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Aminomethylation of Aryl Halides using α -Silylamines Enabled by Ni/Photoredox Dual Catalysis

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Abstract

A protocol for the aminomethylation of aryl halides using α -silylamines via Ni/photoredox dual catalysis is described. The low oxidation potential of these silylated species enables facile single electron transfer (SET) oxidation of the amine followed by rapid desilylation. The resulting α -amino radicals can be directly funneled into a nickel-mediated cross-coupling cycle with aryl halides. The process accomplishes aminomethylation under remarkably mild conditions and tolerates numerous aryl- and heteroaryl halides with an array of functional groups.

Graphical Abstract

Keywords

aminomethylation; radicals; nickel/photoredox dual catalysis; visible light; cross-coupling

The aminomethyl subunit is found in many compounds of interest and is often a crucial linker group between complex fragments.¹ In addition to serving as a useful synthon, the aminomethyl motif is frequently found embedded within the structure of bioactive compounds, such as alkaloids derived from various plant species or in leading

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Notes

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures and characterization data for all compounds (PDF)

pharmaceuticals (Figure 1). An array of classical methods are available to install this nitrogen-containing moiety.^{2–4} Reactions in which the C–N bond is the targeted disconnection are common (e.g., reductive amination and nucleophilic displacement).² Equally as common are approaches that rely on an electrophilic α -carbon, wherein the C–C bond linking the aminomethyl group to the target of interest is formed *via* alkylation of iminium ions by carbon nucleophiles (e.g., Mannich, Strecker, or aza-Prins type reactions).³ The umpolung strategy, wherein the α -carbon serves as the nucleophile, is much less common, owing to difficulties in generating such species. To accomplish this, surrogates, such as nitroalkanes, are employed, and further functional group manipulation is required to obtain the desired aminomethylated products (i.e., reduction in the case of nitroalkanes).⁴

Transition metal-mediated cross-coupling drastically simplifies this process by enabling the direct, one-step installation of an aminomethyl unit onto aryl- and heteroaryl halides. This approach has been realized previously via the efforts of Molander, Tanaka, and Dumas.⁵ This catalytic approach nicely complements existing “go-to” approaches for aminomethylation (e.g., reductive amination or alkylation of amines) because the electrophilic partners are aryl halides or sulfonate esters as opposed to aromatic aldehydes or benzylic halides. Indeed, the latter are not as stable to long term storage, and furthermore, there are easily thousands more commercially available aryl- and heteroaryl halides than aryl/heteroaryl aldehydes or benzylic halides. Consequently, one can easily argue that structural diversity and the development of new chemical space is best served by aminomethylation of aryl- and heteroaryl halides as opposed to more traditional methods.

Although cross-couplings may provide ideal aminomethylation platforms, current protocols typically require high temperatures, designer ligands, and strongly alkaline conditions, thus limiting their broad applicability.⁵ The harsh nature of aminomethylation via cross-coupling is due, in part, to the inherent thermodynamic penalty paid to transmetalation when attempting to forge C_{sp^2} – C_{sp^3} bonds. As a general resolution to this mechanistic impediment, an odd-electron activation mode involving the concerted action of a Ni complex and visible light activated photocatalyst was conceived and simultaneously realized by our group and the groups of Mac-Millan and Doyle.^{6,7} By engaging C_{sp^3} -hybridized radicals generated by photoredox-mediated SET events with transition metal catalysts *via* facile radical metalation, C_{sp^3} – C_{sp^2} bonds can be forged under remarkably mild conditions. Utilization of the so-called “single electron transmetalation” paradigm has resulted in numerous methods for the installation of various fragments onto sp^2 -hybridized electrophiles (aryl halides, aryl triflates, alkenyl halides, and alkenyl triflates) and has been extended to C_{sp^2} –Y bond construction (Y = N, O, S, and P).⁷

