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Cationic versus Neutral Ru^{II}–N-Heterocyclic Carbene Complexes as Latent Precatalysts for the UV-Induced Ring-Opening Metathesis Polymerization

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Abstract: A series of cationic and neutral Ru^{II} complexes of the general formula $[Ru(L)(X)(t\text{BuCN})_4]^+X^-$ and $[Ru(L)(X)_2(t\text{BuCN})_3]$, that is, $[Ru(CF_3SO_3)\{NCC(CH_3)_3\}_4(IMesH_2)]^+[CF_3SO_3]^-$ (**1**), $[Ru(CF_3SO_3)\{NCC(CH_3)_3\}_4(IMes)]^+[CF_3SO_3]^-$ (**2**), $[RuCl\{NCC(CH_3)_3\}_4(IMes)]^+Cl^-$ (**3**), $[RuCl\{NCC(CH_3)_3\}_4(IMesH_2)^+Cl^-]/[RuCl_2\{NCC(CH_3)_3\}_3(IMesH_2)]$ (**4**), and $[Ru(NCO)_2\{NCC(CH_3)_3\}_3(IMesH_2)]$ (**5**) (IMes = 1,3-dimesitylimidazol-2-ylidene, $IMesH_2$ = 1,3-dimesityl-imidazolin-2-ylidene) have been synthesized and used as UV-triggered precatalysts for the ring-opening metathesis polymerization (ROMP) of different norborn-2-ene- and *cis*-cyclooctene-based monomers. The absorption maxima of complexes **1**–**5** were in the range of 245–255 nm and thus perfectly fit the emission band of the 254 nm UV source that was used for activation. Only the cationic Ru^{II}-complexes based on ligands capable of forming μ^2-complexes such as **1** and **2** were found to be truly photolatent in ROMP. In contrast, complexes **3**–**5** could be activated by UV light; however, they also showed a low but significant ROMP activity in the absence of UV light. As evidenced by ^1H and ^{13}C NMR spectroscopy, the structure of the polymers obtained with either **1** or **2** are similar to those found in the corresponding polymers prepared by the action of $[Ru(CF_3SO_3)_2(IMesH_2)(CH\text{-}2\text{-}(2\text{-PrO})\text{-}C_6H_4)]$, which strongly suggest the formation of Ru-based Grubbs-type initiators in the course of the UV-based activation process. Precatalysts that have the $IMesH_2$ ligand showed significantly enhanced reactivity as compared with those based on the IMes ligand, which is in accordance with reports on the superior reactivity of $IMesH_2$-based Grubbs-type catalysts compared with IMes-based systems.

Keywords: carbenes · metathesis · photochemistry · ring-opening polymerization · ruthenium

Introduction

Ring-opening metathesis polymerization (ROMP) is strongly associated with two classes of well-defined metal alkylidene-based initiators, that is, molybdenum-based Schrock-type and ruthenium-based Grubbs-type initiators.[1–2] Most Grubbs-type initiators work at room temperature or require only gentle warming to work properly. More recently, an increasing number of reports appeared on latent Ru-based initiators that can be triggered thermally.[3–5] Such precatalysts are of particular interest in technical applications of ROMP because they allow for the premixing 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"). By contrast, surface modification and functionalization require precatalysts that are stable in the presence of monomers but that can be activated by UV light. Few such systems have been reported to date.[6–10] Most of these systems, however, either show low activity, which results in low polymer yields (< 30 %) in the photochemically triggered process, or an irradiation wavelength necessary to trigger ROMP of 360 nm or higher.[11] In the latter case, the thermal stability of the initiator is generally poor,[12] thereby aggravating their application in photoinduced ROMP. We recently reported on novel, thermally

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stable, truly UV-triggered precatalysts for ROMP and their application in surface functionalization.[13] In this contribution, we have broadened the range of potentially useful precatalysts by using different anionic ligands and have compared the influence of these different anions on both the latency of the precatalyts and the catalytic activity.

