

A Mild and Ligand-Free Ni-Catalyzed Silylation via C–OMe Cleavage

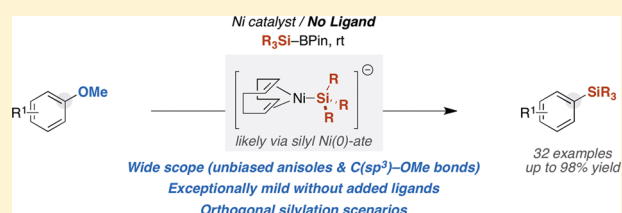
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S Supporting Information

ABSTRACT: Metal-catalyzed transformations that forge carbon–heteroatom bonds are of central importance in organic synthesis. Despite the formidable potential of aryl methyl ethers as coupling partners, the scarcity of metal-catalyzed C–heteroatom bond formations via C–OMe cleavage is striking, with isolated precedents requiring specialized, yet expensive, ligands, high temperatures, and π -extended backbones. We report an unprecedented catalytic *ipso*-silylation of aryl methyl ethers under mild conditions and without recourse to external ligands. The method is distinguished by its wide scope, which includes the use of benzyl methyl ethers, vinyl methyl ethers, and unbiased anisole derivatives, thus representing a significant step forward for designing new C–heteroatom bond formations via C–OMe scission. Applications of this transformation in orthogonal silylation techniques as well as in further derivatizations are also described. Preliminary mechanistic experiments suggest the intermediacy of Ni(0)-ate complexes, leaving some doubt that a canonical catalytic cycle consisting of an initial oxidative addition of the C–OMe bond to Ni(0) species comes into play.

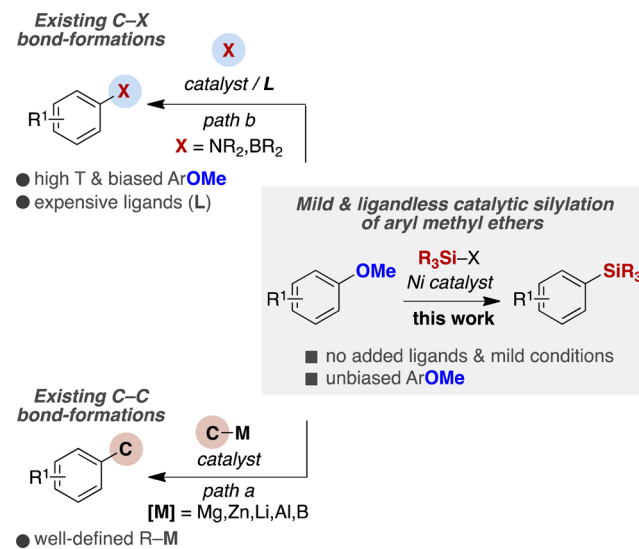


INTRODUCTION

Over the past decade, C–O electrophiles have matured into robust and reliable alternatives to organic halides within the cross-coupling arena owing to the low cost, ready availability, and benign character of phenol.¹ Unlike the use of relatively activated C–O electrophiles that easily undergo oxidative addition, such as aryl sulfonates, esters, or carbamates, the employment of aryl methyl ethers, arguably the simplest and most atom-economical derivatives in the phenol series, has received considerably less attention.² This observation is probably attributed to the remarkably high activation barrier required for effecting C(sp²)-OMe cleavage and the lower tendency of methoxy residues to act as leaving groups.² Indeed, a close look into the literature data reveals that the vast majority of cross-coupling reactions of organic electrophiles, such as aryl halides, esters, carbamates, or sulfonates, among others, perfectly tolerate the presence of aryl methyl ethers, evidencing their lower propensity to undergo C–OMe cleavage.³

At present, catalytic cross-coupling reactions of aryl methyl ethers remain largely confined to C–C bond-forming endeavors based on stoichiometric, highly reactive, and in most instances air-sensitive organometallic reagents (Scheme 1, path a).² Although metal-catalyzed carbon–heteroatom bond-forming reactions are of central importance in organic synthesis,⁴ it comes as a surprise that these transformations have rarely been designed with aryl methyl ethers as coupling partners. The existing precedents for tackling this challenge are currently based on amination or borylation protocols, necessarily requiring the inclusion of electron-rich and expensive ligands such as PCy₃ or *N*-heterocyclic carbenes (NHCs), as well as rather elevated temperatures (Scheme 1,

