



## Priority Communication

## Nickel-catalyzed cross-coupling reaction of carbamates with silylmagnesium reagents

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## ABSTRACT

The C–O bonds are kinetically inert in cross-coupling reactions compared to those of carbon–halogen bonds. Thus, developing methodologies for the activation of C–O bonds in cross-coupling reactions remains a major challenge. We disclose an unprecedented nickel mediated cross-coupling of carbamates with silylmagnesium reagents that does not require the expensive silylboranes. Silylmagnesium reagents were prepared from either silyllithium or silyl iodides. This methodology is distinguished by the synthesis of trimethylsilyl coupled product and its synthetic applications. Kinetic studies and radical clock experiments revealed the rate-limiting C–O bond cleavage, half order with respect to the catalyst and a non-radical transition state.

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## 1. Introduction

Over the past few decades, aryl halides emerged as powerful electrophiles in cross-coupling reactions though they generate toxic halide waste [1]. On the other hand, the phenolic derivatives are highly attractive electrophiles since they are more abundant, environmentally benign and affordable [2]. They often utilized in the form of sulfonates that further undergo Pd mediated cross-coupling reactions, less attention has been paid for the development of cross coupling reactions involving esters like carbamates which can be readily obtained. It is due to the inertness of C(aryl)–O bond especially in Pd catalysis and the presence of multiple reactive C–O sites [2]. Fortunately, nickel complexes possess an exceptional reactivity towards the cleavage of C(aryl)–O bond [3] and the carbamates have been successfully coupled with various nucleophiles [4–6]. In particular, aryl carbamates can be *ortho* and *para* functionalized prior to the cross-coupling event via directed *ortho* metalation (DoM) [7] or C–H activation strategies [8], whereas the ethers and pivalates are reported to be modest [4d,7a].

Organosilanes have widespread application in synthetic organic chemistry [9], medicinal [10] and material science [11]. In recent years, silylboranes ( $R_3SiBpin$ ) are regularly employed as nucleophilic coupling partner in order to introduce a silicon functional group and they are synthesized from either silyllithium or silane

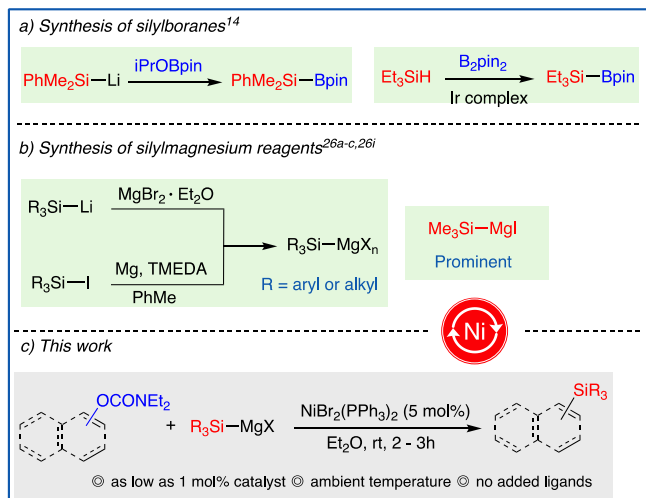
as shown in Scheme 1a [6c,12,13]. Notably, silylboranes require the use of stoichiometric base or activator for transmetalation [14]. Strategies that are atom-economical and highly efficient for the construction of C–Si bonds are compelling. Inspired by the earlier work [15,16]. We wondered if the silylmagnesium reagents can be used to cross-couple the inactive carbamate derivatives [17]. Although the silylmagnesium reagents are known for a long time (Scheme 1b) [18], they have not been explored in cross-coupling reactions [19]. Importantly, the synthesis and cross-coupling of  $Me_3SiMgI$  is crucial since the coupled product  $ArSiMe_3$  has wider scope in synthetic applications than the commonly employed  $PhMe_2Si-Bpin$  and  $PhMe_2SiMX_n$  nucleophiles [20]. Herein, we report a nickel catalyzed cross-coupling of various silylmagnesium reagents with aryl, alkenyl and benzyl carbamates, their mechanistic studies by kinetics and radical clock experiment. The pivotal role of aryl carbamates in orthogonal reactivity and its synthetic applications are also discussed.

