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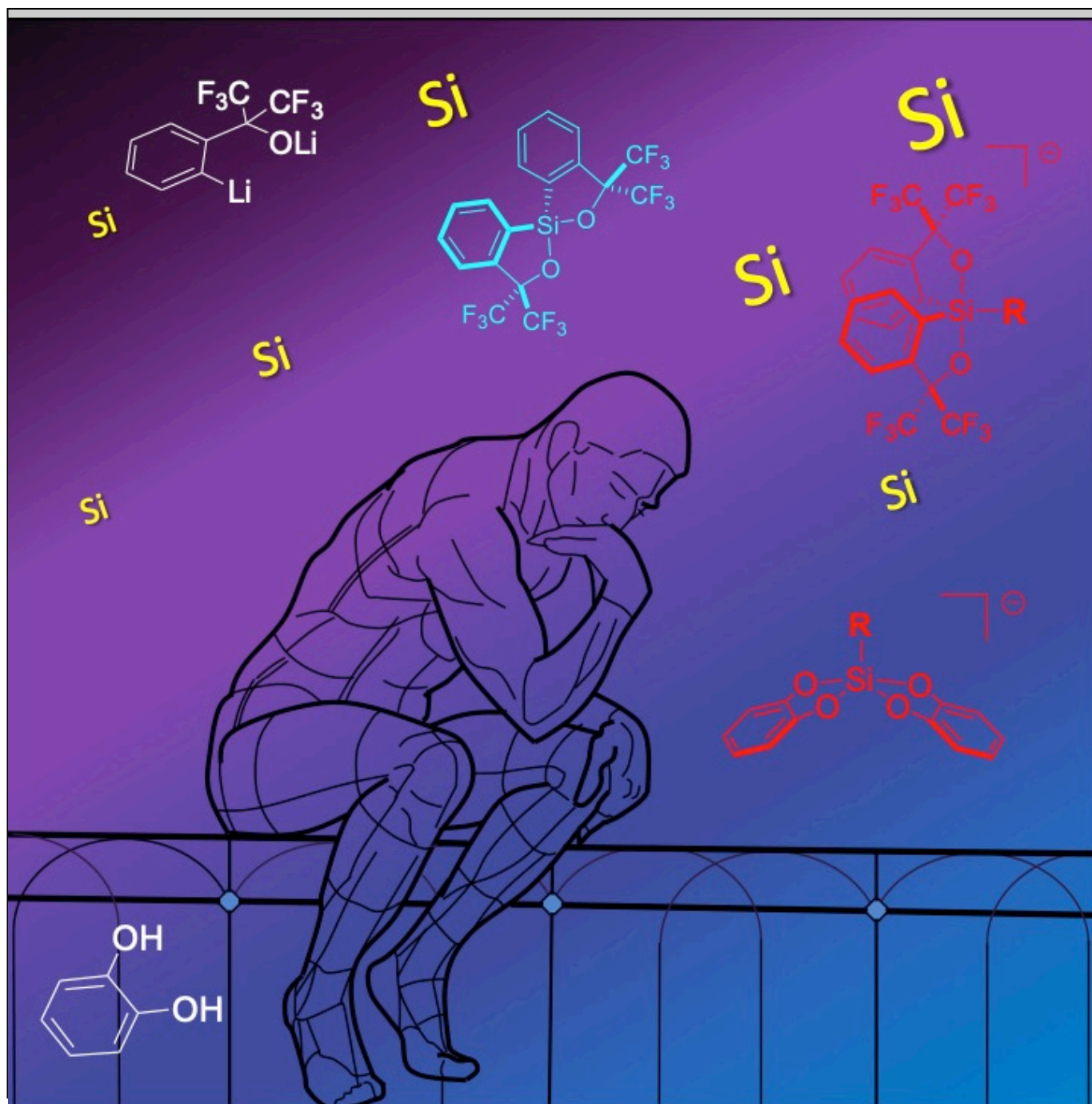
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# A Parisian Vision of the Chemistry of Hypercoordinated Silicon Derivatives

Gilles Lemière<sup>\*[a]</sup>, Alexandre Millanvois<sup>[a]</sup>, Cyril Ollivier<sup>\*[a]</sup>, and Louis Fensterbank<sup>\*[a]</sup>

Dedicated to Scott Sieburth, a visionary of silicon chemistry



**Abstract:** Less than ten years of acquaintance with hypercoordinated silicon derivatives in our lab is described in this account. Martin's spiroasilane derivatives open new opportunities as ligands and as agents for the activation of small molecules and bis-catecholato silicates have proven to be exquisite radical precursors in photoredox conditions for broad synthetic applications.

## 1. Introduction: why hypercoordinated silicon derivatives?

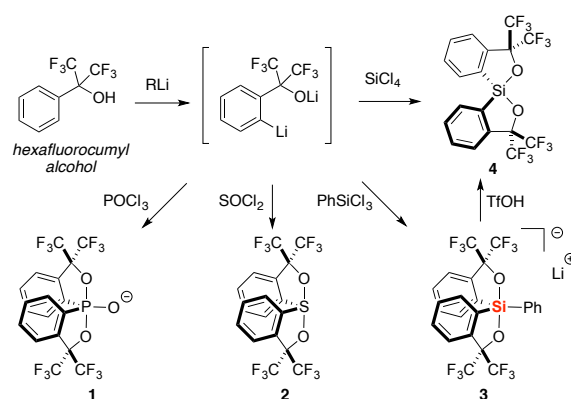
Just below carbon in the periodic table, silicon is much more than a pale imitation of carbon. While organosilicon compounds featuring a C-Si bond are very common, silicon, due to its lower electronegativity compared to carbon, the longer bonds by which it connects to neighboring atoms, its high affinity for fluoride and alkoxy ligands and its propensity to form hypercoordinated derivatives offers unique opportunities in organic chemistry. The first example of a hexavalent silicon derivative ( $\text{SiF}_4 \cdot 2\text{NH}_3$ ) was reported at the beginning of the 19<sup>th</sup> century by Gay-Lussac and Davy.<sup>1</sup> But it was the following century that saw the major discoveries that laid the foundations for the modern chemistry of hypercoordinated organosilicon compounds as conceptualized in the 1980s by Voronkov,<sup>1</sup> Holmes<sup>2</sup> and Corriu<sup>3</sup> just to name a few.<sup>4</sup> As nicely highlighted in 2005 by Oestreich,<sup>5</sup> the hypercoordinated mode can be transiently generated to trigger valuable reactivities such as the Brook rearrangement, the Tamao-Fleming oxidation or the Hiyama cross coupling just to name a few. But stable adducts can also be prepared, isolated and fully characterized.<sup>6</sup> Our acquaintance with organosilicon compounds has a long history featuring arylsilanates as metalation directing groups,<sup>7</sup> silicon tethered Diels-Alder reactions,<sup>8</sup> bromomethylsilyl ethers as precursors of radical cascades,<sup>9</sup> epoxysilanes,<sup>10</sup> silapiperidines.<sup>11</sup> In this story, we will focus on two more recent stories. The first one deals with the use of Martin's spiroasilane and derivatives as Lewis acids and their reactions toward various nucleophiles. The second one focuses on the introduction of bis-catecholato silicates as precursors of radicals in photooxidative conditions.