Scheme 1. Cross-Coupling Reactions via C–OMe Cleavage



path b).⁵ Additionally, π -extended backbones are essential for these reactions to occur unless appropriate activating groups are located at either *ortho* or *para* position relative to the targeted methoxy group.⁵ It is worth noting that these features are recurrent prerequisites found in a myriad of C–O bond-functionalization reactions, significantly limiting the synthetic

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utility and prospective impact of these rather appealing processes.^{6,7}

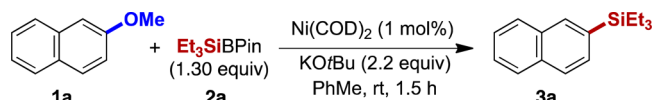
Prompted by the perception that C(sp²)-OMe functionalization might occur by pathways other than “classical” oxidative addition,⁸ we recently questioned whether a mild C-heteroatom bond-forming reaction via C(sp²)-OMe cleavage without recourse to any added dative ligand, harsh conditions, or highly reactive stoichiometric organometallic reagents could ever be implemented.⁹ We anticipated that the successful realization of such a catalytic technique could provide a palette of conceptually new tactics not apparent at first sight while significantly improving our knowledge when using simple aryl methyl ethers as coupling partners via C-OMe scission. As part of our ongoing interest in catalytic C-O functionalization reactions,¹⁰ we describe herein a mild Ni-catalyzed *ipso*-silylation of aryl methyl ethers en route to aryl silanes, privileged intermediates of utmost relevance in organic synthesis and materials science (Scheme 1, right pathway).¹¹ This catalytic protocol is distinguished by its ligandless conditions¹² and wide substrate scope at room temperature with exceptional ease, including the coupling of benzyl and vinyl methyl ethers as well as the always-elusive *unbiased* anisole derivatives. The unique features of this transformation are illustrated in orthogonal silylation scenarios as well as in further derivatization techniques. Initial mechanistic studies reveal that a canonical catalytic cycle consisting of an initial oxidative addition of the C-OMe bond to Ni(0)L_n does not come into play, suggesting the involvement of Ni(0)-ate complexes.

RESULTS AND DISCUSSION

We started our investigations by studying the reaction of **1a** with **2a**, an easily accessible silyl boronate, in bulk quantities and in a single step.^{13,14} After some experimentation,¹⁵ we found that a simple cocktail containing Ni(COD)₂ (1 mol%) and KOtBu in PhMe at room temperature provided the best results, affording **3a** in 88% isolated yield after 1.5 h (Table 1, entry 1). This outcome was unexpected, as the available literature data on catalytic C(sp²)-OMe cleavage,² particularly with heteroatom-based nucleophiles, unanimously encouraged the employment of electron-rich ligands at elevated temperatures and higher catalyst loadings.⁵ As shown in entries 2 and 3, Ni precatalysts other than Ni(COD)₂ resulted in lower conversions to **3a**, even at higher catalyst loadings. Although tentative, these results suggest that COD may serve as a noninnocent ancillary ligand within the catalytic cycle.¹⁶ As shown in entry 4, 2-naphthyl ethyl ether provided lower yields of **3a**, indicating an intimate interplay of reactivity with steric effects.¹⁷ As expected, the basic conditions employed resulted in quantitative formation of 2-naphthol via C(acyl)-O cleavage when using 2-naphthyl pivalate as substrate (entry 5). Although the use of PCy₃ or bulky NHCs has shown to be critical in other C-heteroatom bond formations,⁵ the inclusion of these ligands was inconsequential (entries 6 and 7).