Results and Discussion

Synthesis of precatalysts 1–5: Complexes $[Ru(CF_3SO_3)\{NCC(CH_3)_3\}_4(IMesH_2)]^+[CF_3SO_3]^-$ (**1**), $[Ru(CF_3SO_3)\{NCC(CH_3)_3\}_4(IMesH)]^+[CF_3SO_3]^-$ (**2**), and $[Ru(NCO)_2\{NCC(CH_3)_3\}_3(IMesH_2)]$ (**5**) (IMes = 1,3-dimesitylimidazol-2-ylidene, $IMesH_2$ = 1,3-dimesitylimidazolin-2-ylidene) were obtained through the in situ reaction of either $[RuCl_2(IMesH_2)(p\text{-cymene})]$ or $[RuCl_2(IMes)(p\text{-cymene})]$[14] with 2 mol equiv of $AgOSO_2CF_3$ or AgOCN followed by addition of an excess of *t*BuCN and heating to reflux. Compounds **1**, **2**, and **5** were obtained in an analytically pure form without further purification. The complexes $[RuCl\{NCC(CH_3)_3\}_4(IMes)^+]Cl^-$ (**3**) and $[RuCl\{NCC(CH_3)_3\}_4(IMesH_2)]^+Cl^-$/$[RuCl_2\{NCC(CH_3)_3\}_3(IMesH_2)]$ (**4**) were obtained through the reaction of $[RuCl_2(IMesH_2)(p\text{-cymene})]$ or $[RuCl_2(IMes)(p\text{-cymene})]$[14] with excess *t*BuCN under reflux. Compounds **1**–**5** were obtained as yellow solids in 43 to 60% yield; they are thermally stable and can be handled under air. The ^1H and ^{13}C NMR and mass spectroscopic data of compounds **1**–**3** reveal the presence of one N-heterocyclic carbene (NHC) ligand, four *t*BuCN ligands, and two inequivalent anionic ligands ($CF_3SO_3^-$ and Cl^-, respectively), suggesting cationic Ru^{II} complexes for **1**, **2**, and **3**. This is also supported by the ^{19}F NMR data for compounds **1** and **2**, which show two inequivalent trifluorosulfonates ($\delta = -78.9$ and -79.0 ppm for **1**; $\delta = -78.8$, -79.0 ppm for **2**). Compound **4a** is not selectively formed but exists also in form of a neutral isomer, **4b**, which has three *t*BuCN ligands. All efforts to synthesize or isolate a pure cationic or neutral compound from the mixture failed, suggesting an equilibrium between these two species. The neutral nature of compound **4b** was confirmed by single-crystal X-ray analysis. Crystals that were suitable for X-ray analysis were obtained through the layering of *n*-pentane over a concentrated dichloromethane solution of **4b**, producing light-yellow needle-type crystals. Compound **4b** crystallizes in the orthorhombic space group *Pnma* (no.62), $a = 1833.38(7)$, $b = 2186.43(3)$, $c = 1101.89(4)$ pm, $\alpha = \beta = \gamma = 90°$, $Z = 4$. Its structure and relevant bond lengths and angles are shown in Figure 1. The complex can be described as slightly distorted octahedral and one chloro ligand and three *t*BuCN ligands occupy meridional positions, whereas the second chloro ligand occupies the axial position and is *trans* to the NHC ligand. In contrast to most of the other ruthenium complexes, the two chloro ligands in compound **4b** are in a *cis* arrangement. Bond lengths and angles (Figure 1) are in the usual range,[13,15] with the exception of Ru–Cl(2) that is positioned *trans* to the NHC ligand, which is longer than in comparable complexes reported in literature (253.44(9) vs. 236.62 pm).[15]

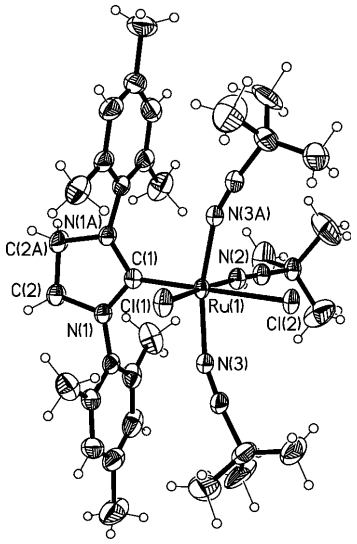
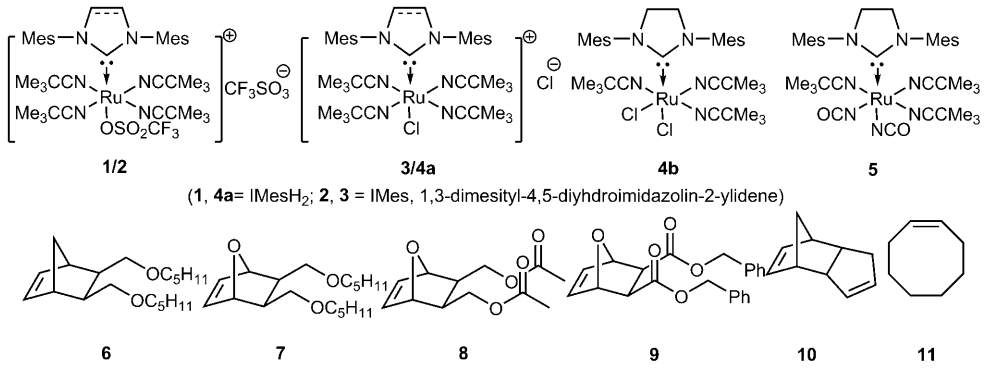


Figure 1. X-ray structure of **4b** and selected bond lengths [pm] and angles [°]: Ru(1)–N(2) 200.3(3), Ru(1)–C(1) 201.3(3), Ru(1)–N(3) 201.4(2), Ru(1)–Cl(1) 239.69(9), Ru(1)–Cl(2) 253.44(9); C(1)-Ru(1)-Cl(1) 89.89(10), C(1)-Ru(1)-Cl(2) 179.11(9).

Reaction of complex $[RuCl_2(IMesH_2)(p\text{-cymene})]$ with silver cyanate selectively resulted in the formation of compound **5**, which is a neutral Ru^{II} complex with both isocyanate ligands bound to the Ru center. The isocyanate bonding of the ligand to the Ru center was unambiguously clarified by FTIR and ^{13}C NMR measurements. In the ^{13}C NMR spectra, the signals for the isocyanate carbon of **5** were found at $\delta = 128.0$ ppm. No additional signals around 110 ppm, which would be indicative for cyanate, were observed. To distinguish between isocyanate and cyanate coordination further we recorded the IR spectra of **5** and the values for the $\tilde{\nu}_{CN}$ band at 2247 cm^{-1} were in accordance with those of other Ru–isocyanate complexes.[16–17]

ROMP with precatalysts 1–5/UV activation: Upon mixing of the precatalysts **1**–**5** with monomers **6**–**9** and **11** (Scheme 1) no reaction was observed for precatalysts **1** and **2** either at room temperature or by heating the mixture for 24 h to 50 °C. These two cationic complexes have trifluoromethansulfonate ligands, which are known to be capable of binding to the metal centers through μ^2-coordination.[18] In the absence of light, these precatalysts did not even react with the highly reactive (distilled) dicyclopentadiene (DCPD, **10**), neither at room or elevated temperatures ($RT < T < 45$ °C). In contrast to precatalysts **1** and **2**, the dichloro-based cationic precatalyst **3** displays a reduced latency. Thus, also in the absence of light it possesses a low but measurable polymerization activity for monomers **6**, **7**, **8**, and **10** at room temperature, which significantly increases up to 100% for monomer **8** at higher temperature (Table 1). However, the mixture of **4a**/**4b** and the neutral compound **5** show virtually no latency at all, especially **5**, which quantita-



Scheme 1. Structures of precatalysts **1–5** and monomers **6–11**.

