A Mild Ni/Cu-Catalyzed Silylation via C−O Cleavage

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Ⓢ *Supporting Information*

ABSTRACT: A Ni/Cu-catalyzed silylation of unactivated C−O electrophiles derived from phenols or benzyl alcohols is described. This transformation is characterized by its wide scope and mild conditions, providing a direct access to synthetically versatile silylated compounds. The protocol allows for the coupling of C(sp^2)−O and even C(sp^3)−O bonds with similar efficiency.

Multimetallic catalysis has recently received a considerable interest for designing unconventional synthetic strategies that are unattainable by other means.[1] Among these, the use of Pd and Cu catalysts has shown to be particularly effective in methodologies that have changed the landscape of organic synthesis, such as the Sonogashira−Hagihara coupling[2] or the Wacker−Tsuji oxidation,[3] among others. While Ni catalysts play a dominant role in the cross-coupling arena,[4] it comes as a surprise that the combination of Ni and Cu catalysts has been virtually unexplored in homogeneous catalysis.[5] Therefore, the discovery of new protocols within this field might lead to novel synthetic routes toward advanced intermediates, counterintuitive at first sight, thus increasing our organic chemist's repertoire.

In recent years, the utilization of C−O electrophiles has received considerable attention due to their lack of toxicity and the readily availability of phenol as compared to commonly employed organic halides.[6] Unlike the use of activated aryl sulfonates, a limited knowledge has been acquired when employing simpler aryl esters via catalytic C−O cleavage. This is probably due to the high activation barrier for C−O cleavage, the proclivity of esters toward hydrolysis under strong basic conditions, and the site-selectivity issues in the presence of multiple C−O reaction sites.[6] Despite the advances realized, the vast majority of C−O bond-cleavage reactions are restricted to the formation of C−C bonds. Indeed, the development of catalytic C-heteroatom bond-forming reactions remains an elusive task in the cross-coupling arena when utilizing unactivated C−O bonds.[7] We envisioned that organic silanes, valuable synthetic intermediates of considerable interest in medicinal and material science,[8] could be within reach by a C−Si bond-forming event from unactivated C−O electrophiles under certain reaction conditions. Such a method would constitute an alternative to classical metal/halogen exchange (Scheme 1, path a),[9] the coupling of aryl halides with R$_3$SiH[10a−c] or (R$_3$Si)$_2$ counterparts[10d−f] (path b) and C−H[11a−d] or C−CN functionalization techniques[11e,f] that are conducted at high temperatures[11] and using *ortho*-directing groups[11a−d] (path c). As part of our ongoing studies in this field,[12] we report herein the discovery of a Ni/Cu catalytic couple that allows for a C−Si

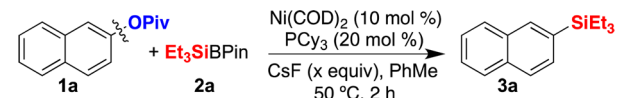## Scheme 1. Synthesis of Aryl and Aliphatic Silanes
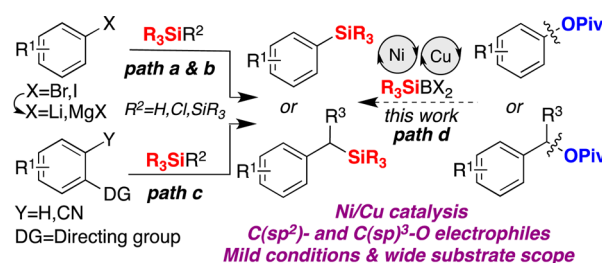
bond-forming reaction via cleavage of unactivated C−O bonds in ester derivatives (path d).[13] The method is distinguished by its mild conditions, robustness, and wide substrate scope, including the formation of particularly elusive C(sp^3)−Si bonds,[14] without compromising its application profile.

We began our investigations by examining the reactivity of **1a** using nickel catalysts (Table 1).[15,16] While silylboranes have extensively been employed for promoting silylborylation of unsaturated C−C bonds,[17] to the best of our knowledge their utilization en route to aryl silanes has not been explored. As shown in entry 3, we found promising results when employing readily available **2a**,[18] Ni(COD)$_2$ as the catalyst, and PCy$_3$ as the supporting ligand at 50 °C. In line with our studies in the field, we found that the absence of COD had a deleterious impact on reactivity (entries 1 and 2), suggesting that non-innocent ancillary ligands might stabilize the active species within the catalytic cycle.[12] As anticipated,[17] additives played a crucial role by activating the Si−B bond (entries 4−15). As shown in entries 6−8, the inclusion of AgF or CuF$_2$ was rather promising for our purposes, suggesting the intermediacy of MSiEt$_3$ species (M = Ag(I), Cu(II)).[19] While the addition of CsF (1 equiv) in combination with CuF$_2$ (30 mol %) had a cooperative effect on reactivity, obtaining a 90% isolated yield of **3a** (entry 10), the use of structurally related KF and more soluble fluoride sources such as TBAF or K$_3$PO$_4$, among others, had a deleterious effect (entry 9). We believe these results indicate an intimate and unique interplay of CuF$_2$ and CsF and suggest that CuF$_2$ does not simply act as a soluble fluoride source.[20] Such perception was further corroborated when comparing the results shown in entry 5 and entries 7−9 with entry 10. A simple filtration of the crude mixture through a plug of Celite was necessary, thus greatly simplifying the workup. Interestingly, the counterion and oxidation state of the additives utilized were found to be critical factors for success (entries 12−15). Control experiments in which the Ni catalyst

