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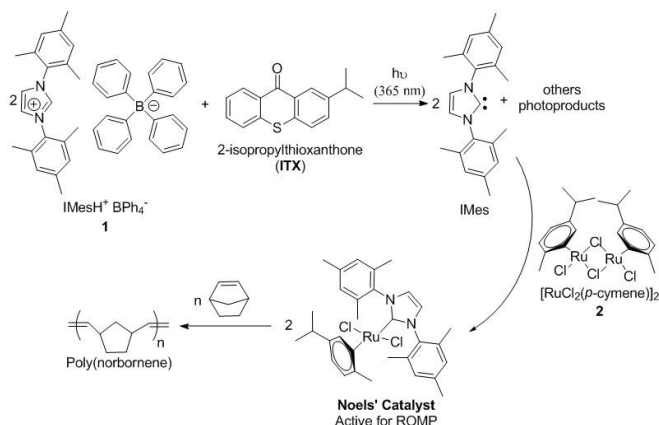
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In Situ Generated Ruthenium-Arene Catalyst for Photoactivated Ring-Opening Metathesis Polymerization Through Photolabile *N*-Heterocyclic Carbene Ligand

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Abstract: 1,3-Bis(mesityl)imidazolium tetraphenylborate (IMesH⁺ BPh₄⁻) can be synthesized in one step by anion metathesis between the corresponding imidazolium chloride and sodium tetraphenylborate. In the presence of 2-isopropylthioxanthone (sensitizer), IMes *N*-heterocyclic carbene (NHC) ligand can be photogenerated under irradiation at 365 nm through coupled electron/proton transfer reactions. By combining this tandem NHC photogenerator system with metathesis inactive [RuCl₂(*p*-cymene)]₂ precatalyst, the highly active RuCl₂(*p*-cymene)(IMes) complex can be formed *in situ*, enabling a complete ring-opening metathesis polymerization (ROMP) of norbornene in the matter of minutes at room temperature. To the best of our knowledge, this is the first example of a photogenerated NHC. Its exploitation in photoROMP has resulted in a simplified process compared to current photocatalysts, because only stable commercial or easily synthesized reagents are required.



Scheme 1: Sensitized photogeneration of IMes NHC from imidazolium salt **1**. Subsequent reaction with inactive Ru precatalyst **2** forms *in situ* the catalytically active Noels' catalyst triggering the ROMP of norbornene.

Since its discovery in the 1950s, olefin metathesis has evolved from a restricted use in petroleum cracking processes to the standard method for creating C-C double bonds. Progress has been driven by a variety of increasingly advanced and well-defined olefin metathesis catalysts.^[1] These developments have predominantly benefited preparative organic chemistry and the synthesis of polymer materials. Many useful polymers such as poly(norbornene) or poly(dicyclopentadiene) can be prepared by ring-opening metathesis polymerization (ROMP), and have led to successful commercial applications as optical components, high impact thermosets or shock absorbers.^[2] However, their implementation at industrial scale has been held back by air sensitivity and lack of processability under ambient conditions of most late transition metal-based catalysts.^[3] Designing ROMP catalysts in a way that allows the on-demand release of highly reactive transition metal alkylidenes is a very attractive goal to ease storage, handling, and processing.^[4] Compared to heat or pH, UV-vis irradiation is certainly one of the most sought-after activating stimuli.^[5] Energy-saving, room-temperature process

and spatio-temporal accuracy are some of the distinctive strengths of a UV-vis radiation induced polymerization.^[6] To date, however, only radical and cationic chain-growth processes have enabled photopolymerization to be harnessed as a technology capable of delivering innovative materials such as photoresists, industrial coatings, or inks.^[7]

With the exception of photoredox catalysts,^[8] photoinduced ROMP (photoROMP) has been built on two types of organometallic catalysts whether or not containing an alkylidene moiety from the beginning.^[3] Currently, the most common strategy is to start from a preformed Ru alkylidene complex made inactive by a sound choice of chelating ligands^[9] or electron-rich carbene moieties.^[10] Activation is driven subsequently by photoinduced ligand dissociation/rearrangement^[9a] or isomerization reactions.^[9b-f] Originally, the first photolabile precatalysts were photosensitive alkylidene-free complexes in which the propagating metal carbene species was generated *in situ* by a photodisplacement of the ligand.^[11] Despite the variety of precatalysts and photochemical mechanisms, very few systems can boast full thermal stability and high activity at room temperature. In almost all cases, photolysis relies on the direct excitation of the precatalyst bearing a photoactive group.

