

Metal complex based photocatalyst systems: A quest for new possibilities and application to photopolymerization reactions

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ABSTRACT

Novel perspectives in the development of metal complex based photocatalysts operating through an oxidation or a reduction cycle are investigated. Several systems (Fe, Ni, Co, Al, Ru, Ir organometallic complexes) working under soft irradiation conditions are presented. Their photochemistry is studied by steady state photolysis and ESR experiments to define the key points responsible for a high reactivity. Some of them are tested as photoinitiator catalysts in multi-component combinations usable in photopolymerization reactions.

KEYWORDS: photocatalysts, photoinitiators, photopolymerization, metal complexes, sulfonium salts, chlorosilane

INTRODUCTION

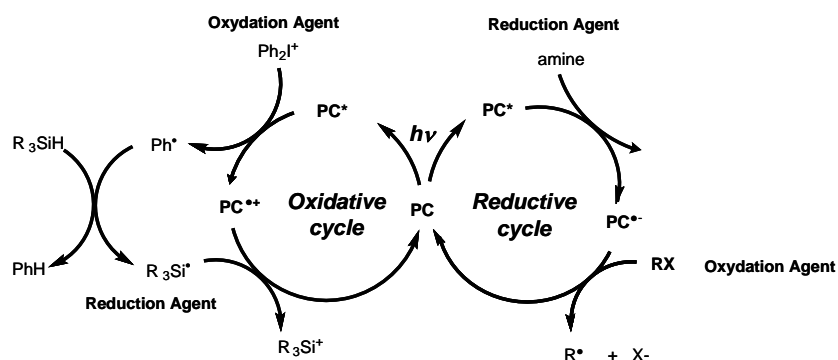
Metal complex based photocatalysts PC are largely used in photochemical sciences for applications in various areas such as organic chemistry synthesis, homogeneous and heterogeneous photocatalysis, nanotechnology, polymer chemistry, etc. For example, organometallic complexes when introduced in various photosensitive formulations [1] (e.g. PC/iodonium salt/silane or PC/amine/phenacyl bromide) work through either an oxidation

or a reduction cycle (Scheme 1 where PC refers to the photocatalyst, e.g. a ruthenium complex). These formulations can be considered as potential sources of radicals and cations usable in photochemical applications. The present paper will illustrate their reactivity towards double bonds and epoxide rings through applications to photopolymerization reactions.

In the particular photopolymer area, organometallic compounds have known a revival of interest as photoinitiators PI [1-2] in photoinitiating systems PIS for the free radical photopolymerization (FRP) of acrylates M (1), cationic photopolymerization (CP) of epoxides Ep (2), free radical promoted cationic photopolymerization (FRPCP) of epoxides Ep (3). These kinds of PIs were reported many years ago (see a review in [3]) but, except some particular examples in the metallocene series, they were not extensively used. Later on, they were reconsidered in some papers dealing with e.g. Cr, Ti, Fe, Rh, W, Ru, Ir metal based derivatives [1, 4-6]. More recently, a photoredox catalysis type behaviour (as it is well known and used in organic synthesis [7]) has been introduced provided a suitable selection of the photoinitiating system is realized [1, 8]. This way allows a PI regeneration while keeping a high reactivity/efficiency. In that case, the PI can be seen as a photoinitiator catalyst PIC. Moreover, it appears as particularly suitable for reactions under very soft irradiation conditions (e.g. Xe lamps, household fluorescence or LED bulbs, halogen

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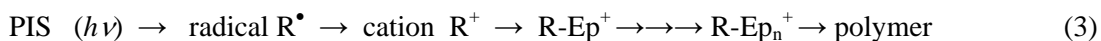
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Scheme 1

lamps, diode lasers, sunlight). This approach opens up a new way for the design of a novel class of high performance PIs for FRP, CP and FRPCP and brings new properties, for example: i) almost no initiator is consumed, ii) the spectral photosensitivity extends from the UV to the visible range, iii) excitation under green or red laser lines is feasible, iv) low light intensity

light sources can be used, v) the production of the initiating radicals in the FRP of acrylates or the cationic species in the CP or FRPCP of epoxides is quite easy. A dual behavior (the simultaneous generation of radicals and cations could ensure the formation of e.g. an epoxy/acrylate interpenetrated network IPN) can be sometimes achieved.



In Scheme 1, the metal complex as well as the oxidation and/or the reduction agents obviously play a pivotal role for the efficiency of these reactions. Ruthenium organometallic complexes exhibit an excellent visible-light absorption, long lived excited states and suitable redox potentials have been mostly applied for many years [8]. More recently, iridium based derivatives were recognized as interesting systems (e.g. for getting a final photoluminescent material) [9]. During the last year, zinc [10] (as examples of low cost metal containing organometallic complexes) and platinum [11] centered compounds were proposed as new photoinitiators.