Another noteworthy observation concerns the nature of the base and escorting counterion. Specifically, a comparison of entry 1 vs entries 8 and 9 showcases the unique competence of K⁺, suggesting that the counterion may play a more important role than initially anticipated. These results are somewhat reminiscent of recent literature data that demonstrates the noninnocent role of counteranions in reactions of aryl ethers,^{8a-c} contributing to the perception that a “nonclassical” scenario might come into play. As shown in entries 10 and 11, no reactivity was found for KOMe or KHMDS, evidencing that

Table 1. Optimization of the Reaction Conditions^a

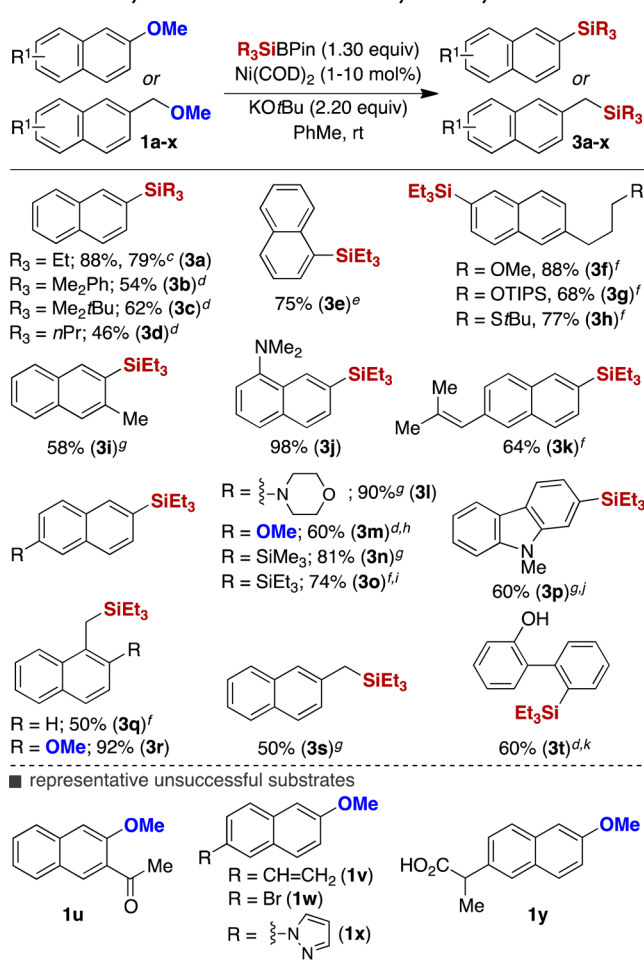


entry	deviation from standard conditions	3a (%) ^b
1	none	100 (88) ^c
2	using NiBr ₂ ·DME (5 mol%) for 16 h	41, 39 ^d
3	using Ni(acac) ₂ for 16 h	62, 72 ^d
4	using 2-naphthyl ethyl ether instead of 1a	79
5	using 2-naphthyl pivalate instead of 1a	0
6	using PCy ₃ (2 mol%)	100
7	using IPr-HCl (2 mol%)	88
8	NaOtBu instead of KOtBu	0
9	Mg(OtBu) ₂ instead of KOtBu	0
10	KOMe instead of KOtBu	0
11	KHMDS instead of KOtBu	0
12	CsF or KF instead of KOtBu	0
13	THF instead of PhMe	14
14	DME instead of PhMe	2
15	HMPA instead of PhMe	0
16	T = 0 °C for 16 h	100
17	using (Et ₃ Si) ₂ instead of 2a	0
18	no Ni(COD) ₂ or no KOtBu	0

^aReaction conditions: **1a** (0.25 mmol), **2a** (1.30 equiv) mmol, Ni(COD)₂ (1 mol%), KOtBu (2.20 equiv), PhMe (0.20 M), 25 °C, 1.5 h. ^bGC yields using decane as internal standard. ^cIsolated yield. ^dZn (1.0 equiv).

a subtle balance of nucleophilicity and steric bulk of the base is required. Although fluoride salts have shown to be competent in related silylation events,^{10c} no conversion to **3a** was observed when using these reagents (entry 12). Equally striking was the influence of the solvent utilized, as THF and DME were equally unsuitable (entries 13 and 14). Similarly, highly polar solvents such as HMPA, previously shown to effectively promote nucleophilic aromatic silylation of aryl halides,¹⁸ failed to provide the targeted **3a** (entry 15). It is worth noting that the reaction can be efficiently conducted at 0 °C,¹⁵ albeit prolonged reaction times were required to reach full conversion (entry 16). Interestingly, the use of disilanes as silicon sources resulted in no conversion of **1a** to **3a** (entry 17), demonstrating the unique reactivity of **2a**. Rigorous control experiments in the absence of either Ni(COD)₂ or KOtBu revealed that these reaction parameters were crucial for the C-OMe silylation to occur (entry 18).¹⁹

