Highly Efficient Activation of Organosilanes with η^2-Aldehyde Nickel Complexes: Key for Catalytic Syntheses of Aryl-, Vinyl-, and Alkynyl-Benzoxasiloles

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S *Supporting Information*

ABSTRACT: An η^2-aldehyde nickel complex was utilized as an effective activator for an organosilane in order to generate a hypervalent silicate reactant for the first time. This method was successfully applied to the highly efficient syntheses of 3-aryl-, vinyl-, and alkynyl-2,1-benzoxasiloles from benzaldehydes with aryl-, vinyl-, and alkynylsilyl groups at the *ortho* position. Initial mechanistic studies revealed that an intermolecular aryl transfer process was involved in the reaction mechanism. The formation of an η^2-aldehyde complex was directly confirmed by NMR.

Aldehydes are versatile carbonyl compounds and are frequently employed as a key component in a wide range of chemistry fields. When they are used in organic synthesis, an activation of the carbonyl group is often required.[1a] A number of methods have been developed with typical and transition metals, in which aldehydes are activated through a coordination to the metals. An η^1 coordination of the carbonyl oxygen to Lewis acidic metals is well-known (Scheme 1a).[1] An enhancement of the

Scheme 1. Activation of Aldehyde via (a) η^1 or (b) η^2 Coordination
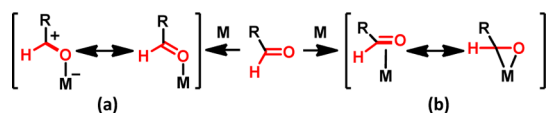
electrophilicity at the carbonyl carbon is expected via this η^1 coordination, which allows the aldehyde to react with a variety of nucleophiles. On the other hand, application of the η^2 coordination of aldehydes has been rather limited in transition-metal-catalyzed organic syntheses,[2,3t] even though many examples of the η^2-aldehyde complexes have been reported in the coordination chemistry field.[3,4] The reactivity of the η^2-aldehyde complex is very intriguing since both the carbonyl oxygen and the carbon show nucleophilic reactivity with the contribution of an oxametallacyclopropane resonance form (Scheme 1b).[3g,s,t] Nevertheless, this type of distinctive reactivity of the η^2-aldehyde complexes has rarely been utilized in the reported catalytic transformation of aldehydes.[5]

We have reported the electrophilic addition of Me$_3$SiOTf to $(\eta^2$-PhCHO)Ni(PCy$_3$)$_2$ giving $(\eta^1:\eta^1$-Me$_3$SiOCH(Ph))-Ni-(PCy$_3$)OTf.[3s,t] This result would show that η^2-aldehyde nickel complexes are sufficiently reactive toward organosilicon compounds. Then, we envisioned the generation of a hypervalent silicate that could be triggered by the activation of an aldehyde via back donation from an electron-rich nickel(0) complex and its application toward organic synthesis (Scheme 2).[6] Herein, we report the syntheses of 3-aryl-, vinyl-, and

Scheme 2. Generation of Hypervalent Silicate Triggered by Activation of Aldehyde via Back Donation from Nickel(0)
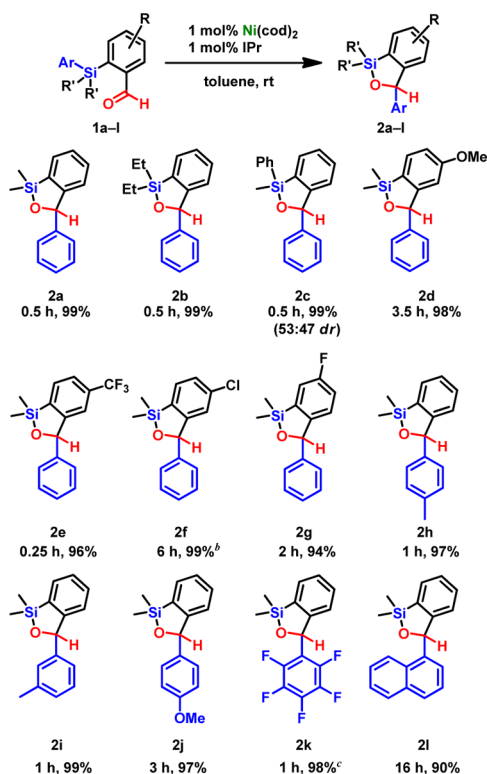

alkynyl-2,1-benzoxasiloles from benzaldehydes with aryl-, vinyl-, and alkynylsilyl moieties at the *ortho* position, which would proceed via a hypervalent silicate intermediate generated by the electrophilic addition of the organosilyl moiety to the η^2-aldehyde nickel complex. These reactions proceeded with 100% atom efficiency under very mild reaction conditions ($\sim$60 °C) without the addition of external bases to activate the organosilanes, which were essential in most of the reported transition-metal-catalyzed addition reactions of organosilanes.[7]