In an effort to improve catalyst performance, versatility, latency and ease of synthesis, we believed that an indirect activation method of the precatalyst based on an exogenous photosensitive species could provide significant advantages. Previous work has shown that a metathesis inactive Ru alkylidene complex could be converted into an active system by a commercial photoacid generator.^[12] Taking a distinctive indirect approach, we report our efforts to develop a highly active photoinitiated catalytic system based on the combination of a photosensitive imidazolium salt (**1**) acting as a

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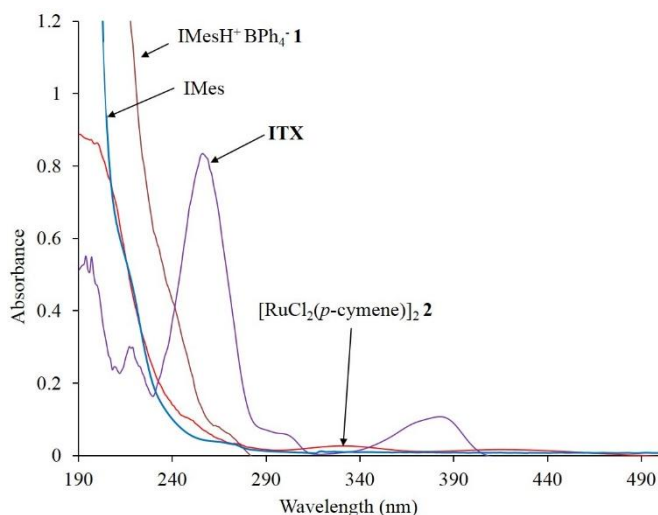


Figure 1: UV-vis absorption spectra of IMesH⁺ BPh₄⁻, IMes, ITX and [RuCl₂(*p*-cymene)]₂ in acetonitrile (2.0×10^{-5} M).

photogenerator of *N*-heterocyclic carbene (NHC) ligand and the well-known inactive [RuCl₂(*p*-cymene)]₂ dimer (**2**) (Scheme 1). Indeed, It is recognized that the simple reaction of Ru precatalyst **2** with a suitable NHC imidazolidene ligand (such as 1,3-bis(mesityl)imidazol-2-ylidene, abbreviated as IMes) is a means to generate *in situ* the highly active ruthenium-arene complex RuCl₂(*p*-cymene)(NHC), also known as Noels' catalyst.^[13] Obviously, part of the challenge lies in the design of an NHC photogenerator. So far, all latent NHCs are triggered thermally or mechanically,^[14] and the synthesis of an efficient photolabile NHC has yet to be developed.

To photogenerate the well-established IMes, we propose the imidazolium tetraphenylborate salt IMesH⁺ BPh₄⁻ **1** as a potential NHC photogenerator. The photochemistry of tetraarylborates has been well examined,^[15] and previous work showed its utilization as a photobase generator *via* a photoinduced proton transfer reaction.^[16] For its synthesis, simple treatment in ethanol of NaBPh₄ with the commercial imidazolium salt IMesH⁺ Cl⁻ resulted in a quantitative anion exchange to provide the desired photolabile NHC cleanly and in excellent yield (94 %).^[17] Compound **1** appears as white crystals with a melting point at 212 °C and a decomposition threshold at 292 °C (see a complete characterization in Fig. S1 of the supporting information). Its electronic absorption (Figure 1) spans only the UV-C region (100-280 nm) with an intense peak at 198 nm ($\epsilon_{198} = 1.38 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and a weak peak at 254 nm ($\epsilon_{254} = 7.30 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 1). A comparison with NaBPh₄ and IMesH⁺ Cl⁻ salts (Fig. S2) clearly established that both the anion (BPh₄⁻) and cation (IMesH⁺) of **1** are chromophores. However, an absorption range limited to short wavelengths represents a drawback for a broad use of **1** in photopolymerization due to competitive absorption with most cyclic olefin monomers. To extend spectral sensitivity at higher wavelengths, the photodecomposition of **1** was sensitized by 2-isopropylthioxanthone (ITX). ITX absorbs within the UV-A range (320 – 400 nm, Figure 1), which is the most suitable for photochemistry. Through its broad and intense absorption band at 365 nm ($\epsilon_{365} = 4.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), a wider range of radiation sources can be used, in particular the near UV light-emitting