With robust conditions in hand, we turned our attention to examine the preparative scope and limitations of our Ni-catalyzed *ipso*-silylation of aryl methyl ethers.¹⁹ As shown in Table 2, a host of differently substituted π -extended aryl methyl ethers reacted perfectly well, including those bearing aliphatic ethers (**3f**), silyl ethers (**3g**), thioethers (**3h**), amines (**3j**, **3l**), or even heteroaromatic rings (**3p**), delivering the targeted aryl silanes in good to excellent yields. Extensions to silyl boronates other than **2a** required higher catalyst loadings and elevated temperatures (**3b-3d**), an observation likely attributed to a combination of optimal steric and electronic effects. As shown for **3t**, the C(sp²)-O bond of dibenzofuran posed no problems in the silylation event. Particularly noteworthy was the observation that low catalyst loadings generally suffice to effect the silylation at room temperature, suggesting that the reactivity of our active Ni catalyst might surpass that of related NiL_n species (L = PCy₃, NHC) used in previous C-heteroatom

Table 2. Silylation of π -Extended Aryl Methyl Ethers^{a,b}

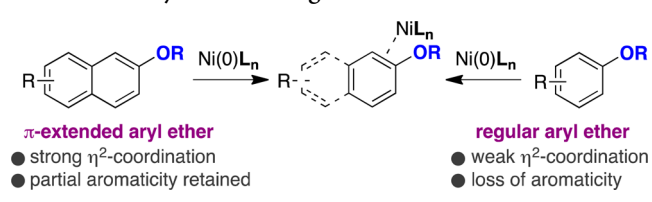
^aAs Table 1 (entry 1). ^bIsolated yields, average of at least two independent runs. ^c**1a** (10 mmol). ^d $\text{Ni}(\text{COD})_2$ (10 mol%) at 95 °C. ^e40 °C. ^f $\text{Ni}(\text{COD})_2$ (5 mol%). ^g $\text{Ni}(\text{COD})_2$ (10 mol%). ^h**1o**:**2a** = 3.3:1 ratio. ⁱ**2a** (2.60 equiv), KOtBu (4.40 equiv). ^j**2a** (1.75 equiv), KOtBu (4.50 equiv). ^kUsing dibenzofuran as substrate at 40 °C.

bond formations.⁵ Importantly, the reaction of **1a** can be conducted at 10 mmol scale without significant erosion in yield (**3a**, 79%). Substrates bearing more than one methoxy group could be subject to mono- or bis-silylation by carefully adjusting the stoichiometry of the reaction (**3m**, **3o**). Electronically unbiased substituents at the position *ortho* to the reactive site did not impede the silylation (**3i**), albeit moderate yields were obtained in these cases. While no competitive silaboration, silylation, or isomerization was observed at the alkene terminus in **3k**,¹⁴ conjugated terminal alkenes resulted in a formal hydrosilylation (**1v**). The presence of ketones (**1u**) or pyrazole residues did interfere (**1x**); while silyl anion attack across the carbonyl–oxygen double bond accounts for the former,²⁰ the lack of reactivity of the latter is attributed to irreversible binding to $\text{Ni}(0)$. Unfortunately, the presence of acidic hydrogens was not tolerated, even with excess amounts of KOtBu , recovering **1y** unaltered. Interestingly, bis-silylation at the C–Br and C–O bond was mainly observed with **1w**, a result that is in contrast with the borylation of carbon–halogen bonds with silyl boronates.²¹ As shown for **3q–3s**, the reaction could be extended to benzylic $\text{C}(\text{sp}^3)$ –OMe bonds with similar ease. It is worth mentioning that significant amounts of $\text{C}(\text{sp}^2)$ –H silylation were observed when exposing **1q** or **1s** in the absence

of $\text{Ni}(\text{COD})_2$, an observation that is consistent with a recent C–H silylation mediated by KOtBu .²²