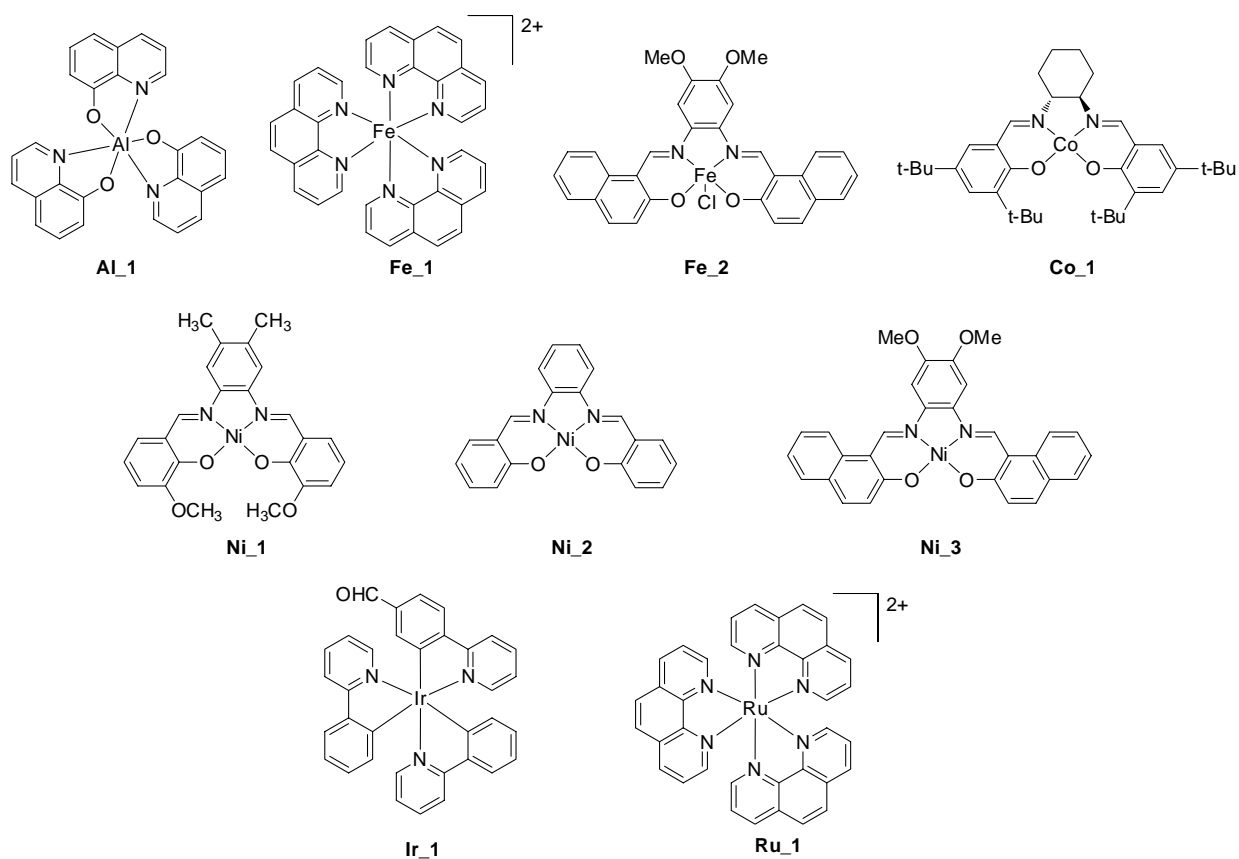
The search for other metal centered PICs as well as oxidation and reduction compounds remains fascinating not only in polymer photochemistry but also e.g. in organic photochemistry under soft irradiation conditions or photocatalysis. In the present paper, Ru, Ir, Fe, Ni, Co and Al

organometallic complexes (Scheme 2) and suitable photosensitive formulations PIS will be tentatively considered. We will evaluate i) the ability of different metal complexes in these catalytic cycles (see again Scheme 1) ii) the use of sulfonium salts in the oxidative catalytic cycle and iii) the change of alkyl halides for chlorosilanes in the reductive cycle. The PIC excited state reactivity and the involved photochemical/ chemical mechanisms will be investigated in detail by ESR experiments. Finally, these systems will be tested in photopolymerization reactions occurring under low light intensity irradiation sources.

EXPERIMENTAL PART

i. Organometallic complex synthesis

The investigated PICs shown in the Scheme 2 were prepared according to the following procedures. All reagents and solvents were



Scheme 2

purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. ^1H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^1H (400 MHz) and ^{13}C (100 MHz). The ^1H chemical shifts were referenced to the solvent peak DMSO- d_6 (2.49 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak DMSO- d_6 (39.5 ppm). *Tris*(8-hydroxyquinolinato)aluminium (AlQ_3) **Al_1** was synthesized by adapting a literature procedure [12]. Complexes **Fe_2** and **Ni_3** were prepared by complexation of the salphen ligand **L_1** with one equivalent of iron (III) chloride hexahydrate and

nickel (II) sulfate respectively. Heteroleptic complex **Ir_1** [8e] and [[2,2'-(1,2-cyclohexanediyl)bis[(nitrilo-kN)methylidyne]]bis[3,5-di-*tert*-butylphenolato-kO]] (2-)]cobalt (II) **Co_1** [13] were synthesized according to literature procedures. Ru-1 ($\text{Ru}(\text{phen})_3\text{Cl}_2$) and Fe-1 ($\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$) were obtained from Aldrich.

Synthesis of *tris*(8-hydroxyquinolinato)aluminium (III) **Al_1**

1.5 g (7.35 mmol) of aluminum isopropoxide and 3.21 g (22.05 mmol) of 8-hydroxyquinoline were suspended in 30 mL dry methanol and the solution was refluxed overnight. After cooling, the yellow solid was filtered off, washed with methanol and acetone, and dried under vacuum (2.84 g, 84% yield). NMR characterizations were consistent with those previously reported [14]. ^1H NMR (DMSO- d_6) δ (ppm): 6.76 (d, 1H, $J = 7.6$ Hz), 6.91 (dd, 2H, $J = 7.5$ Hz, $J = 4.7$ Hz),

7.17-7.20 (m, 3H), 7.34 (d, 1H, $J = 4.2$ Hz), 7.45 (dd, 1H, $J = 4.7$ Hz, $J = 8.1$ Hz), 7.47-7.51 (m, 3H), 7.59 (dd, 1H, $J = 4.7$ Hz, $J = 8.3$ Hz), 7.68 (dd, 1H, $J = 8.3$ Hz, $J = 4.7$ Hz), 8.52 (dd, 2H, $J = 8.1$ Hz, $J = 3.3$ Hz), 8.58 (d, 1H, $J = 7.7$ Hz), 8.63 (d, 1H, $J = 4.2$ Hz), 8.76 (d, 1H, $J = 4.1$ Hz); HRMS (ESI MS) m/z : theor: 460.1236 found: 460.1238 ($[M+H]^+$ detected); Anal. Calc. for $C_{27}H_{18}AlN_3O_3$: C, 70.58; H, 3.95; N, 9.15 Found: C, 70.47; H, 3.99; N, 9.28%.

