**TITLE:**

Photogeneration of N-Heterocyclic Carbenes: Application in Photoinduced Ring-Opening Metathesis Polymerization

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**KEYWORDS:**

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**SUMMARY:**

We describe a protocol to photogenerate N-heterocyclic carbenes (NHCs) by UV irradiation of a 2-isopropylthioxanthone/imidazolium tetraphenylborate salt system. Methods to characterize the photoreleased NHC and elucidate the photochemical mechanism are proposed. Protocols for ring-opening metathesis photopolymerization in solution and miniemulsion illustrate the potential of this 2-component NHC photogenerating system.

**ABSTRACT:**

We report a method to generate the N-heterocyclic carbene (NHC) 1,3-dimesitylimidazol-2-ylidene (IMes) under UV-irradiation at 365 nm, to characterize it and to determine the corresponding photochemical mechanism. Then we describe protocols to perform ring-opening metathesis polymerization (ROMP) in solution and in miniemulsion using this NHC-photogenerating system. To photogenerate the NHC IMes, a system comprising 2-isopropylthioxanthone (ITX) as photosensitizer and 1,3-dimesitylimidazolium tetraphenylborate (IMesH+BPh4-) as NHC protected form is employed. IMesH+BPh4-can be obtained in a single step by anion exchange between 1,3-dimesitylimidazolium chloride and sodium tetraphenylborate*.* A real-time steady-state photolysis set up is described, which hints that the photochemical reaction proceeds in two consecutive steps: ITX triplet is photoreduced by the borate anion, subsequent proton transfer takes place from the imidazolium cation to produce the expected NHC IMes. Two separate characterization protocols are implemented: firstly, CS2 is added to the reaction media to evidence the photogeneration of NHC through the formation of the IMes-CS2 adduct, and secondly, amount of NHC released *in situ* is quantified using acid-base titration. The use of this NHC photogenerating system for the ROMP of norbornene is also commented on. In solution, a photopolymerization experiment is conducted by mixing ITX, IMesH+BPh4-, [RuCl2(p-cymene)]2 and norbornene in CH2Cl2 and by irradiating the solution in a UV reactor. In dispersed medium, a monomer miniemulsion is first formed, then irradiated inside an annular reactor to produce a stable poly(norbornene) latex.

**INTRODUCTION:**

In chemistry, N-Heterocyclic Carbenes (NHCs) species fulfill the twofold role of *ligand* and *organocatalyst*1*.* In the former case, the introduction of NHCs has resulted in the design of metal transition catalysts with improved activity and stability2. In the latter case, NHCs have proved to be superior catalysts for manifold organic reactions3, 4. Despite this versatility, handling of bare NHCs is still a significant challenge5 and producing these highly reactive compounds in a way that they could be released *in situ* and “on demand” is a very attractive goal. Consequently, several strategies have been developed to release NHCin the reaction media, which mostly rely on the use of thermolabile progenitors6–8. Surprisingly, while it would unleash a novel generation of photoinitiated reactions useful for macromolecular synthesis or preparative organic chemistry6, their generation using light as stimulus has been scarcely explored. Only very recently, a first photogenerating system able to produce NHC has been unveiled9. It consists of 2 components: 2-isopropylthioxanthone (ITX) as photosensitive species and 1,3-dimesitylimidazolium tetraphenylborate (IMesH+BPh4-) acting as NHC protected form. Consequently, in the following paragraphs, we report a method to generate the N-heterocyclic carbene (NHC) 1,3-dimesitylimidazol-2-ylidene (IMes) under UV-irradiation at 365 nm, to characterize it and to determine the photochemical mechanism associated with. Then we describe protocols to perform ring-opening metathesis polymerization (ROMP) in solution and in miniemulsion using this NHC photogenerating system.

In a first part, we report herein a synthesis protocol to produce IMesH+BPh4-. This protocol is based on anion metathesis between the corresponding imidazolium chloride (IMesH+Cl-) and sodium tetraphenylborate (NaBPh4). Then, to demonstrate the *in situ* formation of NHC, two protocols have been developed involving the irradiation at 365 nm of a IMesH+BPh4-/ITX solution in a photoreactor. The first one consists in monitoring the deprotonation of the imidazolium cation IMesH+ through 1H NMR spectroscopy. Direct evidence for the formation of the desired NHC (IMes) is provided in a second experiment where the adduct IMes-CS2 is successfully isolated, purified and characterized.