As judged by the wealth of literature data, π -extended arenes have routinely been employed in C–OMe functionalization,^{2,6} providing consistently higher rates than regular anisole derivatives. Such difference in reactivity likely reflects the better ability of π -extended arenes for η^2 -coordination to low-valent complexes and/or the ability to undergo other dearomatization pathways (Scheme 2).^{7,23} Despite the greater

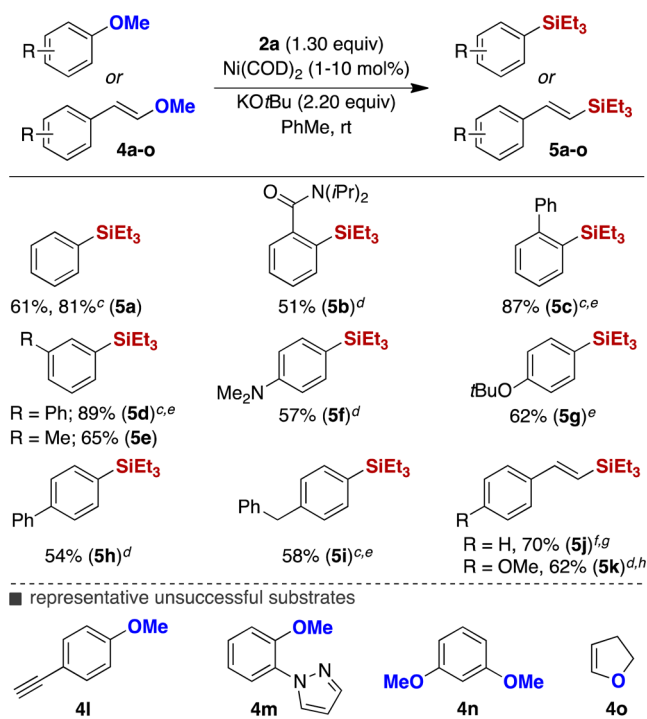
Scheme 2. Polyarenes vs Regular Arenes



accessibility of simple anisole derivatives,² their use in cross-coupling reactions is not as commonly practiced as one might anticipate. Indeed, the cross-coupling of *unbiased* anisoles lacking *ortho* or *para*-activating groups to the methoxide function has only been possible within the realm of C–C bond formations using stoichiometric organometallic species, typically using high temperatures and/or electron-rich ligands.²⁴ Therefore, it is a worthwhile endeavor to search for alternate catalytic techniques that would expand our current cross-coupling portfolio of *unbiased* anisole derivatives, particularly in C–heteroatom bond formations and under mild conditions.

As shown in Table 3, a variety of regular anisole derivatives could be coupled under otherwise identical conditions to those shown in Table 2.¹⁹ In contrast to the prevailing perception that *ortho*- or *para*-activating groups generally provide higher yields when coupling anisole derivatives,² we found that **5b** resulted in lower yields than regular anisole (**5a**).²⁵ Particularly intriguing was that **4m**, previously shown to be suited for C–OMe cleavage,^{6f} remained unaltered, suggesting that the pyrazole motif may compete with substrate binding. Strikingly, *unactivated* anisoles possessing electron-rich groups at the *para* position could equally be silylated in good yields (**5f**, **5g**). These results are noteworthy taking into consideration the higher activation energy required for C–OMe cleavage in electron-rich anisoles,² as well as the lack of reactivity of **4n**, even under more forcing conditions.²⁶ These results challenged the conviction that electronic effects on the arene are the only factor coming into play when tackling C–OMe cleavage. Unfortunately, no silylation took place with substrates possessing terminal alkynes (**4l**), whereas TMS-protected acetylenes resulted in competitive silyl attack to the ethynyl moiety. Although no $\text{C}(\text{sp}^2)$ –O cleavage occurred in dihydrofuran (**4n**) or furan, we found that our protocol could be extended to acyclic vinyl ethers (**5i**, **5j**), thus giving access to synthetically versatile vinyl silanes¹¹ with an exquisite stereoselectivity profile, regardless of the configuration of the substrate employed.²⁷