Synthesis of *N,N'*-Bis((2-hydroxy-1-naphthylidene))-4,5-dimethyl-1,2-phenylene diamine **L₁**

2-Hydroxy-1-naphthaldehyde (4.50 g, 26.12 mmol, 2.2 eq.) and 1,2-diamino-5,6-dimethoxy-benzene (2 g, 11.89 mmol) were dissolved in ethanol (150 mL) and the reaction mixture was stirred at 50°C overnight. The resulting light-red precipitate was filtered, washed with ethanol and ether and dried under vacuum (5.27 g, 93% yield). 1H NMR (THF- d_8) δ (ppm): 3.95 (s, 6H), 7.09 (d, 2H, $J = 9.1$ Hz), 7.21 (s, 2H), 7.29 (t, 2H, $J = 7.8$ Hz), 7.46 (t, 2H, $J = 8.4$ Hz), 7.75 (d, 2H, $J = 7.7$ Hz), 7.82 (d, 2H, $J = 9.1$ Hz), 8.35 (d, 2H, $J = 8.5$ Hz), 9.65 (s, 2H), 15.2 (s, 2H, OH); 1H NMR (DMSO- d_6) δ (ppm): 3.95 (s, 6H), 7.09 (d, 2H, $J = 8.9$ Hz), 7.37 (t, 2H, $J = 7.2$ Hz), 7.40 (s, 2H), 7.56 (t, 2H, $J = 8.4$ Hz), 7.83 (d, 2H, $J = 7.6$ Hz), 7.94 (d, 2H, $J = 8.0$ Hz), 8.54 (d, 2H, $J = 8.3$ Hz), 9.67 (s, 2H), 15.4 (s, 2H, OH); ^{13}C NMR (DMSO- d_6) δ (ppm): 56.2, 103.4, 109.3, 120.7, 121.2, 123.4, 126.9, 127.9, 128.9, 131.7, 132.9, 136.0, 148.6, 156.5, 167.3 HRMS (ESI MS) m/z : theor: 477.1809 found: 477.1801 ($[M+H]^+$ detected).

Synthesis of *N,N'*-Bis((2-hydroxy-1-naphthylidene))-4,5-dimethyl-1,2-phenylene diamine]iron(III) chloride **Fe₂**

500 mg (1.049 mmol) of 1,1'-((1E,1'E)-((4,5-dimethoxy-1,2-phenylene)bis(azanylylidene))bis(methanylylidene))bis(naphthalen-2-ol) **L₁** was suspended in 25 mL methanol. 284 mg (1.049 mmol) of iron (III) chloride hexahydrate was added and the color changed immediately. The solution was heated at 60°C for 1 hour during which time a precipitate formed. It was filtered off, washed with methanol and dried under vacuum (516 mg, 87% yield). Anal. Calc. for $C_{30}H_{22}ClFeN_2O_4$: C, 62.68; H, 3.92; N, 4.95 Found: C, 63.72; H, 4.04; N, 4.90%.

Synthesis of *N,N'*-Bis(3-methoxysalicylidene)-4,5-dimethyl-1,2-benzenediamine] nickel (II) **Ni₁**.

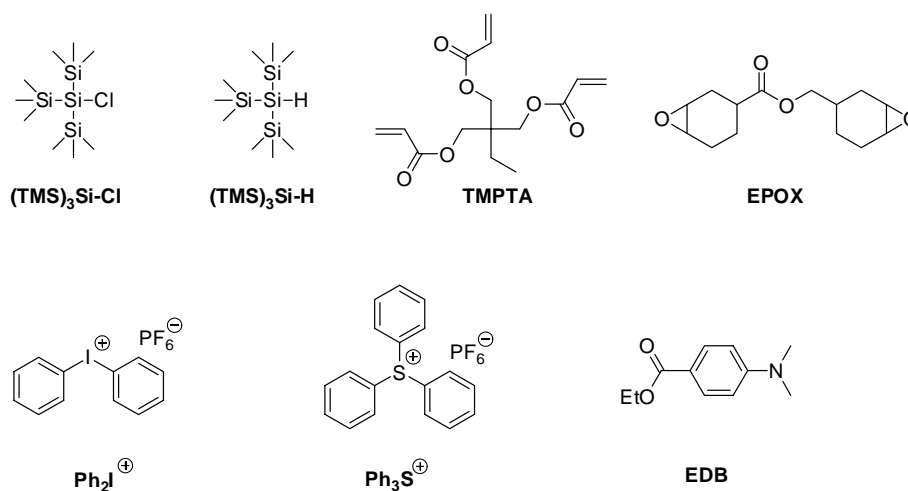
2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) (2.98 g, 19.6 mmol) in methanol (200 mL) and THF (200 mL) was first treated with $NiSO_4$ (2.07 g, 13.38 mmol) and the mixture was stirred for 5 min at room temperature. Then 4,5-dimethyl-1,2-diaminobenzene (1.21 g, 8.9 mmol) was added into the solution. A red precipitate formed immediately and stirring was maintained at room temperature overnight. The precipitate was washed with water and a mixture of pentane/ether: 4/1 and dried under vacuum (4.54 g, 72% yield). 1H NMR (DMSO- d_6) δ (ppm): 2.31 (s, 6H), 3.58 (s, 6H), 6.55 (t, 2H, $J = 7.7$ Hz), 6.85 (d, 2H, $J = 7.2$ Hz), 7.16 (d, 2H, $J = 8.2$ Hz), 7.91 (s, 2H), 8.75 (s, 2H); HRMS (ESI MS) m/z : theor: 461.1006 found: 461.1010 ($[M+H]^+$ detected); Anal. Calc. for $C_{24}H_{22}N_2NiO_4$: C, 62.51; H, 4.81; N, 6.07 Found: C, 62.58; H, 4.94; N, 6.11%.

Synthesis of *N,N'*-Bis(salicylidene)-1,2-diaminobenzene]nickel (II) **Ni₂**

Salicylaldehyde (2.05 mL, 19.6 mmol) in methanol (200 mL) and THF (200 mL) was first treated with $NiSO_4$ (2.07 g, 13.38 mmol) and the mixture was stirred for 5 min at room temperature. Then 1,2-diaminobenzene (0.96 g, 8.9 mmol) was added into the solution. The mixture was stirred at reflux overnight. Upon reflux, the solution turned deep red and a red precipitate formed. The solution was concentrated to the third of its initial volume and the red precipitate was filtered off, washed with ether and dried under vacuum. Upon drying, the initial red solid turned light brown (3.98 g, 78% yield). 1H NMR (DMSO- d_6) δ (ppm): 6.68 (td, 2H, $J = 6.9$ Hz, $J = 0.9$ Hz), 6.89 (d, 2H, $J = 8.1$ Hz), 7.31-7.37 (m, 4H), 7.61 (dd, 2H, $J = 8.0$ Hz, $J = 1.7$ Hz), 8.14-8.17 (m, 2H), 8.90 (brs, 2H, NH); HRMS (ESI MS) m/z : theor: 373.0482 found: 373.0480 ($[M+H]^+$ detected); Anal. Calc. for $C_{20}H_{14}N_2NiO_2$: C, 64.40; H, 3.78; N, 7.51 Found: C, 64.31; H, 3.69; N, 7.54%.

