Photochemistry

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A Light-Activated Olefin Metathesis Catalyst Equipped with a Chromatic Orthogonal Self-Destruct Function

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Abstract: *A sulfur-chelated photolatent ruthenium olefin metathesis catalyst has been equipped with supersilyl protecting groups on the N-heterocyclic carbene ligand. The silyl groups function as an irreversible chromatic kill switch, thus decomposing the catalyst when it is irradiated with 254 nm UV light. Therefore, different types of olefin metathesis reactions may be started by irradiation with 350 nm UV light and prevented by irradiation with shorter wavelengths. The possibility to induce and impede catalysis just by using light of different frequencies opens the pathway for stereolithographic applications and novel light-guided chemical sequences.*

Light is quite certainly the most valuable and perennial of our energy resources. It has been regularly exploited by chemists and nature to promote specific chemical reactions, most rewardingly in the area of photocatalysis.[1] Perhaps one of the most widely studied families of catalysts during the last twenty years has been the ruthenium-based olefin metathesis complexes based on the original Grubbs catalyst.[2] Judicious modifications of the ligand sphere have led to remarkable advances by endowing the catalysts with greater stability and efficiency and by providing them with special functions. Catalyst development has even allowed the emergence of switchable catalysts which may be activated by external stimuli such as light,[3] heat,[4] ultrasound,[5] acids,[6] or redox switches.[7] The impressive work invested on improving and tuning the Grubbs-type catalysts leaves no doubt that the continued design and development of smart catalysts will lead to novel applications with enhanced capabilities. For instance, in the field of three-dimensional (3D) printing by stereolitography,[8] it would be quite useful to permanently turn off a catalyst after it has printed the desired pattern on the thin layer so that it will not continue to react when the new layer coated above is irradiated. If this could be achieved, the layers may be made thinner and the lithography resolution could be increased. With this challenge in mind we envisaged a latent catalyst which could be activated when light shines on it at a specific wavelength and could be permanently deactivated when another light frequency is used. Such a catalyst could also be useful in chromatic orthogonal processes,[9] especially if nonmetathetic reactions[10] of the ruthenium catalyst could be involved in part of the desired sequences.

Here we detail the design, synthesis, and applications of a latent olefin metathesis catalyst which can be activated by irradiation with 350 nm light and is decomposed by 254 nm light.

To produce such a catalyst, the first obstacle to tackle was to introduce photoactivation and photodeactivation functions to the appropriate complex. Our group has recently developed sulfur-chelated ruthenium benzylidenes (e.g. $\mathbf{1_{Ru}}$) which show selective activation when irradiated with 350 nm UV light (Figure 1).[11] In addition, it was shown that short-

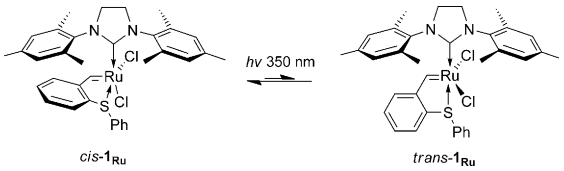

Figure 1. Photoactivation of a sulfur-chelated NHC/Ru complex.

wavelength UV light ($\lambda = 254$ nm) neither activated nor decomposed the catalyst.[12] Taking into account that functional groups on the N-heteerocyclic carbene (NHC) ligand of ruthenium benzylidenes have a strong effect on catalyst activity,[13] and having observed that the photodeprotection of supersilyl groups under certain conditions promoted the decomposition of Grubbs type catalysts,[12] we set out to examine whether adding the supersilyl directly on the NHC could provide an orthogonal chromatic self-destruct mechanism.

One of the most practical ways to attach substituents to the NHC is through the *para* position of the aromatic substituent. Thus, we employed a direct Buchwald–Hartwig-type amination[14] of ethylene diamine with 4-bromo-3,5-dimethylphenol to produce the novel secondary diamine **1** (Scheme 1). Notably, the reaction proceeded without the need for protecting groups and with the hydroxyl group in the *para* position. Indeed, this procedure may be used to readily produce starting materials for several NHC-type ligands, as the free phenol may be used as a suitable handle to attach other substituents to the NHC side arms, and it is conveniently achieved in a single step.[15] Next, the supersilyl group

