

# Towards Visible-Light Photocatalytic Reduction of Hypercoordinated Silicon Species

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Dedicated to Philippe Renaud in celebration of his 60th birthday and with all our friendship

Nowadays, the quest of new radical precursors based on heteroatom complexes occupies an increasingly prominent position in contemporary research. Herein, we investigated the behavior and the limitations of hexaor pentacoordinated organochlorosilanes and related pentacoordinated silyliums as new families of complexes for the generation of radicals under photocatalytic reductive conditions. Particularly, treatment of chlorophenylbis[N,S-pyridine-2-thiolato(–)]silicon(IV) or the related silylium derivative with the *fac*-Ir(ppy)<sub>3</sub> (5 mol-%)/NEt<sub>3</sub> (1.5 equiv.) system under blue LEDs irradiation generates a thiopyridyl radical which can participate in the formation of a carbon–sulfur bond by reaction with an allylsulfone. Computational studies supported this experimental finding, and particularly by showing that homolytic fragmentation of C–Ts bond is favored over the fragmentation of thiopyridyl radical.

**Keywords:** chlorosilane, silylium, hypercoordinated silicon compounds, photoreduction, radicals, cyclic voltammetry, C–S bond, allylation.

## Introduction

Over the last few decades, organosilicon compounds have received a great deal of attention in organic synthesis,<sup>[1,2]</sup> and particularly radical synthetic chemistry, with the generation of transient siliconcentered radicals from silvl hydrides,<sup>[3-8]</sup> behaving both as an effective mediator of radical reactions starting from a range of radical precursors (halides, chalcogens, xanthates, etc...) and as substrates for radical functionalization such as the hydrosilylation of unsaturated systems.<sup>[3-8]</sup> The homolytic Si-H cleavage can be obtained for instance with the (TMS)<sub>3</sub>SiH Chatgilialoglu's reagent<sup>[3-6,9,10]</sup> or the Et<sub>3</sub>SiH/RSH system for polarity reversal catalysis introduced by Roberts.<sup>[11]</sup> More anecdotal, silyl radicals can be generated by photolysis of a Si-B bond for the silvlboration of olefins<sup>[12]</sup> or by photocatalytic oxidation of the supersilanol (TMS)<sub>3</sub>SiOH to perform halogen abstraction for Nickel/photoredox sp<sup>3</sup>-sp<sup>3</sup> crosscoupling reactions.<sup>[13]</sup> As another interesting property, organosilicons with an activated C–Si bond as well as hypercoordinated – penta- or hexacoordinated – silicon derivatives<sup>[14–17]</sup> have revealed as a potential source of carbon-centered radicals under oxidative conditions, which can participate in further synthetic transformations.

A SET oxidation-desilylation of benzyltrimethysilanes involving visible-light excited chiral iminium ions,<sup>[18]</sup> 9-mesityl-10-methylacridinium perchlorate salt<sup>[19]</sup> or graphitic carbon nitride<sup>[20]</sup> as a catalytic and strong photooxidant, allowed the formation of benzylic radicals which can be trapped by ground-state iminium ions or *Michael*-type acceptors respectively. In the same vein,  $\alpha$ -alkoxymethyl radicals were successfully generated from the corresponding  $\alpha$ -silyl ethers<sup>[21–23]</sup> by photocatalyzed oxidation, as well as acyl radicals from acyl silanes.<sup>[24]</sup> But interestingly, what about the reactivity of hypercoordinated silicon derivatives under oxidative conditions? This question