Synthesis of *N,N'*-Bis((2-hydroxy-1-naphthylidene))-4,5-dimethyl-1,2-phenylene diamine]nickel(II) **Ni₃**

Ligand **L₁** (1 g, 2.10 mmol, 1.1 eq.) in methanol (100 mL) and THF (100 mL) was treated with



Scheme 3

NiSO₄ (0.31 g, 1.91 mmol) and the mixture was refluxed for 48 hours. During that time a brown precipitate formed. The precipitate was washed with water and a mixture of pentane/ether: 4/1. The brown powder was dried under vacuum and used without any further purification (3.54 g, 73% yield). HRMS (ESI MS) *m/z* : theor : 473.0795 found : 473.0793 ([M+H]⁺ detected); Anal. Calc. for C₃₀H₂₂N₂NiO₄: C, 67.58; H, 4.16; N, 5.25 Found: C, 67.49; H, 4.11; N, 5.18%.

ii. Chemicals

Tris(trimethylsilyl)silane ((TMS)₃Si-H), diphenyliodonium hexafluorophosphate (Ph₂I⁺), triphenylsulfonium hexafluorophosphate Ph₃S⁺ PF₆⁻, ethyldimethylaminobenzoate EDB, tris(trimethylsilyl)chlorosilane (TMS)₃Si-Cl were obtained from Aldrich and used with the best purity available (Scheme 3). Trimethylolpropane triacrylate (TMPTA; from Cytec) and (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX from Cytec; Uvacure 1500) were selected as monomers (Scheme 3).

iii. Irradiation sources

Several lights were used: i) polychromatic light from a Xe lamp (Hamamatsu L8253); ii) a Hg lamp emitting at 366 nm (Omnicure S1000) and iii) monochromatic light delivered by a

laser diode at 457 nm (MBL-III-BFIOPTILAS; I₀ ≈ 100 mW cm⁻²).

iv. Photopolymerization

All the experimental conditions are given in the Figure captions. The photosensitive formulations were deposited on a BaF₂ pellet (20 μm thick). In CP and FRPCP experiments, the evolution of the EPOX band content is followed by real time FTIR spectroscopy (JASCO FTIR 4100) (as in [6, 8]) at ~ 790 cm⁻¹ and the Si-H conversion in (TMS)₃Si-H at ~ 2050 cm⁻¹. In FRP experiments, the evolution of the double bond content of the TMPTA films was monitored at ~ 1630 cm⁻¹ (as in [15]).

v. ESR spin trapping (ESR-ST) experiments

ESR-ST experiments were carried out using a X-Band spectrometer (MS 400 Magnetech or Bruker EMX-plus). The radicals were produced at RT under the halogen lamp exposure (except otherwise noted) and trapped by phenyl-*N*-tbutylnitron (PBN) according to a procedure described in detail in [6, 8, 15].

RESULTS AND DISCUSSION

1. Absorption spectra

The considered PICs exhibit interesting absorption properties in the visible light wavelength range (Figure 1). For the references Ru₁ and Ir₁ complexes, intense light absorption in the visible range was already reported in [8c, 8e].

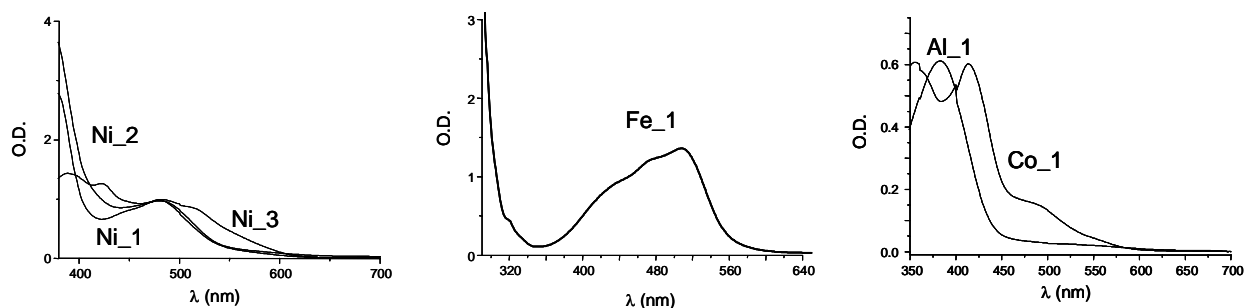


Figure 1. UV-visible absorption spectra of the different PICs in acetonitrile.

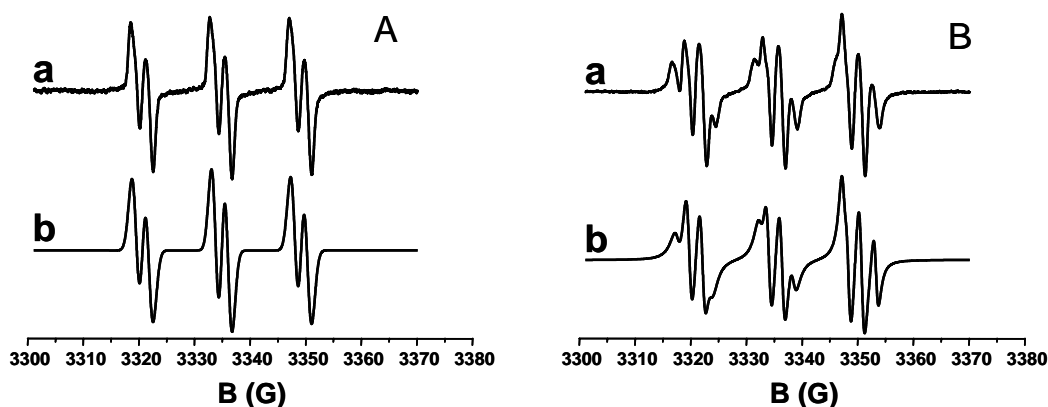


Figure 2. ESR spectra obtained after a Xenon lamp irradiation of (A) Ni_1/Ph₂I⁺ and (B) Ni_1/(TMS)₃Si-H/Ph₂I⁺; in *tert*-butylbenzene: experimental (a) and simulated (b) spectra. Phenyl-*N*-*tert*-butylnitron (PBN) [PBN] = 0.01 M is used as spin-trap.