## 2. Martin's spiroasilanes as an entry for stable peculiar silicates

### 2.1. Martin's spiroasilane, a valuable Lewis acid

James Cullen Martin a.k.a. J. C. Martin is mainly known for his

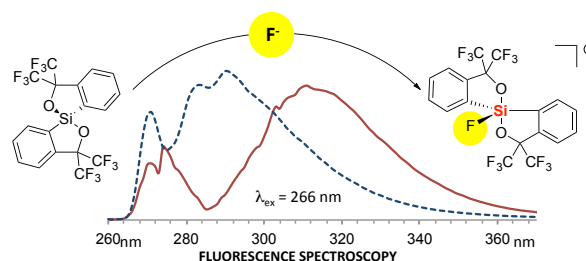
invention of the Dess-Martin reagent. Nevertheless in 1979, he made a seminal report on the use of the dilithio derivative of hexafluorocumyl alcohol as a bidentate ligand that can be appended twice on heteroatoms such as phosphorus, sulfur and silicon to give the corresponding phosphoranoxides **1**, sulfurane **2** and silicate **3**.<sup>12</sup> When treated with  $\text{SiCl}_4$ , hexafluorocumyl alcohol dianion provides a direct access to spiroasilane **4** that can also be obtained from the treatment of silicate **3** with triflic acid (Scheme 1). Due to the presence of the highly electronegative bis-trifluoro alkoxy ligand, spiroasilane **4** is a very strong Lewis acid that can react with a variety of charged and neutral nucleophiles.<sup>13</sup>



**Scheme 1.** Attachment of Martin's ligand on phosphorus, sulfur and silicon. Access to spiroasilane **4**

### 2.2. Martin's spiroasilane as a fluoride sensor

For several years, our laboratory has been interested in the reactivity of Martin's spiroasilanes **4** towards neutral or charged nucleophiles in order to obtain original structures. In particular, it was possible to exploit the Lewis acid properties and its ability to easily reach the hypercoordinated form, to use it as a fluoride probe (Scheme 2).<sup>14</sup> The very strong Si-F bond warrants selective and quantitative detection of fluoride ions in solution and the structural reorganization of hypercoordinated silicon structure allows for a diagnostic.



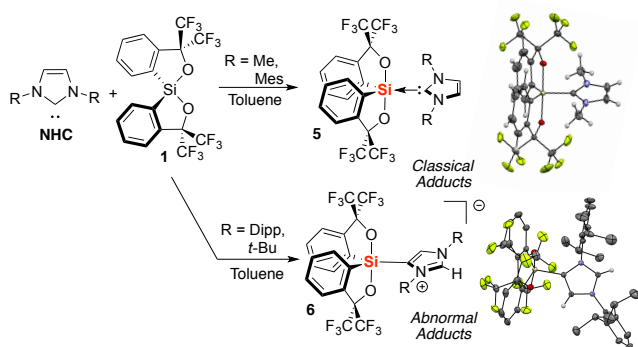
**Scheme 2.** Martin's spiroasilane **4** as a fluoride sensor.

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UV and fluorescence spectroscopy have been used to quantify the fluorosilicate product attaining detection limits as low as 5  $\mu\text{M}$  which is close to the residual concentration of fluoride in some drinking waters. Recently, Greb and coworkers have proposed a bis(alizarinato) spiro silane as chromogenic fluoride sensor which announces further developments in this area.<sup>15</sup>

### 2.3. Interaction of Martin's spiro silane with N-heterocyclic carbenes (NHCs)

Recently, we have studied the interactions of the Martin's spiro silane with neutral Lewis bases displaying various strength and steric hindrances. It has been established that the outcome of these interactions was very dependent on both parameters.<sup>16</sup> Indeed, in the presence of weakly hindered NHCs Lewis base of imidazolylidene type (Ime, IMes), new neutral adducts **5** originating from classical Lewis acid-base interactions were obtained in which the pentacoordinated silicon adopts a trigonal bipyramid (TBP) geometry (Scheme 3), as highlighted by their X-ray diffraction (XRD) analyses. Conversely, when the size of the free carbene becomes larger (IPr, ItBu), no direct interaction between the silicon and the divalent carbon of the NHCs can be noticed by <sup>1</sup>H NMR monitoring. Considering the strength of the Lewis partners involved, the non-interaction is unambiguously diagnostic of Frustrated Lewis Pair (FLP) behaviors highlighting the bulkiness of the spiro silane to some extent. After some time, the mixtures evolves nonetheless towards the formation of an "abnormal adduct" **6** where a covalent bond is created between the silicon atom and one of the two trivalent carbons located on the NHC backbone. As it can be visualized on the XRD structure of **6** (R = Dipp), the ligands surrounding the hypercoordinated silicon are quite distorted due to the steric congestions and deviates from the perfect TBP.