The second section describes two protocols to shed light onto the photochemical mechanism involving the NHC two-component photogenerating system: IMesH+BPh4-/ITX. Firstly, an original real-time steady state photolysis experiment reveals that electron transfer is induced by photo-excitation of ITX in the presence of tetraphenylborate. Electron donor properties of this borate anion10 drives a photoreduction of 3ITX\* triplet excited state into ITX●- radical anion in a so-called photo-sensitized reaction. The formation of NHC confirms that ITX●- species may further abstract a proton from IMesH+ to produce the desired NHC. Based on acid/base titration using phenol red pH indicator as titrant, a second original protocol is implemented which allows the determination of the yield of released NHC.

In the third section, we describe protocols where the above-mentioned photogenerated IMes can be exploited in photopolymerization. Of primary interest is ring-opening metathesis polymerization (ROMP) because this reaction is still at a very preliminary stage of development with regard to photoinitiation11, 12. Initially limited to ill-defined and highly sensitive tungsten complexes, photoinduced ROMP (photoROMP) has been extended to more stable complexes based on W, Ru and Os transition metals. Despite the variety of precatalysts, almost all photoROMP processes rely on the direct excitation of a single photoactive precatalyst13. By contrast, we use radiation to create the NHC imidazolidene ligand (IMes), which can react subsequently with a non-photoactive Ru precatalyst [RuCl2(*p*-cymene)]2 dimer9.In our process, the photogeneration of NHC ligand drives the *in situ* formation of a highly active ruthenium-arene NHC complex: RuCl2(*p*-cymene)(IMes) (Noels’ catalyst)14, 15. Using this indirect methodology, two distinct photoROMP experiments of norbornene (Nb) are performed: in solution (dichloromethane) and in aqueous dispersed system from a monomer miniemulsion16.

**PROTOCOL:**

**1. NHC PHOTOGENERATING SYSTEM: SYNTHESIS AND REACTIVITY**

**1.1 Synthesis of 1,3-dimesitylimidazolium tetraphenylborate (IMesH+BPh4-)**

* + 1. Preparation of the solution of 1,3-dimesitylimidazolium chloride (IMesH+Cl-) in ethanol.
       1. Add 1.00 g (2.93 mmol) of 1,3-dimesitylimidazolium chloride to a 50 mL round bottom flask equipped with a stir bar.

1.1.1.2 Dissolve the 1,3-dimesitylimidazolium chloride in 30 mL of ethanol.

* + 1. Preparation of the solution of sodium tetraphenylborate (NaBPh4) in ethanol.
       1. Add 1.35 g (3.92 mmol) of sodium tetraphenylborate to a 50 mL round bottom flask equipped with a stir bar.

1.1.2.2 Dissolve the sodium tetraphenylborate in 30 ml of ethanol.

* + 1. Generation of 1,3-dimesitylimidazolium tetraphenylborate (IMesH+BPh4-)
       1. Add dropwise the solution of sodium tetraphenylborate into the solution of 1,3-dimesitylimidazolium chloride under stirring.
       2. Stir the reaction mixture for 10 min at room temperature.
       3. Remove the stir bar and filter the white precipitate using vacuum and a fritted glass filter of pore size 3.
       4. Wash the precipitate with 30 mL of ethanol and filter it (fritted glass filter pore size 3).
       5. Wash the precipitate with 30 mL of deionized water and filter it (fritted glass filter pore size 3).
       6. Dry the white precipitate at 60 °C for 15 h.

1.1.3.7 Analyze the product by 1H and 13C NMR in DMSO-d6 according to reported procedure9.

* 1. **Photogeneration of NHC 1,3-dimesitylimidazol-2-ylidene, also known as IMes, by UV irradiation of the dimesitylimidazolium tetraphenylborate in the presence of isopropylthioxanthone (ITX)**
     1. Add 39 mg (0.062 mmol, 2 equiv.) of 1,3-dimesitylimidazolium tetraphenylborate, 7.8 mg (0.031 mmol, 1 equiv.) of ITX and 0.5 mL of deuterated THF (previously stored over 3Å molecular sieves) in an NMR tube.
     2. Place the NMR tube inside the photochemical reactor equipped with a circular array of 16 fluorescent tubes emitting a monochromatic radiation at 365 nm **and irradiate for 10 min.**
  2. **Monitoring of deprotonation of IMesH+BPh4- by 1H NMR spectroscopy.** 
     1. **Analyze the deprotonation of** IMesH+ into IMes by 1H NMR.

