

A Thermo- and Photo-Switchable Ruthenium Initiator For Olefin Metathesis

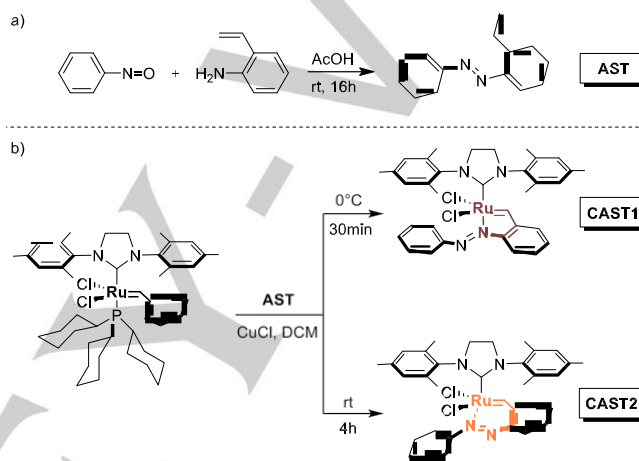
Volodymyr Sashuk*, and Oksana Danylyuk

Abstract: A ruthenium carbene complex bearing azobenzene functionality is reported. The complex exists in the form of two isomers differing by the size of chelate ring. Both isomers were isolated by applying kinetic or thermodynamic control during the synthesis and characterized by X-ray diffraction. The isomerization of the complex was studied by UV-Vis spectroscopy. The stable isomer was tested as a catalyst in olefin metathesis. The complex was activated at about 100°C to promote ring-closing and ring-opening polymerization metathesis reactions. The activation took place also at room temperature under middle ultraviolet radiation.

Olefin metathesis is a convenient chemical tool for creating carbon-carbon double bonds.^[1] Being known for a long time the reaction has become popular only after the discovery of the well-defined ruthenium Grubbs-type catalysts.^[2] Since the inception the ruthenium catalysts were developed primarily towards increasing their efficacy.^[3] With time, the focus on catalyst design was however shifted. Nowadays, an increasing interest is observed for the catalysts capable of switching the reactions on demand.^[4] It is highly desirable to have catalytic systems which are dormant at ambient conditions but able to be activated under external stimuli. The most promising are physical stimuli which hardly change the chemical composition of catalytic system and can be applied with good spatial and temporal resolution.^[5] The temperature and light are arguably the simplest and the most used physical triggers for olefin metathesis. The general strategy to achieve the thermal switching is based on the use of strongly chelating ligands containing atoms such as nitrogen,^[6] phosphorus,^[7] sulfur^[8], oxygen^[9] or even iodine.^[10] On other hand, when the labile ligands are employed, the catalysts are readily activated by light^[11] or sound^[12] irradiation. At the first glance, the requirements for thermal- and light-responsiveness seem to be incompatible. Fortunately, there are plenty of other light-activation mechanisms which can be utilized to make a strongly chelated catalyst photoswitchable.^[5c] Lemcoff *et al* has recently shown that *cis*- to *trans*-dichloro isomerization induced by light gives rise to the metathesis activity of a thermally switchable ruthenium catalyst containing *S*-chelating moiety.^[13] Surprisingly, this was the only report on the dual-responsiveness so far. Therefore, we decided to expand the portfolio of orthogonally activated metathesis initiators.

Here we present a new olefin metathesis catalyst which can be switched either by temperature or light. The catalyst contains *N*-chelating azo benzene moiety which coordinates to ruthenium center through either of the two nitrogen atoms leading to ring size isomerism. A five-membered chelate ring complex (**CAST1**) is a kinetic product which converts quickly in

solution into a six-membered thermodynamically favored isomer (**CAST2**). The latter is switched on at elevated temperatures to promote ring-closing (RCM) and ring-opening polymerization (ROMP) metathesis reactions. Also, it initiates the ROMP at room temperature under UV irradiation.