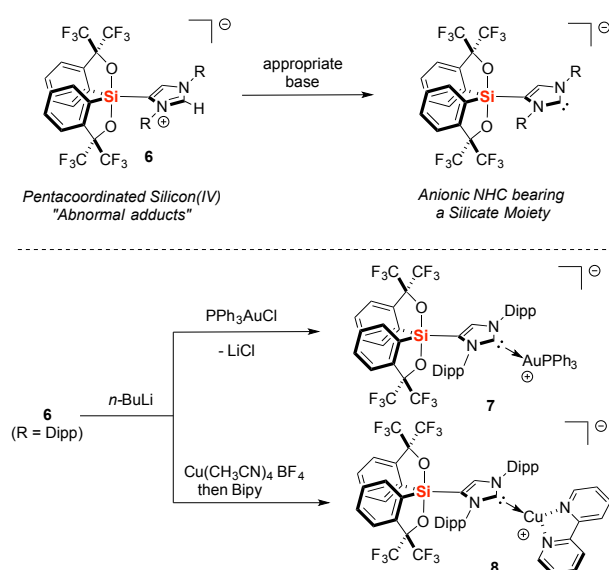


Scheme 3. Interaction between Martin's spiro silane **1** and NHCs

### 2.4. Anionic NHC ligand featuring hypercoordinated silicon

The abnormal adducts **6** have been later used as precursors for new anionic NHC carbene ligands possessing within their backbone a poorly coordinating anion.<sup>17</sup> As a matter of fact,

structures **6** are neutral species that could be seen as imidazolium rings attached to a silicate anion. Basically, the deprotonation of the positively charged heterocycles by using an appropriate base would lead to carbene ligands that can interfere with metals to form original organometallic complexes. From this perspective, the abnormal adducts **6** were cleanly deprotonated using *n*-butyllithium as a base, to be subsequently trapped with Au(I) or Cu(I) species affording complexes of type **7** and **8**, respectively (Scheme 4). It is noteworthy that the anionic nature of the ligand and the presence of the lithium cation presumably favors the chloride dissociation from ClAuPPh<sub>3</sub> to provide the corresponding neutral complexes. The strong  $\sigma$ -donor ability of these new anionic NHC ligands was confirmed by density-functional theory (DFT) calculations.

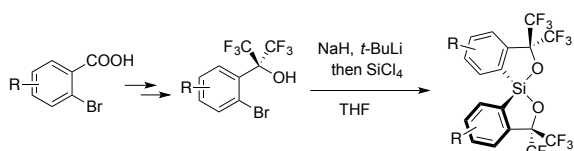


Scheme 4. Silicate-imidazolium zwitterions as precursors for anionic NHC ligands.

### 2.4. Spirosilanes as Lewis acid partners in FLP chemistry

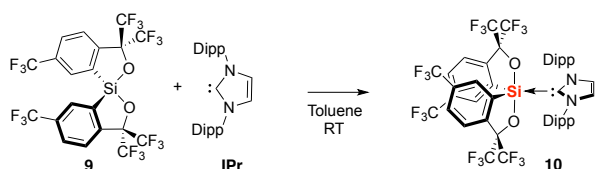
As previously mentioned, the Martin's spiro silane **4** exhibits a FLP character when confronted to encumbered NHCs. The same trend was also observed with other hindered bases such as *tert*-butylphosphine and 2,2,6,6-tetramethylpiperidine since in both cases, no adducts are formed when they are in presence of silane **4**.<sup>18</sup> This behavior is similar to that of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, the most employed Lewis acid in FLP chemistry.<sup>19</sup> For the sake of comparison, the Lewis acidity of Martin's spiro silane **4** was assessed using the Gutmann-Beckett parameter.<sup>20</sup> Although the understanding of the Lewis acidity is very complex and depends on many parameters, this method based on the shift of triethylphosphine oxide in <sup>31</sup>P NMR spectroscopy represents a convenient way to roughly compare the electrophilicity of various species. The acceptor number of **4** was evaluated as AN = 84.4 which is slightly higher than the one calculated for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (AN = 81.4).<sup>21</sup>

Theoretically, the Lewis acid properties of the Martin's spiroisilane **4** can be modulated by introducing substituents on the aromatic rings. For that purpose, a synthesis strategy of analogous structures of spiroisilane **4** has been previously developed in our laboratory.<sup>22</sup> It consists in the spirocyclization of functionalized hexafluorocumyl ligands that are readily available from the corresponding 2-bromobenzoic acid derivatives (Scheme 5).



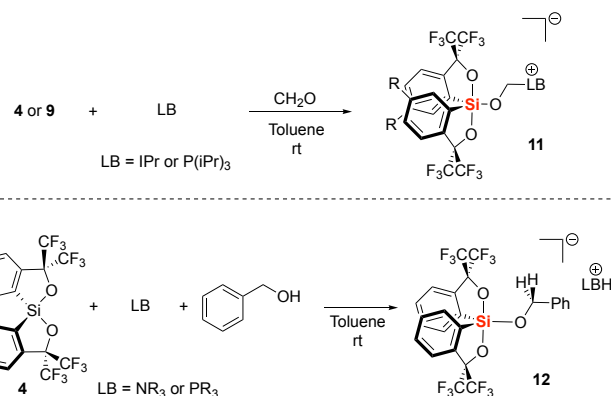
**Scheme 5.** Synthesis of Martin's spiroisilane analogues.

With this method, the synthesis of a spiroisilane **9** bearing one trifluoromethyl group on each aromatic ring was achieved. The presence of an electron-withdrawing group has a great effect on the electronic properties of the silicon atom and the acceptor number was calculated as AN = 89.2. That makes spiroisilane **9** a remarkable Lewis acid particularly prone to reach hypervalency. The high electrophilicity of the CF<sub>3</sub> derivative **9** was confirmed since a classical Lewis adduct **10** was formed in the presence of a bulky NHC (IPr) which has never been observed in the case of the simpler spiroisilane **4** (Scheme 6). DFT calculations revealed that the presence of CF<sub>3</sub> groups on the spiroisilane increases the Gibbs free enthalpy of formation of the conventional adduct by at least 10 kcal.mol<sup>-1</sup>.



**Scheme 6.** Formation of classical Lewis adduct by reaction of spiroisilane **9** with IPr

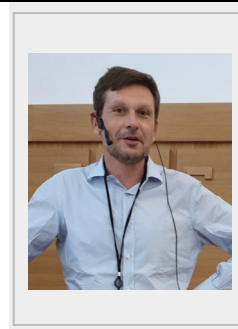
Although for the moment, Lewis acid partners **4** and even more Lewis acidic **9** proved to be inefficient for the activation of H<sub>2</sub> and CO<sub>2</sub>, activation of formaldehyde was possible with the IPr NHC and tri-isopropylphosphine. In these cases, the zwitterionic adducts of type **11** could be isolated (Scheme 7).