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was first answered by Kumada who reported the oxidation of organopentafluorosilicates to provide organic radicals which can react with a second equivalent of copper chloride and liberate the chlorinated product. However, this transformation required stoichiometric amount of copper salts and the low solubility of these substrates limits their use for synthesis.<sup>[25,26]</sup> In that context, Nishigaishi reported the photoallylation<sup>[27,28]</sup> of benzyl-type derivatives and dicyanobenzene with the more soluble allyl biscatecholato silicate,<sup>[29]</sup> but these studies were limited to the generation of allylic radical. Following our initial work on the oxidation of alkyltrifluoroborates in 2010,<sup>[30]</sup> we prepared a series of bench stable alkyl biscatecholato silicates with a low oxidation potential (<1 V vs. SCE) and tested them under visible-light photooxidative condition<sup>[31]</sup> in order to generate functionalized alkyl radicals and particularly primary ones.<sup>[32,33-49]</sup> The scope of substrates for simple radical trapping and also for photoredox/nickel dual catalysis proved to be quite large from primary to tertiary radicals.<sup>[31,32,50–54]</sup>

To date, the use of hypercoordinated silicon derivatives in radical synthesis has been limited to the generation of radicals under oxidative regimes and no attempt has been made in a reductive manner. Herein, we reported the first results about the behavior of hypercoordinated chlorosilanes and the related cationic silicon derivatives under visible-light photoreductive conditions to generate radical species. We presumed that the presence of hypercoordinated ligands or the formation of silylium salts would favor the labilization of the Si–Cl bond during the reduction step to provide the formation of hypercoordinated silyl radicals. The latter may subsequently expel a carbon- or heteroatom-centered radical (R<sup>1</sup> or X, respectively) (*Scheme 1*).

## **Results and Discussion**

We thus tested the photoreduction of a set of hypercoordinated chlorosilanes whose synthesis has already been described in the literature. We started to investigate the reactivity of hexacoordinated silicon compounds with bidentate N,O ligands such as 8oxyquinolinato ligands. We first prepared compound **1a** from phenyltrichlorosilane and 8-hydroxyquinoline using the procedure developed by *Wägler* in 2014 (*Scheme 2*).<sup>[55]</sup> We tried to evaluate the reduction potential of **1a** by cyclic voltammetry (CV) but, due to the insolubility of this organosilicon in acetonitrile and Previous studies



**Scheme 1.** Hypercoordinated silicon compounds as a source of radicals under photooxidative or photoreductive conditions.



**Scheme 2.** Synthesis of hexacoordinated silicon compound **1a** with 8-oxyquinolinato ligands and reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions.

THF, it could not be determined. Nevertheless, we explored the photoreduction of **1a** using the highly reductant photocatalyst *fac*-lr(ppy)<sub>3</sub> (5 mol-%, E lr (IV)/ lr (III)\* = -1.7 V vs. SCE) under blue LEDs irradiation in the presence 1.5 equiv. of allyl sulfone **2** as a radical acceptor and 1.5 equiv. of N,N-diisopropylethylamine (DIPEA) as sacrificial electron donor for the regeneration of the photocatalyst (*Scheme 2*). Whatever the nature of the solvent (0.1 mol/L), acetonitrile (CH<sub>3</sub>CN) or dimethylformamide (DMF), no reaction occurred leaving the allylsulfone **1a** unchanged. Butyl and benzyl chlorosilanes were also efficiently synthetized (86% and 84% yield, respectively) and investigated but no reaction was observed.

In a second phase, we looked at more soluble silicon derivatives. In 2012, Tacke's group reported the formation of pentacoordinate chlorosilicon(IV) complexes with tridentate dianionic O,N,O ligands such as 2-{(*E*)-[(3*Z*)-4-hydroxypent-3-en-2the tridentate vlidene]amino}phenol ligand.<sup>[56]</sup> We then synthesized the corresponding complex **3** as reported in *Scheme 3* and measured its reduction potential by CV. To our delight, we were pleased to see that the reduction potential of the hypercoordinated species 3 is higher than the tetravalent phenyl trichlorosilane (PhSiCl<sub>3</sub>), that is, -1.60 V vs. SCE compared to -1.95 V vs. SCE (see cyclic voltammogram of 3 (Figure 1) and Supporting Information). This suggests that this tridentate ligand significantly increases the ability of the chlor-



Scheme 3. Synthesis of pentacoordinated silicon compound 3, using  $2-\{(E)-[(3Z)-4-hydroxypent-3-en-2-ylidene]amino\}$ phenol ligand, and the corresponding silylium derivatives 4a and 4b as well as their reactivity in the presence of allylsulfone 2 under visible-light photoreductive conditions.