Table 1. Polymerization results for monomers **6–11** with precatalysts **1–5**.[a]

Monomer	PI	Yield[d] [%]	Yield[e] [%]	M_n (theoretical) [g mol^{-1}]	M_n [g mol^{-1}]/PDI[e]	*cis*[e]/*cis*[f,g] [%]
6	**1**	0	98[c]	58894	4.2×10^5/2.5	51/68[f]
	2	0	55[b]		oligomer	50/77[g]
	3	<5[b]	91[c]		3.1×10^5/2.3	50/60[h]
	4a/b	40[b]	100[c]		4.8×10^5/2.7	53
	5	100[c]	not latent		5.1×10^4/1.9[d]	–
7	**1**	0	98[c]	59288	2.5×10^5/2.2	50/69[f]
	2	0	<5[b]		–	–
	3	<5[b]	100[c]		1.7×10^5/2.8	38/38[h]
	4a/b	12[b]	100[c]		1.6×10^5/2.8	50
	5	100[c]	not latent		1.9×10^4/1.7[d]	–
8	**1**	0	93[c]	48050	2.8×10^5/2.3	60/81[f]
	2	0	83[b]		4.1×10^5/2.6	48/83[g]
	3	11[b]	100[c]		2.4×10^5/3.3	46/48[h]
	4a/b	100[c]	not latent		2.2×10^5/2.4[d]	–
	5	100[c]	not latent		2.1×10^4/1.9[d]	–
9	**1**	0	96[c]	72878	2.8×10^5/4.9	50/58[f]
	2	0	0		–	–
	3	0	98[c]		3.6×10^5/3.6	44/44[h]
	4a/b	12[b]	100[c]		2.4×10^5/3.3	48
	5	100[c]	not latent		2.3×10^5/1.7[d]	–
10	**1**	<5[b]	100[c]	26440	insoluble	–
	2	0	100[c]		insoluble	–
	3	100[c]	not latent		insoluble	–
	4a/b	100[c]	not latent		insoluble	–
	5	100[c]	not latent		insoluble	–
11	**1**	0	100[b]	22040	oligomer	–
	2	0	68[b]		oligomer	–
	3	13[b]	100[b]		1.0×10^5/1.8	–
	4a/b	50[b]	100[b]		1.7×10^5/2.1	–
	5	100[c]	not latent		8.4×10^4/1.9[d]	–

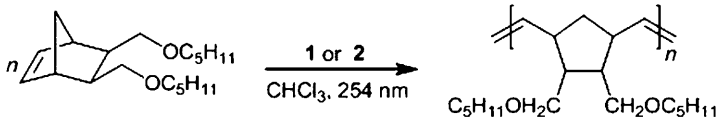
[a] Conditions: In 5 mL of $CDCl_3$, ratio: 200:1. [b] Yields from NMR spectra. [c] Isolated yields. [d] No light, 1 h. [e] UV light (254 nm), 1 h. [f] *cis*-Content of the polymer obtained by the action of [Ru(CF_3SO_3)$_2$-(IMesH$_2$)(CH-2-(2-PrO)-C_6H_4)]. [g] *cis*-Content of the polymer obtained by the action of [Ru(CF_3SO_3)$_2$-(IMes)(CH-2-(2-PrO)-C_6H_4)].[20] [h] *cis*-Content of the polymer obtained with [RuCl$_2$(IMes)(CH-2-(2-PrO)-C_6H_4)].[20]

tively polymerizes all of the monomers within one hour at room temperature in the absence of light. Nevertheless, exposing mixtures of **1** or **2** as well as of **3** or **4a/4b** in $CHCl_3$ with one of the monomers **6–11** to 254 nm UV light at room temperature resulted in the formation of the corresponding polymers in high yield (up to 100% Table 1). Generally, it is worth notifying that the absorption maxima of complexes **1–5** were in the range of 245–255 nm and thus perfectly fit the emission band of the 254 nm UV source that was used for activation.

The molecular weights of the polymers obtained by 254 nm irradiation were three to eight times higher than the theoretical values and were in the range of 1.0×10^5-4.8×10^5 g mol^{-1}. The polydispersity indices (PDI) were generally broad yet monomodal, with polydispersities typically in the range $1.8<\text{PDI}<4.9$. As expected, the polymerization of **10** resulted in the formation of cross-linked, insoluble bulk material. Most probably because of comparably low rates of initiation, which result in the formation of many different propagating species at a given time, we were not able to identify the propagating Ru–carbene species experimentally, that is, by NMR. However, the NMR spectroscopic data on the polymers prepared by **1–4** clearly show ROMP-derived structures (see the Supporting Information). This and theoretical investigations[19] strongly suggest the formation of Ru-based Grubbs-type initiators. The *cis*-content of the double bonds in poly(**6**)–poly(**9**) prepared by the action of the UV-activated precatalysts **1** and **2** varied to a significant extent with the different precatalysts used. Thus, the *cis*-content of these polymers prepared by the action of these precatalysts was in the range of 38–60% and thus lower than that found in the corresponding polymers prepared by the action of [Ru(CF_3SO_3)$_2$(IMesH$_2$)(CH-2-(2-PrO)-C_6H_4)] and [Ru(CF_3SO_3)$_2$(IMes)(CH-2-(2-PrO)-