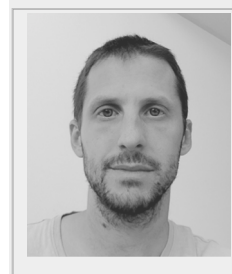
**Scheme 7.** Use of spiroisilanes **4** and **9** in FLP chemistry

In addition, the Martin's spiroisilane **4** could also be used for the activation of alcohols such as benzylic alcohol to form benzyloxysilicates **12** in the presence hindered phosphines or amines. On the <sup>1</sup>H NMR spectrum, adducts **12** displayed AB systems with a large splitting of the two diastereotopic benzylic protons that highlights the intrinsic chirality of the Martin's spiroisilane at the NMR timescale. This interesting feature potentially opens the way for further asymmetric FLP transformations using chiral spiroisilane analogues.

Louis Fensterbank obtained his PhD in 1993 at SUNY Stony Brook under the guidance of Scott Sieburth. After a lecturer position at the Université Pierre & Marie Curie (UPMC), he was appointed in 1995 as a CNRS Chargé de Recherche with Max Malacria. In 2004, he became Professor at UPMC, now Sorbonne Université. His research interests concern the discovery of new molecular transformations relying on radical or organometallic processes and their applications to the synthesis of substrates with relevant properties. Co-author of more than 220 publications, he has received several awards, notably the Silver Medal of CNRS in 2017. He is also Fellow of the Royal Society of Chemistry



Gilles Lemière studied chemistry in Paris at the Université Pierre et Marie Curie (UPMC), where he obtained his PhD in 2008 under the supervision of Profs. Louis Fensterbank and Max Malacria. After his PhD on gold-catalysed new organic reactions, he joined the group of Prof. Jonathan Clayden in Manchester as a postdoctoral fellow to work on the total synthesis of natural compounds. In 2010, he was appointed CNRS Researcher at the University of Nice in the group of Elisabet Dunach and moved in 2015 to Sorbonne Université, Paris. His research interests deal with the development of new metal- and acid-catalysed cycloisomerisation processes and silicon chemistry.



Alexandre Millanvois received his Bachelor (UPMC) and master's degree at Sorbonne Université (ex UPMC) with honour. He is currently conducting his joint PhD under the supervision of Prof. Louis Fensterbank, Prof. Tan Choon Hong and Dr. Cyril Ollivier between Sorbonne Université and Nanyang Technological University (NTU). His current research interests are focused on the synthesis of new silicon based radical precursor and their application in asymmetric radical chemistry.



Cyril Ollivier obtained his PhD in 2000 from the University of Fribourg (Switzerland) and UPMC under the guidance of Philippe Renaud in collaboration with Max Malacria. He was awarded a Swiss National Foundation Fellowship to work with Philippe Magnus at the University of Texas at Austin. In 2002, he was appointed *Chargé de Recherche CNRS* at Aix-Marseille University and in 2007, he moved to UPMC/Sorbonne University where he is now *Directeur de Recherche* to develop new directions for research on synthetic radical and organometallic chemistry including photocatalytic processes.

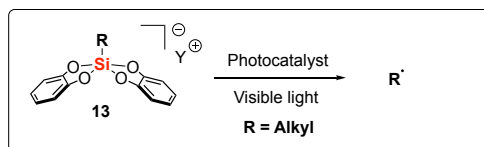


### 3. Bis-catecholato silicates as radical precursors

#### 3.1. Oxidation of soft carbanions

In the quest for new radical precursors, we engaged in the exploration of the oxidation of ate and hypercoordinated derivatives. The idea of such an approach originated from the very inspiring works of Kumada as PI, featuring also the two prominent chemists: Kohei Tamao and the late Jun-ichi Yoshida, on the oxidation of pentafluorosilicates with copper(II) and some organic oxidants.<sup>23</sup> We first tested this idea on alkyltrifluoroborates and showed they could be smoothly oxidized by copper(II) salts or Dess-Martin periodinane to give alkyl radicals including primary ones.<sup>24</sup> We then examined the reactivity of more soluble and user friendly bis-catecholato silicates synthesized by Cecil Frye<sup>25</sup> and Robert Corriu<sup>26</sup>. We were encouraged to do so based on a series of works of Nishigaichi who reported the photoallylation of benzil-type derivatives and dicyanobenzene in moderate yields, but these reactions were limited to the generation of stabilized allyl and benzyl radicals.<sup>27</sup> We therefore decided to prepare a series of bench stable alkyl bis-catecholato silicates **13** and to test them in photooxidative conditions under visible-light irradiation in

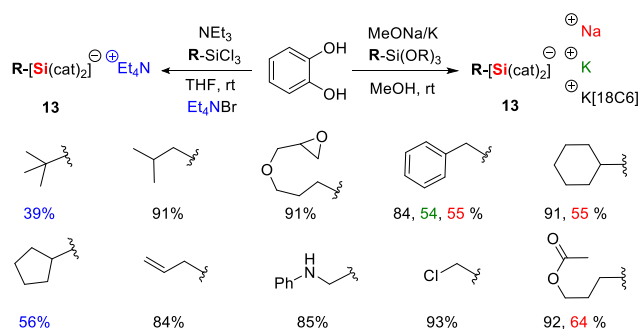
order to generate functionalized alkyl radicals and particularly unstabilized primary ones (Scheme 8).<sup>28</sup>



**Scheme 8.** Generation of alkyl radicals by photooxidation of alkyl bis-catecholato silicates **13** under visible light irradiation

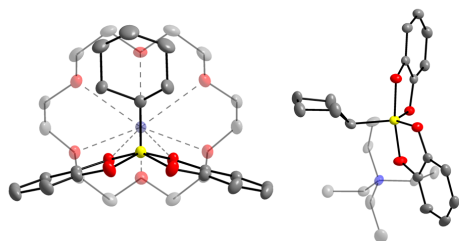
#### 3.2. Oxidation of alkyl bis-catecholato silicates through visible light photoredox catalysis: preliminary screenings

Potassium alkyl bis-catecholato silicates **13** can be easily obtained by reaction of trialkoxysilanes with catechol and potassium methoxide in methanol. The presence of crown ether 18-crown-6 (18-C-6) stabilizes the hypercoordinated species<sup>3</sup> so that a series of primary and secondary alkylsilicates with various functions can be prepared on a large scale and stored for a long time at room temperature with no significant degradation. Sodium silicates **13** are also accessible under the same conditions (MeONa/MeOH) but have shown a reduced stability, even in the presence of 15-crown-5.<sup>29</sup> For cyclopentyl and tert-butyl silicates, the corresponding tetraethylammonium salts were obtained from trichlorosilanes (Scheme 9).<sup>30</sup>



