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Nickel(II)-catalyzed reductive silylation of alkenyl methyl ethers for the synthesis of alkyl silanes†

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A new one pot protocol has been developed for the reductive silylation of alkenyl methyl ethers using Et_3Si–BPin and $HSiEt_3$ with nickel(II) catalyst. Styrene type methyl ethers, multi-substituted vinyl methyl ethers, heterocycles and unconjugated vinyl ethers are all tolerated to form alkyl silanes. Mechanistic study reveals that it is a cascade of a C–O bond silylation and vinyl double bond hydrogenation process. Internal nucleophilic substitution or oxidative addition pathways were both acceptable for C–O bond cleavage. The acquired intermediate alkenyl silanes then proceeded through an unconventional reduction process thus providing alkyl silanes.

Introduction

Organosilanes, prominently with their physical and chemical properties, have significant applications in organic syntheses,[1] drug discovery,[2] bioactive compound preparations,[3] and advanced material developments.[4] Alkyl silanes, as one of the principal research areas among organosilanes, are used as isosteres of quaternary carbons, which have found significant applications in pharmaceutical research (Fig. 1).[5] Therefore, it has attracted much attention on their synthesis. Hydro-silylations of olefins using Pt, Rh, Pd, or Ru catalysts are pioneering works.[6] Recently, instead of noble metal catalysts, several kinds of base metal catalysts such as Fe, Co, Ni, and Mn have been developed for this transformation, generally with elegant catalyst design.[7] Other means including carbene insertion into silanes,[8] cross-coupling with organosilicon reagents,[9] or direct C(sp³)–H silylation[10] all contribute to provide alkyl silanes.

Due to the significant progress made by transition metal catalyzed carbon–heteroatom bond formation *via* unactivated

bond cleavage in synthetic chemistry, especially for C–O bond activation,[11] deoxygenative silylation has been applied for acquiring of multiple silicon compounds. Martin *et al.* reported the vital work in 2014 that Ni/Cu catalyzed C–O bond silylation of aryl or benzyl pivalates with electron rich backbones in mild conditions.[12] This methodology was also introduced to aryl esters which underwent decarbonylative silylation *via* acyl C–O bond activation by Rueping's and Shi's group.[13] Carbamates as appropriate substrates were also discovered using nickel or iron catalysts.[14] Different from esters, cut off the C–O bond of aryl ethers are more difficult because of the high bond energy. Martin *et al.* developed the first nickel catalyzed silylation of aryl methyl ether compounds with silyl borate.[15] Montgomery *et al.* then employed aryl silyl ethers as the source of C–O bond silylation.[16] In addition, pyridine assisted silylation of aryl 2-pyridyl ethers with silyl zinc reagent were realised to generate aryl silanes.[17] Alkyl ethers like benzyl methyl ethers or allyl methyl ethers were succeed as well in nickel catalyzed C–O bond silylation with silyl borate[15] or silyl magnesium reagent[18]. However, vinyl C–O bond silylation was rarely reported, only two styrene type methyl ethers were tested affording alkenyl silicon compounds as the supplementary for silylation of conjugated ethers in Martin's work.[15] In 2017, Studer *et al.* reported ring opening silylation of benzofurans which was similar to alkenyl ethers mediated by a silyl lithium reagent (Scheme 1a).[19] Whereafter, Yorimitsu *et al.* reported CuCl catalyzed ring opening silylation of benzofurans with disilane that made the reaction more tolerable with functional groups (Scheme 1b). Also, an addition–elimination mechanism was proposed for C–O bond cleavage.[20]

Recently, our group has been interested in the valuable conversion of alkenyl ethers employing inexpensive transition metal catalysts.[21] Combined with the high reactivity of nickel species in C–O bond activation, $Ni(acac)_2$ catalyzed one pot reaction of demethoxylative silylation and olefin reduction were
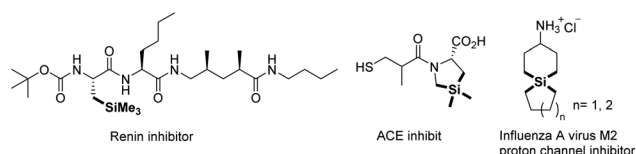

Fig. 1 Pharmaceutical active molecules with tetraalkyl silane skeletons.

