Thermally Switchable Olefin Metathesis Initiators Bearing Chelating Carbenes: Influence of the Chelate's Ring Size

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Received February 28, 2005

Summary: The synthesis, characterization, and ROM polymerization activity of two ruthenium-based metathesis initiators bearing chelating carbene ligands with imine functionalities and N-heterocyclic carbene ligands are presented.

Efficient, well defined, single-component homogeneous catalysts for olefin metathesis have provided powerful tools for C−C bond formation in polymer chemistry and organic synthesis.[1] Ring-opening metathesis polymerization (ROMP) in particular has emerged as one of the key methodologies in the synthesis of speciality polymers.[2] While important issues such as versatility, high polymerization rates, functional-group tolerance, and "livingness" can be provided by state of the art ROMP initiators, there is still need for initiators that can be switched on by a certain event. Stimuli for the switching on can be irradiation with UV or visible light, treatment with acid, or heat. All three alternatives have been demonstrated in the past. Light-induced ROMP can be achieved by irradiation of (η^6-arene)ruthenium derivatives, as shown by the work of Noels et al.[3] Treatment of Ru benzylidenes with strong acids such as HCl led to a rate attenuation in ROMP of norbornene derivatives.[4] Most work has been done on thermally switchable initiators.[7−11] Several groups followed different design concepts to obtain latent initiators. Commonly employed strategies are illustrated in Chart 1.

As it is generally believed that dissociation of a donor ligand (e.g. L^2) is necessary for starting the polymerization event,[5] the trigger for switching on is readily identified: one has to think of slowing down or even preventing the dissociation of L^2 at room temperature. Motif A, an inert ligand L^2 in a position trans to L^1, which is mostly a phosphine such as tricyclohexylphosphine (PCy_3) or an N-heterocyclic carbene such as 1,3-bis(mesityl)-4,5-dihydroimidazol-2-ylidene (H_2IMes), has not been realized up to now. It seems that even ligands which are known to form commonly strong and inert bonds to ruthenium(II) centers are too labile in this special ligand environment. A way to overcome this problem is to take advantage of the chelate effect (examples B and C). Thus, ligand L^2 is either attached to the carbene (motif B) or via X (motif C, where X is oxygen, for example) to the central ruthenium atom. Motif B is based on Hoveyda-type catalysts[6] and was first realized by van der Schaaf et al. for the purpose of fine-tuning gel times for better handling of ROMP in technical processes.[7] More recently, related N-heterocyclic carbene based initiators have been presented.[8] Different approaches utilizing motif C were followed in the past. Grubbs and later Verpoort studied bidentate Schiff base ligands,[9] while Herrmann et al. combined chelating pyridinyl−alcoholato ligands with an N-heterocyclic carbene ligand.[10] Reasonable ROMP activity at elevated temperatures was reported in all studies. Another possibility is to use Fischer carbenes instead of Schrock carbenes (motif D), where X is O or S, for example.[7,11] Design concepts B and D enable fast propagation after retarded initiation in comparison to strategy C. In C the chelating ligand competes not only during initiation but also during propagation with the incoming alkene substrate for the vacant coordination site. This results in comparably low propagation rates.[5,9,10,12] We therefore consider concepts B and D superior for the development of thermally switchable and rapidly curing ROMP initiators.

Herein we describe the synthesis of ruthenium complexes that contain an N-heterocyclic carbene ligand and Schiff base based chelating carbene ligands. The effect

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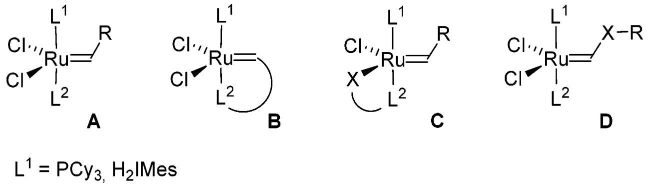
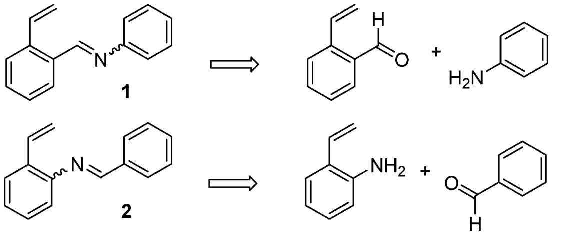
10.1021/om050141f CCC: $30.25

Chart 1. Design Concepts for Thermally Switchable Initiators



Scheme 1. Preparation of the Ligands



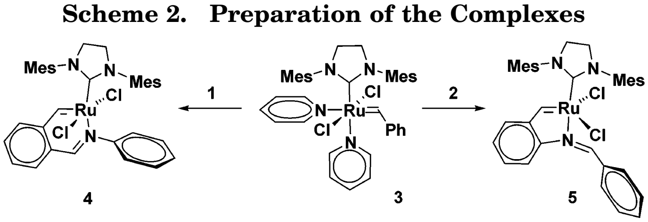
of the ring size of the chelating carbene ligands on the initiation behavior has been studied. Additionally we suggest an experiment to benchmark thermally switchable initiators.

