

Dehydrogenative Coupling of Hydrosilanes and Alcohols by Alkali Metal Catalysts for Facile Synthesis of Silyl Ethers

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Cross-dehydrogenative coupling (CDC) of hydrosilanes with hydroxyl groups, using alkali metal hexamethyldisilazide as a single-component catalyst for the formation of Si–O bonds under mild condition, is reported. The potassium salt [KN(SiMe₃)₂] is highly efficient and chemoselective for a wide range of functionalized alcohols (99 % conversion) under solvent-free conditions. The CDC reaction of alcohols with silanes exhibits first-order kinetics with respect to both catalyst and substrate concentrations. The most plausible mechanism for this reaction suggests that the initial step most likely involves the formation of an alkoxide followed by the formation of metal hydride as active species.

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Introduction

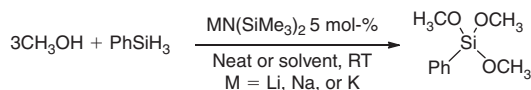
Silyl ethers are among the most frequently used protecting groups for alcohols in organic synthesis.^[1] A large number of silyl ethers are also used as reaction intermediates^[2] in various organic syntheses, material preparation,^[3] and sol–gel preparations,^[4] and as precursors for silicon-based polymers.^[5] Therefore, the improvement of various synthetic routes to prepare silyl ethers has garnered considerable attention from researchers. Traditional approaches, used over the past decades, for the formation of Si–O bonds consist of reactions between various alcohols and several silylation reagents such as halosilanes, hexamethyldisilazanes, and hydrosilanes.^[6] As alcohols are relatively less efficient for achieving electrophilic attack on silanes, the presence of strongly nucleophilic or electrophilic catalysts is desired for silanes to undergo alcoholysis.^[7] Substituting a halogen-free process for a process that employs an organic halide should be considered a fascinating, environmentally benign chemical process. Thus, the catalytic dehydrogenative coupling of alcohols with hydrosilanes represents the most attractive and atom-economical route to obtain silyl ethers as this process produces hydrogen gas as the sole by-product. A wide variety of homogeneous metal complexes including early-, middle-, and late-transition metal complexes, such as Ti^{IV},^[8] Mn^{II},^[9] Re^{IV},^[10] Fe^{II},^[11] Ru^{II},^[12] Rh^{II},^[13] Ir^{II},^[14] Ni^{II},^[15] Cu^{II},^[16] Au^I,^[17] Pt^{II},^[18] and Zn^{II},^[19] have been reported as catalysts for the production of silyl ethers. In addition, metal-free organo-catalysts, such as [(B(C₆F₅)₃)₂] and N-heterocyclic carbenes (NHCs),^[21] have been used as efficient catalysts for the preparation of compounds containing Si–O bonds. Among all the reported catalysts, only a few display high reactivity and selectivity, along with decent functional-group tolerance.^[9,10,19] Thus, in order to achieve highly active and

selective catalysts, further improvement of the process is necessary.

We have recently developed the process of cross-dehydrogenative coupling (CDC) of a variety of amines with hydrosilanes^[22] and boranes^[23] through the use of alkali hexamethyldisilazides as active pre-catalysts under mild conditions. We have demonstrated that alkali metal salts [MN(SiMe₃)₂] act as effective pre-catalysts for the CDC of various amines, with either hydrosilanes to give aminosilanes^[22] or boranes to yield aminoborane.^[23] As alkali metal amides are commercially available, non-toxic, and inexpensive, we were keen to explore their use as pre-catalysts in various CDC reactions. In this context, our strategy for the synthesis of silyl ethers was to use alkali metal amides as active pre-catalysts. Here, we report the facile synthesis of silyl ethers by the coupling reaction of various hydrosilanes with several alcohols using alkali metal amides as active pre-catalysts.