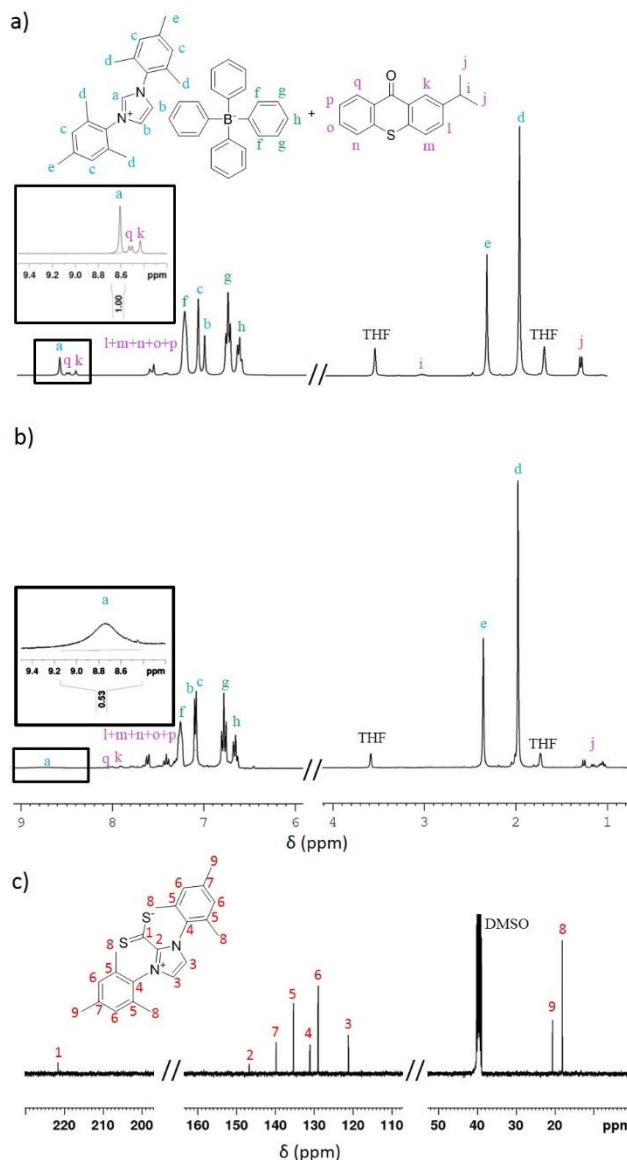
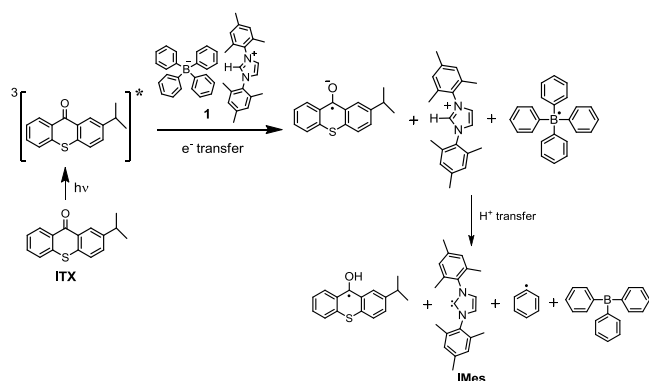