The reaction of *o*-dimethylphenylsilylbenzaldehyde (**1a**) with 10 mol % Ni(cod)$_2$ and PCy$_3$ was examined in toluene at 60 °C, giving 3-phenyl-2,1-benzoxasilole (**2a**) in 47% yield after 18 h through the Ph group migration from the silicon to the carbonyl carbon (Table S1).[8] This result might support the generation of a hypervalent silicate intermediate, as we envisioned (*vide supra*). Even at room temperature, the reaction took place more efficiently in the presence of 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr). With 1 mol % Ni(cod)$_2$ and IPr, the reaction was completed within 0.5 h to furnish **2a** in 99% yield (Table 1). These reaction conditions are very similar to that of the Ni[0]-catalyzed Tishchenko reaction;[5f,g] however, no formation of an ester was observed. When neither, nor both,

Table 1. Highly Efficient Synthesis of Arylbenzoxasiloles with Ni[0] Complex[a]

2a
0.5 h, 99%

2b
0.5 h, 99%

2c
0.5 h, 99%
(53:47 dr)

2d
3.5 h, 98%

2e
0.25 h, 96%

2f
6 h, 99%[b]

2g
2 h, 94%

2h
1 h, 97%

2i
1 h, 99%

2j
3 h, 97%

2k
1 h, 98%[c]

2l
16 h, 90%

[a]General conditions: **1** and Ni(cod)$_2$/IPr (0.02 mmol) were reacted in toluene (2 mL) at room temperature. Yields of isolated products are given. [b]**TNI** (4 mol %) was used at −30 °C. [c]Ni(cod)$_2$/IPr (4 mol %) was used.

Ni(cod)$_2$ and/or IPr were used, **2a** was not obtained even at more than 80 °C and more than 12 h of reaction time.[8] The reaction of **1a** with CsF, ^{n}Bu$_4$NF, or [(Me$_2$N)$_3$S][F$_2$SiMe$_3$] as an activator of the silicon was examined at 80 °C, and **2a** was not obtained (Table S1).[8] These results showed that the (η^2-aldehyde)Ni(IPr) complex would be a highly efficient reagent in the generation of a hypervalent silicate under this reaction condition.

The present methodology can be applied to the synthesis of various 3-aryl-2,1-benzoxasiloles **2a−l** (Table 1). Alkyl substituents on the silicon did not affect the efficiency of the reaction (**2a** and **2b**), but it was reported that this difference would influence the stability of benzoxasiloles toward silica gel chromatography.[8,9] o-Diphenylmethylsilylbenzaldehyde (**1c**) gave **2c** in 99% yield as a mixture of diastereomers (53:47 dr).[10] Introducing an electron-donating methoxy group into the para position with respect to the dimethylphenylsilyl group retarded the transformations; however, the yield of **2d** was also excellent (3.5 h, 98%). By contrast, the reaction of **1e**, which equips an electron-withdrawing CF$_3$ group, was completed within 0.25 h to give **2e** in 96% yield. In the presence of 10 mol % Ni(cod)$_2$ and IPr, the reaction of chlorine-substituted **1f** did not take place at room temperature or 100 °C due to the deactivation of the catalyst by the oxidative addition of the Ar−Cl bond to the Ni[0] center. Although lowering the reaction temperature might have been effective in preventing this deactivation pathway, this would have caused a significant decrease in the solubility of Ni(cod)$_2$ toward toluene. Thus, we employed (η^6-toluene)Ni-(IPr) (**TNI**) as a Ni[0]/IPr source since **TNI** dissolves easily into

toluene even at −78 °C.[11] With 4 mol % **TNI**, the target benzoxasilole **2f** was obtained in 99% yield at −30 °C. Substrates with a 4-fluorobenzaldehyde structure (**1g**) gave **2g** in 94% yield. A variety of aryl groups on the silicon, such as tolyl (**1h** and **1i**), 4-methoxyphenyl (**1j**), pentafluorophenyl (**1k**), and 1-naphthyl (**1l**), were successfully applied to the present system. Prolongation of the reaction time was required for **1j** and **1l**, showing that both electronic and steric environment around the silicon influenced the reaction rate.