Encouraged by our findings, we anticipated that orthogonal silylation strategies could be within reach when using aryl methyl ethers as substrates. As shown in Scheme 3 (top), exposure of **6** to $[\text{Rh}(\text{coe})_2\text{OH}]_2/\text{L1}$ and $\text{Me}(\text{OTMS})_2\text{SiH}$ resulted in a regioselective $\text{C}(\text{sp}^2)$ –H silylation at the less-electron-rich aromatic ring.²⁸ In contrast, KOtBu -mediated $\text{C}(\text{sp}^2)$ –H silylation with Et_3SiH predominantly led to **7b** in

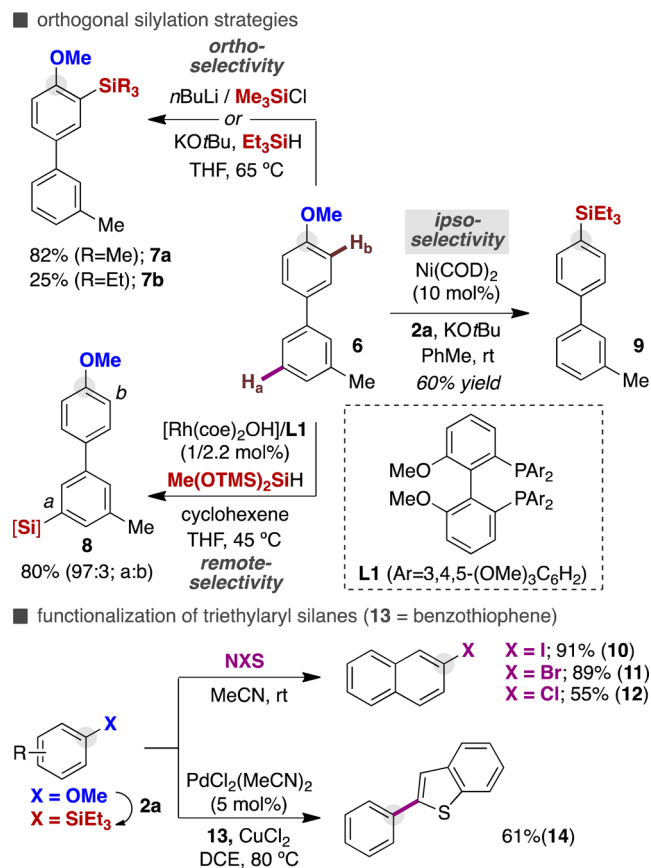
Table 3. Silylation of Non- π -Extended Backbones and Vinyl Ethers^{a,b}

^aAs Table 1 (entry 1). ^bIsolated yields, average of at least two independent runs. ^c2a (2.0 equiv), KOtBu (6.50 equiv). ^dNi(COD)₂ (10 mol%). ^eNi(COD)₂ (5 mol%). ^f50 °C. ^gUsing (Z)-4i. ^hE:Z = 20:1, using 4j (E:Z = 1.5:1).

25% yield,²² together with trace amounts of benzylic silylation.¹⁵ This result could be significantly improved via *ortho*-metalation with *n*BuLi followed by Me₃SiCl quench (7a).²⁹ To put these results into perspective, we found that **9** was exclusively formed under our silylation conditions. Taken together, these results stand as a testament to the potential of our silylation protocol, representing a reactivity mode complementary to “classical” *ortho*-metalation²⁹ or modern catalytic C–H silylation techniques.³⁰ The synthetic applicability of our Ni-catalyzed silylation of aryl methyl ethers is further illustrated in Scheme 3 (bottom). As shown, **1a** could be smoothly converted into **10–12**, hence representing a formal *ipso*-halogenation of aryl methyl ethers under mild conditions. Furthermore, we found that the corresponding triethylaryl silanes could successfully be engaged in a Pd-catalyzed oxidative C(sp²)–H functionalization of benzothio- phene, giving rise to **14** in good yield and excellent regioselectivity at the β -position.³¹