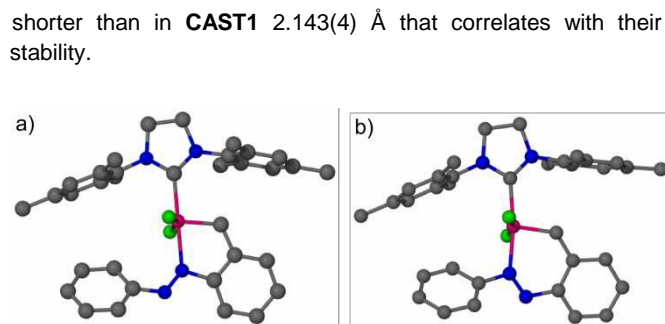
Scheme 1. Synthesis of: a) **AST** ligand, yield: 20%; b) **CAST1** complex, yield: not determined due to instability, and **CAST2** complex, yield: 67%.

The **CAST1** and **CAST2** catalysts were prepared by carbene exchange reaction using Grubbs-II ruthenium complex (**GII**) and (*E*)-1-phenyl-2-(2-vinylphenyl)diazene (**AST**). The latter was readily accessible in one step from commercially available nitrosobenzene and 2-vinylaniline. The reaction schemes for ligand and catalyst preparation are presented in Scheme 1. The carbene exchange reaction was complete at room temperature within 15 minutes yielding both isomers as indicated by thin layer chromatography (TLC). To obtain pure thermodynamic product the reaction mixture was aged for additional few hours. The product was isolated by chromatography and then crystallized by vapor diffusion technique from DCM-pentane solvent system at -30°C. The complex **CAST2** is extremely stable both in solid and solution. Being dissolved the product showed no signs of decomposition after one month at room temperature. The kinetic product was obtained by conducting the reaction at 0°C for half an hour. The product was crystallized directly from the reaction mixture using conditions outlined above. The crystal structures of both isomers are shown in Figure 1.

The isomers **CAST1** and **CAST2** crystallize in the orthorhombic space group *Pbcn*. The coordination geometry of ruthenium centre in both crystalline complexes is a deformed square pyramid with two chloro ligands in a *trans* arrangement. The base of the pyramid consists of two chloro ligands, the azobenzene nitrogen and carbon atom of the *N*-heterocyclic carbene, while alkylidene atom is on the top of the pyramid. The bond length and angles are very similar in two complexes. However, Ru-N distance in **CAST2** 2.057(8) Å is somewhat

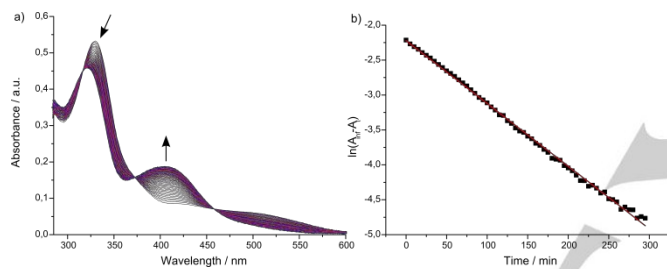
[a] Dr. V. Sashuk, Dr. O. Danylyuk
Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-210 Warsaw (Poland)
E-mail: vsashuk@ichf.edu.pl

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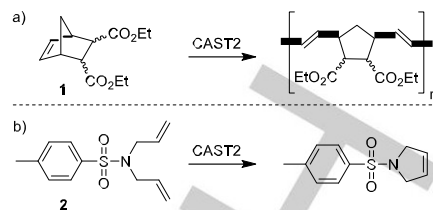
13 **Figure 1.** X-ray structures of **CAST1** (a) and **CAST2** (b).

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15 The transformation of the kinetic **CAST1** to the
16 thermodynamic **CAST2** was studied by UV-Vis spectroscopy
17 (Figure 2). The experiment was carried out at 22°C in toluene.
18 The transformation process obeys first order kinetics. The
19 calculated rate of the transformation $k=0.54 \text{ h}^{-1}$ that gives 77
20 minutes for the half-life of the kinetic complex **CAST1**.
21



32 **Figure 2.** UV-Vis (a) and corresponding kinetic (b) traces for **CAST1**→**CAST2**
33 isomerization, toluene, 22°C.