**Figure 1.** Electrochemical studies: Cyclic voltammogram of **3** (10 mM) performed at 22 °C in dried and degassed THF containing  $Bu_4NPF_6$  (100 mM) as the supporting electrolyte at a scan rate of  $0.1 \text{ V s}^{-1}$ . Glassy carbon, platinum plate and saturated calomel were used as working, counter and reference electrodes, respectively.

osilane to be reduced. Compound **3** was then subjected to the same reaction conditions used for **1a**, but again no reaction was observed by TLC and confirmed by <sup>1</sup>H-NMR (*Scheme 3*). Only starting materials were recovered. Even after addition of additives such as TMSI or TMSOTf to generate *in situ* the corresponding electron deficient silylium derivatives **4a** and **4b** (not characterized),<sup>[57]</sup> no product was obtained, and only degradation was seen. Switching from *fac*-Ir(ppy)<sub>3</sub> to a highly reducing organic photocatalyst such as *N*-phenylphenothiazine (Ph-PTZ) (E Ph-PTZ<sup>+-</sup>/Ph-PTZ<sup>\*</sup> = -2.5 V vs. SCE),<sup>[58]</sup> did not afford any product either.

Thereafter, we were particularly interested in the photoreduction of hexacoordinated silicon complexes with two bidentate N,S-pyridine-2-thiolato ligands.<sup>[57]</sup> In this case, we may benefit from the possible stabilization of the generated silvl radical by the sulfur atom as already observed in the disulfide bond.<sup>[59]</sup> Chlorophenylbis[N,S-pyridine-2-thiolato(–)]silicon(IV) (5a) was then synthesized following the protocol reported by Tacke in 2013 as outlined in Scheme 4. Its reduction potential can be estimated by CV and showed a value of about -1.49 V vs. SCE (Figure 2), higher than the reduction potentials previously determined for the hypercoordinated silicon species 3 (vide supra). This increase of potential should facilitate the reduction of compound 5a by the excited state of the photocatalyst fac-lr(ppy)<sub>3</sub> (Scheme 4). This substrate was then treated under the same conditions as 1a and 3. Allylsulfide 6, resulting from the addition of the ligand 2-thiopyridine to the allylsulfone 2, was obtained in a 24% yield. We wondered if the yield in 6 can be improved and if this transformation involves a radical or an ionic pathway.



**Scheme 4.** Synthesis of hexacoordinated silicon compound **5a**, using *N*,*S*-pyridine-2-thiolato ligand followed by their reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions. Formation of allylsulfide **6**.







**Figure 2.** Electrochemical studies: Cyclic voltammogram of **5a** (10 mM) performed at 22 °C in dried and degassed THF having  $Bu_4NPF_6$  (100 mM) as the supporting electrolyte at a scan rate of 0.1 V s<sup>-1</sup>. Glassy carbon, platinum plate and saturated calomel were used as working, counter and reference electrodes, respectively.

Encouraged by these preliminary results, we first optimized the reaction conditions by screening the nature of the photocatalyst or the electron donor, by using different solvents and by modulating the reaction time or the ratio radical trap/hypercoordinated silicon (2/5a). Both DMF and CH<sub>3</sub>CN have proved to be beneficial solvents for the reaction, while the reaction was less effective in THF (*Table 1, Entries 1–3* and *9*). With respect to the sacrificial electron donor, changing DIPEA to triethylamine gave

