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Primary Alkyl Bis-Catecholato Silicates in Dual Photoredox/Nickel Catalysis: Aryl- and Heteroaryl-Alkyl Cross Coupling Reactions

Christophe Lévêque,^a Ludwig Chenneberg,^a Vincent Corcé,^a Jean-Philippe Goddard,^{*b} Cyril Ollivier^{*a} and Louis Fensterbank^{*a}

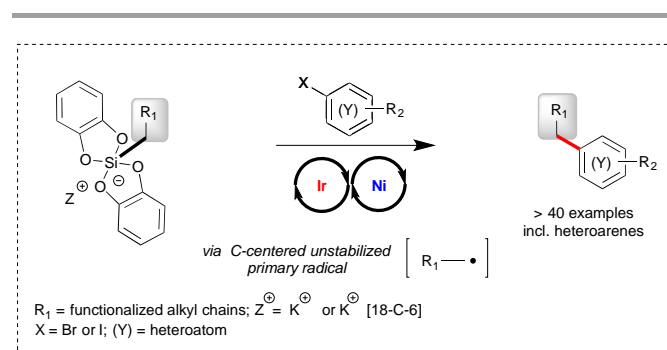
Primary alkyl bis-catecholato silicates have been successfully engaged with aryl and heteroaryl bromide substrates in photoredox/nickel dual catalysis to provide aryl- and heteroaryl-alkyl cross coupling products. The scope of the transformation is wide and the process appears to be tolerant of various functional groups present. Of note, most examples rely on the challenging use of highly reactive primary radicals which constitutes a significant advance in these cross coupling reactions.

Dedicated to John Murphy

Photoredox/nickel dual catalysis^{1,2} has recently emerged as a novel opportunity to form C-C bonds and rapidly couple functionalized fragments for the elaboration of more complex molecules.³ A key advantage of this strategy is to merge the mildness of visible light photoredox catalysis for the generation of hot radical entities⁴ with the robustness of nickel catalyzed cross coupling reactions.⁵ While the electrophilic partner involved in the oxidative addition to nickel has so far consisted of aryl halides and related substrates,⁵ more functional variation has been brought on the radical source. To the best of our knowledge, all works have involved α -amino,^{2b,6,7} α -O,^{2b,6} α -phenyl,^{2b,8} α -oxo,⁹ and secondary⁶ carboxylic acids, mixed anhydrides,¹⁰ dimethylaniline,^{2b} benzyl,^{2a,11} secondary^{2a,9,12} and activated (α -O) primary trifluoroborates.¹³ More recently, potassium and ammonium bis-catecholato silicates have been reported by us¹⁴ as a valuable source of C-centered radicals upon visible light photooxidation using Ir[(dF(CF₃)ppy)₂(bpy)](PF₆) as catalyst. The silicate substrates offer neat advantages over the related trifluoroborates in terms of solubility, of byproducts (no gas release, no fluoride, no boron) and of the scope of the possibly generated radicals (from stabilized alkyl ones to highly reactive primary ones). As a perspective, it was also found that they

could be engaged in photoredox/nickel dual catalysis for C_{sp2}-C_{sp3} cross-coupling reactions, notably involving unstabilized primary radicals.^{14a,15}

The limited sampling of these preliminary findings drove us to gain more insight into this transformation and define its scope by varying both partners (silicates and arylbromides, see Scheme 1). Subsequent to the first report of these cross coupling reactions by us,^{14a} the group of Molander described similar transformations of related ammonium bis-catecholato secondary and primary alkyl silicates with aryl- and heteroaryl-bromides.¹⁶ Herein, we focus on primary radical intermediates and bring a complementary picture to these highly powerful reactions.



Scheme 1. Photoredox/nickel dual catalysis involving primary radicals from silicates

We first prepared a series of potassium silicates **1**. As found before,¹⁴ the latter are rendered rock stable by admixing the 18-C-6 crown ether additive. Nevertheless, we could show that