Instead of the commonly used 2-(3-butenyl)pyridines,[7,8] phenyl(2-vinylbenzylidene)amine (**1**) and benzylidene-(2-vinylphenyl)amine (**2**) were employed as the carbene precursors (Scheme 1). We anticipated that **1** will form a six-membered and, accordingly, **2** a five-membered chelating carbene, which might allow studying the influence of the chelating carbene ring size on the ROM polymerization. Moreover, both molecules constitute the simplest member of a whole family of ligands. Simply by varying the amine in the case of **1** or the aldehyde component in the case of **2** an electronic and steric tuning of the nitrogen donor atom should be easily conceivable, making these ligand classes particularly interesting.

The synthesis of **1** was performed by using 2-vinylbenzaldehyde[13] and aniline (slight excess) in the presence of $TiCl_4$ as the water-removing agent.[14] By doing so, complete consumption of 2-vinylbenzaldehyde was achieved, as monitored by NMR spectroscopy.[15] The absence of 2-vinylbenzaldehyde is crucial for the further steps, because 2-vinylbenzaldehyde would produce (H_2IMes)(κ^2(C,O)-2-formylbenzylidene)Cl_2Ru, as reported elsewhere.[16] Usually, the crude aldehyde-free product was used for the next step without further purification. The same synthetic route was used for the preparation of **2**. In this case total conversion of 2-vinylphenylamine had to be guaranteed by adding a slight excess of benzaldehyde.[17]

As shown in Scheme 2, (H_2IMes)(κ^2(C,N)-2-(phenyliminomethyl)benzylidene)Cl_2Ru (**4**) and (H_2IMes)(κ^2-(C,N)-2-(benzylideneamino)benzylidene)Cl_2Ru (**5**) were prepared by a carbene exchange reaction of (H_2IMes)(pyridine)$_2$(Cl)$_2$Ru=CHPh (**3**)[18] with the vinyl derivatives described above. A mixture of 1 equiv of **3** and 2 equiv of crude **1** (or **2**) was stirred in CH_2Cl_2 at room temperature, according to a protocol similar to that used to obtain complexes of the type (H_2IMes)(PR_3)(Cl)$_2$Ru=CHPh (e.g. R = Ph, *n*-Bu, *p*-$CF_3C_6H_4$).[19] **4** and **5** were isolated in good yield (89% and 86%) as green microcrystals by precipitation upon addition of Et_2O.

Scheme 2. Preparation of the Complexes



Elemental analyses were in agreement with the calculated values in both cases. The spectroscopic data of **4** and **5** were all similar and were in accordance with the proposed stoichiometry and the classical trans stereochemistry of the halide ligands (cf. Scheme 2). Particularly diagnostic were the corresponding proton and carbon resonances of the carbene moieties. In the ^{1}H NMR the corresponding singlet was found at 18.74 ppm (**4**), while in **5** the signal was detected at a distinctly higher field (17.07 ppm). Imine proton and carbon resonances were 8.65 and 167.6 ppm for **4** and 9.32 and 164.8 ppm for **5**.

To elucidate the solid-state structures of the compounds, crystals were grown from saturated solutions of the complexes in CH_2Cl_2 by layering with Et_2O. The resulting crystals, **4** and **5**·(solv), were subjected to X-ray structure analysis. As the most important result the coordination geometry of Ru in both solids is a distorted square pyramid with the two chloro ligands in a trans arrangement (*SPY-5-31* configuration[16]). The base of the square pyramid is formed by the two chloro ligands Cl(1) and Cl(2), the imine nitrogen N(49) in **4** or N(48) in **5**·(solv), and the C(11) atom of the H_2IMes ligand, while the carbene carbon atom C(41) forms the apex. Important bond lengths and angles can be found in the captions of Figures 1 and 2. Further crystallographic details are given in the Supporting Information. The basic layout of the two complexes (e.g. the Cl(1)−Cl(2) vector being essentially perpendicular to the dihydroimidazole main plane) as well as the bond lengths and angles agree well with related complexes studied in recent years.[20] However, the two compounds stand out by being comparatively crowded on the open side of the Ru coordination by the presence of the bulky phenyl ring C(51)−C(56). Therefore, the PhCH=NPh moieties (C(41)−C(56)) are not planar but show mutual benzene−benzene twist angles of 62.4(2)° in **4** and 32.6(4)° in **5**·(solv). Moreover, the agostic interaction H(52)−Ru = 2.75 Å is present in **4**, whereas in **5**·(solv) the corresponding distance is larger by 0.2 Å.

