

# Copper-Catalyzed 1,2-Addition of Nucleophilic Silicon to Aldehydes: Mechanistic Insight and Catalytic Systems

Christian Kleeberg,<sup>\*,[a]</sup> Evgenia Feldmann,<sup>[a]</sup> Eduard Hartmann,<sup>[b]</sup>  
Devendra J. Vyas,<sup>[b, c]</sup> and Martin Oestreich<sup>[b]</sup>

**Abstract:** Activation of the Si–B interelement bond with copper(I) alkoxides produces copper-based silicon nucleophiles that react readily with aldehydes to yield  $\alpha$ -silyl alcohols (that is,  $\alpha$ -hydroxysilanes) after hydrolysis. Two independent protocols were developed, one employing a well-defined NHC–CuOtBu complex and one using the simple CuCN–NaOMe combination without added ligand. The mechanism of the aldehyde addition was investigated in detail by stoichiometric and

catalytic experiments as well as NMR spectroscopic measurements. The primary reaction product of the addition of the Si–B reagent and the aldehyde (a boric acid ester of the  $\alpha$ -silyl alcohol) and also the “dead-end” intermediate, formed in the competing [1,2]-Brook rearrangement, were char-

acterized crystallographically. Based on these data, a reasonable catalytic cycle is proposed. The NHC–CuOtBu catalytic setup performs nicely at elevated temperature. A more reactive catalytic system is generated from CuCN–NaOMe, showing fast turnover at a significantly lower temperature. Both aromatic and aliphatic aldehydes are transformed into the corresponding  $\alpha$ -silyl alcohols in good to very good yields under these mild reaction conditions.

**Keywords:** aldehydes • copper • nucleophilic addition • silicon • transmetalation • X-ray diffraction

## Introduction

The copper-catalyzed transfer of silicon nucleophiles<sup>[1]</sup> onto various electrophiles, for example,  $\alpha,\beta$ -unsaturated carbonyl and carboxyl compounds,<sup>[2–4]</sup> imines,<sup>[5]</sup> alkynes,<sup>[6]</sup> allylic<sup>[7]</sup> and propargylic<sup>[8,9]</sup> chlorides, involving the Si–B interelement linkage<sup>[10]</sup> as the source of nucleophilic silicon, has recently gained considerable attention. The actual nucleophile is assumed to be a Cu–Si complex that transfers the silicon moiety onto the acceptor, followed by its regeneration through transmetalation of an intermediate Cu–O complex and the Si–B reagent. The new methodology is particularly attractive as it provides a facile access to copper-based silicon reagents without using strongly basic precursors. These are necessary in the established chemistry of silicon-based cuprates as stoichiometric reagents.<sup>[11]</sup> We recently reported an efficient catalytic system for the copper-catalyzed silyla-

tion of imines and proposed a catalytic cycle involving a Cu–Si complex as the silyl transfer reagent.<sup>[5]</sup> The active catalyst in this system is generated in situ from CuCN–NaOMe in the presence of an Si–B compound. We now decided to apply the same strategy in carbonyl addition reactions as it might provide a convenient direct route to  $\alpha$ -silyl alcohols (that is,  $\alpha$ -hydroxysilanes) from commercially available aldehydes.

Aside from the *retro*-[1,2]-Brook rearrangement of transient  $\alpha$ -silyloxy-substituted lithium carbanion pairs,<sup>[12]</sup> the majority of literature-known methods<sup>[13]</sup> for the preparation of  $\alpha$ -silyl alcohols are based on the (asymmetric) reduction of acyl silanes,<sup>[14–19]</sup> or the hydrogenation of enolsilanes.<sup>[20]</sup> However, the synthesis of the acyl silanes usually requires several steps.<sup>[21]</sup> An alternative but lesser used approach is the addition of a silicon nucleophile to a carbonyl group.<sup>[22–25]</sup> Hiyama et al. had introduced a fluoride-catalyzed Si–Si bond cleavage followed by the addition of the thus released silicon nucleophile to aldehydes.<sup>[22]</sup> Yields were, however, found to be diminished by partial [1,2]-Brook rearrangement.<sup>[23]</sup> Barrett and Hill then elaborated a practical procedure that is based on the addition of easy-to-make Me<sub>2</sub>PhSiLi to aliphatic and aromatic aldehydes.<sup>[24a]</sup> Neither  $\alpha$ -deprotonation (high chemoselectivity for enolizable aldehydes) nor Brook rearrangement were competing with the 1,2-addition. Despite these efforts, the use of strongly basic lithium silicon nucleophiles is not without problems for functionalized aldehydes, and there is a noteworthy report that the stoichiometric use of a silicon-based cuprate overcomes that issue.<sup>[24c]</sup> The copper-mediated mild generation of nucleophilic silicon from Si–B com-