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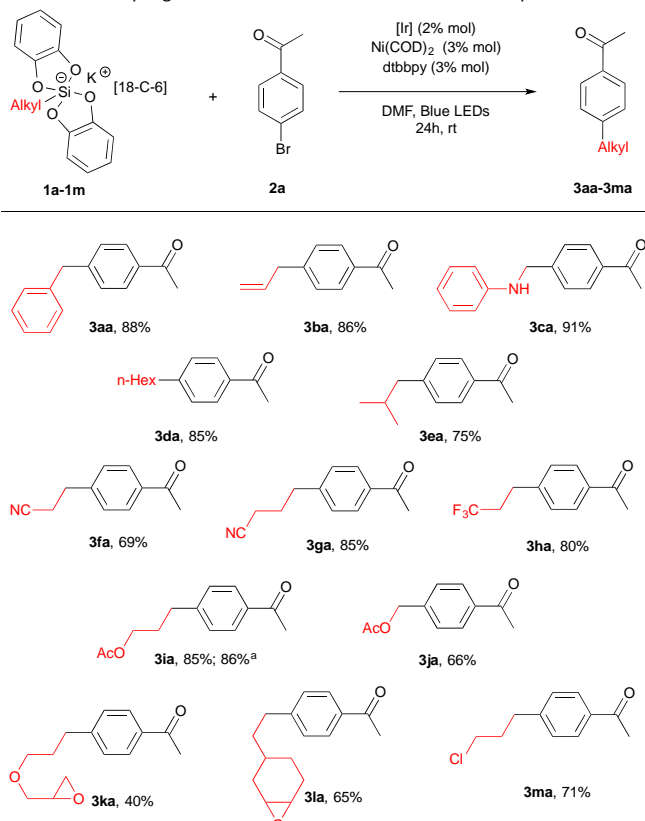
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this additive is not necessary to promote homolytic reactivity (see below). A preliminary screening of conditions with a given arylbromide, namely 4-bromoacetophenone **2a** led us to the following protocol. To a DMF solution of silicate **1** (1.5 equiv, 0.1 M) in the presence of Ir[(dF(CF₃)ppy)₂(bpy)](PF₆) (2 mol%), Ni(COD)₂ (3 mol%) and dtbbpy (3 mol%) as ligand was added 4-bromoacetophenone **2a** (1 equiv). After stirring for 24 h at rt, excellent yields of coupling products **3aa-3ca** were obtained from benzyl, allyl and α -amino silicates (**1a-c**). Gratifyingly, less stabilized radicals could also be involved furnishing the corresponding coupling products **3** in 40 – 85 % yields bearing various functional groups such as an ester (**3ia, 3ja**), a nitrile (**3fa, 3ga**) an oxirane (**3ka, 3la**) or a chloride (**3ma**). Interestingly, a comparison was made with the corresponding benzyltrifluoroborate precursor and showed in our conditions a more productive reaction (adduct **3aa**) from the silicate **1a** (88% vs. 58% yield). Also, potassium silicate **1i'** with no 18-C-6 also provided a good yield (86%) of coupling product **3ia**.

Table 1. Cross coupling reactions of silicates **1** with 4-bromoacetophenone **2a**

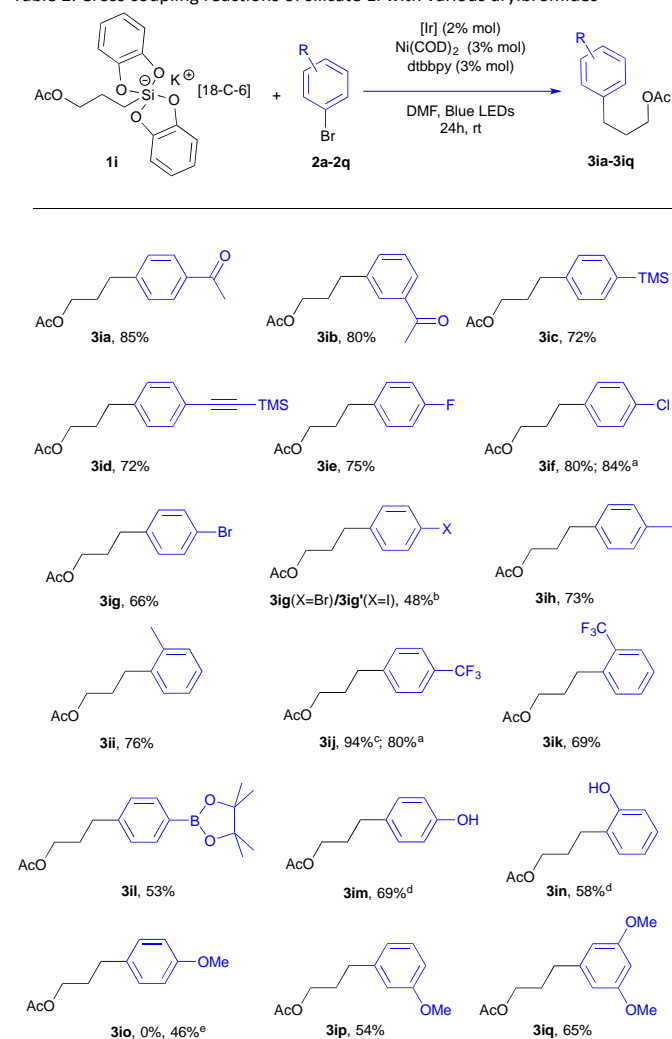


^a Starting from the corresponding potassium silicate with no 18-C-6 **1i'** and **2a**.