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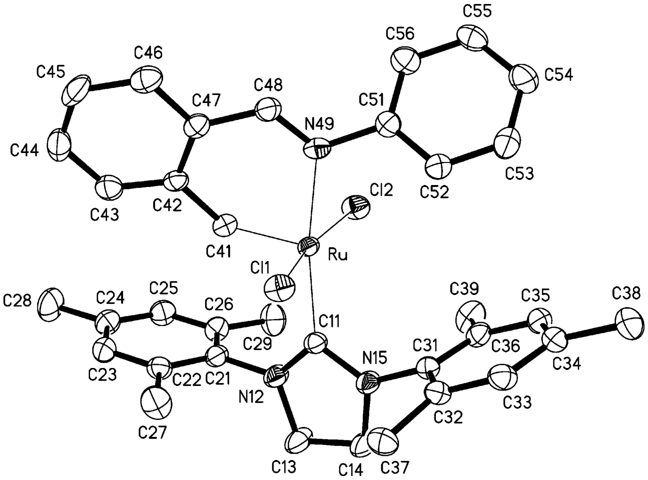

Figure 1. ORTEP plot of **4** (20% ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(41) = 1.827(4), Ru−N(49) = 2.083(3), Ru−C(11) = 2.085(3), Ru−Cl(1) = 2.347(1), Ru−Cl(2) = 2.370(1), C(41)−C(42) = 1.463(5), C(47)−C(48) = 1.421(6), C(48)−N(49) = 1.277(5), N(49)−C(51) = 1.456(5); C(41)−Ru−N(49) = 88.35(16), C(41)−Ru−C(11) = 101.25(15), C(41)−Ru−Cl(1) = 95.64(14), C(41)−Ru−Cl(2) = 96.03(14), C(11)−Ru−N(49) = 170.24(12), Cl(1)−Ru−Cl(2) = 167.57(4), C(42)−C(41)−Ru = 127.5(3), C(47)−C(48)−N(49) = 124.0(4), C(48)−N(49)−C(51) = 119.4(3).

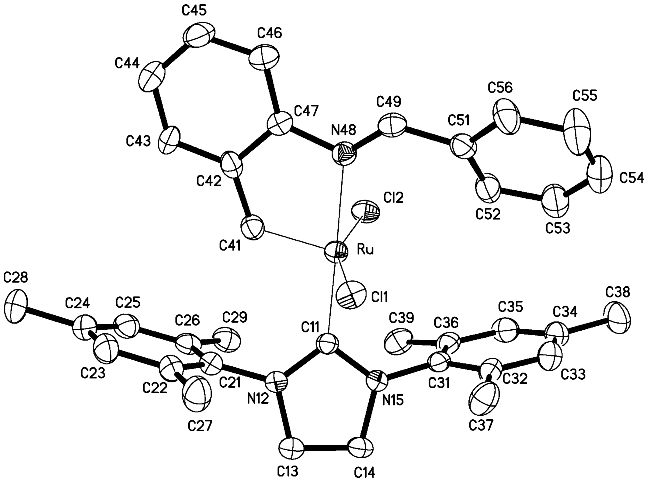

Figure 2. ORTEP plot of **5** in **5**·(solv) (20% ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(41) = 1.823(7), Ru−C(11) = 2.041(6), Ru−N(48) = 2.194(5), Ru−Cl(1) = 2.339(2), Ru−Cl(2) = 2.345(3), C(41)−C(42) = 1.430(10), C(47)−N(48) = 1.435(8), N(48)−C(49) = 1.282(8), C(49)−C(51) = 1.459(10); C(41)−Ru−C(11) = 99.4(3), C(41)−Ru−N(48) = 80.7(3), C(41)−Ru−Cl(1) = 105.6(2), C(41)−Ru−Cl(2) = 96.4(2), C(11)−Ru−N(48) = 172.2(2), Cl(1)−Ru−Cl(2) = 156.7(1), Ru−C(41)−C(42) = 120.6(5), C(47)−N(48)−C(49) = 118.9(6), N(48)−C(49)−C(51) = 127.2(6).

To gain information on the latency of compounds **4** and **5** in ROMP, we conducted model polymerizations utilizing (±)-*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (**6**) as the monomer. The polymerizations were monitored by means of DSC. The initiator (1 equiv) and the monomer (500 equiv) were placed in DSC pans, which were then transferred into the apparatus. A heating ramp of 3 °C/min commenced, and the reaction exotherm was read out as a function of temperature.