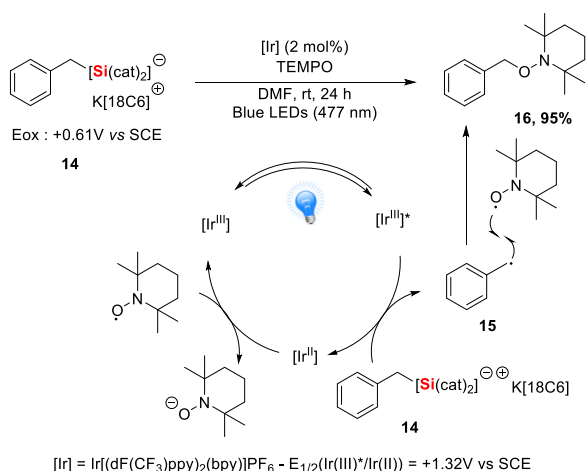
**Scheme 9.** Synthesis of functionalized sodium, potassium, ammonium and potassium[18-C-6] alkyl bis-catecholato silicates **13**

The structures of the silicates **13** were studied by X-ray crystallography and showed a continuum between a quasi-square planar pyramidal (SP) geometry (R = cyclohexyl, K<sup>+</sup>[18C6]) and a trigonal bipyramidal (TBP) (R = cyclopentyl, Et<sub>4</sub>N<sup>+</sup>), as already observed by Holmes<sup>31</sup> (Scheme 10). The oxidation potentials of these silicates were determined by cyclic voltammetry that provided values < +1.0 V vs. saturated calomel electrode (SCE) for both activated and non-activated alkylsilicates **13**. These values were found to be lower than those of the corresponding carboxylates<sup>32</sup> and trifluoroborates<sup>33, 34</sup> and suggest that some photoexcited ruthenium or iridium-based photocatalysts can oxidize all the alkylsilicates.



**Scheme 10.** X-ray crystallography of cyclohexyl (SP) and cyclopentyl (TBP) bis-catecholato silicates

Initially, benzylsilicate **14** was found to be capable of generating benzyl radical **15** under photooxidation conditions (Scheme 11).<sup>30</sup> Based on a screening of photocatalysts including  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (bpy = bipyridine) as well as  $\text{Ir}[(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bpy})]\text{PF}_6$  ( $\text{dF}(\text{CF}_3)\text{ppy}$  = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine), the latter revealed to be the most effective under blue light-emitting diodes (LEDs) irradiation leading to the 2,2,6,6-tetramethylpiperidinyl-oxide (TEMPO) adduct **16** in good yield. The low value of the oxidation potential of the benzylsilicate (**14**,  $E_{\text{ox}} = +0.61$  V vs. SCE) fitted with the potential of the photoactivated catalyst ( $\text{Ru}^{\text{II}*}/\text{Ru}^{\text{I}} = +0.77$  V vs. SCE in  $\text{CH}_3\text{CN}$ ,  $\text{Ir}^{\text{III}*}/\text{Ir}^{\text{II}} = +1.32$  V vs. SCE in  $\text{CH}_3\text{CN}$ ) and suggests that this one can oxidize the silicate. Stern-Volmer plot showed a linear relation between the intensity of the fluorescence and the concentration of quencher. Based on these experiments, a mechanism, where the photoactivated catalyst oxidizes the silicate and the benzyl radical **15** is trapped by TEMPO, was proposed (Scheme 11). The photocatalyst would be regenerated by the reduction of TEMPO (present in excess).

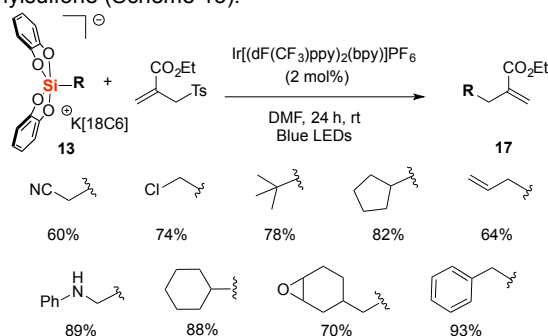


**Scheme 11.** Visible-light photooxidation of benzyl bis-catecholato silicate **14**, spin-trapping experiments with TEMPO and proposed mechanism

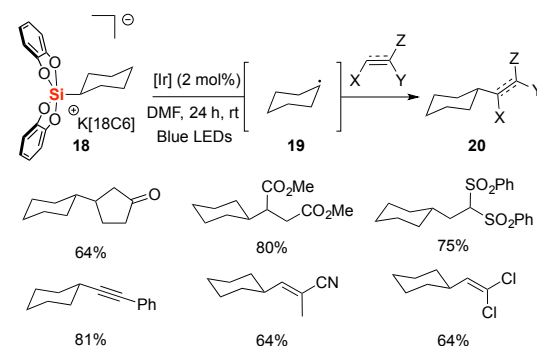
### 3.3. Carbon-carbon bond formation by radical addition from alkyl bis-catecholato silicates

The formation of carbon-carbon bond was explored by focusing mainly on the allylation of alkyl bis-catecholato silicates **13** with allylsulfones (Scheme 12).<sup>30</sup> The range of substrates proved to be quite wide, from primary to tertiary alkylsilicates. We can mention in particular the generation of non-activated primary radicals, as well as new examples of aminomethylation and chloromethylation. A similar mechanism was proposed except that the radical adds to allylsulfone and after fragmentation, the sulfonyl radical participates to the regeneration of the photocatalyst, as already proved by MacMillan.<sup>35</sup> As detailed below, radical chain mechanism in these allylations was excluded based on light/dark experiments and the determination of quantum yields.<sup>36</sup>

We next examined the reactivity of cyclohexyl silicate **18** toward various radical acceptors. The cyclohexyl radical **19** generated was then engaged in Giese-type reactions with various activated olefins. Vinylation can be reached by addition/fragmentation with vinylsulfones, bromides or chlorides, and alkynylation using an alkynylsulfone (Scheme 13).