Table 1. Optimization of the Reaction Conditions[a]
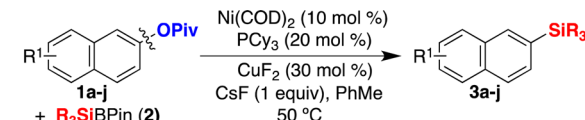
entry	Ni catalyst	CsF (x)	additive (mol %)	3a (%)[b]
1	Ni(PCy$_3$)$_2$(C$_2$H$_4$)	0	—	1
2	NiCl$_2$(PCy$_3$)$_2$	0	—	0[c]
3	Ni(COD)$_2$	0	—	11
4	Ni(COD)$_2$	0	CsF (30)	10
5	Ni(COD)$_2$	0	CsF (100)	10
6	Ni(COD)$_2$	0	AgF (30)	20
7	Ni(COD)$_2$	0	CuF$_2$ (30)	10
8	Ni(COD)$_2$	0	CuF$_2$ (50)	18[d]
9	Ni(COD)$_2$	0	CuF$_2$ (30)	0[e], 1[f], 24[g]
10	**Ni(COD)$_2$**	**1**	**CuF$_2$ (30)**	**94(90)[h]**
11	Ni(COD)$_2$	1	CuF$_2$ (30)	88 (85)[h,i]
12	Ni(COD)$_2$	1	AgF (30)	21
13	Ni(COD)$_2$	1	CuBr$_2$ (30)	0
14	Ni(COD)$_2$	1	CuSO$_4$ (30)	20
15	Ni(COD)$_2$	1	CuI (30)	0
16	—	1	CuF$_2$ (30)	0

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.30 mmol), Ni(COD)$_2$ (0.025 mmol), PCy$_3$ (0.05 mmol) in toluene (2.0 mL), 50 °C, 2 h. [b]GC yields using decane as an internal standard. [c]Zn (0.25 mmol) was used. [d]Similar result was obtained with CuF$_2$ (100 mol %). [e]TBAF (1 equiv) as additive. [f]K$_3$PO$_4$ (1 equiv) as additive. [g]KF (1 equiv) as additive. [h]Isolated yield. [i]110 °C.

was omitted resulted in no product formation (entry 16). Similarly, little conversion was observed in the absence of CuF$_2$ (entries 3 and 5), suggesting that both Ni and Cu assist the C−O cleavage/C−Si bond-forming event. Although silylboranes have been used as a platform for preparing aryl boronates,[18,21] no traces of C−B bond-formation were detected by NMR spectroscopy of the crude mixture, hence showing the distinctive features of our protocol.
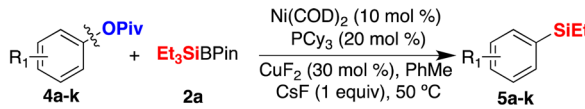
Next, we turned our attention to study the preparative scope of our reaction. As shown in Table 2, the outcome was largely insensitive to changes in the electronic nature of the substrates utilized, obtaining the desired compounds in excellent yields using **2a** as coupling counterpart. Interestingly, we found that the coupling of **2aa** resulted in moderate yields of **3aa**, hence showing the superior activity of **2a**.[22] The chemoselectivity profile of the method is nicely illustrated by the fact that ethers (**3b**, **3d**), esters (**3e**, **3h**), amides (**3g**), or silyl ethers (**3i**) were perfectly tolerated under our optimized protocol. As shown for **3h**, the reaction was not seriously hampered by the presence of *ortho*-substituents, although slightly higher temperatures were required in this case. While C(sp^2)−F bonds are prone to oxidative addition in the presence of Ni catalysts with PCy$_3$ as supporting ligand,[23] we found that such motifs remained intact under our reaction conditions (**3f**). Similarly, the presence of nitrogen-containing heterocycles did not interfere with the productive C−Si bond-forming reaction (**3j**).