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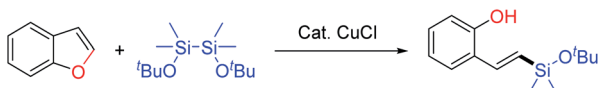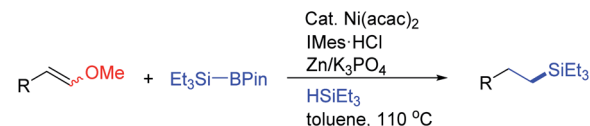
(a) Ring opening silylation with silyllithium (Studer's work)

(b) Copper-catalyzed ring opening silylation with disilane (Yorimitsu's work)

(c) Nickel-catalyzed reductive silylation with Si–B reagent (**this work**)

Scheme 1 C–O bonds silylation of benzofurans and alkenyl methyl ethers.

performed with silyl borate and hydrosilane (Scheme 1c), which offers an alternative process for late-stage functionalization of alkenyl ethers.

Results and discussion

Our investigation was started by testing the reaction of styrene methyl ether **1a** with **2**, a silyl borate usually applied for silylation reactions and easily accessible in bulk quantities.[22] After careful optimization, we found a cocktail of cheap and air-stable catalyst Ni(acac)$_2$ (10 mol%), N-heterocyclic carbene ligand IMes·HCl (10 mol%), catalytic amount of zinc powder (20 mol%), HSiEt$_3$ (3 equiv.) and K$_3$PO$_4$ (1.5 equiv.) in toluene at 110 °C gave the best results, affording phenethyl silane **3a** as the main product in 76% isolated yield. The ratio of **3a** and double-bond reserved byproduct **4a** was 97 : 3 (Table 1, entry 1). NiI$_2$ instead of Ni(acac)$_2$ gave a low yield of **3a** and increased the amount of **4a** (Table 1, entry 2). When using other nickel catalyst like Ni(OTf)$_2$, obvious decrease of **3a** took place (Table 1, entry 3). IMes·HCl was crucial for this transformation, other NHC or phosphine ligands showed little or no reaction of **1a** (Table 1, entries 4 and 5). The reaction could not happen without nickel catalyst (Table 1, entry 6), which negated zinc's catalytic activity. While no Zn had little effect to this transformation which could be largely owing to the same reducing property of HSiEt$_3$ (Table 1, entry 7). No reaction occurred when silyl borate was absent indicated that direct hydrosilylation followed by β-O elimination pathway was not possible (Table 1, entry 8). The additional base K$_3$PO$_4$ was essential and irreplaceable for this reaction. As shown in entries 9–12, no reaction was found with other sylvite, phosphate or other base indicating that a subtle balance was required for nucleophilicity and steric bulk of the base. Without HSiEt$_3$, the yield of **3a** dropped dramatically and **4a** was obtained as the main product (Table 1, entry 13). A possible reason might be concluded from this result that **4a** was an intermediate product and was hydrogenated by HSiEt$_3$, and **4a** could be partly reduced to **3a** with little amount of H$_2$O in reaction mixture when HSiEt$_3$ was absent. To prove this, extra hydrogen sources such as H$_2$O, MeOH and PhMe$_2$SiH were added instead