Results and Discussion

The screening of alkali metal (Li, Na, K) salts as catalysts for the CDC of methanol (MeOH) and phenylsilane (PhSiH₃) was carried out to examine the efficacy of various catalysts (Scheme 1). Table 1 summarizes the results of the initial screening of the catalytic activity of alkali metal hexamethyldisilazides [MN(SiMe₃)₂] (M = Li, Na, K) in the selective formation of alkoxy silanes from hydrosilanes. In each case, the CDC reaction was carried out using PhSiH₃ and MeOH at a molar ratio of 1 : 3 in the presence of 5 mol-% catalyst at 30°C. All three alkali metal salts proved to be effective catalysts at 30°C and led to high reaction selectivity of reactions, consequently generating high yields up to 99 % after 1 h of reaction



Scheme 1. Alcoholysis of silanes under different reaction conditions. RT, room temperature.

Table 1. Screening of catalysts for the alcoholysis of silanes

Pre-catalyst (5 mol-%) was loaded into a Schlenk tube followed by addition of alcohol (3 mmol) and silane (1 mmol). After 1 h, the mixture was transferred into an NMR tube, and chloroform (0.6 mL) was added. Conversions were obtained on the basis of the consumption of PhSiH_3 from integration of signals in the ^1H NMR spectra

| Entry | Catalyst | Time [h] | Solvent | Conversion of alcohol [%] |
|-------|-------------------------------|----------|---------|---------------------------|
| 1 | $\text{LiN}(\text{SiMe}_3)_2$ | 1 | Neat | 99 |
| 2 | $\text{NaN}(\text{SiMe}_3)_2$ | 1 | Neat | 95 |
| 3 | $\text{KN}(\text{SiMe}_3)_2$ | 1 | Neat | 99 |
| 4 | $\text{KN}(\text{SiMe}_3)_2$ | 1 | THF | 99 |
| 5 | $\text{KN}(\text{SiMe}_3)_2$ | 1 | Toluene | 99 |
| 6 | $\text{KN}(\text{SiMe}_3)_2$ | 1 | Benzene | 99 |

(Table 1, entries 1–3). The results from this initial assessment indicate that the use of 5 mol-% alkali metal salts at 30°C can be considered as the optimized process for the facile synthesis of silyl ethers. To prepare several silyl ethers, the potassium salt [$\text{KN}(\text{SiMe}_3)_2$] was preferentially used over the other alkali salts because of its greater availability. It is noted that the use of solvents such THF, toluene, and C_6H_6 did not affect the overall yield (Table 1, entries 4–6), and almost complete conversion of silanes was achieved at 30°C . Thus, we performed all subsequent reactions under neat conditions.

The initial results inspired us to study the scope of this protocol using potassium hexamethyldisilazide as the catalyst for the reaction of a wide variety of aliphatic and aromatic alcohols, containing different functional groups, with different aromatic silanes, such as PhSiH_3 , Ph_2SiH_2 , and PhMeSiH_2 , and aliphatic silanes such as Et_3SiH and Et_2SiH_2 . We observed that alcohols were easily converted into the corresponding mono-, bis-, and tris-substituted alkoxy silanes at room temperature depending on the stoichiometry of the reaction. The results of the detailed study are summarized in Table 2. Methanol can be completely converted into trimethoxy(phenyl)silane within 1 h at 30°C with vigorous evolution of hydrogen gas when it is reacted with phenyl silane at a molar ratio of 3 : 1 (Table 2, entry 1). Reaction between methanol and diphenylsilane (2 : 1) or triphenylsilane (1 : 1) afforded complete conversion within 2 h to obtain dimethoxy(diphenyl) and methoxy(triphenyl)silane, respectively (Table 2, entries 2 and 3). However, lower silane conversions of 73 % and 90 % were achieved after 3 h of reaction when aliphatic diethylsilane and triethylsilane were used as coupling partners with methanol (Table 2, entries 4 and 5). The gradual decrease in conversion values obtained as the silane is changed from a phenylsilane to an alkyl silane is presumably due to the decreasing reactivity of silanes, which is reported in literature.^[22] The reaction between ethanol and PhSiH_3 , Ph_2SiH_2 , and Ph_3SiH required 3 h to attain conversion values of 90 %, 74 %, and 60 %, respectively, at 30°C . However, complete conversion in each case can be achieved in 2 h at 60°C (Table 2, entries 6–8). Secondary isobutyl alcohols underwent smooth conversion, up to 99 %, within 3 h to give the corresponding alkoxy silanes upon reaction with various

