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Photochemical ROMP

# Cationic Ru$^{II}$ Complexes with N-Heterocyclic Carbene Ligands for UV-Induced Ring-Opening Metathesis Polymerization**

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Metathesis chemistry and, in the context of polymer chemistry, ring-opening metathesis polymerization (ROMP) have gained a strong position in chemistry and materials science.[1–4] ROMP is strongly associated with two classes of well-defined metal alkylidene based initiators, molybdenum-based Schrock and ruthenium-based Grubbs type initiators.[5,6] Despite the tremendous achievements in catalyst development, both families of initiators are still experiencing ongoing, vivid development.[3,7–19] Most Grubbs type initiators work at room temperature or require only gentle warming to work properly.

More recently, an increasing number of reports on latent Ru-based initiators has appeared.[20–22] Such precatalysts are of particular interest in technical applications of ROMP, since they allow for premixing, that is, the preformulation of a monomer/precatalyst mixture, its storage over a longer period of time even at elevated temperatures (usually less than 45 °C), and, most importantly, the shaping and profiling of such mixtures prior to polymerization ("curing"). Numerous latent Grubbs type initiators have been reported recently; however, all these precatalysts are triggered thermally. By contrast, surface modification and functionalization require UV-triggerable precatalysts. Few such systems have been reported to date.

The synthesis of photoactive Schrock type tungsten-based compounds[23] as well as ruthenium and osmium arene compounds of the general formula [Ru(*p*-cymene)Cl$_2$(PR$_3$)] and [Os(*p*-cymene)Cl$_2$(PR$_3$)] (R = cyclohexyl, etc.) were first reported by van der Schaaf et al.[24] They also investigated the photoinduced polymerization of different functionalized norbornenes and 7-oxanorbornenes using various [Ru(solvent)$_n$]X$_2$ complexes, (X = tosylate, trifluoromethanesulfonate) as well as Ru$^{II}$ half-sandwich and sandwich complexes.[25,26] Noels and co-workers reported on the visible-light-induced ROMP of cyclooctene using [RuCl$_2$(IMes)(*p*-cymene)] (IMes = 1,3-dimesitylimidazol-2-ylidene).[27] Some of these systems were also used in ring-closing metathesis reactions.[28]

Most of the systems available to date, however, have significant disadvantages. They either show low activity, resulting in low polymer yields (less than 30 %) in the photochemically triggered process, or the irradiation wavelength necessary to trigger ROMP is 360 nm or higher.[29] In the latter case, the initiators' thermal stability is generally poor,[30] thus discouraging their application in photoinduced ROMP. Thus, none of the systems reported to date was entirely thermally stable above or even at room temperature. Therefore, these systems do not fulfill the requirements of a truly latent photocatalyst. Herein, we report the development of the first thermally stable, truly UV-triggerable precatalysts for ROMP and their application in surface functionalization.

We commenced our investigations with [Ru(IMesH$_2$)(CF$_3$CO$_2$)(*t*BuCN)$_4$)]$^+$ CF$_3$CO$_2^-$ (**PI-1**) and [Ru(IMes)(CF$_3$CO$_2$)(*t*BuCN)$_4$)]$^+$ CF$_3$CO$_2^-$ (**PI-2**), which were prepared from [Ru(CF$_3$CO$_2$)$_2$(L)(*p*-cymene)][31,32] (L = IMes or IMesH$_2$, 1,3-dimesityl-4,5-diyhdroimidazolin-2-ylidene) by reaction with excess *t*BuCN. Both compounds can be handled in air. $^1$H and $^{13}$C NMR spectroscopy data and elemental analysis reveal the presence of one N-heterocyclic carbene (NHC) ligand, two inequivalent trifluoroacetate groups, and four *t*BuCN ligands, suggesting cationic Ru$^{II}$ complexes. The structures of **PI-1** and **PI-2** were confirmed by X-ray analysis; the structure of **PI-1** is shown in Figure 1 (see also the Supporting Information).