C_6H_4)], respectively.[20] In contrast, the *cis*-content of poly(**7**)–poly(**9**) prepared by, prectalyst **3**, for example, was identical to the one found in these polymers prepared by the action of [$RuCl_2$(IMes)(CH-2-(2-PrO)-C_6H_4)].[20] This suggests the formation of probably identical propagating species from precatalyst **3** and [$RuCl_2$(IMes)(CH-2-(2-PrO)-C_6H_4)] through simple re-coordination of the (small) Cl^- anion to the cationic Ru–alkylidene. By contrast, the large $CF_3SO_3^-$ anions might have a lower propensity of re-coordination, resulting in cationic propagating species that give raise to ROMP-derived polymers with different *cis* contents.

Catalytic activity as a function of the nature of the ligand and solvents: Figure 2 shows the catalytic activity of the different catalyst precursors in the photoinitiated ROMP of the monomer **6**. The ligand of the catalysts strongly influences the yields and rates of the photoinduced polymerization. Thus, the polymerization of monomer **6** was completed within 1 hour by the action of precatalyst **1** that has the $IMesH_2$ ligand; however, only 50% conversion of the monomer **6** was obtained by the action of **2** that has the IMes ligand (Figure 2a). Applying first-order kinetics (Figure 2b), the apparent rate constant of polymerization ($k_{p(app)}$) of precatalyst **1** is about 14 times larger than the one for **2**, that is, $k_{p(app)}$ is 0.135 min^{-1} for **1** and 0.009 min^{-1} for **2**, respectively. These results are in accordance with our results[13] and the reports on the superior reactivity of $IMesH_2$-based Grubbs-type catalysts compared wtih IMes-based systems.[21] In addition, the solvent used for the photoinitiated ROMP plays also a very important role as depicted in Figure 3. Although



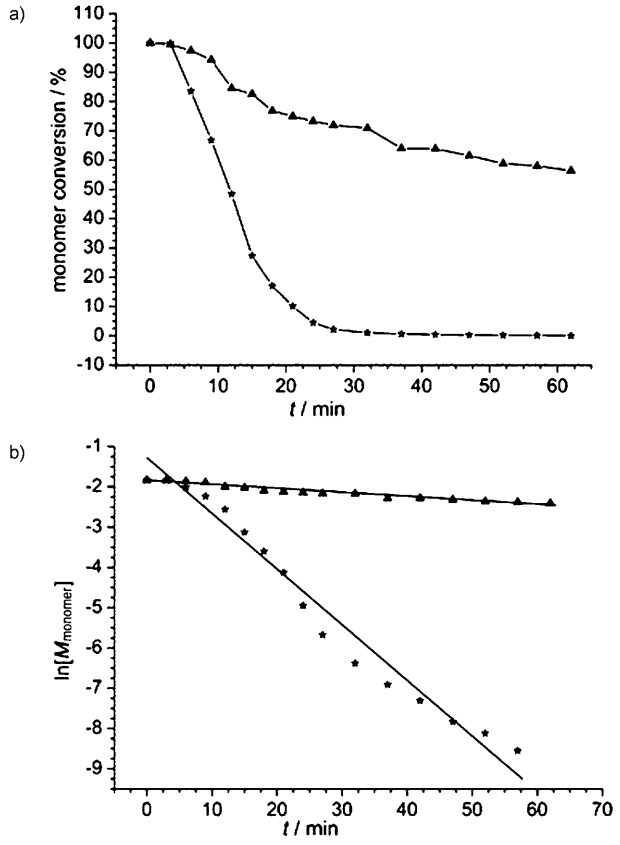


Figure 2. a) Kinetics of photoinitiated ring-opening metathesis polymerization of monomer **6** by the action of **1** and **2**. b) First-order plots for **1** and **2** ([initiator] = 0.8 mM, [6] = 160 mM).