**Table 1.** Optimization of the reaction conditions and control reactions

Entry	Solvent	PCat	Equiv. ( <b>2/5a</b> )	Time [h]	Donor	Yield <sup>[a]</sup>
1	THF	fac-lr(ppy) <sub>3</sub>	1.5/1	24	DIPEA	24%
2	DMF	fac-lr(ppy) <sub>3</sub>	1.5/1	24	DIPEA	35%
3	DMF	fac-lr(ppy) <sub>3</sub>	1.5/1	24	Et₃N	36%
4	DMF	fac-lr(ppy) <sub>3</sub>	1.5/1	24	Hantzsch	0%
					ester	
5	DMF	fac-lr(ppy) <sub>3</sub>	1.5/1	48	Et₃N	37%
6	DMF	fac-lr(ppy) <sub>3</sub>	4/1	24	DIPEA	45%
7	DMF	fac-lr(ppy) <sub>3</sub>	1/2	24	Et₃N	66%
8	DMF	fac-lr(ppy) <sub>3</sub>	1/3	24	Et <sub>3</sub> N	78%
9	MeCN	fac-lr(ppy) <sub>3</sub>	1.5/1	24	Et <sub>3</sub> N	32%
10	MeCN	Fluorescein	1.5/1	24	DIPEA	4%
11	DMF	_	1/3	24	Et₃N	33%
12	DMF	fac-lr(ppy) <sub>3</sub>	1/3	24	_	26%
13	DMF	fac-lr(ppy) <sub>3</sub>	1/3	24	Et₃N	0% <sup>[b]</sup>
14	DMF	-	1/3	24	-	26%
<sup>[a]</sup> NMR yield using TMOP as internal standard. <sup>[b]</sup> In the dark.						

a comparable yield while no reaction was observed with *Hantzsch* ester (*Table 1, Entries 2, 3* and 4). An extended irradiation time from 24 h to 48 h did not improve the photoreductive process (*Table 1, Entries 3* and 5). No more than 45% yield was reached with an excess of allylsulfone **2** (4 equiv., *Table 1, Entry 6*). By contrast, if we consider allylsulfone **2** as the limiting substrate, addition of 2 or 3 equiv. of organochlorosilane **5a** led to 66 or 78% of **6**, respectively (*Table 1, Entries 7* and 8). An organic dye such as fluorescein (F) (E (F<sup>+</sup>/F<sup>\*</sup>) = -1.61 V vs. SCE) was investigated as an alternative to *fac*-lr(ppy)<sub>3</sub>, but only 4% of **6** was obtained after 24 h of irradiation (*Table 1, Entry 10*).

Control experiments have been performed to secure the role of the photocatalyst and a radical process (Table 1, Entries 11–13). Without any photocatalyst and amine, 26% of product was obtained due to the degradation of the silicon complex (Table 1, Entry 14). In the absence of photocatalyst, we ran the reaction under blue LEDs irradiation and allylsulfide 6 was obtained in 33% yield (Table 1, Entry 11). This slight increase of yield in comparison to entry 16 may arise from a photoinduced electron-transfer (PET) between NEt<sub>3</sub> and the organosilane **5a**. No reaction occurred without blue LEDs activation. Only 26% for 6 was obtained when NEt<sub>3</sub> was omitted (due to the degradation of the complex). Even if we showed that the presence of the photocatalyst  $fac-lr(ppy)_3$  is required to reach a good yield, we tested the reactivity between pyridine-2-thiol and acceptor allylsulfone 2 under basic conditions. As expected, no trace of 6 was formed showing that the formation of the allylation adduct does not involve an ionic pathway and a radical process is likely to occur (Scheme 5). Of note, addition of fac-lr(ppy)<sub>3</sub> (5 mol-%) to this mixture led to only 9% yield of 6. From these last studies, we can deduce that most of thiopyridyl radicals were generated by reduction of silane **5a** leading to adduct **6**, and not from the decomposition of 5a. We also can mention that energy transfer instead of electron



**Scheme 5.** Control experiment: reactivity between pyridine-2-thiol and acceptor allylsulfone **2** under basic conditions.



transfer from the iridium complex fac-lr(ppy)<sub>3</sub> is negligible.<sup>1</sup>

In parallel, we examined the behavior of the commercially available *Aldrithiol*<sup>TM</sup> under the same photocatalytic conditions, as a potential source of thiopyridyl radical. Starting from three equivalents of this compound, only a 18% yield of **6** was obtained compared to 78% from **5a**. This study showed all the interest of **5a** as an efficient precursor of thiopyridyl radical for synthetic transformations (*Scheme 6*).