NOTE: 1H NMR spectra were recorded at 25 °C on a NMR spectrometer operating at 400 MHz. TMS was used as internal standards for calibrating the chemical shifts in 1H NMR.

* + - 1. Calibrate the integration parameters so that in the 1H NMR spectra the CH3 singlet of 1,3-dimesitylimidazolium tetraphenylborate (δ = 2.0 ppm) corresponds to six.

1.2.3.2 Determine the integration value of the N-C*H*-N signal area (δ = 8.4 – 9.4 ppm) in order to evaluate the degree of IMesH+ deprotonation. The integration value should vary from 1 when no deprotonation occurred (before irradiation) to 0 when complete deprotonation of IMesH+ has been performed.

* 1. **Formation, isolation and characterization of the 1,3-dimesitylimidazoliumdithiocarboxylate adduct (IMes-CS2)**
     1. Add 0.02 mL of carbon disulfide in the as-irradiated NMR tube. The reaction media changes color from orange/brown to dark red indicating the formation of the IMes-CS2 adduct.
     2. Let react for 12 h. A red precipitate forms assigned to the IMes-CS2 adduct.
     3. Filter the red precipitate (fritted glass filter of pore size 3) and dry it under air at room temperature for 12 h.
     4. Solubilize the red solid in 0.5 mL of deuterated DMSO. Confirm the chemical structure by 1H and 13C NMR spectroscopy.

CAUTION: Carbon disulfide is highly toxic and should be handled with care under a fume hood.

**2. PHOTOCHEMICAL MECHANISM**

* 1. **Real-time photobleaching of IMesH+BPh4- / ITX**
     1. Prepare a stock solution of ITX by adding 0.76 mg (3 x 10-3 mmol) of ITX to 15 mL of dry acetonitrile (previously stored over 3Å molecular sieves).
     2. Transfer 3 mL of ITX solution into a UV quartz cell covered with a rubber stopper containing 1.10 mg of IMesH+BPh4- (1.8 x 10-3 mmol) and a stirring micromagnet. The molar ratio ITX:IMesH+BPh4- is 1:3.
     3. Degas the solution by bubbling nitrogen for 10 min, then irradiate the solution at 365 nm with a medium-pressure Hg-Xe lamp under continuous stirring (63 mW cm-2, power 75 mW).
     4. Monitor the change of UV-absorbance at 365 nm during irradiation by using a spectrometer after passing a transmitted actinide beam.
     5. Apply the same procedure (steps 2.1.1 to 2.1.4) for other experiments replacing IMesH+BPh4- by other quenchers: IMesH+Cl- (0.61 mg, 1.8 x 10-3 mmol) or NaBPh4 (0.62 mg, 1.8 x 10-3 mmol).
  2. **Quantification of photogenerated NHC by spectrophotometric titration** 
     1. Add 1.85 mg of dimesitylimidazolium tetraphenylborate (3 x 10-4 mmol, 3 equiv.) and 0.25 mg of ITX (10-4 mmol, 1 equiv.) to 10 mL of dry acetonitrile.
     2. Transfer 2 mL of this freshly prepared solution into a conventional spectroscopic quartz cell capped with a rubber septum.
     3. Purge the colorless mixture with nitrogen before exposing the cuvette to a 365 nm LED spotlight (power 65 mW) for 1 min.
     4. After each irradiation time, add gradually 0.1 mL portions of phenol red (PR) solution (2 × 10-4 M in dry acetonitrile) into the cuvette. This latter titrating solution was prepared in advance.
     5. Record a UV-vis spectrum after each 0.1 mL addition of PR solution until 1 mL.