Upon mixing of either **PI-1** or **PI-2** with monomers **3**–**8** (Scheme 1), no reaction was observed at room temperature within 24 h. Even highly reactive (distilled) dicyclopentadiene (**4**) did not react with **PI-1** or **PI-2** at room or elevated temperature (RT < $T$ < 45 °C) in the absence of light. Heating a mixture of **8** with **PI-1** or **PI-2** in 1,2-dichloroethane to 60 °C resulted in the formation of much less than 10 % polymer within 24 h. However, exposing mixtures of either **PI-1** or **PI-2** in chloroform with these monomers to 308-nm light at room temperature resulted in the formation of the corresponding polymers. Yields were between less than 5 and 99 % (Table 1).

Increasing the energy of the light by switching from 308 nm to a 254-nm Hg lamp gave raise to high, in most cases virtually quantitative, yields (Table 1). The molecular weights

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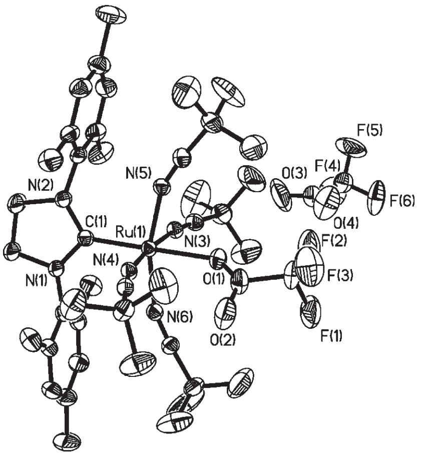
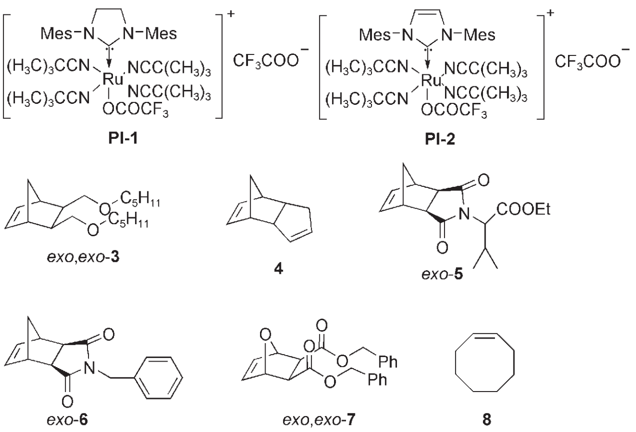


***Figure 1.*** Structure of **PI-1**. Thermal ellipsoids are set at the 30% probability level.



***Scheme 1.*** Structures of **PI-1**, **PI-2**, and monomers **3**–**8**.

***Table 1:*** Polymerization results for monomers **3**–**8** with **PI-1** and **PI-2**.

| | | Yield[a] | | $M_n$/PDI[a] | *cis*/*cis*[c] [%] |
|---|---|---|---|---|---|
| **PI** | monomer | 308 nm | 254 nm | 254 nm | 254 nm |
| **1** | **3** | 40[b] | 95[b] | $4.8\times10^5$/1.8 | 61/51[c] |
| **1** | **4** | 82 | 99 | – | – |
| **1** | **5** | 69 | 85 | $2.1\times10^5$/1.9 | 53/53[c] |
| **1** | **6** | 90 | 92 | $8.8\times10^5$/1.92 | 52/53[c] |
| **1** | **7** | $<5$[b] | 90 | $2.6\times10^5$/3.7 | 49/52[c] |
| **1** | **8** | 33[b] | 99[b] | $4.0\times10^4$/1.2 | – |
| **2** | **3** | 41[b] | 92[b] | – | 61 |
| **2** | **4** | $>99$ | 99 | – | – |
| **2** | **5** | 61 | 67 | $4.4\times10^5$/2.45 | 51 |
| **2** | **6** | 91 | 90 | $8.8\times10^5$/2.0 | 48 |
| **2** | **7** | $<5$[b] | 86 | $4.5\times10^5$/4.53 | 43 |
| **2** | **8** | 21[b] | $>99$[b] | $4.9\times10^4$/1.8 | – |