[a] Dr. C. Kleeberg, E. Feldmann  
Institut für Anorganische und Analytische Chemie  
Technische Universität Carolo-Wilhelmina zu Braunschweig  
Hagenring 30, 38106 Braunschweig (Germany)  
Fax: (+49)0531-3915387  
E-mail: ch.kleeberg@tu-braunschweig.de

[b] E. Hartmann, D. J. Vyas, Prof. Dr. M. Oestreich  
Organisch-Chemisches Institut  
Westfälische Wilhelms-Universität Münster  
Corrensstrasse 40, 48149 Münster (Germany)

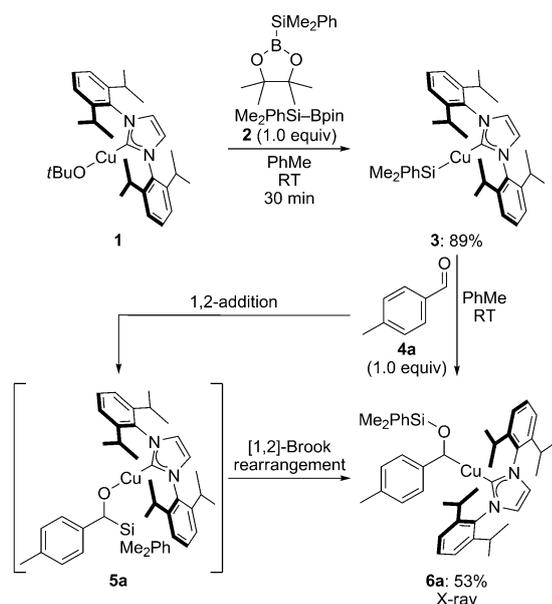
[c] D. J. Vyas  
NRW Graduate School of Chemistry

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pounds<sup>[1-3,5-8]</sup> might therefore be useful in a catalytic one-step access to  $\alpha$ -silyl alcohols from aldehydes. We report here two independent protocols for the catalytic 1,2-addition of a silicon nucleophile to aromatic and aliphatic aldehydes by employing either a well-defined NHC–Cu $\text{O}t\text{Bu}$  complex or the CuCN–NaOMe combination without added ligand. We also present insight into the mechanism of the former catalysis for the first time.<sup>[26]</sup>

## Results and Discussion

The nucleophilic attack of the Cu–Si on the electrophile, that is, the formal insertion of the electrophilic moiety into the Cu–Si bond, is supposed to be crucially involved in catalytic silylation reactions.<sup>[1-3,5-8]</sup> To study this essential step in detail, we employed the complex [(*i*PrNHC)Cu–SiMe<sub>2</sub>Ph] (**3**; *i*PrNHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in stoichiometric reactions with an aldehyde. This complex is readily generated by the reaction of the alcoholato complex [(*i*PrNHC)Cu–O*t*Bu] (**1**) and Me<sub>2</sub>PhSi–Bpin<sup>[27]</sup> (**2**) (pin = pinacolato).<sup>[3,26a]</sup> An exemplary aldehyde, 4-tolyl aldehyde (**4a**), inserts cleanly into the Cu–Si bond upon reaction with **3** under mild conditions, leading to the formation of the benzyl complex **6a** isolated in 53% yield (Scheme 1). Complex **6a** was characterized by a single X-



Scheme 1. Stoichiometric experiment: Aldehyde insertion into the Cu–Si bond, followed by [1,2]-Brook rearrangement.