Computational studies have been realized, namely at the B3LYP-D3/def2-SV(P) level with the TURBOMOLE suite of programs. Upon reduction, it was showed that the SET process is occurring on the  $\pi$  system of the pyridine moiety of **5a** (Figure 3, lower part), in a similar manner to what have been observed with our biscatecholato silicates except that in this case this is an electron capture by the photocatalyst.<sup>[31]</sup> If we compare the various BDEs of the substrates before and after oxidation, this reduction strongly weakens all Si–X (X = C, S, Cl) bonds. Particularly, the energy of the Si-S bond (35 kcal/mol) is lower than the one of the Si-C bond (46 kcal/mol) and the Si-Cl bond (63 kcal/ mol) and should favor the formation of the thiopyridyl radical (Figure 3). We also investigated the non-hypercoordinated tetravalent species with two phenylthio ligands, to directly compare the various BDE values with 5a. This species is plotted on the right side of Figure 3. The reduction process is taking place on the phenylthio moiety, but the energy of the Si-S bond before reduction (76 kcal/mol) is higher than for the hypervalent silane 5a (66 kcal/mol). This comparison shows also that while 5a has a positive electron affinity (10.35 kcal/mol), this is not the case for (PhS)<sub>2</sub>Si (Cl)Ph (-1.96 kcal/mol), highlighting the ease of reduction of 5a. As for 5a, we also observed a small BDE of



**Scheme 6.** Photocatalytic reaction using *Aldrithiol*<sup>TM</sup> as a radical precursor.



**Figure 3.** Computational studies on **5a** and on phenylbis (phenylthiol)chlorosilane. Upper part: bond dissociation energies before and after reduction, in kcal/mol. Lower part: spin density isosurfaces.

27 kcal/mol after reduction. The other bonds are similarly affected by the reduction with the Si–Cl bond having a BDE of 64.5 kcal/mol and the Si–Ph being at 40 kcal/mol.

Based on these experimental studies, DFT calculations and in accordance with the literature,<sup>[33-49]</sup> we can propose the following mechanism where the photoactivated catalyst under blue LEDs irradiation reduces hypercoordinated phenylchlorosilane 5a at the pyridine moiety and promotes preferentially the homolytic cleavage of the Si-S bond between the thiopyridine ligand and silicon atom. The expelled thiopyridyl radical can be trapped by allylsulfone 2. The photocatalyst is regenerated by action of NEt<sub>3</sub> (Scheme 7). It should be mentioned that formation of 6 involved sequential addition of the thiopyridine radical, generation of the transient radical intermediate A and homolytic fragmentation of the C-Ts bond. We were surprised by the fact that intermediate **A** is more prone to give the homolytic fragmentation of the C-Ts bond rather than the reversible extrusion of the thiopyridine radical moiety. It is indeed known in the literature that a thiophenyl radical is a good leaving

<sup>&</sup>lt;sup>1</sup>In response to a referee that we thank for her/his suggestions, we first measured the UV/Visible spectrum which showed a characteristic band centered at 290 nm and a large one between 320 nm and 440 nm. This might explain the formation of thiopyridyl radical both under UV (350 nm) or blue LEDs irradiation. Thus, we performed a reaction with benzophenone as photosensitizer (with a triplet energy (69.1 kcal/mol) higher than that of *fac*-Ir (ppy)<sub>3</sub>) (58.1 kcal/mol) under UV irradiation (350 nm). The yield did not increase significantly which suggests that the energy transfer from the iridium complex *fac*-Ir(ppy)<sub>3</sub> would be negligible compared to the electron transfer process. This was also supported by the photoinduced electron-transfer (PET) reaction observed between NEt<sub>3</sub> and the organosilane **5a** in *Table 1, Entry 11*.