**Table 1** Optimization of reaction conditions[a]

Entry	Variation from standard conditions	Yield of 3a[b] (%)
1	None	76 (97 : 3)
2	NiI$_2$ instead of Ni(acac)$_2$	47 (54 : 46)
3	Ni(OTf)$_2$ instead of Ni(acac)$_2$	23 (78 : 22)
4	IPr·HCl instead of IMes·HCl	n.r.
5	PCy$_3$ or XantPhos instead of IMes·HCl	Trace
6	No Ni(acac)$_2$	n.r.
7	No Zn	62 (97 : 3)
8	No 2	n.r.
9	No K$_3$PO$_4$, 20 mol% NaO^{t}Bu added	n.r.
10	K$_2$CO$_3$ or KO^{t}Bu instead of K$_3$PO$_4$	n.r.
11	K$_2$HPO$_4$ or Na$_3$PO$_4$ instead of K$_3$PO$_4$	n.r.
12	CsF, Na$_2$CO$_3$ or Cs$_2$CO$_3$ instead of K$_3$PO$_4$	n.r.
13	No HSiEt$_3$	26 (35 : 65)
14	H$_2$O instead of HSiEt$_3$	35 (100 : 0)
15	MeOH instead of HSiEt$_3$	48 (100 : 0)
16	PhMe$_2$SiH instead of HSiEt$_3$	56 (90 : 10)

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.6 mmol), HSiEt$_3$ (0.9 mmol) and base (0.45 mmol) were reacted in toluene (1.5 mL) at 110 °C for 24 h under nitrogen atmosphere. [b] Isolated yield, the ratios of **3a** and **4a** in parentheses were determined by GC-MS. n.r. equals to no reaction.

of HSiEt$_3$, **4a** was obtained discrepantly with relatively lower yields (Table 1, entries 14–16).

With robust conditions in hand, we turned to exam the feasible scope and limitations for our Ni(acac)$_2$ catalyzed reductive silylation of alkenyl methyl ethers. Styrene type methyl ethers were first carried out for alkyl silanes preparation (Table 2). Electron-donating group like methyl, tetra-butyl and phenyl at *para-* or *meta*-position were all tolerated providing up to 93% yield of products (**3b–3e**). When 2-pyridyl, a strong *ortho*-directing group, was fixed at *para*-position, 85% yield of **3f** acquired under standard conditions without any C–H activation products detected. We are excited to find that aryl methyl ether which was readily for silylation through nickel catalyst in mild conditions[15] showed no competition against vinyl methyl ether, yet affording 78% yield of **3g**. Substituents with stronger electron donor property seemed to enhance the reactivity in this process. Some disubstituted or trisubstituted styrene methyl ethers all turned out to provide products with higher yields (**3h–3k**). Alkenyl methyl ether bearing benzodihydrofuran skeleton (**1l**) also gave a good result. Fluorine-containing groups such as F (**3m**) or CF$_3$ (**3n**) were proved having no impact on this reaction. The chemical selectivity of this transformation were also demonstrated by employing substrates installing with ester or amide group (**3o**, **3p**), which were deeply explored in nickel catalyzed C–O bond[13] or C–N bond[23] activations. Substrates with sterically hindered o-Me and o-OMe substituents were compatible enough to afford **3q** and **3r** in 47% and 71% yield respectively. Several π-extended alkenyl methyl ethers underwent this process with high reactivity thus providing 90% yield of
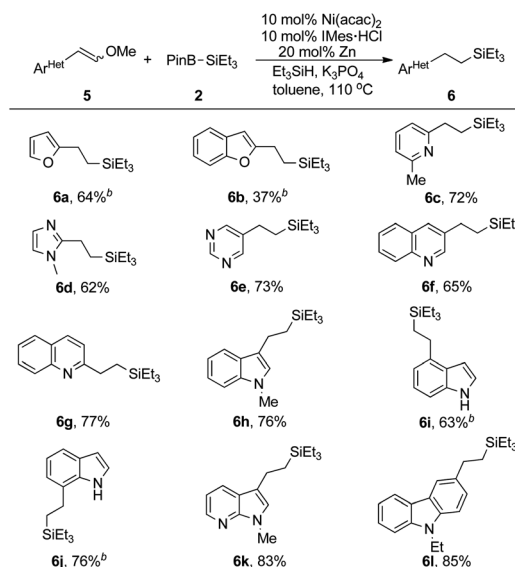
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Table 2 Scope of styrene type methyl ethers[a]
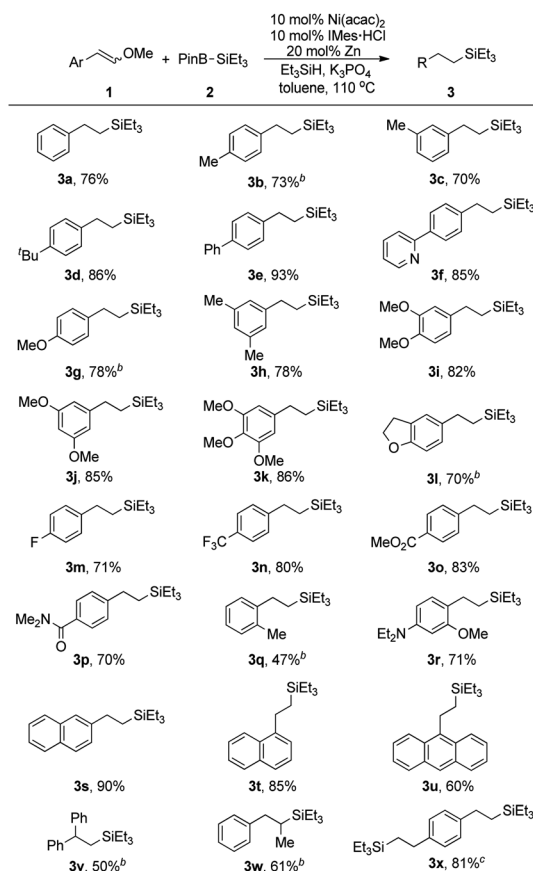
[a] Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), HSiEt₃ (0.9 mmol) and K₃PO₄ (0.45 mmol) were reacted in toluene (1.5 mL) at 110 °C for 24 h under nitrogen atmosphere. Yields were obtained after purification through column chromatography on silica gel. [b] React for 48 h. [c] 20 mol% Ni(acac)₂, 20 mol% IMes·HCl, 40 mol% Zn, **1** (0.3 mmol), **2** (1.2 mmol), HSiEt₃ (1.8 mmol) and K₃PO₄ (0.9 mmol) were reacted in toluene (3 mL) at 110 °C for 24 h under nitrogen atmosphere.