Next, we examined the synthesis of 3-vinyl-2,1-benzoxasilole (**2m**) from o-dimethylvinylsilylbenzaldehyde (**1m**) via vinyl group migration.[13] However, under the same reaction conditions given in Table 1, the formation of **2m** was completely hampered by the formation of (η^2:η^2-CH$_2$=CHSi(Me)$_2$C$_6$H$_4$CHO)Ni-(IPr).[8] As a result of further optimizations (Table S2),[8] **2m** was obtained in 90% yield by employing 2 mol % Ni(cod)$_2$ and 4 mol % IPr in THF at 60 °C (Table 2). Under these reaction

Table 2. Highly Efficient Synthesis of Vinyl- and Alkynylbenzoxasiloles with Ni[0] Complex[a]

2m
2 h, 90%

2n
6 h, 89%[b]
(24 h, 84%)[c]

2o
2 h, 91%

2p
3 h, 95%
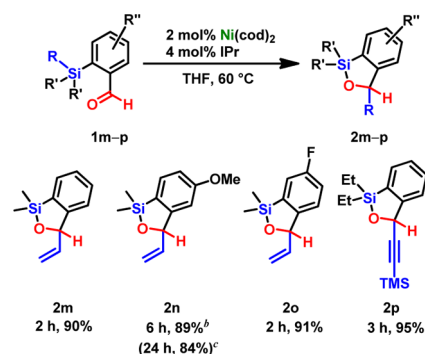
[a]General conditions: **1**, Ni(cod)$_2$ (0.02 mmol), and IPr (0.04 mmol) were reacted in THF (1−2 mL) at 60 °C. Yields of isolated products are given. [b]Ni(cod)$_2$ (1 mol %) and IPr (2 mol %) were used. [c]**1n** (20.0 mmol) was reacted with Ni(cod)$_2$ (1 mol %) and IPr (2 mol %) in THF (20 mL) for 24 h.

conditions, the substituted 3-vinyl-2,1-benzoxasiloles **2n** and **2o** were furnished in 89 and 91% yields, respectively. The procedure was expanded to the gram-scale synthesis of **2n** (17 mmol, 3.71 g). In addition, 3-alkynyl-2,1-benzoxasilole **2p** was also given in 95% yield under the same reaction conditions. In these reactions, the Ni[0]-catalyzed intramolecular hydroacylation of alkenes[5e] or alkynes[5i,14] was not observed.

Since there are chemically labile O−Si and C−Si bonds, benzoxasiloles are very attractive compounds. Therefore, extensive studies have recently been conducted for their application in organic synthesis, and these reports have clearly shown a significant degree of utility of benzoxasiloles.[9,12,15] However, preparation methods for 3-aryl-2,1-benzoxasiloles are limited. Thus, the present method would have utility as well as the advantages of simple experimental procedures, high atom efficiency, and environmentally beneficial conditions (no waste and mild temperature). Moreover, to the best of our knowledge, this is the first report on the synthesis of 3-vinyl- and alkynyl-2,1-benzoxasiloles.[15u,v] The following transformations of **2p** undoubtedly show its potential utility in organic synthesis (Scheme 3). The terminal alkyne-substituted benzoxasilole **2q** was synthesized through the desilylation of the TMS group in **2p** by K$_2$CO$_3$, which might be employed for further functionalization of the alkyne terminal. Treatment of **2p** with KHCO$_3$ and

Scheme 3. Synthetic Applications of 2p[a]
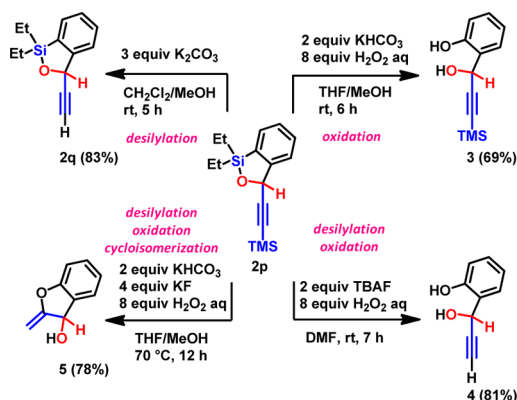
[a]Isolated yields are given.