The unprecedented reactivity observed at room temperature in the absence of electron-rich ligands left a reasonable doubt that a mechanism consisting of an oxidative addition of the C–OMe bond to Ni(0) species would be operative. This interpretation gains credence by the stunning dichotomy exerted by the corresponding counteractions (Table 1, entries 8–12), the excellent reactivity found for particularly electron-rich anisole derivatives (Table 3, **5f** and **5g**), and the formidable activation barrier known for oxidative addition of the C(sp²)–OMe bond to electron-rich Ni(0) complexes.^{8b,d} Prompted by the high reactivity found in the absence of added ligands, we turned our attention to mercury poisoning experiments to identify whether heterogeneous systems participate or not.³²

Scheme 3. Synthetic Applicability



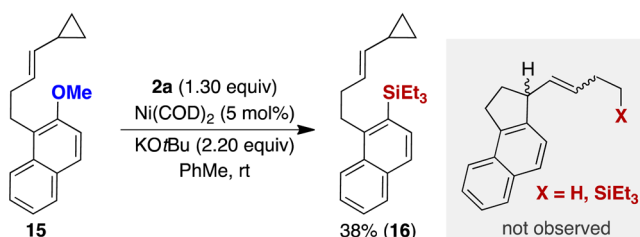
Interestingly, the reaction of **1a** with **2a** was not inhibited in the presence of Hg(0).¹⁵ This observation, together with the absence of heterogeneous metal particles found by TEM analysis of different aliquots during the course of the reaction and the lack of an induction period en route to **3a**, provided compelling evidence for a homogeneous catalyst.^{15,33} Although one might argue that our results could also be interpreted on the basis of an *ortho* C(sp²)–H silylation²¹ followed by C–OMe bond hydrogenolysis,^{34,35} or benzyne-type intermediates,³⁶ we believe that these particular manifolds are highly unlikely. This view is supported by the fact that exclusive *ipso*-silylation was observed for **3i** (Table 2) or **5d,5e** (Table 3), among others.

A priori, the data provided in Tables 2 and 3 do not allow us to rigorously rule out whether single electron transfer (SET) processes intervene or not, as electron-rich Ni(0) species could also act as electron donors,³ leading to carbon-centered radicals. As shown in Scheme 4 (top), **15** was converted exclusively to **16**, regardless of the concentration of Ni catalyst utilized, thus leaving a reasonable doubt about a radical scenario that would have triggered a 5-*exo*-trig cyclization followed by ring-opening of the cyclopropyl motif. The intermediacy of triethylsilyl radicals generated either by homolysis of the Si–B bond³⁷ or from silyl anions via SET³⁸ was also ruled out. Such assumption is based on the observed chemoselectivity (**3k**, Table 2 and **15**, Scheme 4) and the lack of inhibition in the presence of stoichiometric amounts of 1-hexenes or cyclooctenes that would otherwise have resulted in the addition of triethyl silyl radicals to unsaturated C–C bonds (Scheme 4, bottom).³⁹

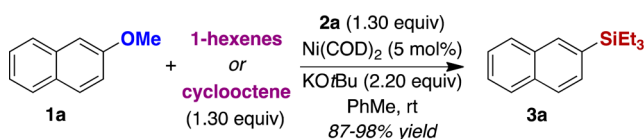
At present, we propose that KOtBu mediates the conversion of **2a** into either Et₃SiK or a silylborate of the formal

Scheme 4. Investigations into Radical-Type Pathways

- participation of carbon-centered radicals via SET processes

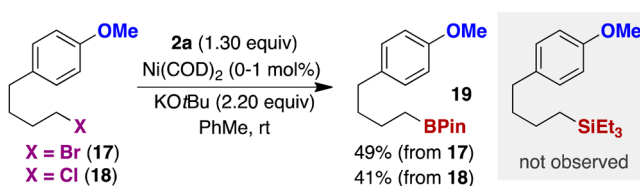


- reactivity with silyl radical scavengers

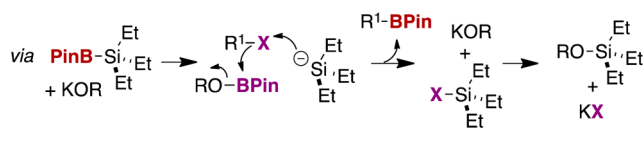


composition [Et₃Si-BPin(OtBu)]K that might act as silyl anion surrogate.⁴⁰ The participation of silyl anionic species was indirectly corroborated by observing exclusively **19** from either **17** or **18** in the presence or absence of Ni(COD)₂, as silyl anions are known to promote nucleophilic attack on the bromine atom, generating a transient carbon nucleophile that reacts preferentially with the boryl unit (Scheme 5).²¹