## 2. Results and discussion

At the outset of our studies, 1-naphthyl diethylcarbamate **1a** was treated with  $PhMe_2Si-Li$  in the presence of 5 mol% of  $NiBr_2(PPh_3)_2$ , unfortunately, the cross-coupled product **4a** was obtained only in 7% yield (entry 2) along with 61% of hydrolyzed 1-naphthol [21]. The use of  $PhMe_2SiZnCl$  was ineffective with most of the carbamate recovered (entry 3). As we expected the involvement of Ni(0) in the catalytic cycle, we employed Ni(0) complexes; such as  $Ni(COD)_2$  and  $Ni(PPh_3)_4$  and observed **4a** in 16% and 76% yields respectively (entries 4 and 7). Although the use of  $CH_3CN$

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**Scheme 1.** Synthesis of organosilanes via C–O bond cleavage.

inhibited the cross-coupling of **1a** (entry 11), the use of toluene and THF offered the cross-coupled products in good yields, (entries 12 and 14) and Et<sub>2</sub>O resulted in remarkable improvement in the yield and reproducibility (entry 1). The greener solvent 2-Me-THF gave moderate yield (entry 15). Virtually none of the silylated product **4a** was formed in the absence of catalyst (entry 10). Furthermore, employing 2-naphthyl dimethylcarbamate **1ab** and 2-naphthyl diisopropylcarbamate **1ac** in place of **1a** resulted in slightly diminished yields (entries 16 and 17). Replacing 1-naphthyl pivalate instead of **1a** gave the aryl silane **4a** only in 13% yield (see S6 in SI). In order to demonstrate the practicability and to further explore the application of this methodology, the reaction was scaled up to 4.0 mmol with just 1 mol% of the catalyst **3** and the reaction was still efficient with slightly diminished yield (entry 18, Table 1).

Having identified the optimal reaction condition, we moved further to explore the scope of aryl and alkenyl carbamates. The results are summarized in Table 2. As expected, 1 and 2-naphthyl diethylcarbamates gave the silanes **4a** and **4b** in 84% and 80% isolated yields, bisilylation with excess of silylmagnesium bromide **2a** resulted in 81% of **4c**. While the fluoride is compatible (product **4q**) under the reaction condition, bromide, chloride and iodide substituents were not compatible and traces of the expected product was observed. We next turned our attention to explore the functional group tolerance, ether substituted carbamates **1d**, **1g** and **1j** offered the cross-coupled product **4d**, **4g** and **4j** in excellent yields (Table 2). Notably, the sterically congested 2-methoxy substituted carbamate **1d**, trimethylsilyl (TMS) substituent (substrate **1e**), terminal alkenes **1f**, **1i–1k**, boronic ester **1r** and morpholine substituent **1w** were well tolerated. Substrates with carbonyl or nitrile functional group are not compatible under the reaction condition [22]. Carbamates derived from enol ethers were also examined, gratifyingly, substrates **1i**, **1j** and **1k** were cross-coupled in 40% (**4i**), 85% (**4j**) and 88% (**4k**) isolated yields. The CF<sub>3</sub> substituted carbamate **1i** was also compatible [23]. It is worth to note that both electron-rich and electron-deficient groups on carbamates were compatible under the optimized condition. As heterocycles are highly attractive in the field of medicinal chemistry [24], we subjected  $\pi$ -deficient quinoline **1o**, pyridines (**1m** and **1n**), and  $\pi$ -rich pyrazole **1l** derivatives in the cross-coupling of silylmagnesium bromide **2a** and observed good to excellent yields of the corresponding *ipso*-silylated products. It has been observed that aryl carbamates with no extended  $\pi$ -system were reluctant to undergo cross-coupling reactions (see SI) [25], but pyridyl-carbamate **1m**