Figure 2: ¹H NMR spectra of **1**/ITX (2/1 eq.) mixture in THF-*d*₈ (0.12 M, relative to **1**): (a) before UV exposure, (b) after 10 min irradiation at 365 nm (0.12 mW cm⁻²) in a Rayonet® photochemical reactor; (c) ¹³C NMR spectra in DMSO-*d*₆ of the precipitate recovered after addition of CS₂. Insets: deprotonation yields were obtained by comparing the integrated area of the H_a proton resonance versus the methyl protons H_d used as internal standard.

diodes (LEDs), allowing very energy efficient, reliable, and simple generation of UV radiation between 365 and 395 nm. Also noteworthy is that ITX has a limited absorption overlap with Ru precatalyst and that the expected NHC (IMes) is inert to incident UV-A wavelengths as it begins to absorb below 280 nm ($\epsilon_{198} = 9.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Herein, we investigate the *in situ* photogeneration of the highly active RuCl₂(*p*-cymene)(IMes) catalyst through a three-component system: PhotoNHC **1**/ Ru precatalyst **2** / Sensitizer ITX (Scheme 1). Such a combination requires only stable commercial or easily synthesized reagents, thus leading to a simple and straightforward photoROMP procedure. First, the ability to photogenerate NHCs was assessed by irradiating a THF-*d*₈ solution of **1**/ITX (2/1 eq) at



Scheme 2: Photolysis mechanism of the 1/ITX tandem system. The primary step is the photochemically induced electron transfer from BPh₄[•] to triplet ITX. The resulting intermediate carbon anion may abstract a proton from IMesH⁺ to release the free NHC IMes. Boranyl and ketyl radicals are the other photoproducts. Carbon-boron cleavage of the boranyl radical may generate triphenylborane and a phenyl radical as described in the literature.^[18]

365 nm for 10 min, followed by ¹H NMR spectroscopy analysis (Figure 2). Proton H_a (δ = 8.63 ppm, Figure 2a) on carbon 2 adjacent to the two nitrogen atoms disappeared partially upon irradiation (53 %, Figure 2b), suggesting a photoinduced proton transfer reaction. Deprotonation was also demonstrated in other solvents (CD₂Cl₂ and acetonitrile-*d*₃, see Fig. S3 and S4). However, direct detection of the *in situ* formed NHC was more challenging because the position of the other protons (H_{b-e}) of IMesH⁺ is almost identical to the free IMes (Fig S5), and therefore, there is no expected shift after irradiation. To determine the precise structure of the generated species, an indirect identification method was undergone by reacting the as-irradiated medium with CS₂. The resultant red precipitate formed in THF-*d*₆ was readily collected, then dissolved in DMSO-*d*₆. The ¹³C spectrum (Figure 2c) displayed the characteristic signals of the pure zwitterionic adduct IMes-CS₂, thereby evidencing the formation of the targeted IMes NHC. Capitalizing on the Brønsted basicity of NHC (pK_a (IMes/IMesH⁺) = 20.8 at 25 °C in water^[19]), the amount of released NHC was evaluated by acid/base titration using phenol red pH indicator as titrant (Fig. S6). A maximum yield of 50 % was achieved after 5 min of irradiation (see SI for experimental details).

With an emission spectrum restricted to UV-A, removing ITX completely suppressed the photoactivity of IMesH⁺ BPh₄[•]. This result confirmed the major role of the photoexcited triplet state ITX in a sensitized reaction. With respect to the reaction mechanism, triplet-triplet energy transfer from ³ITX* to ³PhotoNHC[•] can be discarded since the following triplet energy order, E_T(BPh₄[•]) > E_T(ITX), was determined by conventional computational procedure. On the other hand, the tetraphenylborate anion was proved to have electron donor properties.^[18] Therefore, it is more likely that an electron transfer from BPh₄[•] to ³ITX* may take place as a primary step, to form the radical anion intermediate on the photoinitiator. Subsequent proton transfer from IMesH⁺ may yield IMes and ketyl radical on ITX (-C•(OH)-). Based on a coupled electron/proton transfer, our tentative mechanism (Scheme 2) is close to that of type II radical photoinitiators^[20] which are mixtures of hydrogen acceptors (oxidant, e.g. ketone) and donors (reductant, e.g. tertiary amine). The possibility of electron-transfer upon