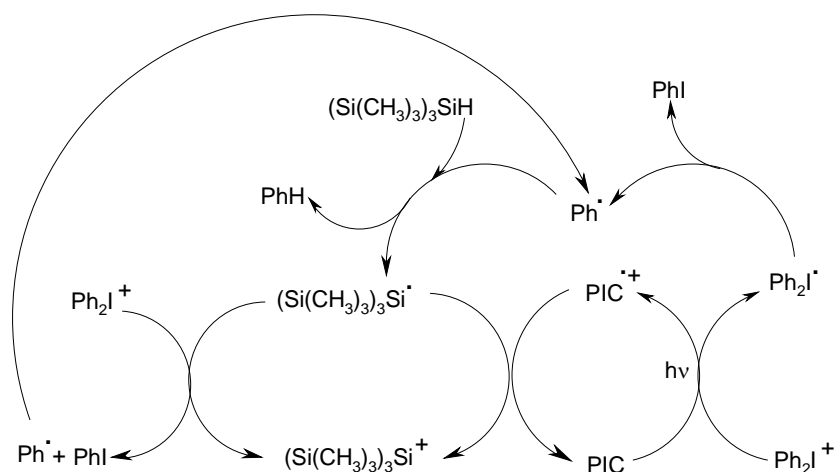
2. The PIC/iodonium salt/silane systems

Upon irradiation of the PIC/Ph₂I⁺ and PIC/(TMS)₃Si-H/Ph₂I⁺, the formation of phenyl Ph[•] and silyl ((TMS)₃Si[•]) radicals, respectively, is well supported by ESR-ST experiments using phenyl-*N*-*tert*-butylnitron (Figure 2): e.g. for PIC = Ni_1, the PBN radical adducts are characterized by a_N = 14.3 and a_H = 2.2 G for Ph[•]; a_N = 14.9 and a_H = 5.8 G for (TMS)₃Si[•] in agreement with known reference data [8]. The presence of these radicals is easily ascribed to i) the oxidation of the PICs by Ph₂I⁺ leading to the formation of Ph[•] and ii) the hydrogen abstraction reaction of Ph[•] on (TMS)₃Si-H generating (TMS)₃Si[•].

As for PIC = Ru or Ir [8, 15], Scheme 4 summarizes the reactions involved in these new PICs (oxidation of PIC by Ph₂I⁺, formation of a phenyl radical Ph[•], hydrogen abstraction between

(TMS)₃Si-H and Ph[•], regeneration of PIC and formation of silylium cations). The silyliums are the initiating species of the FRPCP process.

The polymerization ability of the novel Fe, Ni, Co and Al based PICs as parts of the photoinitiating formulations has been checked. The best conversion-time profiles for the photopolymerization of EPOX under air using a three-component (Fe_1 0.2%/(TMS)₃Si-H 3%/Ph₂I⁺ 2%) photoinitiating system exposed to a Xenon lamp or a diode laser irradiation are shown in Figure 3. Addition of water 0.2% still increases the final conversion (Figure 3B). A tack free coating can be obtained e.g. upon the diode laser irradiation (457 nm) (Figure 3A curve 3; final conversion ~ 50%). No polymerization occurs in the presence of the two-component system (Fe_1 0.2%/Ph₂I⁺ 2%). A significant decrease of the epoxy band at ~ 790 cm⁻¹ accompanied by a high Si-H consumption (~50%)



Scheme 4

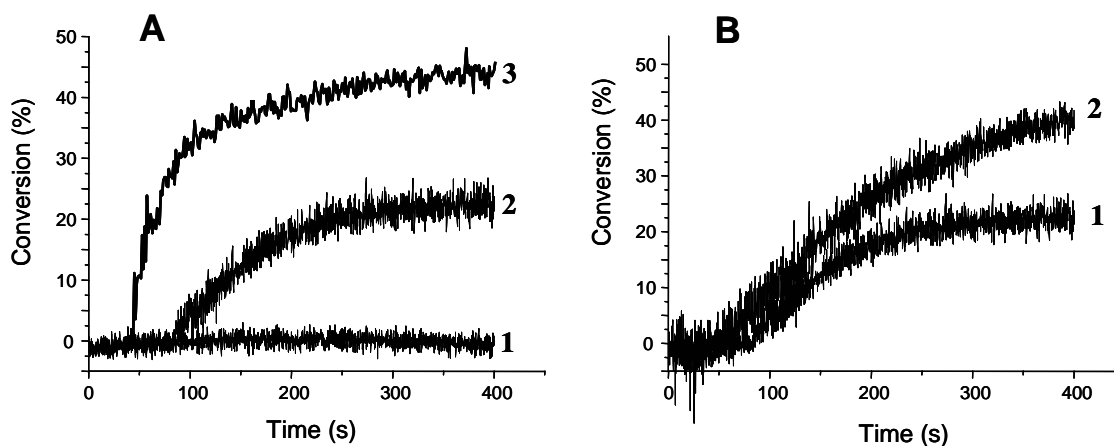


Figure 3. Photopolymerization profiles of EPOX under air upon: **(A)** a Xenon lamp irradiation in the presence of (1) **Fe_1/Ph₂I⁺** (0.2%/2% w/w); (2) **Fe_1/(TMS)₃Si-H/Ph₂I⁺** (0.2%/3%/2% w/w) and (3) a laser diode 457 nm irradiation in the presence of **Fe_1/(TMS)₃Si-H/Ph₂I⁺** (0.2%/3%/2% w/w). **(B)** a Xenon lamp irradiation in the presence of (1) **Fe_1/(TMS)₃Si-H/Ph₂I⁺** (0.2%/3%/2% w/w) and (2) **Fe_1/(TMS)₃Si-H/Ph₂I⁺** (0.2%/3%/2% w/w) + 0.2% (w/w) of water.

is concomitantly observed (Figure 4). UV-visible absorption spectroscopy qualitatively shows a recovery of **Fe_1** during the irradiation. In the presence of water, the efficiency of the polymerization is moderately improved (Figure 3B curve 1 vs. curve 2). This can be ascribed to the presence of a well known activated monomer mechanism for the cationic propagation reaction [16].