hydrosilanes as coupling partners (Table 2, entries 9–11). In contrast, the conversion of benzyl alcohol into benzyloxy (triphenyl)silane, bisbenzyloxy(diphenyl)silane, and tribenzyloxy (phenyl)silane was lower (70 %) upon reaction with the corresponding hydrosilanes with appropriate stoichiometry (Table 2, entries 12–14) at 30°C . However, these reactions required 4 h to achieve such conversion values, and no improvement in conversion was observed even at 60°C . The molecular structure of benzyloxy(triphenyl)silane obtained from the dehydrogenative coupling reaction between benzyl alcohol and triphenylsilane (1 : 1) (Table 2, entry 14) was established by single-crystal X-ray analysis and is shown in Fig. 1.^[24]

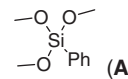
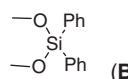
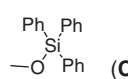
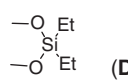
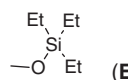
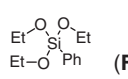
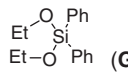
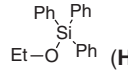
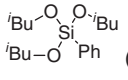
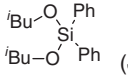
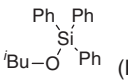
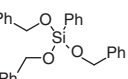
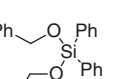
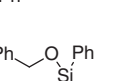
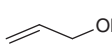
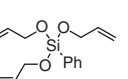
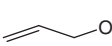
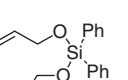
The silyl ether **N** crystallizes in monoclinic space group $P2_1$ having two molecules in the unit cell. The Si1–O1 distance of 1.638(4) Å is similar with the literature reported value.^[25] The geometry around the silicon is distorted tetrahedral with bond angles of O1–Si1–C19 109.63° , O1–Si1–C8 104.02° , C19–Si1–C8 112.40° , and C20–Si1–C8 104.02° .

To appraise the functional-group tolerance of the alkali metal catalyst, we employed several alcohols with different functional groups attached to them. Allyl alcohol was used as a coupling partner for different aliphatic and aromatic silanes, and a satisfactory yield of up to 88 % was obtained within ~3–4 h (entries 15–19, Table 2). This result indicated that the alkene group remained unaffected under the reaction condition employed. We also examined the reaction between alcohols containing halogen functional groups, such as 2-chloroethanol and 2-bromoethanol, and either phenyl silane or diphenyl silane as the reaction partner at 30°C . Excellent conversion (99 %) was achieved after 4 h. Nevertheless, steric influences and the functional groups attached to the various substrates, such as alcohols and silanes, are relevant for them to undergo dehydrogenative coupling to form the Si–O bonds. Similar observations were reported by Cui and Gao when tertiary silane was treated with $t\text{BuOH}$ using NHC as a catalyst.^[21] Thus, potassium hexamethyldisilazide acts as an efficient catalyst for the formation of Si–O bonds with a wide range of substrates. Moreover, to the best of our knowledge, this is the first example of the use of potassium salt as a catalyst for dehydrogenative coupling of hydrosilanes with hydroxyl groups.