Table 1. Photopolymerization results of NB using 1/2/ITX photoinitiating system in CD₂Cl₂ (1.06 M, relative to NB). Irradiation was performed in a Rayonet® photochemical reactor (365 nm, 0.12 mW cm⁻², 10 min irradiation)

Entry	1:2:ITX:NB Eq	Conv. ^[a] %	M _{n-th} ^[b] kg mol ⁻¹	M _{n-SEC} ^[c] kg mol ⁻¹	<i>D</i> ^[c]	σ _{cis} ^[d]
a	10:1:5:540	100	25.4	288.4	1.49	0.50
b	10:1:1:540	100	25.4	188.9	1.87	0.45
c	10:0:1:540	0	-	-	-	-
d	0:1:5:540	19	25.4	357.5	1.90	0.26
e	10:1:0:540	42	25.4	94.7	1.70	0.22

[a] Determined by ¹H NMR after 10 min UV irradiation. [b] Theoretical number average molar mass M_{n-th} = Conv. × $\frac{[NB] \times M_{NB}}{2 \times [2]}$ [c] Experimental number average molar mass obtained after reaching full monomer conversion and determined by triple detection SEC. [d] Fraction of *cis* double bonds as determined by ¹H NMR.

electronic excitation of the oxidant (ITX) was supported by a number of evidences. According to the Rehm-Weller equation, the free energy change for an electron transfer from BPh₄[•] to ³ITX* is favorable (ΔG_{et} = -0.13 eV), but weak. Conversely, a photooxidation of ³ITX* by IMesH⁺ is not thermodynamically feasible (ΔG_{et} = +0.72 eV). Quenching of ³ITX* in the presence of **1** was also proved by Laser Flash Photolysis (LFP) experiments in acetonitrile (Nd-YAG laser excitation at 355 nm). An interaction rate constant was determined by measuring the rate of triplet decay at 600 nm from Stern-Volmer plots (Fig. S7). The estimated quenching rate of 4 × 10⁷ M⁻¹ s⁻¹ was lower than that encountered in the known photochemistry of ³ITX*/amine systems, ranging usually from 10⁸ to 10⁹ M⁻¹ s⁻¹.^[20] Interestingly, IMesH⁺ BPh₄[•] (**1**) and NaBPh₄ showed nearly identical quenching rates, suggesting that BPh₄[•] serves as an efficient electron donor and that the cation IMesH⁺ is not involved in the first step of electron transfer. Accordingly, no deprotonation was observed by ¹H NMR spectroscopy when **1** was replaced by IMesH⁺ Cl⁻ (Fig. S8).

Subsequent efforts were directed toward exploring the catalytic activity of the three-component system 1/2/ITX in ROMP solution reaction of common monomers such as norbornene (NB). Irradiation was performed in a conventional Rayonet® photochemical reactor (λ_{max} = 365 nm) at room temperature. As shown in Table 1 for NB, excellent conversions were achieved after only 10 min of irradiation (entry **a**), suggesting the successful formation of the highly active ruthenium-arene complex bearing an NHC ligand. Even with lower loadings of ITX (entry **b**), conversion was maintained at a very high level. Molecular weights were higher than those predicted, which is indicative of incomplete catalyst activation.^[11c] Polymer with relatively narrow dispersity values (*D* = 1.5) were obtained. While irradiation of a solution devoid of Ru dimer resulted in no reaction (entry **c**), a small conversion was observed without **1** (19 %, entry **d**) or the sensitizer (42 %, entry **e**). Clearly, a direct excitation of the Ru precatalyst **2** at 365 nm is possible (Figure 1), which could generate a small amount of active species without the assistance of NHC. In this case, the required ROMP-active metal-alkylidene fragment may originate from a sequence involving a first photoinduced decooordination of the ⁶η arene ligand to release an unsaturated Ru species able to react with the alkene substrate. Such secondary initiation mechanism has been already reported, but only with mononuclear Ru complex e.g. RuCl₂(arene)(NHC).^[13] However, it proceeds only with highly