[a] In 5 mL $CDCl_3$, monomer/initiator 200:1, 30°C, 1 h, yield of isolated polymer in %. [b] In 5 mL $CDCl_3$, monomer/initiator 200:1, 30°C, 1 h, yield determined by $^1$H NMR spectroscopy. [c] Content of *cis* isomer obtained with $[Ru(CF_3COO)_2(PCy_3)(IMesH_2)(CHPh)]$.

of the polymers obtained at 254 nm were in the range $4.0\times10^4$–$2.1\times10^5$ g mol$^{-1}$; polydispersity indices were in the range $1.2 < PDI < 4.53$. Even the functional monomers **5**–**7** could be polymerized in high yields, particularly by the action of **PI-1**. In general, initiation efficiencies were low with both PIs, particularly for the unfunctionalized monomers **4** and **8**. The comparably low molecular weights of poly(**8**) with both **PI-1** and **PI-2** are believed to result from significant chain transfer. $^1$H und $^{13}$C NMR spectroscopic investigations clearly revealed the ROMP-derived structure of all polymers (see the Supporting Information). The *cis* content of poly(**3**) and poly(**5**–**7**) was very similar to that found in the corresponding polymers prepared by the action of $[Ru(CF_3CO_2)_2(CHPh)(IMesH_2)(PCy_3)]$[17] (Table 1). This finding might be indicative of the formation of at least similar propagating species.

As expected, the polymerization of **4** resulted in the formation of cross-linked bulk material. Though we were not able to identify the propagating Ru carbene species, both the NMR spectroscopy data on the polymer structure and theoretical investigations[32] strongly suggest the formation of $Ru^{IV}$-based Grubbs type initiators from both **PI-1** and **PI-2**. The two species show different reactivity, for example, in the photopolymerization of **5**. Thus, **PI-1** (bearing the $IMesH_2$ ligand) shows significantly enhanced reactivity compared to **PI-2** (based on the IMes ligand), which is in accordance with reports on the superior reactivity of $IMesH_2$-based Grubbs type catalysts compared to IMes-based systems.[33]

We then checked whether the findings for the solution polymerizations described above could be used to establish a surface modification process. For that purpose, glass plates were coated with a mixture of **PI-1** and **4**, covered with a mask, and subjected to irradiation for one minute. Removal of the mask and unreacted monomer provided fully transparent poly(dicyclopentadiene) coatings (Figure 2). Typical contact angles of 95.5° were found for the coating, while the parent glass surface showed an angle of 50.7°.

***Figure 2.*** Poly(**4**) coatings on glass prepared by the action of **PI-1**.

As shown previously,[32] the formation of the ROMP-active Ru alkylidene requires the shift of one H atom from C1 to C2 of the C1=C2 double bond of the alkene π complex. On the basis of quantum chemical calculations (B3LYP/LACVP* level and time-dependent DFT as implemented in the Jaguar 7.0 program,[34] see the Supporting Information), the following mechanism is proposed. Dissociation of one *t*BuCN ligand in **PI-2** proceeds easily (dissociation energy $E_{diss} = 12$ kcal mol$^{-1}$, $\Delta G = -4$ kcal mol$^{-1}$), while dissociation of the $CF_3CO_2^-$ ligand is impossible ($E_{diss} = 160$ kcal mol$^{-1}$). Next, either dissociation of a second *t*BuCN ligand or addition of monomer to form the corresponding π complex might be expected. However, dissociation of a second *t*BuCN ligand is strongly endothermic (ca. 29 kcal mol$^{-1}$, $\Delta G = 15$ kcal mol$^{-1}$), thus indicating that this step does not proceed spontaneously without additional energy. Likewise, formation of the π complex with the monomer is endothermic ($\Delta H = 6$ kcal mol$^{-1}$, $\Delta G = 20$ kcal mol$^{-1}$). However, analysis of the electronic structure of the $\{Ru(IMes)(CF_3CO_2)(tBuCN)_3\}^+$ fragment reveals that the electron distribution in the lowest unoccupied molecular orbital (LUMO) has a strong antibonding character between the Ru center and the N atom of the *t*BuCN ligand, leading to the weakening of the Ru–N bond in the excited (triplet) state. Thus, in agreement with experiments, the possible excess energy for the dissociation of the second tBuCN ligand can only be achieved by excitation of the Ru complex with high-energy UV-B light. This dissociation is reversible in the absence of monomer (see below); however, if monomer is present, a stable π complex with the monomer and subsequent formation of the Ru alkylidene by 1,2-H-shift within the C=C bond of the monomer is observed.[32]