**Scheme 12.** Allylation reactions of a variety of functionalized silicates **13**

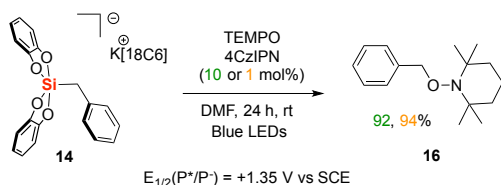


**Scheme 13.** Reactivity of cyclohexyl silicate **18** towards various radical acceptors

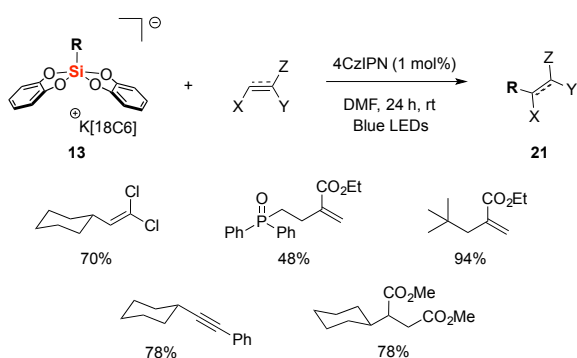
Computational studies on the oxidation of cyclohexyl bis-catecholato silicate by the triplet state of  $\text{Ir}(\text{III})\text{-dF}(\text{CF}_3)$  (triplet state) were carried out by Etienne Derat and showed a single-electron transfer (SET) process from the catecholate ligand of the silicate to the metallic center of the photocatalyst. Comparison of the bond dissociation energy (BDE) of the substrates before and after electron transfer indicates that

oxidation significantly weakens the Si-C bond that undergoes cleavage.<sup>30</sup> These DFT calculations fully validated the proposed mechanism.

As previously mentioned, the oxidation of the bis-catecholato silicates **13** has been accomplished using metal-based photocatalysts, and particularly rare and expensive polypyridine complexes of ruthenium or iridium. In order to provide greener reaction conditions, the reactivity of organic dyes as an alternative to metal complexes was explored.<sup>34,37</sup> First, we found that only the more oxidant Fukuzumi acridinium photocatalyst revealed to be the most efficient in spin trapping experiments with benzylsilicate **14** and no reaction was observed with Eosin and Fluorescein even if their oxidation potentials at the excited state also match with the silicate.<sup>34</sup> In 2012, Adachi *et al.* described a new carbazolyl dicyanobenzene complex, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN), which demonstrated a high photoluminescence quantum yield (94.6%) and a long life-time (5.1  $\mu$ s) at the excited state.<sup>38</sup> Later, Zhang measured the oxidative potentials of 4CzIPN and of related structures. He was also the first one to apply these carbazole derivatives as photocatalysts for the photooxidation of stabilized carboxylate and trifluoroborate.<sup>39</sup> The potential of 4CzIPN at the excited state was recently revised by Waser at + 1.59 V vs. SCE.<sup>40</sup> Based on these physico-chemical data and not surprisingly, benzylsilicate **14** gave the TEMPO adduct **16** in 94% yield with a catalytic loading in 4CzIPN of only 1 mol% (Scheme 14). Vinylation, allylation, alkynylation and Giese-type adducts **21** were also obtained in good yields with a variety of alkylsilicates (Scheme 15).

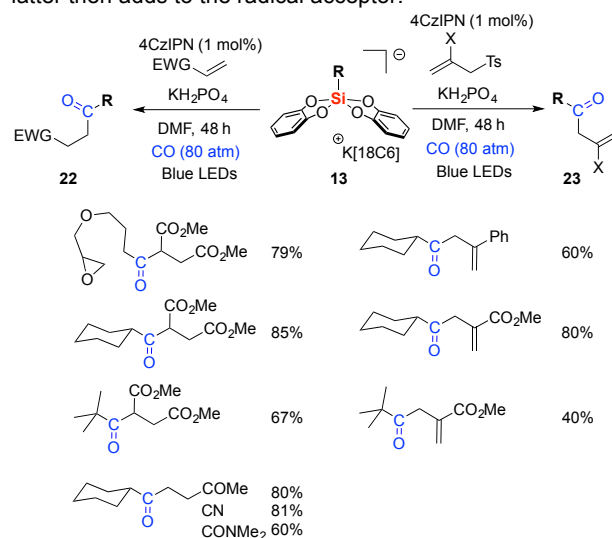


**Scheme 14.** Photooxidation of benzyl bis-catecholato silicate **14** with the organic dye 4CzIPN



**Scheme 15.** Photooxidation of alkylsilicates **13** by 4CzIPN with various C-radical acceptors

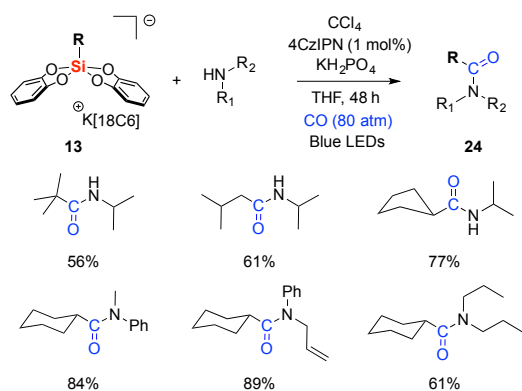
A new methodology of radical carbonylation of alkyl bis-catecholato silicates **13** under photocatalyzed oxidation conditions was developed in collaboration with the group of Ilhngong Ryu and Takahide Fukuyama from Osaka Prefecture University and could be implemented in multicomponent reactions. Thus, alkyl radicals generated by photooxidation of the corresponding organosilicates with 4CzIPN, participate in radical carbonylation with carbon monoxide (CO) in the presence of electron-deficient alkenes as radical acceptors, providing a series of unsymmetrical ketones **22** and **23** via an acyl radical intermediate. These optimized conditions were applied to a variety of alkylsilicates. The carbonylation of primary, secondary and tertiary radicals worked well and led to the corresponding ketones in good yields (Scheme 16). Gratifyingly, we tested different alkenes as radical acceptors. For instance,  $\alpha,\beta$ -unsaturated ketones participated in these three-component to afford 1,4-diketones. Transformations with *N,N*-dimethyl acrylamide and acrylonitrile were equally effective as well as those carried out with an allylsulfone. "Light-dark" experiments conducted in the absence of CO and quantum yield measurements supported a catalytic photoredox process and not a radical chain pathway. In this case, a SET oxidation of the silicate by the excited photocatalyst results in the formation of the alkyl radical that adds to CO to form an acyl radical. The latter then adds to the radical acceptor.