The indicator solution is initially transparent and contains the bis-protonated form H2PR. After its addition, acid/base reaction with NHC causes the formation of the pink bivalent anion PR2- with a maximum absorption at 580 nm. Plotting the absorbance at 580 nm as a function of the titrant volume gives two intersecting straight lines, indicative of the titration end-point.

2.2.6 Repeat the same operations (steps 2.2.1 to 2.2.5) with the same ITX/IMesH+BPh4- solution irradiated for longer times: 2 min, 5 min and 10 min. For each time, a new must be prepared.

At the equivalence point in the acid-base titration:

(1)

where is the concentration of photogenerated IMes released in the UV cuvette, is the initial volume of IMesH+BPh4- / ITX solution, [PR] is the concentration of PR and is the total volume of PR added into the UV cuvette at the titration end-point. Therefore, the yield of IMes released upon irradiation of IMesH+BPh4- /ITX solution was obtained from equation (2):

(2)

where is the initial concentration of IMesH+BPh4-.

The validity of the method is checked by titrating a free IMes solution (1 × 10-4 M in acetonitrile) using a similar acetonitrile PR solution as titrant (2 × 10-4 M).

**3. PHOTOINDUCED RING-OPENING METATHESIS POLYMERIZATION**

**3.1 PhotoROMP of Nb in solution**

3.1.1 Add 1 g (11 mmol, 540 equiv.) of Nb, 120 mg (0.196 mmol, 10 equiv.) of 1,3-dimesitylimidazolium tetraphenylborate, 12 mg (19.6 mmol, 1 equiv.) of dichloro(para-cymene)ruthenium dimer and 25 mg (0.098 mmol, 5 equiv.) of ITX in a 20 mL test tube equipped with a stir bar.

3.1.2 Dissolve the solids in 10 mL dichloromethane and cap the tube with a rubber septum.

3.1.3 Purge the mixture by bubbling nitrogen gas through a syringe needle for 15 min.

3.1.4 Place the tube inside the photochemical reactor equipped with a circular array of 16 **fluorescent lamps (emitting at 365 nm) and irradiate for 10 min. The solution becomes viscous indicating that high-molecular weight polyNb is formed.**

3.1.5 Precipitate the polymer by pouring the solution into 300 ml of methanol.

3.1.6 Filter the polymer (fritted glass filter pore size 3) and dry it at 60°C for 8h.

3.1.7 Analyze the polymer by 1H NMR according to reported procedure9 by dissolving about 10 mg of polymer in 0.5 ml of CD2Cl2.

3.1.8 Analyze the polymer by size exclusion chromatography according to reported procedure9, using THF as eluent and by dissolving 10 mg of polymer in 1 mL of THF.

**3.2. PhotoROMP of Nb in miniemulsion**

3.2.1 Preparation of Nb miniemulsion:

3.2.1.1 Dissolve 15.0 g of neutral surfactant **Polyoxyethylene (100) stearyl ether** in 150 mL of milliQ water

3.2.1.2 Introduce the aqueous phase in the annular LED photoreactor closed with rubber septum and place the reactor under the airtight sonication probe.

3.2.1.3 Degas the solution by bubbling nitrogen during 1 h.

3.2.1.4 Mix 4.94 g of Nb (5.2 10-2 mol; 510 equiv.; 25 w-%), 2.85 mL of hexadecane (10 w-%) and 6 mL of dichloroethane (32.5 w-%) in a 50 mL round bottom flask closed with a rotaflo and degas the solution with freeze-pump-thaw cycle.

3.2.1.5 Add 6 mL of dichloroethane (32.5 w-%) in a second 50 mL round-bottom flask closed with a rotaflo. Degas the solution by Freeze-pump-thaw. Add 162 mg of 1,3-dimesitylimidazolium tetraphenylborate (2.6 10-4 mol, 5 equiv.), 33 mg of ITX (1.3 10-4 mol, 2.5 equiv.) and 30 mg of dichloro(p-cymene)ruthenium(II) dimer (4.9 10-5 mol, 1 equiv.) under inert atmosphere (glovebox) to the flask.

3.2.1.6 Mix the two organic solutions containing the monomer and the catalytic mixture under a nitrogen flux and introduce 15 g of the final organic solution inside the photoreactor containing the aqueous phase under stirring.