**Table 1**  
Optimization of the reaction condition.<sup>a</sup>

Entry	Deviation from standard conditions	Time (h)	Yield (%) <sup>b</sup>
1	None	1	89 (84) <sup>c</sup>
2	PhMe <sub>2</sub> SiLi instead of <b>2a</b>	2	7 <sup>d</sup>
3	PhMe <sub>2</sub> SiZnCl instead of <b>2a</b>	18	14
4	Ni(COD) <sub>2</sub> instead of <b>3</b>	18	16
5	NiBr <sub>2</sub> instead of <b>3</b>	18	64 <sup>e</sup>
6	NiBr <sub>2</sub> + diglyme instead of <b>3</b>	18	17
7	Ni(PPh <sub>3</sub> ) <sub>4</sub> instead of <b>3</b>	18	76
8	Ni(acac) <sub>2</sub> instead of <b>3</b>	18	77 <sup>e</sup>
9	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> instead of <b>3</b>	18	80 <sup>e</sup>
10	without <b>3</b>	12	ND
11	CH <sub>3</sub> CN instead of Et <sub>2</sub> O	18	ND
12	Toluene instead of Et <sub>2</sub> O	18	79
13	Et <sub>2</sub> O 0.1 M instead of 0.15	18	69
14	THF instead of Et <sub>2</sub> O	18	60
15	2-Me-THF instead of Et <sub>2</sub> O	18	59
16	<b>1ab</b> instead of <b>1a</b>	1	73 (70)
17	<b>1ac</b> instead of <b>1a</b>	1	80 (74)
18	1 mol% of <b>3</b> instead of 5 mol%	4	(75) <sup>f</sup>
19	Fe(acac) <sub>3</sub> /dtbbpy instead of <b>3</b>	18	70 <sup>g</sup>

<sup>a</sup> Reaction condition: 0.2 mmol of **1a**, 0.3 mmol of **2a** (0.45 M in THF), 5 mol% of NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**3**), Et<sub>2</sub>O, 0.15 M, rt (26–28 °C), 2 h.

<sup>b</sup> Determined by GC analysis using *n*-decane as internal standard, value in parentheses are isolated yield.

<sup>c</sup> Repeated a minimum of four times.

<sup>d</sup> Hydrolyzed product 1-naphthol was observed in 61% GC yield.

<sup>e</sup> Traces of reduced product naphthalene was seen.

<sup>f</sup> 4 mmol of **1a** was used.

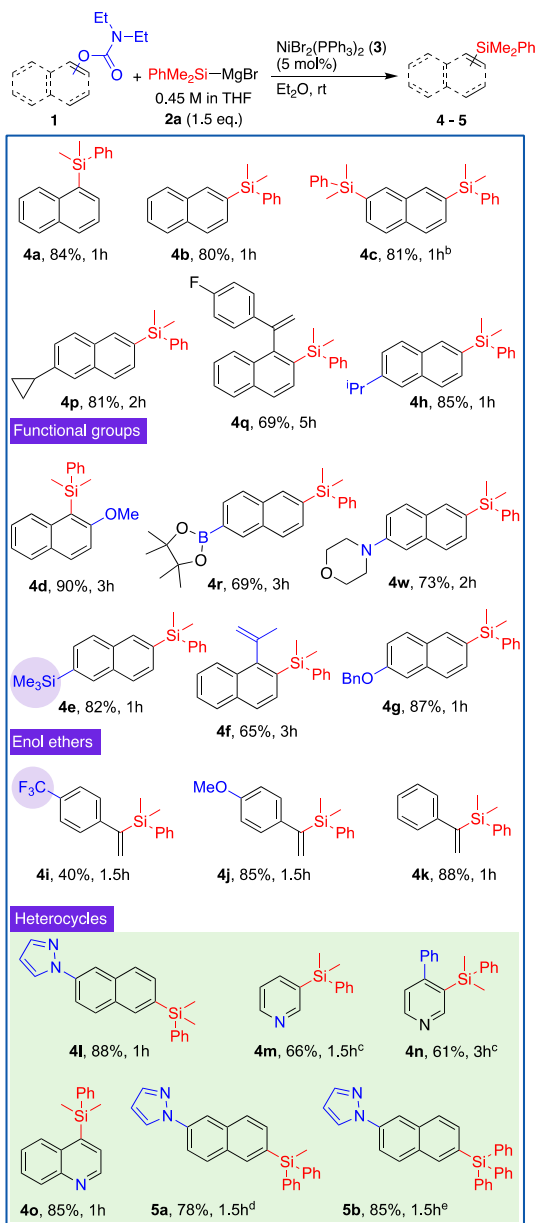
<sup>g</sup> 10 mol% of Fe(acac)<sub>3</sub> was used. Et<sub>2</sub>O: diethyl ether. ND: Not detected. **1ab**: 2-Naphthyl dimethylcarbamate, **1ac**: 2-naphthyl diisopropylcarbamate.