Kinetics Study


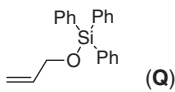

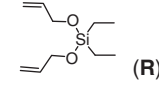

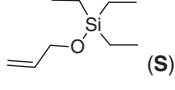
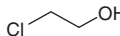
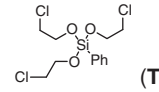
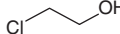
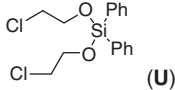
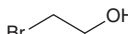
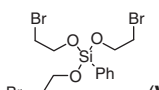
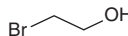
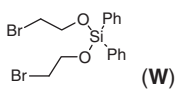
To explore the mechanism of the reaction, we performed kinetics studies. In situ NMR experiments were performed. Known amounts of the catalyst [$\text{KN}(\text{SiMe}_3)_2$] (to achieve concentrations of 0.025, 0.03, 0.035, 0.04, and 0.045 M) were added to a solution containing Ph_3SiH (0.130 g, 0.5 mmol), MeOH (0.016 g, 0.5 mmol), and C_6D_6 (0.4 mL). The solution was set at 30°C . At indicated time intervals, the solution was analyzed by ^1H NMR (see Figs S4–S14, Supplementary Material). The NMR spectra showed that with increase in time, the singlet peak signal of ^1SiH at 5.01 ppm gradually decreased clearly, indicating the formation of Si–O bond. The study showed that the KN (SiMe_3)₂-catalyzed dehydrocoupling reaction of MeOH with Ph_3SiH has a first-order dependence on the concentration of the catalyst $\text{KN}(\text{SiMe}_3)_2$. The reaction rate increased with increase in the amount of catalyst in a linear fashion (Figs 2 and 3). The result suggests that the active catalyst is a mononuclear intermediate in the catalytic cycle and this agrees with the proposed mechanism shown in Scheme 2 where the alkali metal complex reacts with alcohol to generate a metal alkoxide **i** via elimination of $\text{HN}(\text{SiMe}_3)_2$. The metal alkoxide acts as the

Table 2. Substrate scope for the dehydrocoupling of alcohols with various silanes at room temperature
Catalyst [KN(SiMe₃)₂] (5 mol-%), neat, room temperature. Yields were calculated from the isolated compounds

| Entry | Alcohol | Silane | Alcohol/silane | Time [h] | Product | Yield (Conversion) [%] |
|-------|---|----------------------------------|----------------|----------------|---|------------------------|
| 1 | CH ₃ OH | PhSiH ₃ | 3 : 1 | 1 |  (A) | 99 (99) |
| 2 | CH ₃ OH | Ph ₂ SiH ₂ | 2 : 1 | 2 |  (B) | 99 (99) |
| 3 | CH ₃ OH | Ph ₃ SiH | 1 : 1 | 2 |  (C) | 99 (99) |
| 4 | CH ₃ OH | Et ₂ SiH ₂ | 2 : 1 | 3 |  (D) | 72 (73) |
| 5 | CH ₃ OH | Et ₃ SiH | 1 : 1 | 3 |  (E) | 88 (90) |
| 6 | EtOH | PhSiH ₃ | 3 : 1 | 2 ^A |  (F) | 96 (99) |
| 7 | EtOH | Ph ₂ SiH ₂ | 2 : 1 | 2 ^A |  (G) | 93 (99) |
| 8 | EtOH | Ph ₃ SiH | 1 : 1 | 2 ^A |  (H) | 94 (99) |
| 9 | ⁱ BuOH | PhSiH ₃ | 3 : 1 | 3 |  (I) | 97 (99) |
| 10 | ⁱ BuOH | Ph ₂ SiH ₂ | 2 : 1 | 3 |  (J) | 96 (99) |
| 11 | ⁱ BuOH | Ph ₃ SiH | 1 : 1 | 3 |  (K) | 95 (99) |
| 12 | BnOH | PhSiH ₃ | 3 : 1 | 4 |  (L) | 68 (70) |
| 13 | BnOH | Ph ₂ SiH ₂ | 2 : 1 | 4 |  (M) | 68 (70) |
| 14 | BnOH | Ph ₃ SiH ₂ | 1 : 1 | 4 |  (N) | 57 (60) |
| 15 |  | PhSiH ₃ | 3 : 1 | 3 |  (O) | 88 (90) |
| 16 |  | Ph ₂ SiH ₂ | 2 : 1 | 3 |  (P) | 82 (86) |

(Continued)