3.2.1.7. Stir the two phases during 1 h to form a rough macroemulsion.

3.2.1.8. Sonicate during 10 min (Power 50%; pulse-on time: 5 s, off-time: 5 s) to form the miniemulsion.

3.2.2. Photopolymerization of NB miniemulsion

3.2.2.1 Replace the airtight sonication probe by the LED lamp equipped with a water cooling system and protected by a cladding tube under a nitrogen flux.

3.2.2.2 Place the closed reactor inside the photocabinet to prevent exposure to UV radiation.

3.2.2.3 Irradiate the monomer miniemulsion for 100 min in order to obtain polymer latex. During irradiation, particle size and monomer conversion can be determined as explained below.

3.2.3 Determination of particle size, conversion and molecular weight

3.2.3.1 Collect 4 mL of miniemulsion sample during irradiation process.

3.2.3.2 Add 20 µL of miniemulsion in a glass cuvette containing 5 mL water to prepare a 250 times diluted sample for particle size analysis by dynamic light scattering (DLS).

3.2.3.3 Dissolve 100 µL of miniemulsion in 500 µL of THF to measure the Nb conversion by gas chromatography (GC) with hexadecane as internal standard (GC retention times: tGCNb = 1.77 min; tGCdodecane = 13.25 min).

3.2.3.4 Precipitate the rest of the sample in 20 mL of acetone. Filter the polymer. Dry the polymer under vacuum and measure the molecular weight by size exclusion chromatography (SEC) (SEC in tetrahydrofuran (THF) (1 mL min-1) with trichlorobenzene as the flow marker, using both refractometric and UV detectors).

CAUTION (Part 1-3): Possibly hazardous sources of light emitting in the UV and visible range are used in the described experiments. These lamps can present a reasonably foreseeable risk of harming the eyes and skin of workers. Consequently, all measures possible should be put in place by the experimenter to reduce the risks to as low as is reasonably practicable. A list of common measures includes isolation of the light source inside a protective casing (photocabinet for example), training of all workers, placing the hazardous sources of light in well designated laboratories or fume hood with restricted access, providing suitable safety gears: safety goggles blocking UVA irradiation are sufficient for all described protocols and displaying appropriate warning and safety signs.

**REPRESENTATIVE RESULTS:**

**Protocol 1.1** describes the efficient anion metathesis between 1,3-dimesitylimidazolium chloride (IMesH+Cl-) and sodium tetraphenylborate (NaBPh4) to yield 1,3-dimesitylimidazolium tetraphenylborate (IMesH+BPh4-). The desired photolatent NHC is obtained in excellent yield (98 %). Figure 1 shows a 1H and 13C NMR spectra, both testifying that a pure product exhibiting the correct structure is obtained.

**Protocol 1.2** describes how to generate the N-HC IMes by irradiating the mixture IMesH+BPh4- / ITX (2/1 equiv.) in THF-d8 solution.

**Protocol 1.3** shows that it is possible to assess the conversion of IMesH+ in IMes by monitoring the deprotonation of IMesH+BPh4- through 1H NMR spectroscopy. Figure 2 shows that proton Ha (8.63 ppm, Figure 2a) on carbon 2 adjacent to the two nitrogen atoms disappears partially after 10 min irradiation (53 %, Figure 2b). The reaction was performed by irradiating the mixture IMesH+BPh4- / ITX (2/1 equiv.) in THF-d8 solution.

**Protocol 1.4** shows that it is possible to isolate the formed NHC by reacting the as-irradiated medium (see protocol 1.2) with CS2. The red precipitate formed in THF-*d*8 is collected, dried and dissolved in DMSO-*d*6. As it can be seen in the 13C NMR spectrum (Figure 2c), all the characteristic resonances are consistent with IMes-CS2 adduct. This result confirms indirectly the *in situ* generation of the targeted IMes NHC.

**Protocol 2.1** Thioxanthone derivatives are a well-established class of photoinitiators generally employed in combination with a second component referred to as “co-initiator”. Their absorption spectra appear with a maximum in the range 340-420 nm. The nature of the co-initiator determines the mechanism of initiation. Three general initiation mechanisms have been described: ❶ Triplet-triplet energy transfer (in the present case from 3ITX\* to 3BPh4-\*);❷ electron transfer from the electron donor BPh4- to 3ITX\*; and, ❸ direct H abstraction of IMesH+ by 3ITX\*. Mechanism ❶ can be discarded since the following triplet energy order, ET(BPh4-) > ET(ITX) is established by conventional computational procedure.