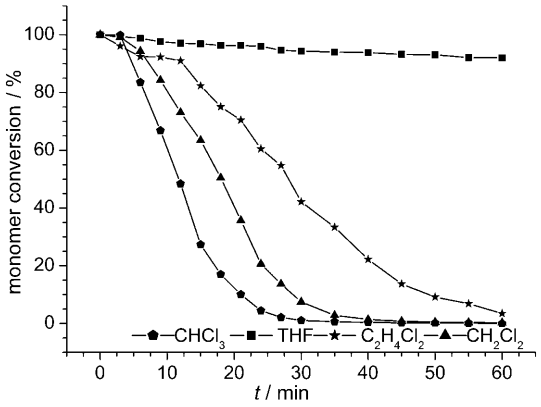


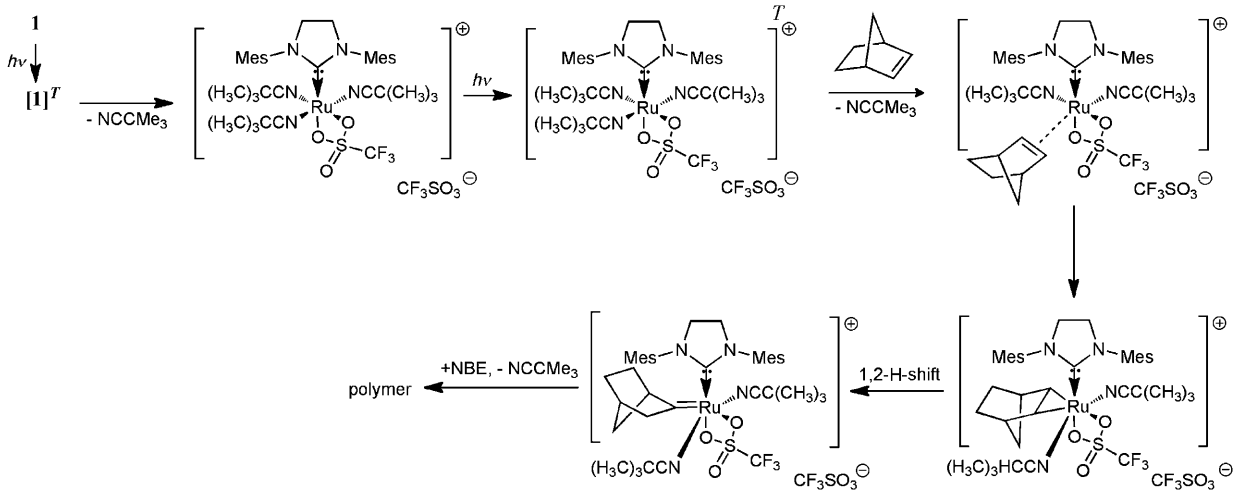
Figure 3. Influence of the solvent on the polymerization of *exo*-**6** by the action of precatalyst **1**.

the absorption maxima of chloroform, dichloromethane, dichloroethane, and THF are <230 nm, the polymerization reaction does not start at all in THF. It can only be carried out in chloroform, dichloromethane and dichloroethane, for which chloroform seems to be the best choice for photo-ROMP.

Generally, these results strongly support our recently proposed mechanism,[13] in which only cationic Ru complexes with chelating ligands such as $CF_3CO_2^-$ were found to be photolatent in ROMP. Thus, upon irradiation/heating of complexes of the general formula [Ru(X)($IMesH_2$)-(*t*BuCN)$_3^+$]X^- only one *t*BuCN ligand is removed and simultaneously [Ru(μ-X)($IMesH_2$)(*t*BuCN)$_3^+$]X^- (X = CF_3COO^-, $CF_3SO_3^-$) species that are stable intermediates in the absence of monomer are formed. Further photolysis of these species in the presence of monomer then finally leads to the release of a second *t*BuCN ligand, coordination of the monomer and, most probably thorough a 1,2-sigmatropic H shift,[19] to the active Ru–alkylidene complex (Scheme 2).

Conclusion

In summary, a series of new Ru^{II} complexes based on [Ru(L)(X^-)(*t*BuCN)$_4$)]$^+X^-$ and [Ru(L)(X)$_2$(*t*BuCN)$_3$)] have been successfully synthesized, structurally characterized, and were used for UV-induced ROMP with different kinds of norborn-2-ene- and *cis*-cyclooctene-based monomers. Particularly the cationic precatalysts **1** and **2** that have trifluoro-



Scheme 2. Proposed UV-based activation process.

methanesulfonate ligands and are capable of μ^2-coordination show very good UV latency for all of the monomers investigated. In contrast, (neutral) complexes based on chloride (**4a**/**b**) and isocyanate ligands (**5**) show virtually no latency for the set of monomers investigated. These results do not only enlarge the armor of Ru^{II}-based precatalysts for photo-ROMP but also further support our recently proposed mechanism, which proposed that ligands capable of μ^2-coordination were essential for UV latency.

Experimental Section

All manipulations were performed under a nitrogen atmosphere in a glove box (LabMaster 130, MBraun, Germany) or by standard Schlenk techniques. Purchased starting materials were used without any further purification. THF and dichloroethane were distilled under nitrogen from sodium benzophenone ketyl and CaH_2, respectively. Pentane, diethyl ether, toluene and CH_2Cl_2 were dried by an MBraun solvent purification system. NMR data were obtained at 250.13 MHz for proton and 62.90 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 250 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. IR spectra were recorded on a Bruker Vector 22 using ATR technology. Molecular weights and PDIs of the polymers were performed on a Waters RID-2410 refractive index detector equipped with a CTO-10AC column oven and three columns from Polymer Standards Service GmbH (PSS, Germany). $[Ru(CF_3SO_3)_2(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$, $[Ru(CF_3SO_3)_2(IMes)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$, and $[RuCl_2(IMes)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ were prepared as described previously.[20] Compounds **7** and **8**, were synthesized according to the literature.[22]