Table 3 Scope of heterocycle conjugated vinyl methyl ethers[a]

[a] Reaction conditions: **5** (0.3 mmol), **2** (0.6 mmol), HSiEt₃ (0.9 mmol) and K₃PO₄ (0.45 mmol) were reacted in toluene (1.5 mL) at 110 °C for 24 h under nitrogen atmosphere. Yields were obtained after purification through column chromatography on silica gel. [b] React for 48 h.

such as pyridine, imidazole, pyrimidine, quinoline, indole, pyrrole, and carbazole were all acquired with good results (**6c–6h**, **6k**, **6l**). It was worth noting that unprotected indole products **6i** and **6j** were obtained without observably decline in yields implying the efficiency of this C–Si bond forming strategy.

In order to excavate the applicability of this transformation, some unconjugated alkenyl methyl ethers were put into reaction (Scheme 2). Disubstituted alkenyl ethers were suitable for this reaction affording **8a** and **8b** with good results. Yet **8c** and **8d** was obtained in a lower yield presumably due to the steric effect caused by trisubstituted alkenyl methyl ethers.

Subsequently, some mechanistic studies were carried out to give a closer understanding of this process. Compounds E-**4a** and Z-**4a**, acquired from known report,[24] were investigated under standard conditions and **3a** was obtained in our

(naphthalen-2-yl)ethyl silane (**3s**) and 85% yield of (naphthalen-1-yl)ethyl silane (**3t**). Even bulky 9-anthryl ethyl silane (**3u**) was obtained with 60% yield. To our delight, this reaction was not limited to simple disubstituted alkenyl methyl ethers, trisubstituted alkenyl methyl ethers could result in structurally diverse alkyl silanes in moderate yields (**3v**, **3w**). Besides, aryl dienyl methyl ether (**1x**) reacted as well providing **3x** through dual reductive silylation process with high reactivity.

