innovation and Technology (project II 2.2). K.G. and C.S. thank the European Community for generous support, which was provided through the Seventh Framework Program (grant no. CP-FP 211468-2 EUMET).

Supporting Information Available: Complete characterization of all new compounds, catalytic procedures, X-ray crystallographic tables, and data in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.