Complex 1: $[\{RuCl_2(p\text{-cymene})_2\}_2]$ (61.2 mg, 0.101 mmol) was suspended in THF and a solution of 1,3-dimesitylimidazolin-2-ylidene (61.1 mg, 0.201 mmol) in THF was added dropwise. The mixture was stirred for 2 h at room temperature and then cooled to −36 °C. A chilled solution of CF_3SO_3Ag (102.0 mg, 0.401 mmol) in THF was added dropwise. The solution was stirred for another 2 h, allowing it to reach room temperature. During that time a white precipitate of AgCl was formed. The reaction mixture was filtered through a short bed of celite and the THF was removed in vacuo. CH_2Cl_2 was added to dissolve the residue and the solution was again filtered through glass-fiber paper and concentrated in vacuo. The remaining solid was suspended in absolute trimethylacetonitrile (5 mL). This mixture was then heated to 90 °C overnight. After the mixture had been cooled to room temperature, all volatiles were removed in vacuo, and the residue was washed with diethyl ether, and then dried (yield: 90.0 mg, 43 %). ^{1}H NMR ($CDCl_3$): $\delta = 7.00$ (s, 4H), 3.86 (s, 4H), 2.34 (s, 6H), 2.31(s, 12H), 1.31 ppm (s, 36H); ^{13}C NMR ($CDCl_3$): $\delta = 207.1$, 139.1, 138.7, 136.6, 132.6, 130.3, 121.6 [q, $^1J(^{19}F,^{13}C) = 321.5$ Hz; CF_3], 119.7 [q, $^1J(^{19}F,^{13}C) = 319.3$ Hz; CF_3], 53.6, 30.8, 28.3, 21.5, 18.6 ppm; ^{19}F NMR ($CDCl_3$): $\delta = -78.9$, −79.0 ppm; IR (ATR): $\tilde{\nu} =$ 2982.9 (w), 1690.2 (s), 1481.5 (m), 1149.9 (s), 1018.1 (s), 800.0 (m), 726.3 (m), 651.8 cm^{-1} (w); UV/Vis ($CHCl_3$): $\lambda_{max} = 250$ nm; MS (ESI$^+$): m/z calcd for $C_{43}H_{62}F_6N_6O_6RuS_2$: $M = 1038.31$ g mol^{-1}; found: 889.36 $[M - CF_3SO_3^-]^+$.

Complex 2: The complex was synthesized from $[\{RuCl_2(p\text{-cymene})_2\}_2]$ (61.2 mg, 0.101 mmol), 1,3-dimesitylimidazol-2-ylidene (60.9 mg, 0.201 mmol), and CF_3SO_3Ag (102.4 mg, 0.401 mmol) as described for complex **1** (yield: 95.0 mg, 46 %). ^{1}H NMR ($CDCl_3$): $\delta = 7.04$ (s, 4H), 6.94 (s, 2H), 2.39 (s, 6H), 2.11 (s, 12H), 1.31 ppm (s, 36H); ^{13}C NMR ($CDCl_3$): $\delta = 170.0$, 140.1, 137.9, 136.3, 132.6, 129.8, 127.0, 121.6 [q, $^1J(^{19}F,^{13}C) = 321.4$ Hz; CF_3], 119.7 [q, $^1J(^{19}F,^{13}C) = 319.1$ Hz; CF_3], 30.8, 28.3, 21.5, 18.4 ppm; ^{19}F NMR ($CDCl_3$): $\delta = -78.8$, −79.0 ppm; IR (ATR): $\tilde{\nu} =$ 2983.3 (w), 1689.9 (s), 1480.0 (m), 1374.2 (s), 1143.0 (s), 1026.3 (s), 930.4 (s), 865.9 (m), 745.0 (m), 703.5 cm^{-1} (w); UV/Vis ($CHCl_3$): $\lambda_{max} = 255$ nm; MS (ESI$^+$): m/z calcd for $C_{43}H_{60}F_6N_6O_6RuS_2$: $M = 1036.30$ g mol^{-1}; found: 887.36 $[M - CF_3SO_3^-]^+$.

Complex 3: $[\{RuCl_2(p\text{-cymene})_2\}_2]$ (61.2 mg, 0.101 mmol) was suspended in THF and a solution of 1,3-dimesitylimidazol-2-ylidene (60.9 mg, 0.201 mmol) in THF was added dropwise. The mixture was stirred for 2 h at room temperature and then cooled to −36 °C. The mixture was filtered through a short bed of celite and the THF was removed in vacuo. Then the residue was suspended in 5 mL of absolute trimethylacetonitrile. This mixture was then heated to 90 °C overnight. After being cooled to room temperature, all volatiles was removed in vacuo, and the residue was washed with diethyl ether before being dried again (yield: 80.0 mg, 50 %). ^{1}H NMR ($CDCl_3$): $\delta = 6.95$ (s, 4H), 6.91 (s, 2H), 2.33 (s, 6H), 2.06 (s, 12H), 1.24 ppm (s, 36H); ^{13}C NMR ($CDCl_3$): $\delta = 175.8$, 139.1, 137.7, 135.5, 130.7, 128.9, 125.5, 29.9, 28.3, 21.2, 17.8 ppm; IR (ATR): $\tilde{\nu} = 2970.1$ (w), 1466.2 (s), 1392.4 (m), 1299.2 (m), 1240,2 (s), 873.3 (m), 694.5 cm^{-1} (m). UV/Vis ($CHCl_3$): $\lambda_{max} = 250$ nm; MS (ESI$^+$): m/z calcd for $C_{41}H_{60}Cl_2N_5Ru$: $M = 808.33$ g mol^{-1}; found: 773.36 $[M - Cl^-]^+$.

