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 Et3Si–BPin and HSiEt3 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 alkyl 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 silylation10 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 catalzed 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 magnesium 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 borate18 or silyl magnesium reagent19. 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.20 In 2017, Studer et al. reported ring opening silylation of benzo[5]furans which was similar to alkenyl ethers mediated by a silyl lithium reagent (Scheme 1a).21 Whereafter, Yorimitsu et al. reported CuCl catalyzed ring opening silylation of benzo[5]furans 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.22

Recently, our group has been interested in the valuable conversion of alkenyl ethers employing inexpensive transition metal catalysts.23 Combined with the high reactivity of nickel species in C–O bond activation, Ni(acac)2 catalyzed one pot reaction of demethoxyative silylation and olefin reduction were

Fig. 1 Pharmaceutical active molecules with tetraalkyl silane skeletons.
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. After careful optimization, we found a cocktail of cheap and air-stable catalyst Ni(acac)₂ (10 mol%), N-heterocyclic carbene ligand IMes, and phosphorus oxochloride (0.45 mmol), NaOH (0.6 mol%), and base (0.45 mmol) were reacted in toluene (1.5 mL) at 110°C for 24 h under nitrogen atmosphere. With robust conditions in hand, we turned to examine 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 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 (1f) also gave a good result. Fluorine-containing groups such as F (3m) or CF₃ (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 or C–N bond activations. Substrates with stERICly hindered o-Me and o-OMe substituents were compatible enough to afford 3q and 3r in 47% and 71% yield respectively. Several r-extended alkenyl methyl ethers underwent this process with high reactivity thus providing 90% yield of

Table 1 Optimization of reaction conditions

| Entry | Variation from standard conditions | Yield of 3a (%) |
|-------|-----------------------------------|-----------------|
| 1     | None                              | 76 (97 : 3)     |
| 2     | NiI₂ 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     | PCy₃ or XantPhos instead of IMes·HCl | Trace         |
| 6     | No Ni(acac)₂                      | n.r.            |
| 7     | No Zn                             | 62 (97 : 3)     |
| 8     | No Ni(al)₃                       | n.r.            |
| 9     | No K₂PO₄, 20 mol% NaOEt added     | n.r.            |
| 10    | K₂CO₃ or KO'Et instead of K₂PO₄  | n.r.            |
| 11    | K₂HPO₄ or Na₂PO₄ instead of K₂PO₄ | n.r.            |
| 12    | CsF, Na₂CO₃ or Cs₂CO₃ instead of K₂PO₄ | n.r.        |
| 13    | No HSiEt₃                         | 26 (35 : 65)    |
| 14    | H₂O instead of HSiEt₃             | 35 (100 : 0)    |
| 15    | MeOH instead of HSiEt₃            | 48 (100 : 0)    |
| 16    | PhMe₂SiH instead of HSiEt₃        | 56 (90 : 10)    |

a Reaction conditions: 1a (0.3 mmol), 2 (0.6 mmol), HSiEt₃ (0.9 mmol) and base (0.45 mmol) were reacted in toluene (1.5 mL) at 110°C for 24 h under nitrogen atmosphere. Isolated yield, the ratios of 3a and 4a in parentheses were determined by GC-MS. n.r. equals to no reaction.
(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 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 mechanic 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

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**Table 2** Scope of styrene type methyl ethers

| Ar | CMe + PinB-SeEt3 | R | SiEt3 |
|----|-----------------|---|-------|
| 1a | Me              | 2a | 3a, 76% |
| 2a | F               | 2b | 3b, 73% |
| 3a | Ph              | 3b | 3c, 70% |
| 4a | OMe             | 4b | 3d, 66% |
| 5a | Me              | 5b | 3e, 85% |
| 6a | Ph              | 6b | 3f, 85% |
| 7a | SiEt3           | 7b | 3g, 87% |
| 8a | Me              | 8b | 3h, 85% |
| 9a | Ph              | 9b | 3i, 85% |
| 10a| SiMe3           | 10b| 3j, 52% |

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.

**Table 3** Scope of heterocycle conjugated vinyl methyl ethers

| Ar                                  | CMe + PinB-SeEt3 | R | SiEt3 |
|-------------------------------------|-----------------|---|-------|
| 5a                                  | Me              | 2a | 6a, 64% |
| 6a                                  | F               | 2b | 6b, 37% |
| 7a                                  | Ph              | 2b | 6c, 72% |
| 8a                                  | OMe             | 2b | 6d, 65% |
| 9a                                  | Me              | 2b | 6e, 65% |
| 10a                                 | Ph              | 2b | 6f, 65% |
| 11a                                 | OMe             | 2b | 6g, 77% |
| 12a                                 | Ph              | 2b | 6h, 73% |
| 13a                                 | OMe             | 2b | 6k, 85% |
| 14a                                 | Ph              | 2b | 6l, 85% |

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.

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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, an internal nucleophilic substitution mechanism, supported by DFT calculations, was possible for C–O bond silylation. As in our process, K3PO4 was supposed to play an important role in the convention of 2 to either Et3SiK or [(Et3Si–Bpin)3]K complex that might be regarded as a silyl anion surrogate. A tendency of a discrete [Ni(IMes)–SiEt3]K complex might be acquired when in situ generated Ni0 species exposed to IMes·HCl, 2, and K3PO4. 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 Ni0 inserted into C–O bond followed by transmetalation with 2, reductive elimination then occurred forming the key intermediate 4a. Path b exhibited a constant Ni0 mediated nucleophilic substitution mechanism, where Ni–Si complex C acted as a nucleophile, and methoxy from 1a was substituted by SiEt3 to provide intermediate 4a. Unconventional hydrogenation of 4a with HSiEt3 proceeded to generate 3a in this strategy, which was commonly seen as a side reaction appeared in transition metal catalyzed hydrosilylation of alkenes. The byproduct siloxane instead of disilane was isolated (see ESI† for details) which not only excluded the continues oxidative addition path of forming SiEt3–Ni–SiEt3 complex but also suggested trace amount of moisture in the reaction mixture maybe have some effect for this transformation.

**Conclusions**

In summary, we have provided a Ni(II) catalyzed one pot reaction of alkynyl 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 alkynyl 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 HSiEt3 is fully presented. Further mechanistic studies as well as functionalization of alkynyl or alkyl C–O bond are in progress in our lab.
Author contributions

X. Q. conceived the project and analysed the data. L. Z. and H. W. performed the experiments and analysed the data. L. L. helped with the substrates synthesis and analysed experimental data. Y. L. and Y. Z. participated in the mechanism discussion. The manuscript was written by X. Q. and Y. Z. contributed to the editing.

Conflicts of interest

There are no conflicts to declare.

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