Table 2. (Continued)

| Entry | Alcohol | Silane | Alcohol/silane | Time [h] | Product | Yield (Conversion) [%] |
|-------|---|----------------------------------|----------------|----------|--|------------------------|
| 17 |  | Ph ₃ SiH | 1 : 1 | 3 |  (Q) | 75 (80) |
| 18 |  | Et ₂ SiH ₂ | 2 : 1 | 4 |  (R) | 82 (85) |
| 19 |  | Et ₃ SiH | 1 : 1 | 4 |  (S) | 70 (72) |
| 20 |  | PhSiH ₃ | 3 : 1 | 4 |  (T) | 87 (90) |
| 21 |  | Ph ₂ SiH ₂ | 2 : 1 | 4 |  (U) | 95 (99) |
| 22 |  | PhSiH ₃ | 3 : 1 | 4 |  (V) | 92 (90) |
| 23 |  | Ph ₂ SiH ₂ | 2 : 1 | 4 |  (W) | 96 (99) |

^aReaction was performed at 60°C.

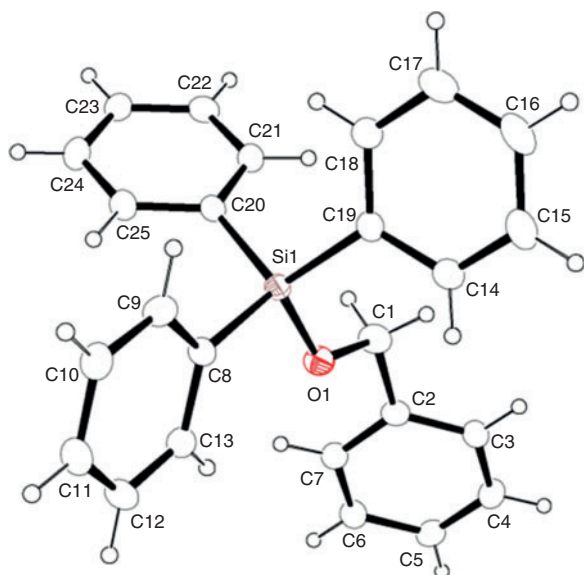


Fig. 1. ORTEP drawing of benzyloxy(triphenyl)silane **N** obtained under the reactions conditions listed in entry 14 of Table 2.

catalytically active species, and at higher concentrations, the reaction proceeds faster. Several reactions were attempted at varying concentrations of methanol, while the concentrations of [KN(SiMe₃)₂] and triphenylsilane remained constant (Table 3);

the observed reaction rate constant (K_{obs}) increased linearly with increasing concentrations of MeOH ranging from 0.4 to 0.8 M. The linear dependence of the reaction rate on methanol concentration confirms the first-order kinetics of the reaction. The same results could be observed upon varying the concentration of silane, while maintaining the constant concentrations of [KN(SiMe₃)₂] and methanol. Under these conditions, an empirical rate law can be obtained as follows:

$$-d[\text{Ph}_3\text{SiH}]/dt = k_{\text{obs}}[\text{Ph}_3\text{SiH}][\text{KN}(\text{SiMe}_3)_2]^1[\text{Ph}_3\text{SiH}]^1[\text{MeOH}]^1$$

This empirical rate law is consistent with the mechanism shown in Scheme 2. Specifically, Scheme 2 describes a plausible mechanism for the CDC reaction between alcohols and silanes mediated by group 1 hexamethyldisilazido pre-catalysts. This mechanism is based on the recently proposed catalytic cycle for the alkali metal-catalyzed CDC of amine with silane^[22] and borane,^[23] as well as the catalysis of N–H/H–B CDC reactions promoted by alkaline earth metals.^[26] In the first step, the alkali metal complex reacts with the alcohol to generate a metal alkoxide **i** via elimination of HN(SiMe₃)₂. The metal alkoxide acts as the catalytically active species. In the next step, nucleophilic attack of the O atom on the electrophilic Si centre of the incoming silane, denoted as R₃SiH in Scheme 2, furnishes the intermediate **ii**, featuring the transient intermediate **iii**. However, the transient intermediate **iii** rapidly undergoes β-hydrogen transfer to yield the transient metal hydride MH.