These calculations were supported by laser flash and steady-state photolysis experiments to investigate the primary reaction steps of the photoactivation of **PI-1**. For this purpose, solutions of **PI-1** in 1,2-dichloroethane were activated by a laser pulse. Immediately after the laser pulse, the depletion of the parent compound and a new weak absorption band centered around 400 nm, which has not yet been assigned, are evident from the transient spectrum at 200 ns (Figure 3, ◆). There was no indication of a long-lived triplet-state absorption, thus suggesting a fast cleavage process from either the excited singlet state, a higher excited triplet state, or a dissociative *LF (ligand field) state. Thus, a short-lived triplet state, as suggested by quantum chemical calculations, that exists below the time resolution of the laser flash setup ($\tau <$ 1 ns) cannot be excluded.

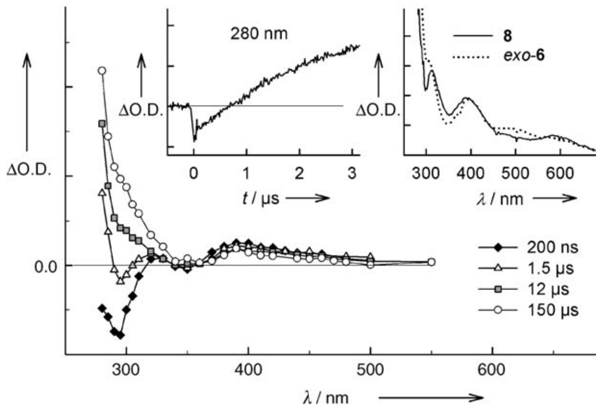


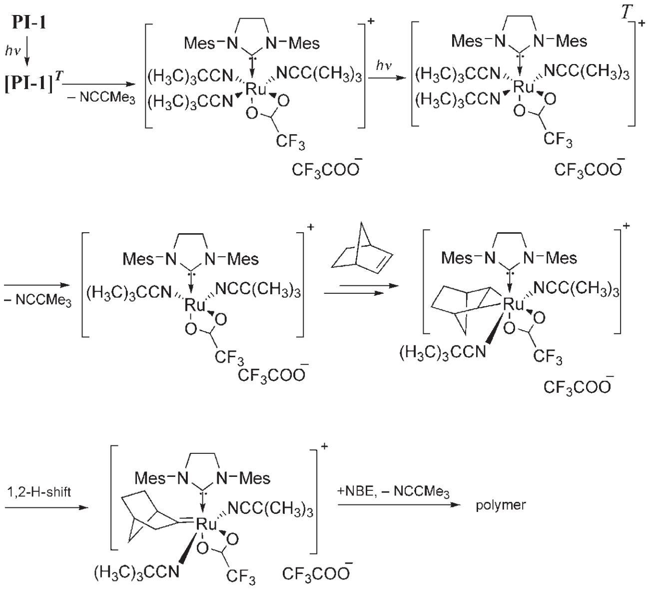
***Figure 3.*** Laser flash photolysis of a $N_2$-saturated $2\times10^{-4}$ mol L$^{-1}$ solution of **PI-1** in 1,2-dichloroethane (times after the flash as indicated); O.D. = optical density. Insets: formation of the metastable transient (left); spectra observed in solutions containing **8** and **6** five minutes after irradiation (right).