Scheme 5. Intermediacy of Silyl Anionic Species



- proposed mechanism (see ref. 21)

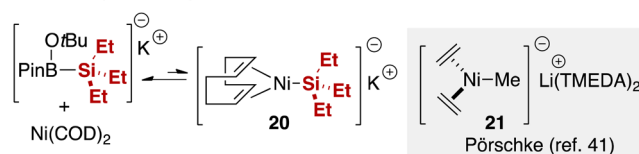


Additional support for silyl anions came from the observation that PhSiMe₂Li (**2e**) was found to be competent as a reaction intermediate en route to **3a**, either in the absence or in the presence of KOtBu, albeit in lower yields (34%).¹⁵ The lower reactivity of PhSiMe₂Li is tentatively ascribed to its partial decomposition, the use of THF as cosolvent (**2e** consists of a 1 M THF solution), or the lower nucleophilicity of PhSiMe₂Li vs Et₃SiK.

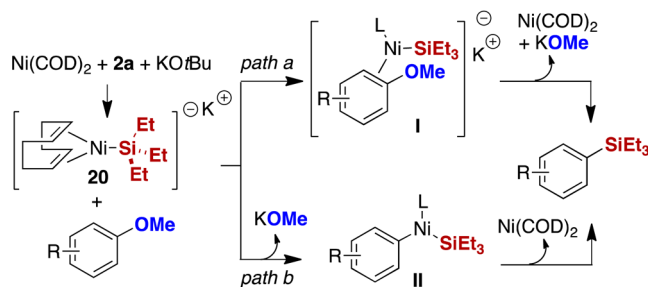
Based on our empirical data, we currently favor a mechanistic rationale consisting of the intermediacy of a discrete [Ni(COD)SiEt₃]K complex (**20**) that might be generated *in situ* upon exposure of Ni(COD)₂ to **2a** and KOtBu (Scheme 6, top pathway). This conclusion is reminiscent of the structurally well-defined, yet exceptionally sensitive, Ni(0)-ate complex **21** reported by Pörschke that can be obtained by reaction of Ni(COD)₂ with MeLi in ethylene atmospheres, the identity of which was rigorously proven by X-ray diffraction analysis.^{41,42} Unfortunately, and despite extensive experimentation, isolation of **20** or direct spectroscopic evidence for such putative intermediate was not possible, probably due to its expected exceptional sensitivity and limited lifetime. In a formal sense, the reaction of **20** with an aryl methyl ether could be visualized

Scheme 6. Ni(0)-Silyl-Ate Species and Mechanistic Rationale

- Ni(0)-silyl ate complexes



- proposed mechanistic rationale (L = COD)



as an internal metal-catalyzed nucleophilic aromatic substitution assisted by complexation of the K⁺ counterion with the lone pair of the ethereal oxygen atom (Scheme 6, path a).⁴³ Alternatively, one could also envision a “nonclassical” oxidative addition of the C(sp²)-OMe bond via Ni(0)-ate complexes assisted by the K⁺ counterion (Scheme 6, path b).^{8b,44} These interpretations could explain the strikingly different behavior found for potassium counterions, in which a Lewis acid might aid the targeted C–O cleavage.^{8,44,45}

CONCLUSIONS

In summary, we have documented a surprisingly facile Ni-catalyzed silylation of aryl methyl ethers that operates without added dative ligands. This protocol is distinguished by its mild conditions and wide scope, including the always-elusive *unbiased* anisole derivatives. Although additional investigations at a molecular level are warranted to shed light on the intermediacy of short-lived and, most likely, exceptionally sensitive Ni(0)-ate entities, we believe that our study constitutes an important step toward a more prolific use of readily available aryl methyl ethers as coupling partners. The role exerted by the escorting counterion in the targeted C–OMe bond cleavage deserves particular attention, as it may set the basis for systematically examining the influence of a priori innocent additives in related cross-coupling reactions. That being said, we anticipate that this strategy will foster further explorations of related transformations via C–OMe scission.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10998.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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