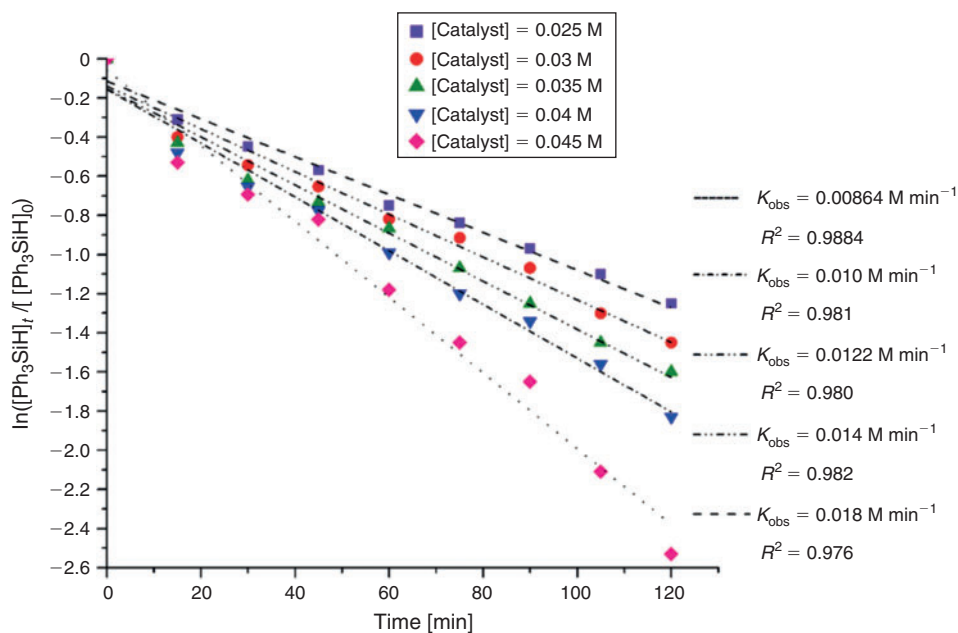


Fig. 2. First-order kinetics plots of $\ln([\text{Ph}_3\text{SiH}]_t/[\text{Ph}_3\text{SiH}]_0)$ as a function of time (t) in C_6D_6 (0.4 mL) at different concentrations of $[\text{KN}(\text{SiMe}_3)_2]$ at 25°C .

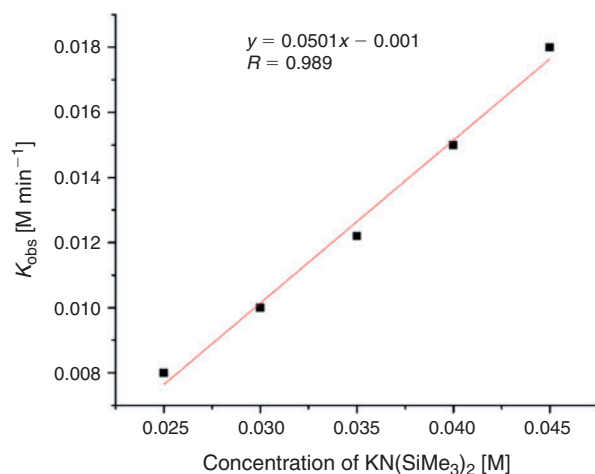
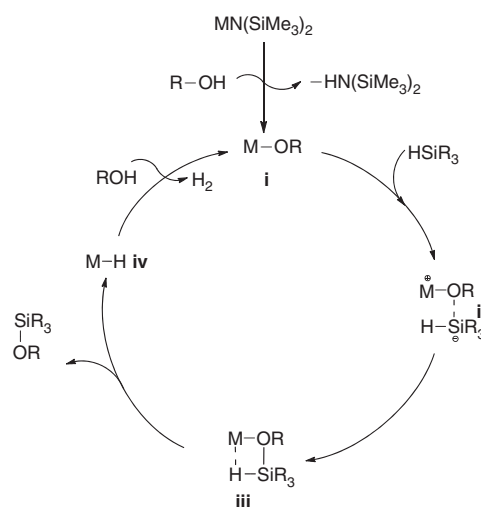