34
35 **CAST2** is practically inactive in olefin metathesis at room
36 temperature. For instance, only traces of metathesis products
37 (below 0.2%) were observed in substrate-catalyst mixtures after
38 two weeks. The employed olefin substrates are shown in
39 Scheme 2. The catalyst, however, becomes active upon heating.
40 To determine precisely the switching temperature of **CAST2** the
41 differential thermal analysis (DTA) was applied. The catalyst was
42 dissolved in a small amount of DCM and mingled with monomer
43 **1** in a ratio of 1:500. The solvent was next evaporated and the
44 sample was placed in a DTA-pan. The reaction thermal profile
45 was recorded at a rate of 3°C/min. The exothermic heat flow
46 with a maximum at 100°C indicated the polymerization reaction
47 (Figure 3). According to the DTA plot the polymer is stable up to
48 300°C after which the decomposition takes place as evidenced
49 by the following endothermic peak.
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Scheme 2. The catalytic reactions tested: a) ring-opening olefin metathesis polymerization; b) ring-closing olefin metathesis.

After the switching temperature was established the benchmark ROMP and RCM reactions were probed. The polymerization of **1** in nearly boiling toluene gave the corresponding product with $M_n=5.8 \cdot 10^5$ and $M_w/M_n=3.23$. Higher molecular weight ($1.1 \cdot 10^6$) and lower polydispersity (2.13) were obtained when the reaction was performed in neat monomer. The experiments in solution and bulk were carried out under identical reaction conditions (110°C, monomer-catalyst ratio 300:1, argon atmosphere). In both cases virtually full conversions (>99%) were attained after 1h. **CAST2** displays also RCM activity. The metathesis experiment was performed in NMR tube at 110°C in deuterated toluene under argon blanket. With 1 mol% catalyst loading the alkene **2** was ring-closed in 73% yield within one day. Further heating did not improve the yield significantly probably due to side isomerization reaction. The highest yield (84%) was obtained four days after the experiment was started. The periodic evacuation of ethylene gas formed during the reaction also had almost no influence both on the reaction rate and the final yield. Importantly, after the reaction was completed, the catalyst was still present in the solution evincing its exceptional thermal stability.

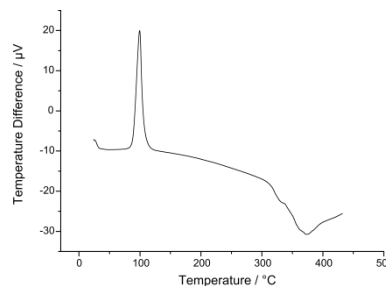


Figure 3. DTA plot for ROMP of **1**, DCM, **CAST2**:**1**=1:500, heating rate 3°C/min.

We envisioned initially that UV irradiation could entail conformational changes in the coordination sphere of ruthenium through trans-to-cis isomerization of azobenzene moiety thereby affecting the catalytic properties of **CAST1**. The most stable isomer, however, appeared to be **CAST2** with the azo bond blocked toward isomerization due to chelation.^[14] Indeed, a trial to prompt the isomerization and catalytic activity of **CAST2** through the excitation of $\pi-\pi^*$ transition band with a maximum located at 320 nm failed. Unexpectedly, switching the light to lower wavelength rendered the catalyst active concomitantly

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1 leading to its fast decomposition. With a 254 nm UV handled
2 lamp (4W) the ROMP reaction proceeded with 54% yield after
3 24h. The reaction was performed at room temperature and
4 **CAST2:1**=1:300 ratio. The polymer obtained was of $M_n=6.7 \cdot 10^4$
5 and $M_w/M_n=2.24$. Although the mechanism of the photoactivation
6 of **CAST2** is not clear it can be similar to that suggested by
7 Buchmeiser for a ruthenium initiator bearing the cognate
8 triazene moiety.^[15]

9 In summary, we demonstrated for the first time a dually
10 latent *N*-chelating ruthenium metathesis catalyst. The catalyst is
11 activated by heating or under exposure to UV light irradiation.
12 The described latent behavior may be useful for the preparation
13 of ready-to-use catalyst-monomer formulations or applied in the
14 polymer patterning technologies. This is also the first report on
15 chelate ring isomerism in the ruthenium carbene complexes.

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25 **Keywords:** carbenes • chelates • metathesis • N ligands •
26 ruthenium

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Layout 2:

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Volodymyr Sashuk*, Oksana Danylyuk

Page No. – Page No.

Title: A Thermo- and Photo-Switchable Ruthenium Initiator For Olefin Metathesis

Text for Table of Contents: **A Double-Faced** ruthenium carbene complex bearing azobenzene moiety is presented. The complex exhibits chelate ring isomerism accessible under kinetic and thermodynamic control. Also, the complex acts as a olefin metathesis catalyst in response to heating or light irradiation.