underwent cross-coupling reaction smoothly. This may due to the requirement of dearomatization during oxidative addition, similar observations were reported by the other research groups [6d,25].

Further studies were carried out to uncover the scope of silylmagnesium reagents [26]. It has been described in the literature that the Ar<sub>3</sub>SiMgBr can be prepared by the cation exchange of Ar<sub>3</sub>SiLi with either in-situ prepared MgBr<sub>2</sub> (from dibromoethane and Mg) [26a] or commercial MgBr<sub>2</sub>·Et<sub>2</sub>O [26b,26c]. As described above in Scheme 1, we initially prepared PhMe<sub>2</sub>SiMgBr from PhMe<sub>2</sub>SiLi which in turn was synthesized from PhMe<sub>2</sub>SiCl via lithium/halogen exchange [15a,26a,26j,27]. This protocol was extended further for the synthesis of silylmagnesium reagents **2b** and **2c** [26a]. Although the reagents **2a–c** offered the cross-coupling product **4** in excellent yields (entries 1–3, Table 3), the synthetic application of **4a** is very limited due to (i) the presence of multiple arenes on silicon center which may cause selectivity issues, (ii) synthetic transformations of biaryl-substituted silanes are rare [28]. This forced us to turn our attention to the synthesis of trimethylsilyl substituted arenes (Ar-TMS) since substrates of this type can readily undergo various transformations [29]. Unlike PhMe<sub>2</sub>SiCl, the direct lithiation of Me<sub>3</sub>SiCl cannot be carried out [30], hence we prepared Me<sub>3</sub>SiLi from hexamethyldisilane (Me<sub>3</sub>Si–Si–SiMe<sub>3</sub>) as described in the literature [27d,31], subsequent cation exchange with MgBr<sub>2</sub>·Et<sub>2</sub>O offered Me<sub>3</sub>SiMgBr, which furnished moderate yield in the cross-coupling of **1a** [21]. Fortunately, we came across a protocol [26i] that uses Me<sub>3</sub>Si–I, magnesium and TMEDA to prepare Me<sub>3</sub>SiMgI and with a little modification we prepared Me<sub>3</sub>SiMgI that gave us excellent yield in the cross-coupling of **1a** (entry 4, Table 3) [32].

Concurrent with the above studies, benzylic carbamates **1v** and **1x** underwent cross-coupling reaction with PhMe<sub>2</sub>SiMgBr to offer

**Table 2**  
Silylation of aryl and alkenyl carbamates: scope.<sup>a</sup>



<sup>a</sup> Reaction condition: 0.45 mmol of **1**, 0.67 mmol of **2a** (0.45 M in THF), 5 mol% of NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**3**), Et<sub>2</sub>O (0.15 M), rt (26–28 °C), isolated yield.