Using **Fe_2** (or **Co_1**, **Ni_1**, **Ni_2**, **Ni_3**, **Al_1**)/**(TMS)₃Si-H/Ph₂I⁺**, low final conversions are noted (< 15% after 400 s of the xenon lamp irradiation).

Under a 457 nm diode laser exposure, **Ni_1/(TMS)₃Si-H/Ph₂I⁺** leads to a ~ 15% conversion within 300s. With **Fe_1**, a better polymerization profile is found with a ~ 50% final conversion (Figure 3A curve 3). With the other PICs (**Fe_2**, **Co_1**, **Ni_2**, **Al_1**), no significant conversion is reached (moreover, **Co_1** is not enough thermally stable).

When using Ir or Ru based systems, higher polymerization rates and final conversions were previously obtained [8]. This highlights the role of the metal PIC for the global efficiency of

the process. The low reactivity/polymerization efficiency of the investigated PICs compared to Ru or Ir complexes can be ascribed to their shorter excited state lifetimes (e.g. 800 ps for Fe_1) leading to less efficient iodonium salt reduction reactions.

Although radicals are generated (see Scheme 4), no efficient photopolymerization of TMPTA, whatever the light source used, was achieved (the fact that the radical concentration is also a function of the competition between the different reactions should not be forgotten).

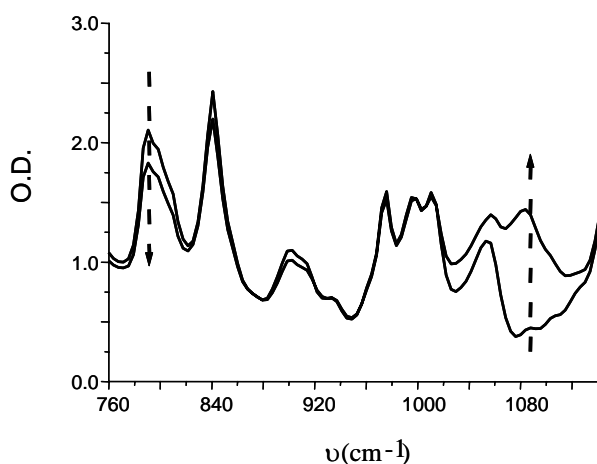


Figure 4. IR spectra recorded during the photopolymerization of EPOX under air upon a Xenon lamp irradiation in the presence of **Fe_1**/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w).

3. The PIC/sulfonium salt/silane systems

As sulfonium salts are more stable than diphenyliodonium salts, the possibility to change Ph₂I⁺ for Ph₃S⁺ as the oxidation agent in Scheme 1 in a PIC based system (where PIC stands e.g. for an iridium complex Ir_1) has been studied. As expected, ESR experiments support the formation of phenyl radicals in Ir_1/Ph₃S⁺ and silyl radicals in Ir_1/(TMS)₃Si-H/Ph₃S⁺ (Figure 5): the PBN radical adducts are characterized by $a_N = 14.2$ and $a_H = 2.2$ G for Ph[•]; $a_N = 15.1$ and $a_H = 5.5$ G for (TMS)₃Si[•] (see above for the discussion of the ESR spectra). This noticeable photosensitized decomposition of the sulfonium salt should also be observed with other PICs such as ruthenium complexes.

A plausible mechanism involved in the Ir_1/(TMS)₃Si-H/Ph₃S⁺ and Ir_1/Ph₃S⁺ systems is depicted in Scheme 5A and 5B, respectively (PIC = Ir). Due to the redox potentials, the silyls cannot be oxidized by the sulfonium salts: compared to what happens in Scheme 4, the silyls are only oxidized by the PIC cation radical (PIC^{•+}).

A typical conversion-time profile for the photopolymerization of EPOX, under air and upon a Hg lamp exposure at 366 nm, using the Ir_1 0.2%/Ph₃S⁺ 1% photoinitiating system, is shown in Figure 6. The final conversion reaches 30% compared to only 20% in the presence of Ph₃S⁺ alone. Addition of the silane still increases the final conversion (>70%) (together with a significant decrease of the epoxy band at ~ 790 cm⁻¹ and the

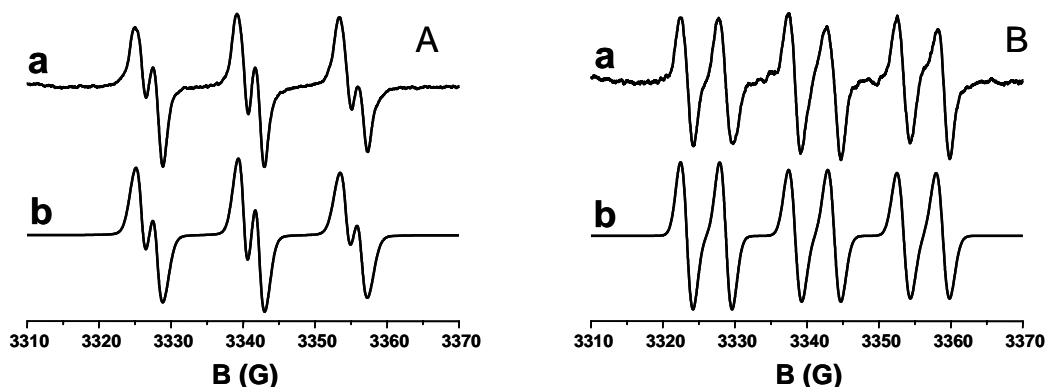
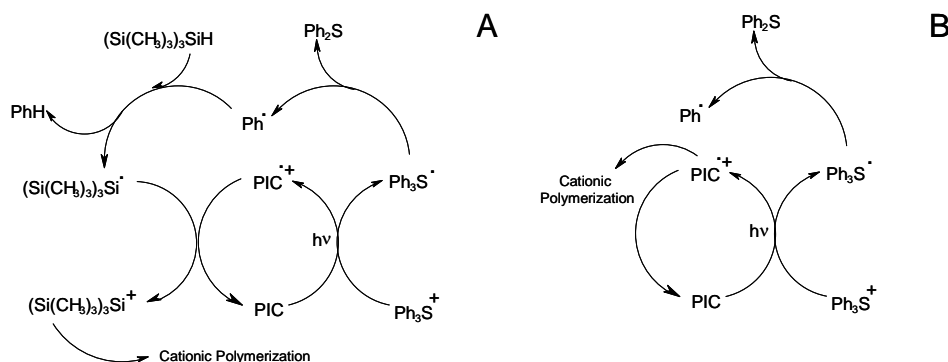