H_2O_2 aq. in THF/MeOH resulted in the formation of phenyl propargyl alcohol **3** in 69% yield, in which the TMS group remained intact. On the other hand, by employing the combination of TBAF and H_2O_2 aq. in DMF, both desilylation and Tamao−Fleming oxidation took place to afford 2-(1-hydroxyprop-2-yn-1-yl)phenol (**4**) in 81% yield. Interestingly, 2-methylenedihydrobenzofuran-3-ol (**5**) was directly synthesized in 78% yield as the sole product from **2p** with $KHCO_3$, KF, H_2O_2 aq. at 70 °C, which is a promising precursor for benzofuranes[16] and spiroketals.[17] It is noteworthy that **5** was previously prepared via Pd-,[16a,b] Cu-,[16c] Ag-,[18] or Au[19]-catalyzed cycloisomerization from 2-(1-hydroxyprop-2-ynyl)phenols.

As part of the initial mechanistic studies, a crossover experiment using **1d** and **1j** was examined (Scheme 4). With 2

Scheme 4. Crossover Experiment with 1d and 1j[a]
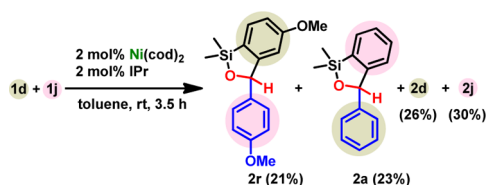
[a]Reaction was monitored by GC analysis, and yields of product were determined with *n*-pentadecane as an internal standard.

mol % $Ni(cod)_2$ and IPr, the reaction gave four benzoxasiloles including crossover products **2r** and **2a** in almost the same yields after 3.5 h (Figure S3).[8] The exchange of the aryl groups between **1d** and **1j** was not observed at all during the reaction. In addition, no aryl exchange reaction between **2d** and **2j** was observed when the isolated **2d** and **2j** were subjected to the reaction conditions. These results indicate that the present reaction involves an intermolecular aryl transfer process.[10]

In order to gain insight into the reaction intermediates, a stoichiometric reaction of **1d** with **TNI** was conducted in toluene-d_8 at −50 °C (Scheme 5). The formation of **6** was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR analyses (Figures S6−8).[8] In the ^{1}H and ^{13}C NMR spectra, the resonances of the carbonyl hydrogen and carbon were observed at δ_H 5.90 and δ_C 86.1, respectively, both of which were shifted upfield compared with those of **1d** (δ_H 9.60 and δ_C 192.4). In addition, the methyl groups on Si in **6** were observed as two diastereotopic peaks due to the formation of a chiral carbon center ligated to the nickel (**6**: δ_H 0.52 (s, 3H), 0.46 (s, 3H); δ_C −0.1, −0.5. **1d**: δ_H 0.59 (s, 6H);

Scheme 5. Stoichiometric Reaction of 1d with TNI[a]
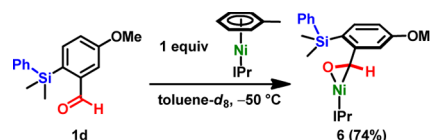
[a]Reaction was monitored by NMR analyses, and yield of **6** was determined with TMS as an internal standard.

δ_C −1.2). In the ^{29}Si NMR spectrum, the resonance of **6** was observed at −8.8 ppm, which was slightly shifted from the −7.6 ppm of **1d**. These results clearly support the η^2 coordination of **1d** toward Ni^0 by C=O;[3s,t,5g,20] however, the interaction between Si and O remains unclear at this time.[6a,12] After warming to room temperature, the quantitative conversion of **1d** to **2d** was confirmed by ^{1}H NMR.

The mechanism of the present reaction might include the following steps. First, a coodination of **1** to Ni^0 gives rise to the formation of an η^2-aldehyde nickel intermediate such as **6**. Through this first step, the aldehyde is activated as a nucleophile that continuously activates the silicon via an intramolecular addition reaction, which affords a hypervalent silicate intermediate. Then, an intermolecular aryl transfer would take place to give the product. In order to clarify the details of the mechanisms, further mechanistic studies are ongoing by our group.

In summary, a synthesis of 3-aryl-, vinyl-, and alkynyl-2,1-benzoxasiloles has been developed, which proceeds via an electrophilic addition of the organosilyl group to the η^2-aldehyde nickel complex as a key step. It is noteworthy that this work represents the first use of the η^2-aldehyde nickel complex as a highly efficient activator of organosilicon compounds. Thus, the present reaction required no additives to activate the silicon and harsh reaction conditions.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details 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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