In addition of the styrene type methyl ethers, we are interested in the transformation containing heteromatic skeletons. Because of the striking impact exhibited by heteroatoms in hydrosilylation process, alkyl silicon compounds containing heteroatoms were really hard to obtain. In our conditions, several type of heteroaryl vinyl methyl ethers were tested. As shown in Table 3, furan was tolerated leading to the preparation of **6a** in 64% yield. While **6b** was obtained in a low yield probably because the competitive side reaction took place on the C–O bond of the benzofuran ring. N-heterocycles were more reactive and corresponding silanes containing heterocyclic ring
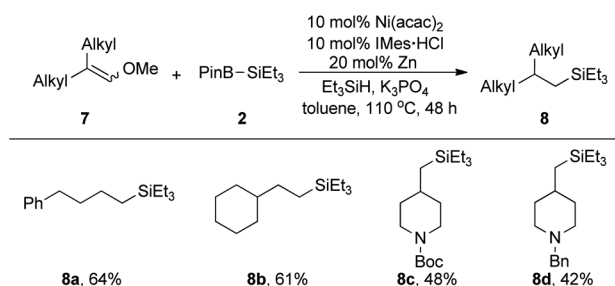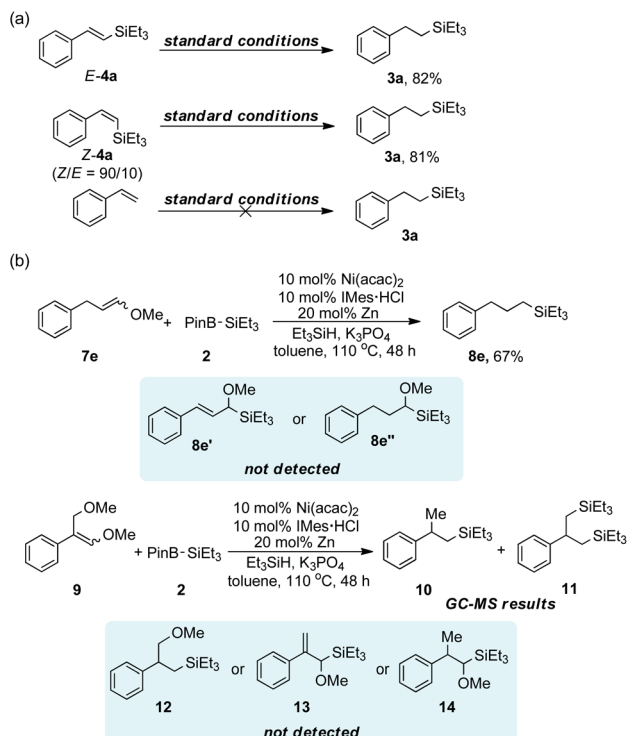

Scheme 2 Reductive silylation with alkyl substituted vinyl methyl ethers. Conditions: **7** (0.3 mmol), **2** (0.6 mmol), HSiEt₃ (0.9 mmol) and K₃PO₄ (0.45 mmol) were reacted in toluene (1.5 mL) at 110 °C for 48 h under nitrogen atmosphere.
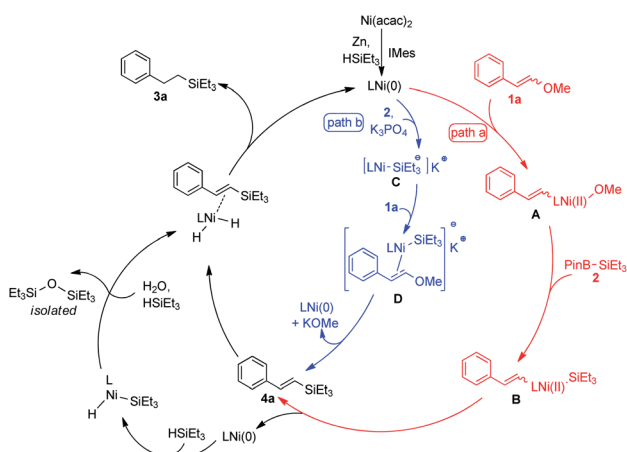
Scheme 3 Mechanistic studies.