<sup>b</sup> 2.5 eq. of **2a**.

<sup>c</sup> Toluene instead of Et<sub>2</sub>O along with 0.3 eq. of AgF.

<sup>d</sup> Ph<sub>2</sub>MeSiMgBr used instead of PhMe<sub>2</sub>SiMgBr.

<sup>e</sup> Ph<sub>3</sub>SiMgBr used instead of PhMe<sub>2</sub>SiMgBr.

the coupled products **4v** and **4x** in 89% and 92% isolated yields (Scheme 2).

In order to explore the synthetic application of the cross-coupled product **4**, trimethyl(naphthalen-1-yl)silane **4u** was subjected to halogenation in the presence of various N-halosuccinimides, and the corresponding 1-chloro, 1-bromo and 1-iodo substituted naphthalenes were isolated in excellent yields (Scheme 3a). Furthermore, **4u** was also employed in the palladium catalyzed coupling of 3-methylthiophene via C–H activation, the cross-coupled 3-methyl-4-(naphthalen-1-yl)thiophene **6b** was isolated in 60% yield (Scheme 3) [29h].

As discussed earlier, aryl carbamates are excellent directed metalation groups (DMG) [7]. In order to demonstrate the synthetic

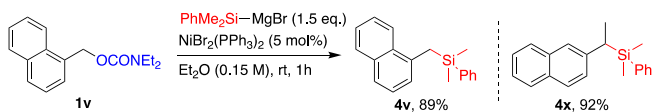
**Table 3**  
The scope of silylmagnesium reagents.

Entry	<b>2</b>	Yield (%) <sup>a</sup>
1	PhMe <sub>2</sub> SiMgBr ( <b>2a</b> )	84
2	Ph <sub>2</sub> MeSiMgBr ( <b>2b</b> )	80
3	Ph <sub>3</sub> SiMgBr ( <b>2c</b> )	82
4	Me <sub>3</sub> SiMgI ( <b>2d</b> )	93 <sup>b</sup>

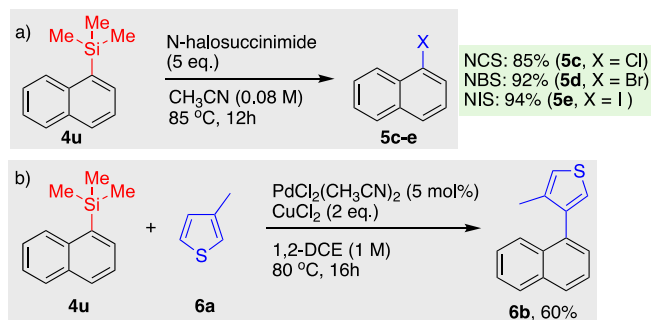
4a: SiMe<sub>2</sub>Ph  
4s: SiMePh<sub>2</sub>  
4t: SiPh<sub>3</sub>  
4u: SiMe<sub>3</sub>

<sup>a</sup> Yields are isolated.

<sup>b</sup> THF was used instead of Et<sub>2</sub>O, 5 h.



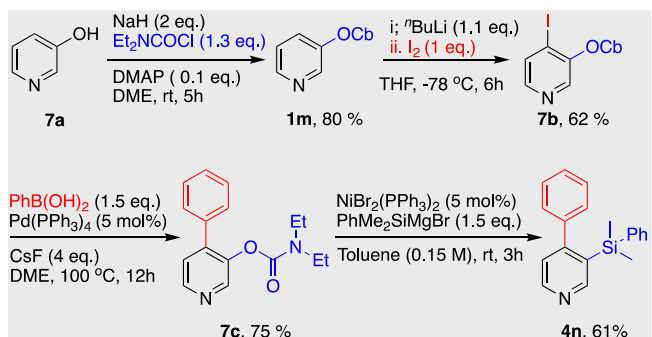
**Scheme 2.** Cross-coupling of alkyl carbamate.