Scheme 7. Proposed mechanism for the formation of 6.

group, presumably better than the phenylsulfonyl one.<sup>[60,61]</sup> To rationalize the observed selectivity, DFT calculations of  $\beta$ -fragmentation processes on intermediate **A** and on an analogous intermediate  $(\mathbf{A}')$ where the pyridine moiety is replaced by a phenyl were thus conducted, at the same level of theory (namely B3LYP-D3/def2-SV(P)). On A', calculations indicate that departure of the tosyl radical is slightly favored over the thiophenyl radical fragmentation (barriers of 8.4 kcal/mol vs. 9.3 kcal/mol). But the situation is different in the case of intermediate A: while the tosyl radical departure is still in the same energetic range with a barrier of 9 kcal/mol, the thiopyridyl radical extrusion proves to be unfeasible with an always increasing potential energy surface (see Figure 4), reaching value over 18 kcal/mol. It turns out that the thiopyridyl radical is particularly unstable, and observation of the geometry highlights that this radical is trying to establish non-covalent interactions between the nitrogen of the pyridine moiety and the homobenzylic C-H to stabilize itself (see Figure 5). Therefore, the mechanism proposed in Scheme 7 is supported by this computational analysis.

Due to the weakness of the Si–S bond and its ability to generate thiyl radicals under reductive conditions, we compared the reactivity of our previous system (**5a**) with the non-hypercoordinated tetravalent phenylsilane bearing three phenylthio ligands **7** (*Scheme 8*). This one was synthesized from phenyl-



**Scheme 8.** Photocatalytic reaction using phenyl[tris(phenylsulfanyl)]silane as a radical precursor.

silane and thiophenol according to the literature procedure.<sup>[62]</sup> Its reduction potential was then measured. A value of -2.00 V vs. SCE was obtained which appears to be lower than the reduction potential of **5a** (*Figure 6*). This difference of potential may explain why no allylation adduct **6** was formed from **5a** under the same reductive conditions (*Scheme 8*).

We next evaluated the reactivity of the hypercoordinated methylchlorosilane 5b under photocatalytic reductive conditions. We first prepared it by using the same procedure as for 5a starting from methyltrichlorosilane, and then we measured its reduction potential, which was estimated by CV at about -1.68 V (vs. SCE) (Figure 7). This value still suggests that the photo-excited photocatalyst fac-Ir(ppy)<sub>3</sub> (E Ir  $(IV)/Ir(III)^* = -1.7 V$  vs. SCE) can reduce this substrate. Treatment of 5b (3 equiv.) with 2 (1 equiv.) in the presence of fac-lr(ppy)<sub>3</sub> (5 mol-%) and Et<sub>3</sub>N (1.5 equiv.) in DMF under blue LEDs irradiation gave 6 in 31% yield (Scheme 9). It should be noted that no addition of the methyl group was observed. For comparison, its benzyl analog 5c has also been investigated. This compound was prepared in-situ from benzyltrichlorosi-



**Scheme 9.** Synthesis of hexacoordinated silicon compounds **5b** and **5c**, using N,S-pyridine-2-thiolato ligand followed by their reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions. Formation of allylsulfide **6**.





**Figure 4.** Calculated  $\beta$ -fragmentation processes for intermediate **A** and **A**', at the B3LYP–D3/def2-SV(P) level.



Pot. CV 4 limits

**Figure 6.** Electrochemical studies: cyclic voltammetry of **7** (10 mM) performed at 22°C in dried and degassed THF containing  $Bu_4NPF_6$  (100 mM) as the supporting electrolyte at a scan rate of  $0.05 \text{ V s}^{-1}$ . Glassy carbon, platinum plate and saturated calomel were used as working, counter and reference electrodes, respectively.