Fig. 2 Probable reaction pathways.

prospection with favourable results despite the original configuration of **4a**. Nevertheless, styrene failed to generate **3a** when employed under the same conditions (Scheme 3a). These all suggested that compound **4a** was probably an intermediate product and a cascade of C–O bond silylation followed with olefin reduction was the possible reaction pathways rather than the way of hydrosilylation to the potential alkenes. All the time it has been difficult to distinguish the oxidative addition mechanism from addition–elimination mechanism in transition metal catalyzed inert bond activation. We tried two substrates **7e** and **9**, derived from which intramolecular competition might exist if Ni–X elimination process would happen when reacting

with **2** under standard conditions, to test the feasibility of addition–elimination pathway for C–O bond silylation (Scheme 3b). Actually, after the reaction of **7e**, no structurally dominant addition–(Ni–H elimination) product **8e′** nor further reductive product **8e″** were detected. Specifically, when **9** was conducted under the same reaction conditions as **7e**, only few amount of compounds **10** and **11** were detected by GC-MS while anticipated product **12** was undiscovered, which suggested that allylic C–O bond scission along with vinyl C–O bond scission occurred in this reaction. No addition–(Ni–OMe elimination) product **13** nor **14** were detected further illuminating the improbability of the Ni–O elimination pathway.

According to Martin's report,[15] an internal nucleophilic substitution mechanism, supported by DFT calculations,[25] was possible for C–O bond silylation. As in our process, K$_3$PO$_4$ was supposed to play an important role in the convention of **2** to either Et$_3$SiK or [(Et$_3$Si–Bpin)$_n$(PO$_4$)]K$_3$ complex that might be regarded as a silyl anion surrogate. A tendency of a discrete [Ni(IMes)–SiEt$_3$]K complex might be acquired when *in situ* generated Ni(0) species exposed to IMes·HCl, **2**, and K$_3$PO$_4$. Unfortunately, isolation of the nickel complex or spectroscopic evidence for this suppositive intermediate was unavailable. Therefore, two feasible pathways were proposed in the C–O bond silylation procedure (Fig. 2). Classic oxidative addition mechanism was shown in path a, in which Ni(0) inserted into C–O bond followed by transmetalation with **2**, reductive elimination then occurred forming the key intermediate **4a**. Path b exhibited a constant Ni(0) mediated nucleophilic substitution mechanism, where Ni–Si complex **C** acted as a nucleophile, and methoxy from **1a** was substituted by SiEt$_3$ to provide intermediate **4a**. Unconventional hydrogenation of **4a** with HSiEt$_3$ proceeded to generate **3a** in this strategy, which was commonly seen as a side reaction appeared in transition metal catalyzed hydrosilylation of alkenes.[26] The byproduct siloxane instead of disilane was isolated (see ESI† for details) which not only excluded the continues oxidative addition path of forming SiEt$_3$–Ni–SiEt$_3$ complex but also suggested trace amount of moisture in the reaction mixture maybe have some effect for this transformation.[27]

Conclusions

In summary, we have provided a Ni(ii) catalyzed one pot reaction of alkenyl methyl ethers with silyl borate through C–O bond silylation and olefin reduction process. This strategy is successfully implemented not only for electron-rich styrene methyl ethers and π-extended alkenyl methyl ethers, but also succeeded in generating alkyl silanes containing electron-deficient aryls, heterocycles, and unconjugated alkyl groups, that provides alternative approaches for carbon–hetero bond formation and extends the scope of unreactive C–O bond activations. Besides, a possible reaction mechanism including oxidative addition or internal nucleophilic substitution for C–O bond scission and nickel mediated double bond reduction by HSiEt$_3$ is fully presented. Further mechanistic studies as well as functionalization of alkenyl or alkyl C–O bond are in progress in our lab.

Author contributions

Conflicts of interest

There are no conflicts to declare.

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