A closer look into the literature data indicates that the inclusion of π-extended systems greatly accelerates the rate of C(sp^2)−O bond-cleavage reactions.[24] Encouraged by the findings in Table 2, we speculated that our mild Ni/Cu-catalyzed silylation event could be even extended to the use of simpler, yet challenging, phenyl pivalates. As shown in Table 3, this was indeed the case, and a wide variety of phenyl pivalates, regardless of the electronic effects on the aryl ring, could be coupled in high

Table 2. Ni-Catalyzed Silylation of Naphthyl Pivalates[a,b]

[a]Reaction conditions: **1** (0.50 mmol), **2a** (0.60 mmol), Ni(COD)$_2$ (10 mol %), PCy$_3$ (20 mol %), CuF$_2$ (30 mol %), CsF (1 equiv) in toluene (3.0 mL) at 50 °C. [b]Isolated yields, average of at least two independent runs. [c]PhMe$_2$SiBpin (**2aa**) was utilized. [d]80 °C.

Table 3. Ni-Catalyzed Silylation of Phenyl Pivalates[a,b]

[a]As for Table 2. [b]Isolated yields, average of at least two independent runs. [c]GC yields using decane as an internal standard due to volatility issues. [d]Reaction conducted at 80 °C. [e]**2a** (1.0 mmol) and CsF (1.70 equiv).

yields (**5a−5k**). It is worth noting that the coupling of phenyl and naphthyl pivalates (Tables 2 and 3) operates under otherwise identical reaction conditions, an observation that demonstrates the robustness and generality of our Ni/Cu-catalyzed event. In analogy with the results in Table 2, the presence of *ortho*-substituents did not hinder the C−Si bond-forming reaction (**5g**, **5h**). Likewise, a number of functional groups such as boronic esters (**5c**), ketones (**5d**), amines (**5f**), acetals (**5i**, **5k**), and

heteroaromatics (**5j**) could also be equally accommodated in good to excellent yields.

To the best of our knowledge, a catalytic C-heteroatom bond-forming reaction via the cleavage of unactivated C(sp^3)−O bonds has no precedents in the literature.[25] Gratifyingly, we observed that primary and even secondary benzylic pivalates could be cross-coupled with **2a** in good yields (Table 4).

Table 4. C(sp^3)−O Cleavage/C−Si Bond Formation^{a,b}

73% (**7a**)^c 46% (**7b**)^c 79% (**7c**)
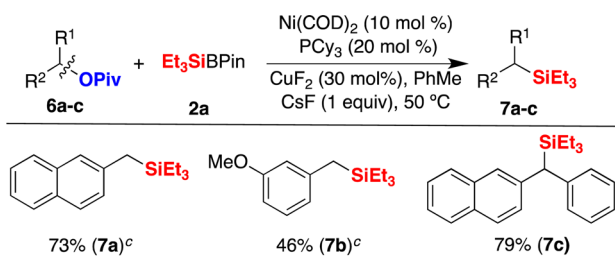
^{a}As for Table 2. ^{b}Isolated yields, average of at least two independent runs. ^{c}Reaction conducted at 80 °C.

Importantly, no reoptimization of the reaction conditions was required, a rather valuable finding that demonstrates the outcome of our method. Overall, we believe the results shown in Tables 2−4 nicely illustrate the excellent reactivity and the wide application profile of our Ni/Cu-catalyzed C(sp^2)− and C(sp^3)−O bond-cleavage protocol, suggesting that other conceivable scenarios might be discovered in the near future.[26]

Although a detailed mechanistic picture requires further studies, we tentatively propose a scenario consisting of two catalytic cycles (Scheme 2). Thus, we favor an initial oxidative

Scheme 2. Mechanistic Proposal
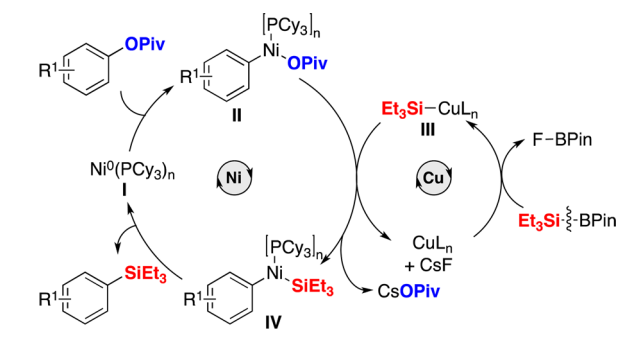
addition of the C(sp^2)−O bond to Ni(0) (**II**).[27] Then, a transmetalation event facilitated by in situ generated **III**,[28,29] followed by a reductive elimination delivers the final product while recovering back the active Ni(0)L$_n$ catalytic species **I**. Whether other mechanistic pictures come into play[30] or the reaction involves single-electron transfer processes is subject of ongoing studies in our laboratory.

In summary, we have discovered a Ni/Cu-catalyzed C−Si bond-forming reaction via C(sp^2)− and even C(sp^3)−O bond cleavage.[31] This study suggests that other related multimetallic scenarios might lead to the foundation of new discoveries within the field of Ni-catalyzed cleavage of unactivated C−O bonds. The wide substrate scope, mild reaction conditions, robustness, and generality of the method suggest that this protocol can be a powerful alternative to existing methodologies for preparing organic silanes from readily available precursors. Further

mechanistic studies and other related transformations are currently underway in our laboratories.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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