In the context of this dual-catalytic process, several groups, including our own, have sought to interface various radical precursors to enhance accessible structural diversity. To date, several classes of C_{sp^3} radical precursors, including potassium alkyltrifluoroborates (R–BF₃Ks), carboxylic acids, ammonium alkylbis(catecholato)silicates, 4-alkyl-1,4-dihydropyridines (DHPs), and even activated C–H bonds, have been incorporated into the Ni/photoredox dual catalytic regime.⁸ Although numerous functional groups can be installed using these radical progenitors, aminomethylation of arenes has proved challenging because of issues related to the synthesis and/or properties of the requisite precursors. In cases where

precursors can be readily synthesized, their structural features prevent successful integration into the dual catalytic process (e.g., unprotected α -aminoalkylsilicates and alkyltri-fluoroborates exist as internal salts).^{8,9} The radicals that result from the theoretical SET oxidation of these species are destabilized by the α -ammonium motif (Figure 2). This is in stark contrast to the success encountered by MacMillan, Doyle, Rueping, and others when using dialkylanilines, where carbon-centered radicals are generated by decarboxylative fragmentation, hydrogen atom transfer (HAT), or deprotonation.^{10–12} The success incurred with these scaffolds can be attributed to their relatively low oxidation potentials coupled with α -amino radical stabilization. However, the same rationale for the successes with these systems ultimately highlight their restrictions, namely that *only activated amines* can succumb to visible light activation.

Several groups recently reported the rapid desilylative fragmentation of α -silyl tertiary amines following SET oxidation by a photo-catalyst to furnish α -amino radicals.¹³ This same fragmentation phenomena had been identified some time ago by Yoon, Mariano, and Pandey in their pioneering photochemical studies using UV irradiation.¹⁴ Because the dual catalytic system is “blind” to the origins of the radical, we surmised that α -silylamines could be integrated into the dual catalytic system (Figure 3).¹⁵ If successful, a dissonant mode of photochemical aminomethylation of aryl halides would be realized and complement existing Ni/photoredox strategies, which are limited to protected amines or aniline-based derivatives.^{9–12}

Encouraged by the extensive electrochemical studies suggesting that α -silyl tertiary amines have relatively uniform oxidation potentials (~ 0.4 – 0.8 vs SCE),¹⁶ we selected **2a** as a representative α -silylamine (which was prepared by a simple S_N2 reaction between chlorotrimethylsilane and piperidine) for optimization (Table 1). Using **1a**, we attempted the aminomethylation using previously established conditions for the dual catalytic process.⁸ We found that conditions typically used with alkylsilicates [DMF, Ru(bpy)₃(PF₆)₂, NiCl₂•dme, dtbbpy] afforded successful aminomethylation.⁸ Control experiments confirmed that this was indeed a dual catalytic process; no reaction occurred in the absence of irradiation, photocatalyst, or nickel (see Supporting Information for details). Comparable results were observed with the preformed [Ni(dtbbpy)(H₂O)₄]Cl₂ complex.

Brief optimization of the process was next pursued. A number of photocatalysts of varying excited state oxidation potentials were examined. Apart from the highly oxidizing mesityl acridinium catalyst, all gave some level of success. The more oxidizing but less reducing Ru photocatalyst, Ru(bpz)₃(PF₆)₂, was inferior to its analogous bpy complex in this process. When using iridium-based catalysts or 4CzIPN, deleterious formation of *p*-chlorobenzonitrile was observed. This latter chlorinated species was not observed when using Ru(bpy)₃(PF₆)₂ and is unreactive in cross-coupling. DMF was found to be superior to other standard solvents.⁸ Finally, two additional pre-formed bipyridyl-based Ni complexes were examined. Although these other complexes performed reasonably well in the reaction, the dtbbpy complex was optimal based on the approximate conversions obtained from GC-FID analysis. In light of these findings and the inexpensive, easily accessible nature of Ru(bpy)₃(PF₆)₂ relative to Ir-based photocatalysts, we moved forward with our initial conditions.