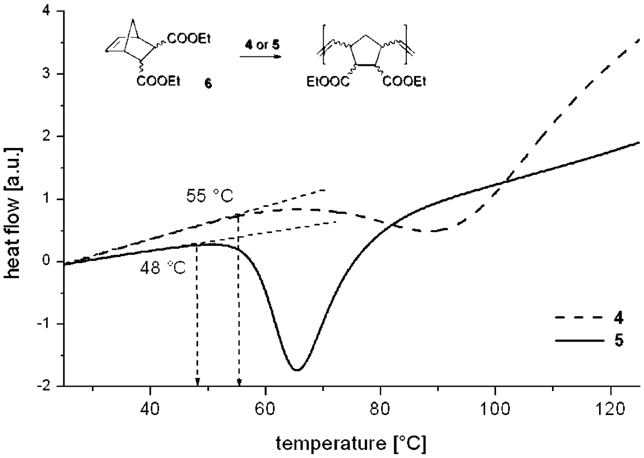

Figure 3. Course of the polymerization of **6** initiated by **4** and **5** (heating rate 3 °C/min, initiator:**6** = 1:500).

A “switching temperature” for the initiators (i.e. the temperature at which, under certain conditions, the polymerization is detectable) can be determined as the temperature at which the first exothermic heat flow is detectable. By means of this method a very easy and convenient way for benchmarking the thermal switchability of newly synthesized initiators is available. Figure 3 shows the corresponding graph.

As is obvious from Figure 3, the two initiators exhibited different rates of polymerization. Since the propagating species is the same in both cases, the difference might be explained by different initiation behaviors. This could be assured by determining the molecular weights of the corresponding polymers. **6** was polymerized with **4** and **5** in a ratio of 300:1 at 110 °C either in solution in toluene or in bulk by mixing **6** with the corresponding amount of **4** or **5**. Reaction times needed for completion of the polymerization were below 5 min in all cases. Determination of the weight average molecular weight (M_w) using gel permeation chromatography in THF revealed distinctly higher M_w values for the polymers prepared with **4** (solution, 1 660 000; bulk, 1 540 000) than for those prepared with **5** (solution, 1 270 000; bulk, 1 340 000). The polydispersity for all polymers was in the range of 1.9−2.3.[21]

Figure 3 suggests, at first view, that the initiators are inactive below 48 °C. When the information with solution polymerizations of **6** was compared, it became readily clear that polymerization at room temperature also occurred, albeit at very low rates. The polymerization of **6** was carried out in NMR tubes utilizing initiators **4** and **5** (solvent $CDCl_3$, initiator:**6** = 1:50, ambient conditions), and the reaction progress was monitored by ^1H NMR spectroscopy. **4** gave 20% conversion, while **5** polymerized 29% of **6** after 15 days. At the same time, in both cases 50% of the initiator was consumed. Since both complexes can be kept in $CDCl_3$ solutions under ambient conditions for at least 2 months without any evidence of decomposition or isomerization to, for example, the corresponding *SPY-5-34* derivative,[8]

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[21] Similar polymerization experiments using cyclooctene were also conducted. While the polymerization initiated by either **4** or **5** in bulk yielded insoluble polymeric materials, solution polymerizations (toluene; 110 °C; 5 min−2 h; initiator:cyclooctene = 1:300) were not successful, as indicated by the recovery of 85% of the cyclooctene upon workup.

the decrease of initiator can be best explained by a moderate sensitivity of the propagating species toward oxygen.

In conclusion, we have described a new class of second-generation metathesis catalysts bearing chelating carbene ligands based on imines. These perfectly stable catalysts are easy to obtain in high-yield synthetic procedures. The application of the compounds as initiators for thermally switchable ROM polymerization revealed pronounced latency at room temperature and very fast polymerization rates at temperatures around 110 °C. The latency of the six-membered chelating ring system in **4** is more pronounced than the latency of the five-membered-ring system of **5**. This explains a higher "switching temperature" and a lower polymerization rate for **4** compared to **5**. Similar effects due to electronic tuning of related oxygen-based bidentate carbene ligands on rates of catalytic activity were observed by the groups of Hoveyda[22] and Blechert.[23]

Perfectly stable and thermally switchable initiators are of great interest in polymer chemistry. It is desired that monomers and initiator(s) can be mixed and stored without concomitant polymerization. The initiators presented constitute a step forward toward these requirements, even though complete inactivity at room temperature was not achieved. Variations of the steric and electronic properties of the chelating carbene ligands and, thus, a fine-tuning of the polymerization characteristics of the presented complexes should be easily accomplished. Research along these lines is currently ongoing in our laboratories.

Acknowledgment. Financial support by the EC Project "DENTALOPT" (No. G5RD-CT2001-00554) is gratefully acknowledged. We cordially thank Materia for providing us with the Grubbs second-generation catalyst.

Supporting Information Available: X-ray crystallographic data in CIF and tabular format for the structures of compounds **4** and **5**, as well as text giving details of the preparations and characterization data for compounds **1**–**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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