Figure 5. ESR spectra obtained after a Xenon lamp irradiation of (A) Ir_1/Ph₃S⁺; (B) Ir_1/(TMS)₃Si-H/Ph₃S⁺; in *tert*-butylbenzene: experimental (a) and simulated (b) spectra. Phenyl-*N-tert*-butylnitron (PBN) ([PBN] = 0.01 M) is used as spin-trap.



Scheme 5

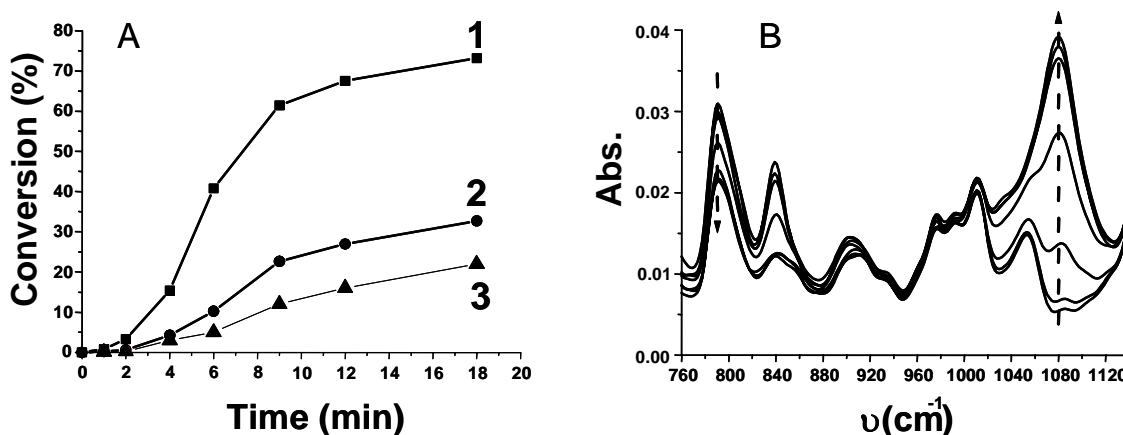


Figure 6. (A) Photopolymerization profiles of EPOX upon a Hg lamp irradiation (366 nm) under air in the presence of (1) Ph_3S^+ (1% w/w); (2) $\text{Ir}_1/\text{Ph}_3\text{S}^+$ (0.2%/1% w/w) and (3) $\text{Ir}_1/(\text{TMS})_3\text{Si-H}/\text{Ph}_3\text{S}^+$ (0.2%/3%/1% w/w). (B) IR spectra recorded during the photopolymerization of (3).

Si-H band at $\sim 2050 \text{ cm}^{-1}$ – Figure 6B); a tack free coating is obtained after 22 mn of irradiation.

The initiation step of the EPOX polymerization is depicted in Scheme 5. Using the $\text{Ir}_1/\text{Ph}_3\text{S}^+$ two-component system leads to the formation of PIC^{++} which is likely the initiating species. In that case, one observes a usual photosensitized cationic polymerization CP (Scheme 5B). When operating with $\text{Ir}_1/(\text{TMS})_3\text{Si-H}/\text{Ph}_3\text{S}^+$, the reaction is a free radical promoted cationic polymerization FRPCP (Scheme 5A) where the initiating species is a silylium cation (the silyl/ PIC^{++} interaction ensures the recovery of the PIC).

4. The PIC/amine/chlorosilane systems

In the reductive cycle (Scheme 1), the PIC (typically a ruthenium complex) is reduced through a

photoinduced electron transfer with an electron donor such as an amine AH (e.g. methyldiethanolamine [15], N,N-diisopropylethylamine or N,N-dimethylformamide [17]) yielding PIC^+ and AH^{++} . A suitable alkyl (e.g. phenacyl) bromide $\text{PhC(=O)CH}_2\text{Br}$ (bromides are the only compounds proposed at the moment in the literature for organic chemistry purposes using a reduction cycle) leads to a regeneration of the PIC and the formation of a phenacyl radical $\text{PhC(=O)CH}_2^{\bullet}$ and an anion Br^- (Scheme 1). Only carbon centered radicals can be generated in this approach. The change of the phenacyl bromide to a compound being able to generate more efficient radicals towards the addition to double bonds is really tempting. One possibility might be to use a Ru_1/amine (EDB)/chlorosilane ($(\text{TMS})_3\text{SiCl}$) system.

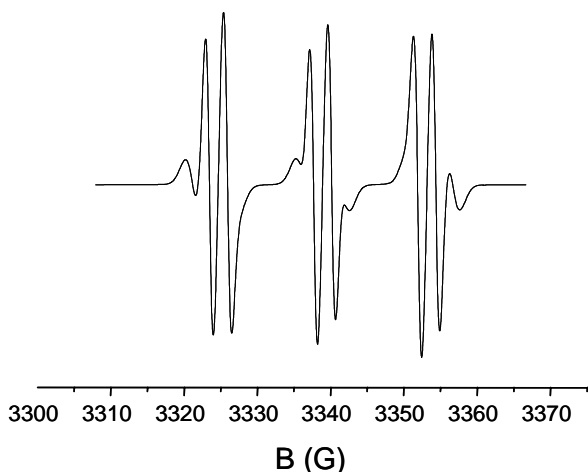
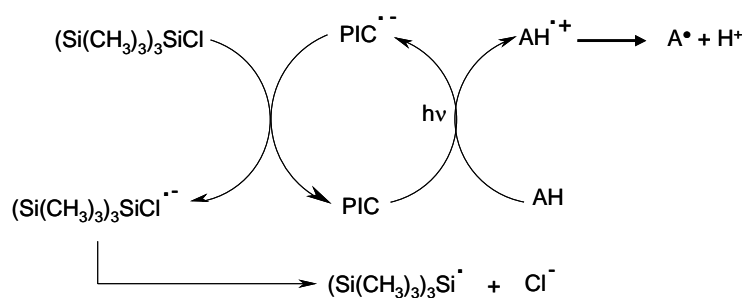