With the conditions established for the aminomethylation process, the scope of the transformation was next explored. In general, the reaction tolerated a number of α -silylamines, giving the cross-coupled adducts in fair to good yield (Table 2). Of note, alteration of the structure of the silyl group had a significant influence on the reaction outcome. Indeed, we later found that the dimethylphenyl variant **3a'** was superior in most cases (speculatively because of the enhanced β -silyl stabilization of the intermediate radical cation),¹⁶ whereas the electronically-poor trimethoxysilane **3a''** gave trace conversion to the aminomethylated product. In addition to being a superior agent for aminomethylation, the dimethylphenyl derivatives were more easily prepared, particularly when using low molecular weight amines. Thus, in the majority of cases, this silyl group was utilized unless it was otherwise difficult to install. Both cyclic and acyclic α -silylamines were tolerated in the dual catalytic aminomethylation process. No regioisomeric products were observed with any of the α -silylamines employed. Moreover, systems bearing chirality adjacent to nitrogen could be prepared without any stereochemical ablation, indicating the fidelity of desilylative fragmentation. Substituted ring systems and acyclic α -silylamines were similarly competent in the dual catalytic process, giving their aminomethylation products in fair yields (**3e** and **3i**). The carbamate **2f** failed to give any observable product when using the standard conditions. This may relate to its known higher oxidation potentials,¹⁶ although only trace product was observed when using a more oxidizing photo-catalyst such as [Ir{dFCF₃ppy}₂(bpy)]PF₆. Finally, performing aminomethylation on a larger scale proved viable (5 mmol, 10-fold increase) for both the trimethylsilyl as well as the dimethylphenyl derivatives without compromising yield (**3a**, **3a'**).

Subsequently, the scope of the process was examined in the context of various aryl halide coupling partners (Table 3). In general, both aryl iodides and aryl bromides performed reasonably well, with aryl iodides proving superior in scope. Indeed, whereas only neutral to electron-deficient aryl/heteroaryl bromides could be successfully aminomethylated, a range of electronically disparate aryl iodides could be incorporated.

Heterocycles such as pyridines, indoles, and quinolines were amenable to aminomethylation (**3n–o**, **3t**, and **3v**) as were strained rings (**3w**) and species that may be prone to H-atom abstraction events (**3x–y**). A system possessing functional handles (**3r**) was amenable to aminomethylation, opening up the possibility for further functionalization. Additionally, some of the prepared substrates that would not be amenable to classical methods for aminomethylation (e.g., S_NAr reactions in systems such as **3n** or **3o**) readily succumbed to the process outlined herein without issue. Likewise, the requisite aldehyde (for reductive amination) or benzyl halides (for *N*-alkylation) of many of the examples shown in Table 3 would be costly or arduous to synthesize.

To understand more fully the selective nature of photochemical oxidation under the reactions conditions, oxidation potentials of select α -silylamines and their corresponding aminomethylation products were obtained using cyclic voltammetry (Table 4). Differences in both structure and electronics were compared. Overall, the potentials of various α -silylamines were rather consistent (with carbamate **2f** being the obvious exception). Indeed, the high potential of **2f** provides a rationale for its failure in the aminomethylation process. The aminomethylated products themselves demonstrated greater variability in oxidation

potential based on structure (i.e., acyclic vs cyclic amines) and electronic perturbation of the arene. In general, the oxidation potentials of the products were ~0.3 V greater than their α -silylamine progenitors and, in most cases, were outside the oxidation potential range of the excited state of the ruthenium photocatalyst used here ($E_{1/2} [^*Ru^{II}/Ru^I] = +0.77$ V vs SCE in CH_3CN).¹⁷ This uniform difference is consistent with the absence of any observed bis-aminomethylated products and the efficiency of Ru as a photocatalyst for these systems.