**Scheme 16.** Three-component radical carbonylation reactions of alkyl bis-catecholato silicates **13** for the synthesis of unsymmetrical ketones **22** and **23**

In the presence of an amine and carbon tetrachloride, the transient acyl radical generates an acyl chloride through chlorine abstraction from  $\text{CCl}_4$  and leads this time to a variety of amides **24** with yields ranging from 34 to 89%. An amine with a potentially reactive alcohol only furnishes the corresponding amide and no trace of ester was observed (Scheme 17).<sup>41</sup>

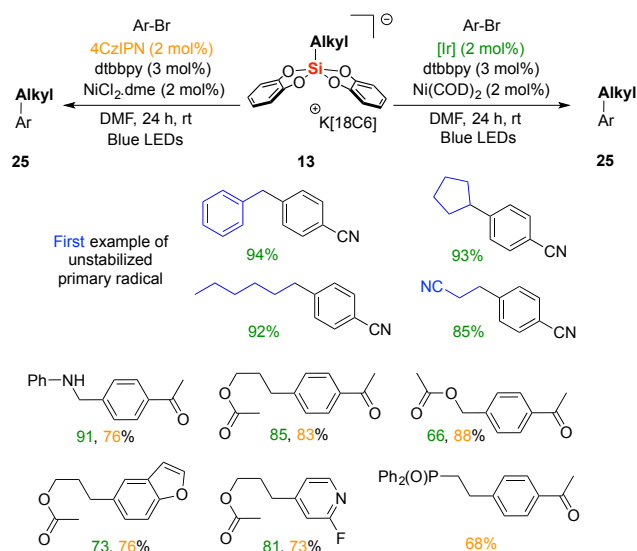




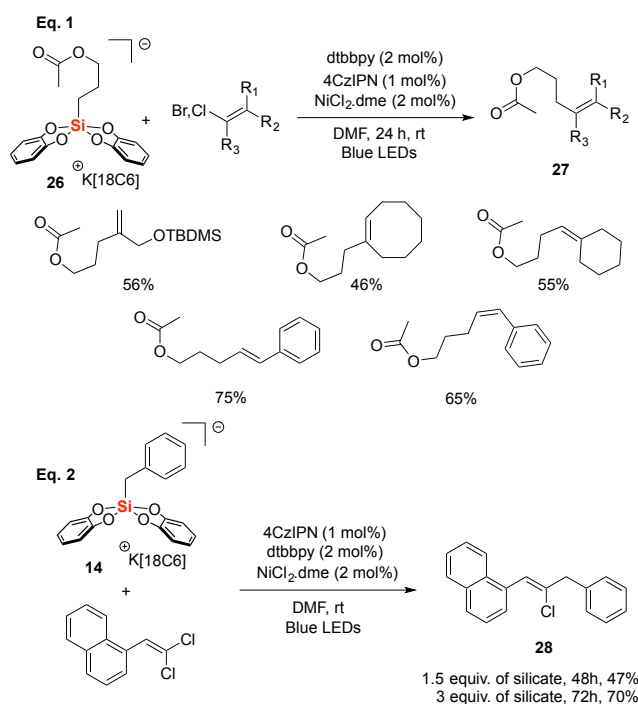
**Scheme 17.** Synthesis of aliphatic amides **24** by radical carbonylation starting from alkyl bis-catecholato silicates **13**

### 3.4. Cross-coupling reactions by dual photoredox/Nickel catalysis

A particularly attractive field concerns dual photoredox/organometallic catalysis. Initially developed through photoreductive processes,<sup>42</sup> the possibility of coupling aromatic electrophiles with radicals, generated by photooxidation, thanks to nickel complexes was recently demonstrated.<sup>43</sup> This type of coupling was first reported by the groups of Molander, MacMillan and Doyle with a primary or a secondary radical obtained respectively from activated trifluoroborates or carboxylic acid derivatives or methylamines as easy oxidation substrates.<sup>44,45</sup> We wished to examine the possibility of introducing silicates in these cross couplings and notably what would be the benefits of their use.<sup>37,46</sup> When treated with Ni(COD)<sub>2</sub>/iridium photocatalyst or NiCl<sub>2</sub>.dme/4CzIPN catalytic systems, silicates **13** could be coupled with electron poor and electron rich (hetero)arylbromides and gave the cross-coupling product **25** with benzyl, allyl,  $\alpha$ -amino methyl and secondary radicals as well as proved successful with unstabilized primary radicals. These results revealed that silicates are partners of choice in the dual catalysis processes, as shown also by the Molander group.<sup>47</sup> The scope of the transformation is broad and the process is tolerant with various functions, such as a pinacol alkylboronate function on the aryl ring. The NiCl<sub>2</sub>/4CzIPN dual catalysis conditions allowed to couple both ethylenic bromides and chlorides with acetoxypropyl bis-catecholato silicate **26** with a high diastereoselectivity (Scheme 19, Eq. 1).<sup>37</sup> Finally, gem-dichlorostyrenes were reacted with primary and secondary (non-)activated alkylsilicates **13** (such as **14**, R = benzyl) and provided exclusively the corresponding monoalkylated cross coupling (Z)-styrylchloride products (**28**) (Scheme 19, Eq. 2).<sup>37,29</sup>



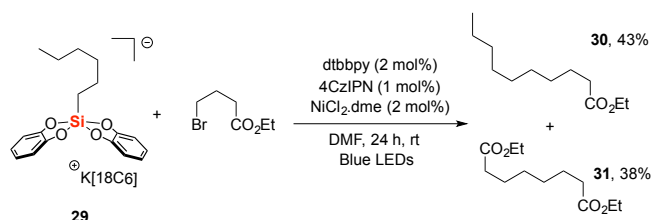
**Scheme 18.** Cross coupling reactions of silicates **13** with various arylbromides



**Scheme 19.** Reaction of bis-catecholato silicates **26** and **14** with alkenyl halides

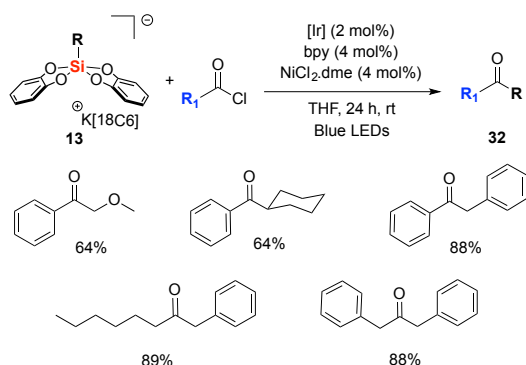
After developing an efficient photoredox/nickel dual catalytic process for C(sp<sup>3</sup>)-C(sp<sup>2</sup>) coupling, alkylsilicates **13** (such as **29**, R = n-hexyl) were involved in cross-coupling reactions with alkyl halides such as 4-bromobutyrate to create C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bonds.<sup>48</sup> The corresponding products (**30**) were obtained in moderate yields, either from primary and also secondary alkylsilicates, along with the homocoupling product (**31**) of the

alkyl halide. The mechanism is still under discussion and needs to be clarified (Scheme 20).