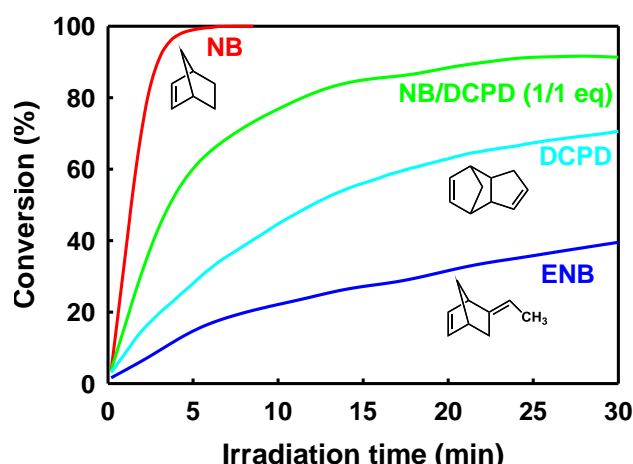


Figure 3. Conversion vs. irradiation time of various monomers. 1:2:ITX:Monomer (10:1:5:510 eq) in CH_2Cl_2 (1 M, relative to monomer). Irradiation: 365 nm LED (irradiance: 65 mW cm^{-2}).

active olefinic substrates such as NB, because no reaction was observed with DCPD. The co-existence of two distinct photochemical pathways was supported by differences in poly(NB) cis fraction. In the presence of **1** (entries **a-b**), σ_{cis} (≈ 0.5) was very similar to that found in the corresponding polymer prepared by the action of Ru-NHC complex,^[21] thereby suggesting the formation of the same ROMP catalyst. Conversely, a lower σ_{cis} was obtained without **1** (entries **d-e**), which agrees with the formation of another propagating species giving rise to a kinetically distinct conformation.

Additionally, photopolymerization kinetics were investigated by real-time FTIR spectroscopy. To achieve this, a 365 nm LED spot source (65 mW cm^{-2} at $\lambda_{\text{max}} = 365 \text{ nm}$) was focused through a light guide on a conventional IR liquid transmission cell containing the NB reactive solution. Reaction progress was monitored *in situ* by following the decreasing C=C stretching mode at 1566 cm^{-1} , only visible for NB and not the resultant polyalkenamer (Figure 3). Using the three-component 1/2/ITX system, full conversion of NB was accomplished in CH_2Cl_2 after 4 min. Upon removing **1**, less than 5 % of NB was converted after the same period of time, confirming the key role played by the NHC in the generation of a highly reactive ROMP catalyst. With the monofunctional monomer 5-ethylidene-2-NB (ENB), consumption was reduced to 40 % after 30 min of irradiation. The method was finally expanded to multifunctional cyclic olefins in an attempt to develop a promising photoROMP UV curing technology. Dicylopentadiene (DCPD) resulted in 70 % conversion while a copolymerization with NB in a 1 to 1 ratio (mol. eq.) increased conversion up to 90 %.

In conclusion, the easily synthesized IMesH⁺ BPh₄⁻ salt has proved to release the IMes-type NHC under UV-irradiation at 365 nm when sensitized by ITX, making it the first example of an NHC photogenerator. In combination with $[\text{RuCl}_2(p\text{-cymene})]_2$, the three-component system 1/2/ITX has allowed the fast photoROMP of NB at room temperature. The design of photosensitive imidazolium salt offers facile synthesis and affordable raw materials. There are other potential advantages: changing the imidazolium cation to broaden the structural diversity of photogenerated NHCs, or the structure of the anion

can help shift the absorption towards near UV-vis region. These attributes and potentialities open new avenues, not only for photoROMP, but also to develop novel NHC organocatalyzed photoreactions and photopolymerizations.