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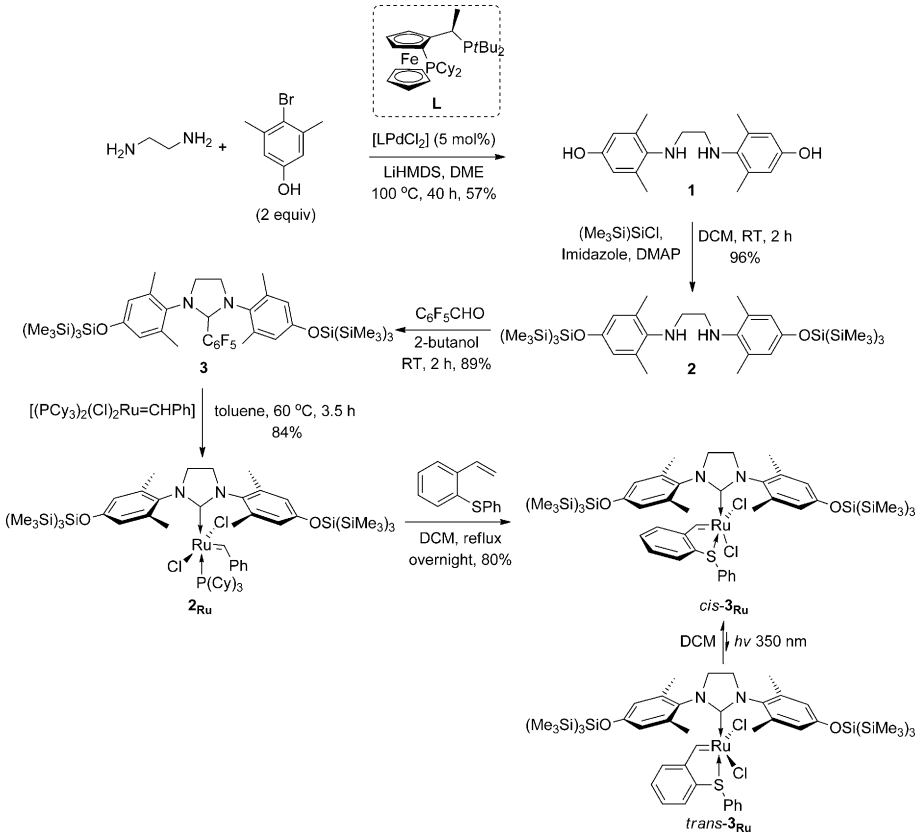
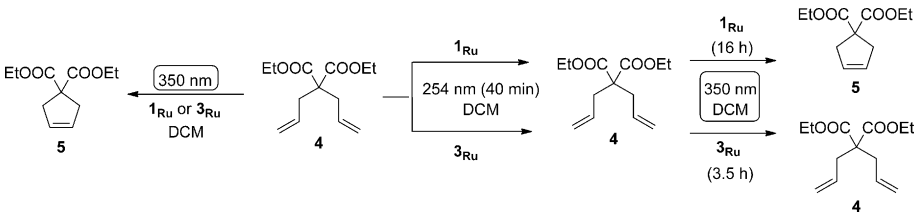


Scheme 1. Synthesis of the super silyl NHC complex $\mathbf{3_{Ru}}$. DCM = dichloromethane, DMAP = 4-(dimethylamino)pyridine, DME = 1,2-dimethoxyethane, HMDS = hexamethyldisilazide,

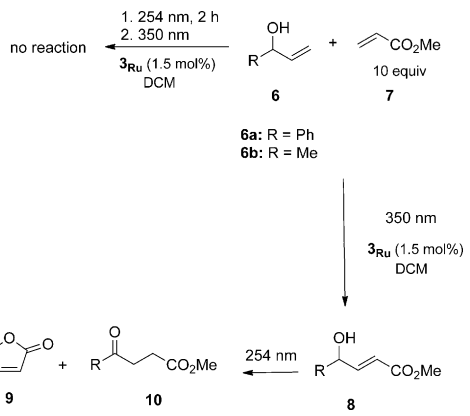
was quantitatively introduced to afford the compound **2**, which was cyclized with pentafluorobenzaldehyde to make the carbene precursor **3** in very satisfactory overall yields.[16] Then, ligand exchange of the Grubbs first-generation catalyst with the carbene, in situ generated from **3**, produced the complex $\mathbf{2_{Ru}}$. Finally, a metathesis reaction of complex $\mathbf{2_{Ru}}$ with styrene phenyl thioether[17] afforded the new latent olefin metathesis catalyst *cis*-$\mathbf{3_{Ru}}$, as confirmed by X-ray diffraction analysis,[18] NMR spectroscopy, and high-resolution mass spectrometry.

In accordance with previous observations for the family of sulfur chelated complexes, *cis*-$\mathbf{3_{Ru}}$ photoisomerized to the catalytically active *trans*-dichloro species when subjected to UV irradiation at $\lambda = 350$ nm. Irradiation of a solution of diethyl diallylmalonate (**4**) and 5 mol% $\mathbf{3_{Ru}}$ in CH_2Cl_2 at $\lambda =$ 254 nm and $\lambda = 350$ nm afforded different results. While irradiation with 350 nm UV light gave 83% conversion to the cyclized product **5**, irradiation with 254 nm UV light did not promote ring-closing metathesis (RCM), and only the starting material was observed (Scheme 2). As a control experiment, **4** was mixed with $\mathbf{3_{Ru}}$ as before, but the solution was first irradiated with $\lambda = 254$ nm light in a quartz NMR tube. After that, the solution was irradiated with 350 nm light, but no **5** was detected. It must be stressed that this result could only achieved by using the precatalyst $\mathbf{3_{Ru}}$, and the use of 254 nm light did not fully inhibit the normal light activated catalyst $\mathbf{1_{Ru}}$ (Scheme 2) as expected from the results of our previous chromatic orthogonal catalytic process.[12]