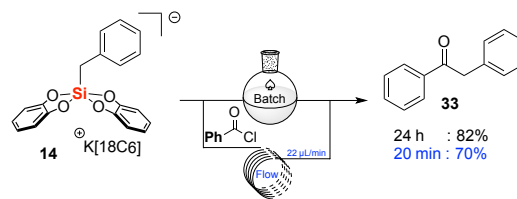


**Scheme 20.** Cross-coupling reactions between *n*-hexyl bis-catecholato silicate **29** and 4-bromobutyrate

Finally, we were interested in the reactivity of silicates **13** towards acyl chlorides in order to obtain benzyl and alkyl ketones **32**, which are of great interest in fragrance and flavors industry, and more generally, as synthetic intermediates.<sup>49</sup> Upon treatment with a complex of iridium as photocatalyst and NiCl<sub>2</sub>.dme under irradiation with blue LEDs, an alkylsilicate **13** can be coupled to an acyl chloride as electrophile to give the expected ketones **32** (Scheme 21). Several silicates **13** were then tested under these conditions. Cyclohexyl, norbornyl and mainly the activated silicates such as the methoxymethylene and benzyl derivatives were able to provide the desired product and notably highly enolizable ketones. The nature of the acyl chloride partner also influenced this coupling since both electron-rich benzoyl chlorides and alkyl ones afforded the corresponding ketones in good yields, including variously substituted dibenzyl ketones (Scheme 21). In collaboration with Michaël Tatoulian, Stéphanie Ognier and Mengxue Zhang from Institut Pierre-Gilles de Gennes in Paris, we used miniaturized flow reactors to accelerate this photooxidative process, without increasing the yield though. Only 20 minutes are necessary to obtain the cross-coupling product **33** from benzylsilicate **14** and benzoyl chloride whereas 24 hours are necessary under normal circumstances (Scheme 22).



**Scheme 21.** Acylation of alkyl bis-catecholato silicates **13** via dual nickel photocatalysis



**Scheme 22.** Continuous flow vs. batch processing

## Perspectives

This survey of our recent works involving hypercoordinated silicon derivatives illustrates, if it was still necessary, that this class of intriguing compounds offer unique opportunities in organic synthesis. At the origin of the described reactivities in this account, lays the Lewis acidity of a silicon center bearing electronegative ligands such as a catecholate<sup>50</sup> or the dianion of hexafluorocumyl alcohol, Martin's, which formally welcomes a nucleophilic addition to generate selectively pentavalent species. The formally resulting bis-catecholato silicates have proven to be excellent precursors of unstabilized alkyl radicals in a series of radical sequences. They position therefore themselves as reagents of choice for the introduction of Csp<sup>3</sup>-rich fragments on (hetero)aryl platforms through dual Ni/photoredox catalysis which is highly praised in medicinal chemistry ("escape from the flatland"). The realm of applications of these reagents is rapidly expanding as illustrated by the contributions of several groups.<sup>51</sup> Martin's spirosilane **4** has been known for more than 40 years but rarely considered as an alternative to the highly encountered B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis acids. Our preliminary works have delivered valuable elements of reactivity that augur well for more sophisticated applications. Interestingly, alkylsilicates obtained by Kano's group from **4** also proved to be sources of radicals. Despite their higher oxidation potentials (> 1.0 V), they also give an access to C-centered alkyl radicals, including the methyl radical.<sup>52</sup> The oxidation mechanism in that case is distinct since it is the C-Si bond that is directly oxidized.

Future research directions along these lines will involve the tuning of the silicon ligands<sup>22</sup> and the study of their effects. Notably, how can their modification by the substitution of the aromatic groups can improve the oxidation process and give access to sp<sup>2</sup>-radicals<sup>53</sup> for instance. Application to radical cascades that open a straightforward access to molecular complexity are envisioned.

## Acknowledgements

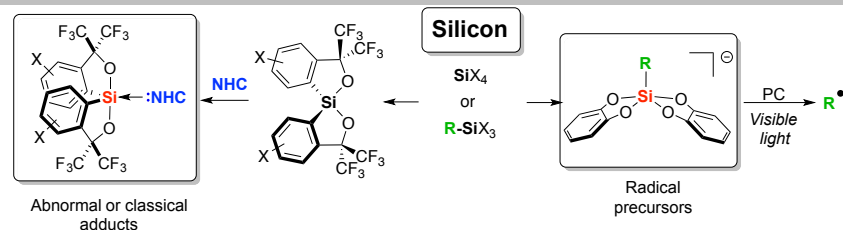
We wish to warmly acknowledge all our collaborators whose works were cited in this manuscript. We also thank Sorbonne Université, CNRS, PSL University, ANR-17-CE07-0018 HyperSiLight.

**Keywords:** Silicon • Lewis acid • silicate • photoredox • radical



## Entry for the Table of Contents (Please choose one layout)

## PERSONAL ACCOUNT



Gilles Lemière\*, Alexandre Millanvois<sup>[a]</sup>,  
Cyril Ollivier\*, and Louis Fensterbank\*

Page No. – Page No.

A Parisian Vision of the Chemistry of  
Hypercoordinated Silicon Derivatives

**Silicon at its best!** Less than ten years of acquaintance with hypercoordinated silicon derivatives in our lab is described in this account. Martin's spirosilane derivatives open new opportunities as ligands and as agents for the activation of small molecules and bis-catecholato silicates have proven to be exquisite radical precursors in photoredox conditions for broad synthetic applications.

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