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Keywords: N-heterocyclic carbenes • photopolymerization • photochemistry • metathesis • ROMP

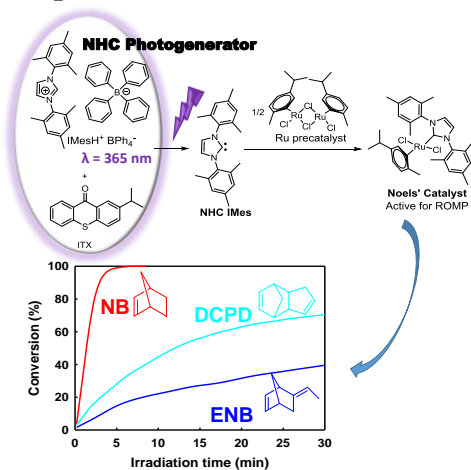
- [1] A. H. Hoveyda, A. R. Zhugralin, *Nature* **2007**, *450*, 243-251.
- [2] J. C. Mol, *J. Mol. Catal. A: Chem.* **2004**, *213*, 39-45.
- [3] S. Naumann, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2014**, *35*, 682-701.
- [4] a) K. A. Ogawa, A. E. Goetz, A. J. Boydston, *Synlett* **2016**, *27*, 203-214; b) S. Monsaert, A. L. Vila, R. Drozdak, P. Van Der Voort, F. Verpoort, *Chem. Soc. Rev.* **2009**, *38*, 3360-3372.
- [5] a) Y. Vidavsky, N. G. Lemcoff, *Beilstein J. Org. Chem.* **2010**, *6*, 1106-1119; b) C. E. Diesendruck, O. Iliashevsky, A. Ben-Asuly, I. Goldberg, N. G. Lemcoff, *Macromol. Symp.* **2010**, *293*, 33-38; c) O. Eivgia, N. G. Lemcoff, *Synth.* **2017**, *49*, DOI: 10.1055/s-0036-1589113; d) O. Reany, N. G. Lemcoff, *Pure Appl. Chem.* **2017**, *89*, 829-840.
- [6] W. Schnabel, in *Polymers and Light*, Wiley-VCH Verlag, **2007**, pp. 273-304.
- [7] R. Schwalm, in *UV Coatings*, Elsevier, Amsterdam, **2007**, pp. 19-61.
- [8] a) A. E. Goetz, A. J. Boydston, *J. Am. Chem. Soc.* **2015**, *137*, 7572-7575; b) K. A. Ogawa, A. E. Goetz, A. J. Boydston, *J. Am. Chem. Soc.* **2015**, *137*, 1400-1403.
- [9] a) D. Wang, J. Unold, M. Bubrin, I. Elser, W. Frey, W. Kaim, G. Xu, M. R. Buchmeiser, *Eur. J. Inorg. J.* **2013**, *2013*, 5462-5468; b) A. Ben-Asuly, A. Aharoni, C. E. Diesendruck, Y. Vidavsky, I. Goldberg, B. F. Straub, N. G. Lemcoff, *Organometallics* **2009**, *28*, 4652-4655; c) E. Levin, S. Mavila, O. Eivgi, E. Tzur, N. G. Lemcoff, *Angew. Chem. Int. Ed.* **2015**, *54*, 12384-12388; d) R. L. Sutar, E. Levin, D. Butilkov, I. Goldberg, O. Reany, N. G. Lemcoff, *Angew. Chem. Int. Ed.* **2016**, *55*, 764-767; e) A. J. Teator, H. L. Shao, G. Lu, P. Liu, C. W. Bielawski, *Organometallics* **2017**, *36*, 490-497; f) V. Sashuk, O. Danylyuk, *Chem. Eur. J.* **2016**, *22*, 6528-6531.
- [10] R. A. Weitekamp, H. A. Atwater, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 16817-16820.
- [11] a) P. A. vanderSchaaf, A. Hafner, A. Muhlebach, *Angew. Chem. Int. Ed.* **1996**, *35*, 1845-1847; b) A. Hafner, A. Muhlebach, P. A. vanderSchaaf, *Angew. Chem. Int. Ed.* **1997**, *36*, 2121-2124; c) L. Delaude, A. Demonceau, A. F. Noels, *Chem. Commun.* **2001**, 986-987; d) L. Delaude, M. Szyba, A. Demonceau, A. F. Noels, *Adv. Synth. Cat.* **2002**, *344*, 749-756; e) D. Wang, K. Wurst, W. Knolle, U. Decker, L. Prager, S. Naumov, M. R. Buchmeiser, *Angew. Chem. Int. Ed.* **2008**, *47*, 3267-3270; f) C. Ernst, C. Elsner, A. Prager, B. Scheibitz, M. R. Buchmeiser, *J. Appl. Polym. Sci.* **2011**, *121*, 2551-2558; g) D. Wang, K. Wurst, M. R. Buchmeiser, *Chem. Eur. J.* **2010**, *16*, 12928-12934; h) D. Wang, J. Unold,