Complex 4: The compound was synthesized from $[\{RuCl_2(p\text{-cymene})_2\}_2]$ (61.2 mg, 0.101 mmol) and 1,3-dimesitylimidazolin-2-ylidene (61.2 mg, 0.201 mmol) as described for complex **3** (yield: 97.0 mg, 62 %). ^{1}H NMR ($CDCl_3$): $\delta = 6.89$ (s, 4H), 3.88–3.79 (m, 4H), 2.43–2.29 (m, 18H), 1.38–1.11 ppm (m, 34H); ^{13}C NMR ($CDCl_3$): $\delta = 212.3$, 206.6, 139.4, 138.5, 138.0, 136.8, 136.6, 136.3, 136.1, 130.7, 129.4, 128.8, 128.5, 53.1, 52.9, 29.9, 28.8, 28.5, 28.3, 21.2, 18.8, 18.6, 18.1 ppm; IR (ATR): $\tilde{\nu} = 2967.67$ (w),

1476.5 (m), 1401.3 (m), 1241.6 (s), 1034.2 (m), 847.4 (m), 717.2 (w), 691.1 cm^{-1} (w); UV/Vis ($CHCl_3$): $\lambda_{max}=255$ nm; MS (ESI^+): m/z calcd for $C_{41}H_{60}Cl_2N_5Ru$: $M=808.33\,g\,mol^{-1}$; found: 775.36 $[M-Cl^-]$. Crystals of (**4b**) suitable for X-ray analysis were obtained by slowly diffusing pentane into a solution of **4a/b** in CH_2Cl_2.

Complex 5: Complex **5** was synthesized from $[\{RuCl_2(p\text{-cymene})_2\}_2]$ (61.2 mg, 0.101 mmol), 1,3-dimesitylimidazolin-2-ylidene (61.2 mg, 0.201 mmol), and AgOCN (60.0 mg, 0.401 mmol) as described for complex **1** (yield: 57.0 mg, 38%). ^1H NMR ($CDCl_3$): $\delta=6.91$ (s, 4H), 3.78 (s, 4H), 2.35–2.30 (m, 18H), 1.39 (s, 6H), 1.35 (s, 3H), 1.15 ppm (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta=211.3$, 140.3, 137.7, 137.5, 129.6, 128.0, 52.9, 30.7, 30.4, 29.1, 28.7, 21.5, 18.4 ppm; IR (ATR): $\tilde{\nu}=2967.67$ (w), 1476.5 (m), 1401.3 (m), 1241.6 (s), 1034.2 (m), 847.4 (m), 717.2 (w), 691.1 cm^{-1} (w); UV/Vis ($CHCl_3$): $\lambda_{max}=245$ nm; MS (ESI^+): m/z calcd for $C_{38}H_{53}N_7O_2Ru$: $M=740.33$; found: 740.33 $[M]^+$.

Typical polymerization procedure: Complex **1** (4.0 mg, 4.0×10^{-3} mmol) and the monomer (0.8 mmol) were dissolved in $CHCl_3$ (5 mL) and transferred into a quartz Schlenk tube. The mixture was either stirred at room temperature or exposed to UV (254 nm) irradiation for 60 min, then it was poured into methanol (50 mL). The polymer was isolated by filtration, washed thoroughly with methanol and pentane, and dried in vacuo overnight at 40 °C.

*Poly(**exo-6**)/(**1**)*: ^1H NMR ($CDCl_3$): $\delta=5.27$–5.17 (m, 2H), 3.36 (brs, 10H), 2.68 (brs, 1H), 2.36 (brs, 1H), 1.97 (brs, 2H), 1.55 (brs, 4H), 1.31 (brs, 8H), 0.90 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=133.7$ (m), 71.1 (m), 50.8–39.8 (m), 29.5, 28.5, 22.5, 14.1 ppm; $M_n=4.2\times10^5\,g\,mol^{-1}$; PDI = 2.5.

*Poly(**exo-6**)/(**3**)*: ^1H NMR ($CDCl_3$): $\delta=5.28$–5.19 (m, 2H), 3.36 (brs, 10H), 2.68 (brs, 1H), 2.35 (brs, 1H), 1.98 (brs, 2H), 1.56 (brs, 4H), 1.32 (brs, 8H), 0.91 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=133.8$(m), 50.8–39.9 (m), 29.5, 28.5, 22.6, 14.1 ppm; $M_n=3.1\times10^5\,g\,mol^{-1}$; PDI = 2.3.

*Poly(**exo-6**)/(**4a/b**)*: ^1H NMR ($CDCl_3$): $\delta=5.27$–5.17 (m, 2H), 3.36 (brs, 10H), 2.68 (brs, 1H), 2.36 (brs, 1H), 1.97 (brs, 2H), 1.55 (brs, 4H), 1.31 (brs, 8H), 0.90 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=133.7$ (m), 47.6–39.9 (m), 29.5, 28.5, 22.5, 14.1 ppm; $M_n=4.8\times10^5\,g\,mol^{-1}$; PDI = 2.7.

*Poly(**exo-7**)/(**1**)*: ^1H NMR ($CDCl_3$): $\delta=5.69$–5.51 (m, 2H), 4.51 (brs, 1H), 4.21 (brs, 1H), 3.47–3.36 (m, 8H), 2.24 (brs, 2H), 1.54 (brs, 4H), 1.30 (brs, 8H), 0.89 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=133.3$ (m), 81.7, 71.2, 68.1 (m), 29.4, 28.4, 22.5, 14.0 ppm; $M_n=2.5\times10^5\,g\,mol^{-1}$; PDI = 2.2.

*Poly(**exo-7**)/(**3**)*: ^1H NMR ($CDCl_3$): $\delta=5.70$–5.53 (m, 2H), 4.52 (brs, 1H), 4.21 (brs, 1H), 3.47–3.37 (m, 8H), 2.26 (brs, 2H), 1.55 (brs, 4H), 1.33 (brs, 8H), 0.90 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=133.3$ (m), 81.6, 71.2, 68.2 (m), 46.8 (m), 29.4, 28.4, 22.5, 14.0 ppm. $M_n=1.7\times10^5\,g\,mol^{-1}$; PDI = 2.8.