Using the same conditions, a series of arylbromides **2a-2q** with varied substitution pattern could be used in conjunction with acetate silicate **1i** or **1i'** (Table 2). First, reaction scope proved to be quite wide. Second, a closer examination of these results revealed interesting features. For instance, the difference of reactivity between a C_{sp2}-Br and a C_{sp2}-I bond was investigated with 1-bromo-4-iodobenzene **2g**. Not surprisingly, a preferred

oxidative addition took place at the carbon-iodide bond¹⁷ giving a 10:1 ratio of products **3ig** (X = Br) and **3ig'** (X = I). This appeared quite opportune for electron enriched aryl substrates.¹⁸ While *meta*-bromo anisoles (**2p** and **2q**) could be effectively used (adducts **3ip** and **3iq**), only starting material was recovered with *ortho*-bromoanisole and *para*-bromoanisole. The reluctant behavior of *para*-bromoanisole could be partly fixed by using the corresponding iodo derivative since cross coupling product **3io** was obtained albeit in modest yield (46%). These findings contrast with Molander's report^{16a} in which electron rich substrates proved to be competent. Their catalytic mixture (5 mol% NiCl₂(dme), 5 mol% dtbbpy, 2 mol% Ru(bpy)₃(PF₆)₂) differs from ours (3 mol% Ni(COD)₂, 3 mol% dtbbpy and 2 mol% Ir[(dF(CF₃)ppy)₂(bpy)](PF₆)) implying interesting metal and ligand effects that we are now investigating.¹⁸

Table 2. Cross coupling reactions of silicate **1i** with various arylbromides



^a Starting from the corresponding potassium silicate with no 18-C-6 **1i'**.

^b Starting from 1-bromo-4-iodobenzene. A 10:1 mixture of **3ig** and **3ig'** was isolated.

^c 2 mol% Ru(bpy)₃(PF₆)₂ was used instead of 2 mol% [Ir].

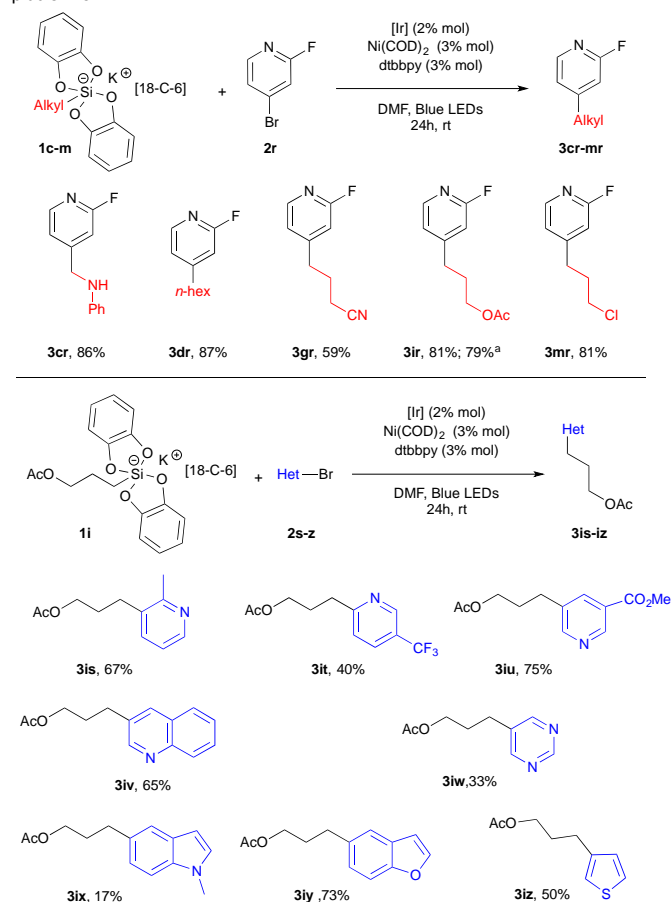
^d Pinacol borane directly oxidized before purification (H₂O₂, NaOH for 30 min at 0°C).