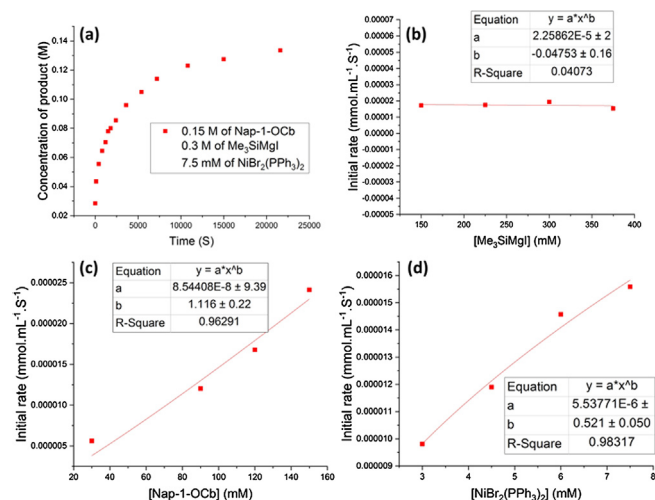
**Scheme 3.** Synthetic application of aryl silane.

application of the methodology, we explored the orthogonal reactivity of the carbamate as shown in Scheme 4 [33], where the *ortho*-lithiation/iodination of **1m** afforded the intermediate **7b**. A chemoselective palladium catalyzed cross-coupling with phenylboronic acid followed by the nickel mediated cross-coupling with silylmagnesium bromide under the optimized condition afforded the cross-coupled product **4n** in 61% yield.

We studied the quantitative kinetics of the reaction between **1a** and Me<sub>3</sub>SiMgI in order to elucidate the mechanism (Fig. 1) [34]. The order of the reaction with respect to each reagent was determined using initial rates (*k*<sub>in</sub>). Plots of initial rate versus the concentration of each reagent are shown in Fig. 1. As expected, a



**Scheme 4.** Orthogonal reactivity.



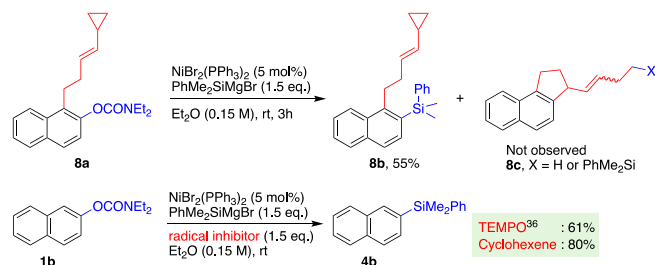
**Fig. 1.** (a) A representative kinetic time-course for the  $\text{NiBr}_2(\text{PPh}_3)_2$  catalyzed cross-coupling of **1a**. (b) Plot of  $k_{\text{in}}$  versus  $[\text{Me}_3\text{SiMgI}]$ . (c) Plot of  $k_{\text{in}}$  versus  $[\mathbf{1a}]$ . (d) Plot of  $k_{\text{in}}$  versus  $[\text{NiBr}_2(\text{PPh}_3)_2]$ .

zero-order ( $-0.0475 \pm 0.166$ ; Fig. 1b) dependence on the concentration of the  $\text{Me}_3\text{SiMgI}$  over a range of 150–375 mM was observed, the reaction showed first-order ( $1.116 \pm 0.22$ ; Fig. 1c) dependence on the concentration of the carbamate **1a** over a range of 30–150 mM. Notably, a half-order ( $0.521 \pm 0.050$ ; Fig. 1d) dependence on the concentration of  $\text{NiBr}_2(\text{PPh}_3)_2$  over a range of 3–7.5 mM was observed and this may be attributed to the dissociation of ligands from  $\text{NiBr}_2(\text{PPh}_3)_2$  or the dimerization of nickel complex [3,34d]. The kinetic data obtained here reveals that the oxidative addition of carbamate to the nickel complex must be the rate-limiting step.