Cross-metathesis (CM) reactions are usually more demanding than RCM reactions, thus it was important to determine if the activation/deactivation protocol could also be used for this type of olefin metathesis. Consequently, the light-induced CM of α-vinylbenzyl alcohol (**6a**) and α-vinyl methyl alcohol (**6b**) with methyl acrylate was studied (Scheme 3). To our satisfaction, irradiation at $\lambda = 350$ nm promoted the desired CM reactions for both alcohols. When the solution was first irradiated with 254 nm UV light, then the catalyst was decomposed and only starting substrates were observed, even after posterior irradiation of the solution with 350 nm light. Interestingly, upon irradiation of the crude reaction



Scheme 2. Chromatic arrest in a photoactivated RCM reaction.



Scheme 3. Chromatic orthogonal CM and nonmetathetic processes.

mixture from the CM reaction with 254 nm UV light, two types of non-metathetic products, the lactones **9** and ketones **10**, were produced. Indeed, Grubbs-type complexes and their decomposition products have been shown to promote non-metathetic catalysis,[10] such as bond isomerization,[19] cycloisomerization,[20] and hydrogenation.[21] Notably, the ratios between the products were dependent on several reaction parameters (see the Supporting Information). While the lactones were obtained through the double-bond isomerization of **8** followed by cyclization, the ketones resulted from double-bond migration and tautomerization.[22] This scheme provides an original light-induced one-pot approach to the synthesis of either furanone derivatives (**9**) or γ-keto esters (**10**), but further optimization and a study of the scope is required to achieve high selectivities.

Naturally, the most significant application for this novel methodology can be found in polymerization reactions.[23] Thus, the photoinduced ring-opening metathesis polymerization (PROMP)[24] of a norbornene derivative (**11**) and cyclooctene (**12**) was studied by using the UV irradiation sequences. Scheme 4 summarizes the results obtained. Irradiation of a monomer solution in CH_2Cl_2 with UV-A light ($\lambda = 350$ nm) in the presence of $\mathbf{3_{Ru}}$ afforded complete polymerization. As usually obtained with the S-chelated latent catalysts, the polymers obtained had high molecular weights and low polydispersities, which are consistent with the 'turnover limited polymerization' mechanism.[25] However, if UV-C light ($\lambda = 254$ nm) was used first, the catalyst was permanently inhibited and no polymer could be obtained after this. As a final proof of concept the chromatic self-destruct function was tested on a polymer layer to simulate the 3D printing process. Two metallic molds containing the monomer **11** with catalyst $\mathbf{3_{Ru}}$ were irradiated either with 350 nm UV light or with a sequence of 254 nm and 350 nm UV light (see the Supporting Information). Figure 2 shows the striking visual contrast between the polymerized and the inhibited samples.

In conclusion, a novel olefin metathesis UV-A photocatalyst, which may be completely deactivated by the removal of a supersilyl protecting group when irradiated with UV-C, was created. The possibility to add an orthogonal chromatic kill switch to the complex and impede catalysis just by using light opens a doorway for stereolitographic applications and adds a new tool for complex light-guided chemical processes.[26]

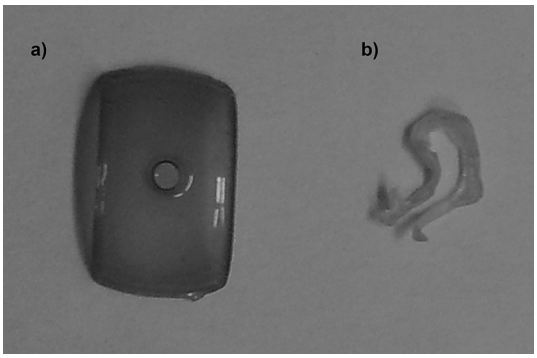
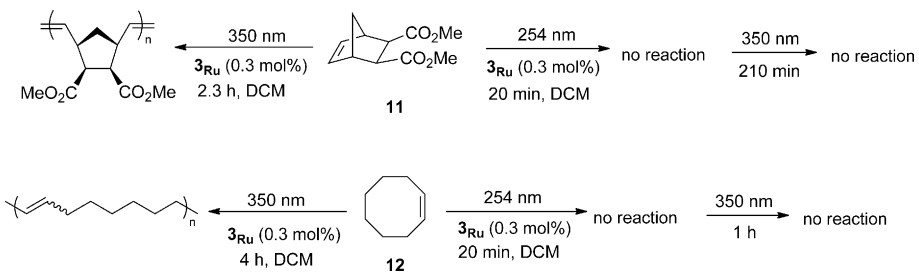


Figure 2. Polynorbornenes derived from **11** as obtained from the metallic molds [6 M monomer solution, 0.05 mol% of $\mathbf{3_{Ru}}$]. a) Irradiated 15 min with 350 nm UV light. b) Irradiated 20 min with 254 nm UV light, and then 15 min with 350 nm UV light.



Scheme 4. Chomatic arrest of PROMP.

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