Fig. 3. Kinetics plots of K_{obs} as a function of $[\text{KN}(\text{SiMe}_3)_2]$. $[\text{Ph}_3\text{SiH}] = 0.05 \text{ M}$, $[\text{MeOH}] = 0.5 \text{ M}$, $\text{C}_6\text{D}_6 = 0.4 \text{ mL}$, temperature = 25°C .



Scheme 2. Plausible mechanism for the dehydrogenative coupling of alcohol with hydrosilane.

Conclusions

We have demonstrated, for the first time, the use of easily available, non-toxic, and cost-effective alkali metal hexamethyldisilazides $[\text{MN}(\text{SiMe}_3)_2]$, acting as effective pre-catalysts, for the CDC of O–H fragments of various alcohols with the Si–H of various silanes. The aryl silanes react faster than the corresponding alkyl silanes with different alcohols. However, the conversion performance of alcohols with halo functional groups was lower, thereby resulting in lower yields when compared with that of un-substituted alcohols. Nevertheless, the potassium hexamethyldisilazide proved to be an effective pre-catalyst for dehydrocoupling of alcohols with silanes under mild conditions.

Table 3. Reaction rates obtained upon varying the concentrations of catalyst $[\text{KN}(\text{SiMe}_3)_2]$, Ph_3SiH , and MeOH at 298 K in the presence of C_6D_6 as solvent

| Entry | Catalyst [$\times 10^{-3} \text{ M}$] | Ph_3SiH [M] | MeOH [M] | Initial rate [$\times 10^2 \text{ M min}^{-1}$] |
|-------|--|--------------------------------|----------------------|--|
| 1 | 5 | 0.3 | 0.5 | 0.009 |
| 2 | 5 | 0.7 | 0.5 | 0.019 |
| 3 | 5 | 0.5 | 0.4 | 0.007 |
| 4 | 5 | 0.5 | 0.6 | 0.013 |
| 5 | 5 | 0.5 | 0.5 | 0.008 |
| 6 | 7 | 0.5 | 0.5 | 0.012 |
| 7 | 8 | 0.5 | 0.5 | 0.014 |

Experimental

General Methods

All manipulations of air-sensitive materials were performed under inert atmosphere in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line interfaced with a high vacuum (10^{-4} Torr) line or in an argon-filled M. Braun glove box. ^1H NMR (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) spectra were recorded on a Bruker AVANCE III-400 spectrometer. All alcohols and silanes were purchased from either Sigma-Aldrich or Alfa Aesar. Alcohols were distilled over sodium metal before use. $\text{LiN}(\text{SiMe}_3)_2$, $\text{NaN}(\text{SiMe}_3)_2$, and $\text{KN}(\text{SiMe}_3)_2$ were purchased from Sigma-Aldrich and used as received. NMR solvents (CDCl_3 and C_6D_6) were purchased from Alfa Aesar.

Typical Procedure for CDC Reactions

Catalyzed CDC reactions were carried out using the following standard protocol. In the glove box, the chosen pre-catalyst (0.05 mmol) was loaded into a Schlenk tube, and subsequently the alcohol ($n \times 0.05$ mmol, n equiv.) followed by silane ($n' \times 0.05$ mmol, n' equiv.) were added. The reaction mixture was stirred at the desired temperature (30°C), which was controlled by an oil bath. After the required period, the reaction was quenched by adding CDCl_3 to the mixture. Substrate conversion was monitored by examination of the ^1H NMR spectrum of the reaction mixture and comparing relative intensities of resonance characteristics of the substrates and products.

Characterization of the Products

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data of known^[27] and newly synthesized silyl ethers are given in the Supplementary Material.

Supplementary Material

Spectral data and kinetics data of the products are available on the Journal's website.

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