**Protocol 2.1** enables to evidence which of the two mechanisms ❷ or ❸ is operating. Figure 3 shows the evolution of absorbance values of characteristic ITX absorption band at 365 nm during irradiation for three different bicomponent mixtures: IMesH+BPh4- /ITX, IMesH+Cl- /ITX and NaBPh4/ITX. The absence of decay for IMesH+Cl- supports the incapacity for electronically excited ITX to abstract a hydrogen from the imidazolium cation (mechanism ❸). In contrast, photobleaching of ITX is visible in the two systems containing the BPh4- anions although the decay rates are different in these two cases. This result emphasizes the critical role played by the tetraphenylborate anion. Consequently, the photoreduction of ITX by tetraphenylborate (mechanism ❷) is proved as the primary step in the formation of the NHC. **Figure 4** displays a hypothetical and complete mechanism where the ITX●- radical anion may abstract a proton from IMesH+ to release the free NHC IMes.

**Protocol 2.2** shows evidence in favor of this mechanism. This method reveals the progressive release of NHC during irradiation. It is a method to determine the amount of released NHC based on acid/base titration using phenol red (PR) pH indicator as titrant. A maximum yield of 50 % is achieved after 5 min of irradiation (**Figure 5**) and control experiment with free IMes enables to validate the method.

**Protocol 3.1** describes photoROMP of NB (540 equiv.) in dichloromethane using a photolatent mixture composed of IMesH+BPh4- /ITX (10/5 equiv.) (to produce NHC IMes) and the well-known inactive [RuCl2(*p*-cymene)]2 dimer (1 equiv.). It is recognized that the simple reaction of Ru precatalyst with the imidazolidene ligand IMes is a means to generate *in situ* the highly active ruthenium-arene complex RuCl2(*p*-cymene)(NHC), also known as Noels’ catalyst. Irradiation is performed in a conventional photochemical reactor (λmax = 365 nm) at room temperature. Complete conversion is achieved after only 10 min of irradiation as measured by 1H NMR spectroscopy (**Figure 6**), suggesting the successful formation of the highly active ruthenium-arene complex bearing an NHC ligand. In addition, polyNb with a number-average molecular weight of 288 kDa and a relatively narrow dispersity values (*Ð* = 1.5) is obtained as determined by size exclusion chromatography.

**Protocol 3.2** describes a miniemulsion photoROMP procedure. High conversions (70-80 %) are achieved (**Figure 7**). As can be seen in **Figure 8**, the initial droplet size measured by DLS is 92 nm. The final particles exhibit a size of 102 nm (0.140) closed to the initial droplet size. TEM observations show perfectly spherical particles with sizes in agreement with DLS data.

**FIGURE LEGENDS:**

**Figure 1.** **NMR characterization of IMesH+BPh4-.** (a) 1H NMR spectrum in DMSO-*d*6 (400 MHz) of 1,3-dimesitylimidazolium tetraphenylborate (IMesH+BPh4-), δppm : 2.13 (s, 12H), 2.36 (s. 6H), 6.69 (t, 4H), 7.17 (m, 20H), 8.27 (s, 2H), 9.64 (s, 1H,); (b) 13C NMR spectrum of the same compound in DMSO-*d*6 (100 MHz), δppm:16.58, 20.23, 121.35, 124.49, 125.02, 129.24, 130.29, 134.00, 135.35, 138.19, 140.06, 162.58. Tm = 212 °C (DSC). This figure has been modified from reference9.

**Figure 2.** **NMR monitoring of IMesH+BPh4- deprotonation and subsequent synthesis of IMes-CS2.** 1H NMR spectra of IMesH+BPh4- /ITX(2/1 equiv.)mixturein THF-*d*8:(a) before UV exposure, (b) after 10 min irradiation at 365 nm (0.12 mW cm-2) in a photochemical reactor; (c) 13C NMR spectra in DMSO-*d*6 of the precipitate recovered after addition of CS2. This figure has been modified from reference9.