^e Starting from 4-iodoanisole.

Remarkably, a pinacol boronate function could also be tolerated in these conditions¹¹ as illustrated by the formation of **3il** that could be utilized for further coupling reactions. Nevertheless, direct isolation of this product after column chromatography was detrimental to the yield. Instead, when the crude reaction mixture was oxidized (NaOH, H₂O₂), a higher yield (69% vs 53% for **3il**) of phenol product **3im** was recorded. Similar protocol was applied to give phenol product **3in**.

Heterocyclic bromides completed the reach of this transformation and established its high synthetic potential. 2-Fluoro-4-bromopyridine **2r** was used as partner of the dual catalysis in the presence of silicates **1c-m** and delivered a small library of new alkylpyridines **3cr-3mr** in satisfactory yields (Table 3). Other pyridyl systems **2s-u** proved to be competent for this cross-coupling transformation. The corresponding products **3is-3iu** were obtained in a 40-75% yield range. Finally, various heterocyclic systems such as quinoline **2v**, pyrimidine **2w**, indole **2x**, benzofuran **2y** and thiophene **2z** were engaged and yielded the corresponding cross coupling adducts **3** from mitigated to fair yields.¹⁹

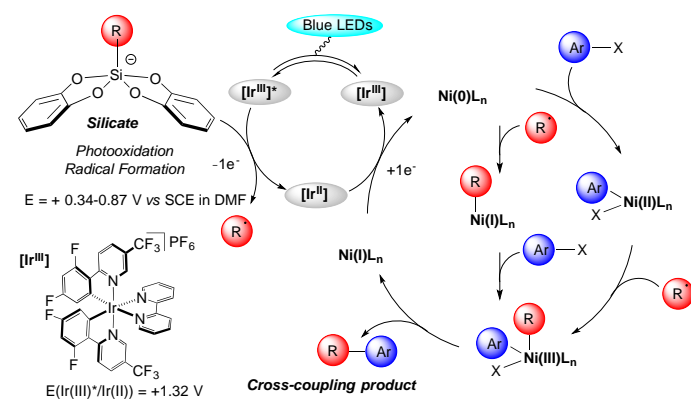
Table 3. Cross coupling reactions of silicates **1** with various heterocyclic platforms.



^a Starting from the corresponding potassium silicate with no 18-C-6 1⁺.

The proposed catalytic cycle is outlined in Scheme 2. It is well established that excitation of photoredox catalyst Ir[(dF(CF₃)ppy)₂(bpy)](PF₆) produces a long-lived photoexcited state ^{*}Ir[(dF(CF₃)ppy)₂(bpy)](PF₆).⁴ The latter acts as a strong oxidant (E [^{*}Ir^{III}/Ir^{II}] = +1.32 V vs SCE in MeCN)²⁰ and undergoes a single electron transfer (SET) with bis-catecholato silicates **1** (E_{ox} between +0.34 and +0.87 V vs SCE in DMF)^{14a} generating a primary alkyl radical which interacts with a Ni species. However, the mechanism of this dual catalysis is still in debate.^{9,21} All proposals converge toward a Ni(III) intermediate which upon reductive elimination delivers the cross coupling product and a Ni(I) intermediate complex, the latter being further reduced (E [Ni^{II}/Ni⁰] = -1.2 V vs SCE in DMF)²² by SET from the iridium(II) (E [Ir^{III}/Ir^{II}] = -1.37 V vs SCE in MeCN)²⁰ to generate a Ni(0) complex. From this zero-valent nickel entity, two possibilities have been advanced. Initial oxidative addition of the ArX gives a Ni(II) species that would trap the nucleophilic radical intermediate. Alternatively, an alkyl Ni(I) species would result from the trapping of the radical intermediate by Ni(0) followed by oxidative addition of the ArX to the Ni(III) intermediate (Scheme 2). Some of our results in Table 2 with the formation of **3ig** and **3io** highlight the importance of the oxidative addition step. However, this will necessitate more investigation to clarify that matter.

In conclusion, this study illustrates that bis-catecholato silicates are very reliable partners for photoredox/nickel dual catalysis. We have focused our efforts on the use of highly reactive primary radicals which so far has remained an uncharted territory. Our generally successful results in terms of yields and structure scope, since notably heteroatomic functions and heterocyclic platforms do not appear as limiting factors in these transformations, augur well for the application of this methodology in different settings.



Scheme 2. Proposed mechanism of the photoredox/nickel dual catalysis using silicates

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