Figure 5. Structure of the intermediate A.





**Figure 7.** Electrochemical studies: Cyclic voltammogram of **5b** (10 mM) performed at 22 °C in dried and degassed THF containing  $Bu_4NPF_6$  (100 mM) as the supporting electrolyte at a scan rate of 0.1 V s<sup>-1</sup>. Glassy carbon, platinum plate and saturated calomel were used as working, counter and reference electrodes, respectively.

lane but could not be isolated. Nevertheless, the photocatalytic reaction was carried on the crude mixture and the allylsulfide **6** was obtained in 15% yield as the only product.

From those experiments, only the thiopyridyl radical was formed as evidenced by trapping experiments with allylsulfone **2**. The phenyl derivative was revealed to be the most reactive and provided the best yield in allylsulfide **6**. Interestingly, formation of phenyl, methyl or benzyl radical was never observed in these studies.

We investigated by DFT calculations the fate of the silyl anion originating from the reduction of hypercoordinated alkylchlorosilanes **5** and subsequent fragmentation of the thiopyridyl radical. We found that chloride anion dissociation occurs with an energy barrier of 8.6 kcal/mol providing the formation of a transient highly reactive silylene.<sup>2</sup>

Finally, we looked at the photoreduction of the highly electron deficient silylium derivative **5d** readily obtained by action of TMSI on the corresponding phenylchlorosilane **5a**.<sup>[57]</sup> Under the optimized photocatalytic conditions determined for **5a**, **5d** provided **6** as the sole product with the same yield as **5a**. This result showed that silylium **5d** can be reduced as

efficiently as phenylchlorosilane **5a** and participate in radical reactions (*Scheme 10*).

Interestingly, as the thiopyridine moiety is encountered in various bioactive molecules (*Figure 8*),<sup>[63,64]</sup> efficient reactions allowing the synthesis of these compounds in mild conditions remains interesting.<sup>[65]</sup>

### Conclusions

In conclusion, we have demonstrated that the modification of the ligands of hexacoordinated chlorosilane derivatives can efficiently modulate their reactivity towards photoreductive conditions. By using a thiopyridine ligand, the corresponding thiyl radical has been liberated and efficiently trapped by an allylsulfone as an acceptor. Even if these radicals could be formed through the oxidation of pyridine thiolate like phenyl thiolate,<sup>[66]</sup> no methodology has already been reported by using a reductive pathway. Experiments are currently ongoing in our laboratory for the formation of carbon-centered radicals by photoreduction of other types of hypercoordinated silicon species.



**Scheme 10.** Synthesis of silylium derivative **5d**, using N,S-pyridine-2-thiolato ligand followed by their reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions. Formation of allylsulfide **6**.



Figure 8. Bioactive molecules containing a thiopyridine scaffold.

<sup>&</sup>lt;sup>2</sup>We are grateful to the referees for their questions on the nature of the generated Si-species generated after the reaction, and particularly the fate of the silyl anion.





## **Experimental Section**

To a *Schlenk* flask was added the silicon complex **5a**–**5d**, *fac*-lr(ppy)<sub>3</sub> (5 mol-%), and allyl sulfone **2**. The degassed solvent (0.1 mol/L or 0.067 mol/L) was then introduced followed by the amine (1.5 equiv.) and the mixture was irradiated with blue LEDs (470 nm) at room temperature for 24 h under an argon atmosphere. The reaction mixture was diluted with diethyl ether, washed with water (two times), dried over MgSO<sub>4</sub> and evaporated under reduced pressure. The crude residue was purified by flash chromatography.

## **Authors Contribution Statement**

*E. L., C. L., L. F.* and *C. O.* conceived and designed the studies and analyzed the data. *E. L.* and *C. L.* performed the experiments. *E. D.* conceived and conducted DFT calculations. *E. L., L. F.* and *C. O.* wrote the manuscript.

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