**Figure 3.** **Evidence for photolysis mechanism.** Real-time photobleaching experiments in acetonitrile (irradiation: 365 nm, 63 mW cm-2): ITX, and ITX with three different quenchers: IMesH+Cl-, NaBPh4 and IMesH+BPh4-. ITX: quencher molar ratio is 1:3. ([ITX] = 2.0 10-4 M).

Figure 4. **Photomechanism pathway to IMes**. Photolysis mechanism of the IMesH+BPh4- /ITX tandem system.

**Figure 5.** **Quantification of IMes amount released.** (a) Change of UV-Vis spectra of an acetonitrile solution of IMesH+BPh4- (3.0 × 10-4 M) and ITX (1 × 10-4 M) irradiated during 2 min (LED, 365 nm, 65 mW cm-2) upon gradual addition of PR (2 × 10-4 M), (b) Titration plot showing the absorbance at 580 nm for the same solution irradiated at 1, 2 or 5 min as a function of PR (titrant) volume. The insert gives the yield of photogenerated NHCs deduced from the spectrophotometric titration curve. This figure has been modified from reference9.

**Figure 6.** **PhotoROMP in solution.** 1H NMR spectrum in CD2Cl2 (400 MHz) of the photopolymerization reaction medium before irradiation (a) and after 10 min irradiation at 365 nm (b).

Figure 7. Evolution of photoROMP in miniemulsion with time. Nb conversion as a function of irradiation time in miniemulsion photoROMP.

Figure 8. Characterization of polyNb particles. DLS data (top) of Nb miniemulsion and polyNb latex obtained after photopolymerization. TEM micrograph of final latex.

**DISCUSSION:**

We have reported an easy and versatile protocol for the in-situ generation of NHC upon UV-irradiation at 365 nm. The anion exchange reaction between 1,3-dimesitylimidazolium chloride and sodium tetraphenylborate provides a straightforward access to the NHC protected form IMesH+BPh4- in quantitative yield. Nevertheless, if employing another starting imidazolium salt, the solvent employed to perform the metathesis reaction should be chosen with care so that it allows the solubilization of both starting salts (imidazolium salts and sodium tetraphenylborate) and the precipitation of the imidazolium tetraphenylborate product. As such, ethanol is most often the appropriate solvent to perform this reaction.

The photogeneration of the NHC IMes by irradiation at 365 nm of the 2 components system IMesH+BPh4-/ITX can produce NHC yields up to 50 % but lower yields can be obtained depending on the experimental conditions employed. In particular, the use of solvents containing water or protic species favors secondary reactions such as the deprotonation of these protic species by BPh4- and/or the reprotonation of IMes, thus decreasing the overall yield of released IMes. Indeed, NHC are known to be sensitive to water and other impurity traces, we thus recommend using dried solvents when attempting to photogenerate the NHC IMes. Despite their water/protic sensitivity, NHCs are much more reactive towards metallic substrates such as [RuCl2(p-cymene)]2, which allows for the ROMP of Nb to be performed in miniemulsion. It has been noticed that the presence of dioxygen can also alter the course of the reaction. Indeed, dioxygen is known to react with ITX triplet, preventing the release of IMes. Because an electron transfer is involved for the generation of NHC, the reaction is also assumed to be highly dependent on solvent polarity. Finally, when attempting at photogenerating IMes from ITX/IMesH+BPH4- in a reaction media, the latter should be chosen so that it provides a good solubilization of the IMesH+BPh4- salt and does not absorb UV light up to 350 nm.

As opposed to other methods that rely on temperature, dilution or change of pH to generate *in situ* NHC, our approach involves radiation as external stimulus with the distinctive advantage of spatial/temporal control of the reaction. Thanks to manifold polymerization reactions catalyzed/initiated by NHC, we envision that a photolatent NHC can foster new photopolymerization reactions such as photoROMP as detailed in this study. In addition, because NHCs are well established stabilizing ligands, we believe that the photochemical preparation of organometallic complexes may benefit from this photogenerating NHC system. Finally, NHCs are employed as reactants or catalysts in many reactions of organic chemistry, their photogeneration should be of interest to chemists who would like to involve NHCs in cascade reactions at the desired time.

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**DISCLOSURES:**

The authors have nothing to disclose.

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