*Poly(**exo-7**)/(**4a/b**)*: ^1H NMR ($CDCl_3$): $\delta=5.69$–5.51 (m, 2H), 4.51 (brs, 1H), 4.21 (brs, 1H), 3.47–3.36 (m, 8H), 2.24 (brs, 2H), 1.54 (brs, 4H), 1.30 (brs, 8H), 0.89 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=133.3$ (m), 81.7, 71.2, 68.1 (m), 29.4, 28.4, 22.5, 14.0. $M_n=1.6\times10^5\,g\,mol^{-1}$; PDI = 2.8.

*Poly(**exo-8**)/(**1**)*: ^1H NMR ($CDCl_3$): $\delta=5.75$–5.60 (m, 2H), 4.52 (brs, 1H), 4.17 (brs, 5H), 2.43 (brs, 2H), 2.06 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=170.6$ (m), 133.1 (m), 81.4, 61.8 (m), 45.8 (m), 20.8 ppm; $M_n=3.5\times10^4\,g\,mol^{-1}$; PDI = 3.6.

*Poly(**exo-8**)/(**2**)*: ^1H NMR ($CDCl_3$): $\delta=5.72$–5.58 (m, 2H), 4.50 (brs, 1H), 4.15 (brs, 5H), 2.41 (brs, 2H), 2.03 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=170.6$ (m), 133.0 (m), 81.4, 61.8 (m), 45.8 (m), 20.8 ppm; $M_n=4.1\times10^5\,g\,mol^{-1}$; PDI = 2.6.

*Poly(**exo-8**)/(**3**)*: ^1H NMR ($CDCl_3$): $\delta=5.72$–5.58 (m, 2H), 4.50 (brs, 1H), 4.15 (brs, 5H), 2.41 (brs, 2H), 2.03 ppm (brs, 6H); ^{13}C NMR ($CDCl_3$): $\delta=170.7$, 133.1 (m), 81.3, 61.8, 45.5 (m), 20.8 ppm; $M_n=2.4\times10^5\,g\,mol^{-1}$; PDI = 3.3.

*Poly(**exo-9**)/(**1**)*: ^1H NMR ($CDCl_3$): $\delta=7.23$ (brs, 10H), 5.80 (brs, 1H), 5.53 (brs, 1H), 5.12–4.63 (m, 6H), 3.01 ppm (brs, 2H); ^{13}C NMR ($CDCl_3$): $\delta=170.1$, 135.3, 132.3, 131.3, 130.8, 128.4, 80.5, 66.8, 53.2–52.1 ppm (m); $M_n=2.8\times10^5\,g\,mol^{-1}$; PDI = 4.9.

*Poly(**exo-9**)/(**3**)*: ^1H NMR ($CDCl_3$): $\delta=7.23$ (brs, 10H), 5.80 (brs, 1H), 5.53 (brs, 1H), 5.12–4.63 (m, 6H), 3.01 ppm (brs, 2H); ^{13}C NMR ($CDCl_3$): $\delta=170.1$, 135.3, 132.3, 131.3, 130.8, 128.4, 80.5, 66.8, 53.2–52.1 ppm (m); $M_n=3.6\times10^5\,g\,mol^{-1}$; PDI = 3.6.

*Poly(**exo-9**)/(**4**)*: ^1H NMR ($CDCl_3$): $\delta=7.23$ (brs, 10H), 5.80 (brs, 1H), 5.55 (brs, 1H), 5.14 (brs, 1H), 4.93 (brs, 4H), 4.62 (brs, 1H), 3.01 ppm (brs, 2H); ^{13}C NMR ($CDCl_3$): $\delta=170.1$, 135.3, 132.3, 131.3, 130.9, 128.4, 80.4, 66.8, 53.2–52.1 ppm (m); $M_n=2.4\times10^5\,g\,mol^{-1}$; PDI = 3.3.

*Poly(cis-**11**)/(**3**)*: ^1H NMR ($CDCl_3$): $\delta=5.38$ (brs, 2H), 1.97 (brs, 2H), 1.26 (brs, 4H); ^{13}C NMR ($CDCl_3$): $\delta=130.3$, 129.9, 32.6, 29.7, 29.6, 29.2, 29.14, 27.2; $M_n=1.0\times10^5\,g\,mol^{-1}$; PDI = 1.8.

*Poly(**cis-11**)/(**4a/b**)*: ^1H NMR ($CDCl_3$): $\delta=5.38$ (brs, 2H), 1.97 (brs, 2H), 1.26 ppm (brs, 4H); ^{13}C NMR ($CDCl_3$): $\delta=130.3$, 129.9, 32.6, 29.7, 29.6, 29.2, 29.14, 27.2 ppm; $M_n=1.7\times10^5\,g\,mol^{-1}$; PDI = 2.1.

X-ray analysis: Data collection for X-ray analysis of **4b** was performed at $T=233$ K on a Nonius Kappa CCD equipped with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda=71.073$ nm) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated by using DENZO[23] and scaled with SCALEPACK.[23] The structures were solved with direct methods SHELXS86[24] and refined against F^2 SHELX97.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms attached to carbon atoms were calculated and refined with isotropic displacement parameters 1.2 or 1.5 times higher than the value of their carbon atoms. In the asymmetric unit is a half molecule, which will be completed by a crystallographic mirror plane. The methyl groups of the *t*BuCN ligands are positional disordered with a ratio of 1:1 at the ligand with the nitrogen atom N(1) and 2:1 at N(2).

CCDC-788839 (**4b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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