In summary, α -silylamines have been successfully integrated with Ni/photoredox dual catalysis, resulting in a mild, room temperature aminomethylation process. Taking advantage of the relatively low, uniform redox potentials of these silylated species, $Ru(bpy)_3(PF_6)_2$ readily facilitates oxidative desilylative fragmentation to yield α -amino radicals of unactivated tertiary amines, which subsequently enter the cross-coupling cycle. A number of aryl halides and α -silylamines can be used successfully in the described aminomethylation process, speaking to the generality of this approach. The developed method further illustrates the versatile nature of the dual catalytic paradigm toward interfacing new radical forebears.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Representative natural or man-made molecules containing the aminomethyl motif.

Figure 2.

Utilization of α -silylamines to overcome restrictions when using α -aminoalkylsilicates or -trifluoroborates.

Figure 3.
Envisioned catalytic cycle integrating α -silyl amines with the dual catalytic manifold.

Table 1

Optimization of the Aminomethylation Process^{a,b}

entry	Dev from std cond	conv to 3a (%)
1	none	82 (60) ^c
2	Ru(bpz) ₃ (PF ₆) ₂	12
3	[Ir{dFCF ₃ ppy} ₂ (bpy)]PF ₆	88 ^d
4	Ir(ppy) ₃	85 ^d
5	MesAcr ⁺ ClO ₄ ⁻ (5 mol %)	0
6	4CzIPN (5 mol %)	89 ^d
7	DMSO	37
8	MeCN	69
9	1,4-dioxane	0
10	acetone	24
11	[Ni(bpy)(H ₂ O) ₄]Cl ₂	75
12	[Ni(diOMebpy)(H ₂ O) ₄]Cl ₂	64

4CzIPN
 $E_{1/2} (^*P/P^{\cdot-}): +1.35 \text{ V}$
 $E_{1/2} (P/P^{\cdot-}): -1.21 \text{ V}$

[Ni(dtbbpy)(H₂O)₄]Cl₂

^aOptimization reactions performed using 0.1 mmol of **1a** and 0.12 mmol of **2a** for 18 h at 27 °C.^bConversions are based on uncorrected GC-FID ratios of starting materials/products and thus are approximate, see Supporting Information for details.^cValues in parentheses indicated isolated yields on a 0.5 mmol scale of **3a** after 24 h.^dComplete consumption of **1a** with the remainder being unreactive *p*-chlorobenzonitrile.

Table 2

Scope of α -silylamines in the aminomethylation process^a

^aUnless otherwise noted reactions were performed using **1a** (1.0 equiv, 0.5 mmol), α -silylamine (1.2 equiv), $[\text{Ni}(\text{dtbbpy})(\text{H}_2\text{O})_4]\text{Cl}_2$ (5 mol %), and $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (2 mol %) in DMF (0.1 M) at rt for 24–36 h; all yields are isolated yields after purification.

^bYields in parentheses indicate yield when performed on 5 mmol scale.

Table 3

Scope of aryl halides in the aminomethylation process^a

^aUnless otherwise noted reactions were performed using **1a** (1.0 equiv, 0.5 mmol), α -silylamine (1.2 equiv), $[\text{Ni}(\text{dtbbpy})(\text{H}_2\text{O})_4]\text{Cl}_2$ (5 mol %), and $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (2 mol %) in DMF (0.1 M) at rt for 24 h; all yields are isolated yields after purification.

Table 4

Measured $E_{1/2}$ of select α -silylamines and their corresponding aminomethylation products

-Silylamines			$E_{1/2}$ (V) vs SCE

2a: +0.71 V	2a': +0.66 V	2b: +0.68 V

2d: +0.71 V	2f: +1.69 V	2h: +0.73 V	
Aminomethylated Products			$E_{1/2}$ (V) vs SCE

3a: +1.37 V	3h: +1.25 V	3d: +1.16 V

3d: +1.15 V	3j: +1.03 V	3p: +1.02 V	