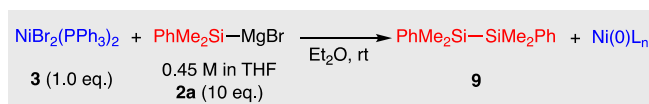
In order to identify the nature of the intermediate, we prepared a radical clock substrate **8a** and subjected to the optimized reaction condition as shown in scheme 5 [12b]. The uncyclized product **8b** was isolated in 55% yield and we have not observed the cyclized product **8c**, also the reaction with TEMPO [35] and cyclohexene did not inhibit the reaction that may rule out a carbon-centered radical as the transition state.

When  $\text{NiBr}_2(\text{PPh}_3)_2$  (1.0 eq.) and  $\text{PhMe}_2\text{SiMgBr}$  (10 eq.) were mixed, instant formation of  $\text{PhMe}_2\text{Si-SiMe}_2\text{Ph}$  was observed. However, the concentration of disilane remains constant throughout the course of the reaction, which may be an indication to the formation of  $\text{Ni}(0)\text{L}_n$  (Scheme 6) [34a]. Subjecting  $\text{PhMe}_2\text{Si-SiMe}_2\text{Ph}$  instead of **2a** did not offer the expected product that rules out  $\text{PhMe}_2\text{Si-SiMe}_2\text{Ph}$  as the source silicon nucleophile [34h,34i].

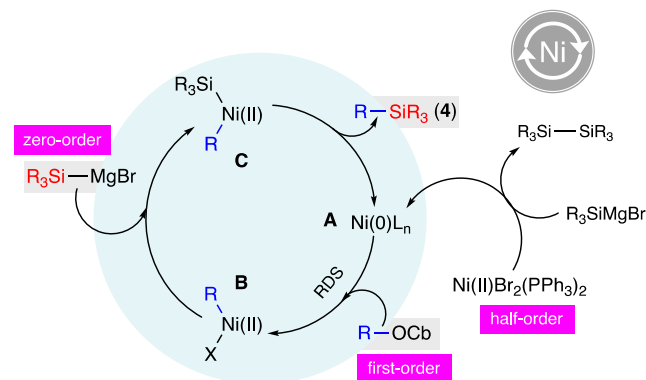
Although a detailed mechanistic study has been initiated, we propose a plausible mechanism based on the above-mentioned studies. We hypothesize the formation of an active  $\text{Ni}(0)$  catalyst **A** upon mixing  $\text{NiBr}_2(\text{PPh}_3)_2$  and  $\text{R}_3\text{SiMgBr}$ . Subsequent oxidative addition (RDS) of the  $\text{R-OCb}$  to  $\text{Ni}(0)\text{L}_n$  (**A**) generates  $\text{Ni(II)}$  intermediate **B** [36]. Further, intermediate **B** undergoes transmetalation



**Scheme 5.** Radical clock experiment.



**Scheme 6.** Formation of disilane and  $\text{Ni}(0)$ .



**Scheme 7.** Mechanistic proposal.

with the silylmagnesium reagent to give intermediate **C**, which releases the cross-coupled product **4** via reductive elimination (Scheme 7).

### 3. Conclusions

In summary, we have developed an unprecedented cross-coupling reaction that utilizes inexpensive, bench-stable catalyst  $\text{NiBr}_2(\text{PPh}_3)_2$ . This methodology has a wide scope with respect to relatively inert  $\text{C}(\text{sp}^2)\text{-O}$  carbamates and silylmagnesium reagents. The  $\text{C}(\text{sp}^3)\text{-O}$  carbamates have also been successfully employed in the cross-coupling reactions. The synthetic application of this methodology was shown in the orthogonal reactivity of the carbamate in combination with directed *ortho* metalation (DoM). Studies aimed at expanding the scope of silylmagnesium reagents in asymmetric cross-coupling reactions are currently advancing in our laboratory.

### Declaration of Competing Interest

There are no conflicts to declare.

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### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2019.07.026>.

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