The delayed formation of a new band in the range of 280–310 nm with a very weak shoulder at 350 nm (Figure 3, spectra for $t \geq 1.5$ μs and left inset), which did not decay during the accessible time window of the laser flash photolysis (sub-millisecond time range), can be assigned to the formation of the (meta)stable (μ-carboxylato) species $[Ru(tBuCN)_3(CF_3CO_2)(IMesH_2)]^+ CF_3CO_2^-$. Excitation at 266 and 308 nm gave similar results in terms of polymer structure and thus mechanism, demonstrating the same photochemical pathways independent of the irradiation of the main band (266 nm) or the lower-energy shoulder (308 nm) of **PI-1**. Furthermore, laser photolysis of aerated solutions did not show significant differences in the kinetics or the transient spectra, confirming the absence of a long-lived triplet-state transient species, which would rapidly be quenched by $O_2$. When monomer was added, the same results were obtained within the first 200 μs, thus indicating that the primary processes are related only to the precatalyst itself and that no associative coordination is involved.

When changes in absorption of a **PI-1** solution in the absence of monomer are monitored on a longer timescale using UV/VIS spectroscopy (100-ms resolution), a transient species with a lifetime of several seconds is observed. The spectrum of this species has a main band around 290–300 nm and a shoulder at 350 nm, fitting well to the spectrum recorded at the end of the laser flash experiment (Figure 3, 150 μs). The evolution of this spectrum is accompanied by a slight red shift of the absorption (final maxima at 310 and 370 nm). The remaining absorption spectrum is again assigned to the (meta)stable (μ-carboxylato) species $[Ru(tBuCN)_3(CF_3CO_2)(IMesH_2)]^+ CF_3CO_2^-$. When monomer was added to this species, a completely new band around 400 nm formed; the intensity of this band continued to increase even after the end of the irradiation, and this band also formed when monomer was added after irradiating a solution of **PI-1**. Surprisingly, essentially the same band at 400 nm (Figure 3, right inset) was observed in the presence of different monomers, for example cyclooctene **8** and monomer **6**, and is most likely indicative of a catalyst–monomer complex.

NMR spectroscopy measurements on **PI-1** after successive irradiations of the precatalyst solution revealed that even at low exposure doses (2.2 mW cm$^{-2}$, 1 min, 308 nm), the intensity of signals of coordinatively bound *t*BuCN decreased while that of the corresponding signals of free *t*BuCN increased linearly with irradiation time (see the Supporting Information). At the same time, the intensities of the other parent NMR spectroscopy signals decreased and new signals appeared that could be clearly assigned to $[Ru(tBuCN)_3(CF_3CO_2)(IMesH_2)]^+$ ($\delta_{\text{N-C-N}} = 215.0$ ppm, $\delta_{\text{N-CH}_2\text{-CH}_2\text{-N}} =$ 53.1 ppm). Quantification of these signals confirmed the quantum chemical calculations and suggests removal of only one *t*BuCN ligand upon irradiation and formation of the (μ-carboxylato) species $[Ru(tBuCN)_3(CF_3CO_2)(IMesH_2)]^+$ in the absence of monomer. Subsequent photolysis of this species in the presence of monomer then finally leads to the active $Ru^{IV}$ alkylidene complex, presumably $[Ru(CF_3CO_2)_2(IMesH_2)L(CHR)]$ (L = *t*BuCN, monomer, Scheme 2).

In summary, we have developed truly UV-triggerable cationic Ru-based ROMP precatalysts with unprecedented activity and elucidated some key steps of initiation. Current



*Scheme 2.* Reaction cascade for the formation of the ROMP active species. NBE = norbornene, *T* = triplet state.

investigations focus on systems with improved initiation efficiencies.

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