-
- M. Bubrin, W. Frey, W. Kaim, M. R. Buchmeiser, *Chemcatchem* **2012**, *4*, 1808-1812; i) A. Hafner, P. A. van der Schaaf, A. Muhlebach, P. Bernhard, U. Schaedeli, T. Karlen, A. Ludi, *Prog. Org. Coat.* **1997**, *32*, 89-96.
- [12] a) B. K. Keitz, R. H. Grubbs, *J. Am. Chem. Soc.* **2009**, *131*, 2038-2039; b) A. Y. Khalimon, E. M. Leitao, W. E. Piers, *Organometallics* **2012**, *31*, 5634-5637.
- [13] L. Delaude, A. Demonceau, *Dalton Trans.* **2012**, *41*, 9257-9268.
- [14] a) S. Naumann, M. R. Buchmeiser, *Cat. Sci. Technol.* **2014**, *4*, 2466-2479; b) M. Fevre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.* **2013**, *42*, 2142-2172.
- [15] a) J. D. Wilkey, G. B. Schuster, *J. Org. Chem.* **1987**, *52*, 2117-2122; b) J. L. R. Williams, J. C. Doty, P. J. Gridale, R. Searle, T. H. Regan, G. P. Happ, D. P. Maier, *J. Am. Chem. Soc.* **1967**, *89*, 5153-5157; c) A. Pelter, R. T. Pardasani, P. pardasani, *Tetrahedron* **2000**, *56*, 7339-7369.
- [16] X. Sun, J. P. Gao, Z. Y. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 8130-8131.
- [17] a) E. Alcalde, I. Dinares, A. Ibanez, N. Mesquida, *Chem. Commun.* **2011**, *47*, 3266-3268; b) E. Alcalde, I. Dinares, A. Ibanez, N. Mesquida, *Molecules* **2012**, *17*, 4007-4027.
- [18] S. Chatterjee, P. D. Davis, P. Gottschalk, M. E. Kurz, B. Sauerwein, X. Yang, G. B. Schuster, *J. Am. Chem. Soc.* **1990**, *112*, 6329-6338.
- [19] E. M. Higgins, J. A. Sherwood, A. G. Lindsay, J. Armstrong, R. S. Massey, R. W. Alder, A. C. O'Donoghue, *Chem. Commun.* **2011**, *47*, 1559-1561.
- [20] S. Dadashi-Silab, C. Aydogan, Y. Yagci, *Polym. Chem.* **2015**, *6*, 6595-6615.
- [21] L. Delaude, A. Demonceau, A. F. Noels, *Curr. Org. Chem.* **2006**, *10*, 203-215.
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Graphical Abstract:



Text for table of content: We describe the first N-heterocyclic carbene (NHC) photogenerator consisting of an air-stable imidazolium tetraphenylborate salt as protected form of NHCs and isopropylthioxanthone (ITX) as sensitizer. A NHC-coordinated complex effective at photoROMP can be made in situ by subsequent reaction with the conventional ruthenium precatalyst [RuCl₂(*p*-cymene)]₂.

Keywords: Carbene Ligands, Photochemistry, Ring-Opening Polymerization, N-Heterocyclic Carbene, Ruthenium