Figure 7. ESR spectra obtained after irradiation of Ru_1/EDB/Si(CH₃)₃SiCl. In *tert*-butylbenzene. Experimental spectra. Phenyl-*N-tert*-butylnitron (PBN) is used as spin-trap.

ESR experiments show that the PBN adducts of the aminoalkyls A[•] and the silyls ((TMS)₃Si[•]) (Figure 7) are formed in a ratio of 70%/30% during the irradiation of the Ru_1/EDB/(TMS)₃SiCl system ($a_N = 14.2$ and $a_H = 2.4$ G for the aminoalkyl; $a_N = 15.0$ and $a_H = 5.5$ G for (TMS)₃Si[•]) and confirm the ability of this system to generate a more efficient radical (silyl vs. phenacyl).

The Ru_1/EDB/(TMS)₃SiCl system likely works in a way similar to that of Ru_1/EDB/PhC(=O)CH₂Br (Scheme 6).

The use of a chlorosilane in a ruthenium complex based system (Ru_1/EDB/ (TMS)₃SiCl) for the photopolymerization of TMPTA under visible lights (diode laser exposure at 457 nm) was checked. The achieved performance (Figure 8)



Scheme 6

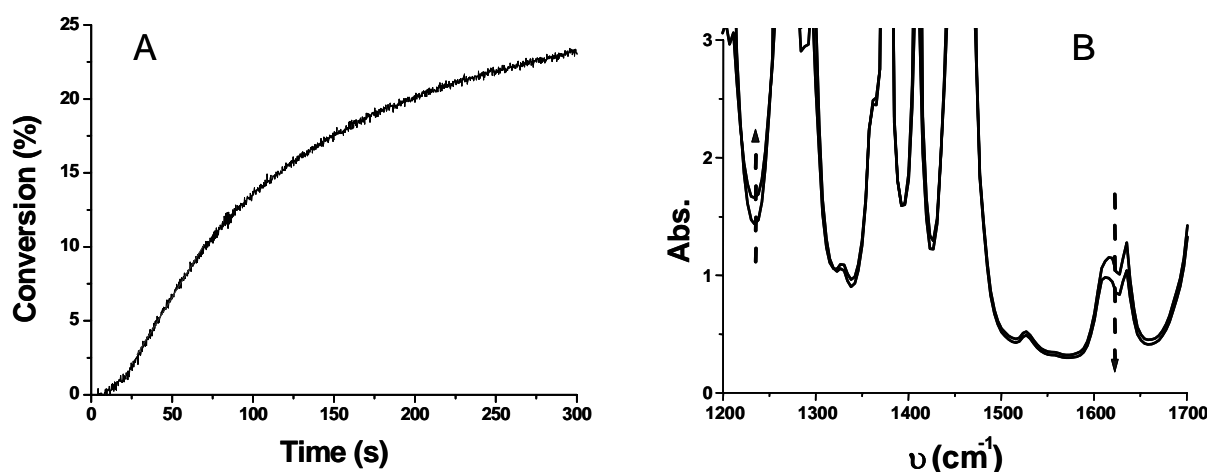


Figure 8. Photopolymerization profiles of TMPTA upon a diode laser exposure at 457 nm in laminate in the presence of Ru_1/EDB/(TMS)₃SiCl (0.2%/4.5%/3% w/w).

unfortunately remains lower compared to the use of Ru₁/EDB/PhC(=O)CH₂Br where a final conversion of ~ 55% can be obtained for 200 s of irradiation. Despite the presence of aminoalkyl and silyl initiating radicals (known as very reactive radicals towards the acrylate addition [18]), the low efficiency of the overall photoinitiation system is presumably due a lower reactivity of Si(CH₃)₃SiCl towards PIC⁻ or/and a lower ability of the Si(CH₃)₃SiCl⁻ radical anion to decompose into a silyl radical and a chlorine anion. To overcome this problem, one way might be to use bromosilanes but these compounds are not easily accessible.

CONCLUSION

In the present paper, several organometallic complexes based on Ru, Ir, Fe, Ni, Co and Al engaged in selected photosensitive formulations have been studied and their reactivity/efficiency evaluated for double bonds and ring opening reactions.

When considering Fe, Ni, Co and Al as photoinitiator catalysts PIC for the FRPCP of an epoxide monomer under soft irradiation conditions, quite good polymerization profiles are only obtained with the Fe derivative based formulation. This highlights the role of the excited state properties which seems mostly inherent to the nature of the metal centers used here. At first sight, for a given metal, the design of other derivatives with different ligands to boost the reactivity is likely not straightforward. It does not actually appear as an easy and promising solution for the development of PICs working in soft experimental conditions, the well known Ru and Ir and the more recent Zn and Pt based PICs being much more efficient.

The change of an iodonium salt for a sulfonium salt in an organometallic (Ir) complex based photoinitiating system allows an interesting photosensitization of the sulfonium salt decomposition under visible lights that is not so trivial; moreover, the addition of a silane leads to a quite efficient FRPCP. To the best of our knowledge, the introduction of a sulfonium salt in a photoredox catalysis process working through an oxidative way has not been reported before, even in organic chemistry.

Although it does not lead to improvement of results for the free radical photopolymerization of an acrylate, the change of the phenacyl bromide for a chlorosilane in a PIC (Ru) based system working through a reduction cycle can be considered, to our opinion, as the first example for a formation of silyl radicals in organophotocatalysis (using such a cycle).

All the three perspectives explored in this paper could open new methodologies in the photopolymerization and organic chemistry areas.

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