ray diffraction study as well as by NMR spectroscopy and its connectivity was unambiguously established. Compound **6a** crystallized as racemate in the centrosymmetric triclinic space group  $P\bar{1}$  with one molecule in the asymmetric unit. The molecular structure of **6a** (Figure 1 and Table 1, left column) is typical for a (*i*PrNHC)Cu complex with a benzyl-

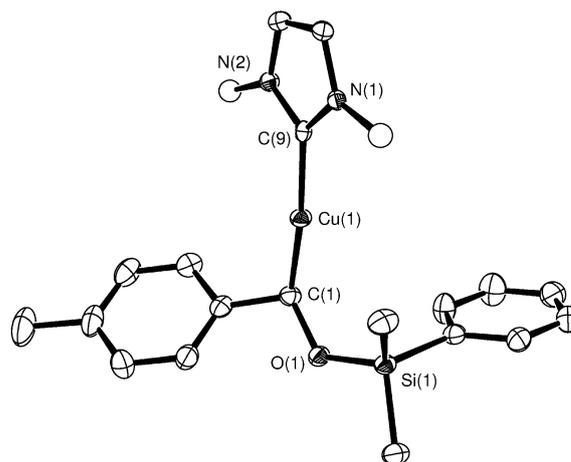


Figure 1. Molecular structure of **6a**. Thermal ellipsoids are given at the 50% probability level. 2,6-Diisopropylphenyl units are represented by the *ipso* carbon atom only (spheres); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–C(9) 1.904(2); Cu(1)–C(1) 1.955(2); C(1)–O(1) 1.473(2); O(1)–Si(1) 1.633(2); C(9)–Cu(1)–C(1) 169.64(8).

Table 1. Selected crystallographic data for **6a** and **7a**.<sup>[31]</sup>

	<b>6a</b>	<b>7a</b>
formula	C <sub>43</sub> H <sub>55</sub> CuN <sub>2</sub> O <sub>Si</sub>	C <sub>22</sub> H <sub>31</sub> BO <sub>3</sub> Si
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	707.52	382.37
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
<i>a</i> [Å]	9.8343(3)	6.4823(5)
<i>b</i> [Å]	10.7270(3)	34.692(3)
<i>c</i> [Å]	20.1244(6)	10.8310(7)
$\alpha$ [°]	74.770(3)	90
$\beta$ [°]	83.437(2)	117.782(7)
$\gamma$ [°]	85.444(3)	90
<i>T</i> [K]	100(2)	100(2)
<i>V</i> [Å <sup>3</sup> ]	2032.3(1)	2154.9(2)
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ], <i>Z</i>	1.156, 2	1.179, 4
crystal dimensions [mm <sup>3</sup> ]	0.36 × 0.35 × 0.27	0.47 × 0.14 × 0.11
color, shape	colorless, block	colorless, column
$\mu$ [mm <sup>-1</sup> ] ( $\lambda$ )	0.599 (0.71073 Å)	0.127 (0.71073 Å)
2 $\theta$ limits [°]	4.5–60.0	4.4–54.0
no. of reflns:		
measured	86 039	31 671
independent	11 639	4682
observed <sup>[a]</sup>	8891	4066
completeness	98.1% to 2 $\theta$ = 60.0°	99.6% to 2 $\theta$ = 54.0°
parameter/restraints	444/0	251/0
<i>R</i> <sub>1</sub> (obs. reflns) <sup>[b]</sup>	0.0518	0.0709
<i>wR</i> <sub>2</sub> (all reflns) <sup>[c]</sup>	0.1158 <sup>[d]</sup>	0.1606 <sup>[e]</sup>
GOF on <i>F</i> <sup>2</sup>	1.044	1.200
max./min. electron density	–0.563/1.267	–0.326/0.705
[eÅ <sup>-3</sup> ]		

[a] Observation criterion:  $I > 2\sigma(I)$ . [b]  $R_1 = \sum |F_o - F_c| / \sum F_o$ . [c]  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ . [d]  $w = [q^2(F_o^2) + (0.0433P)^2 + 1.5631P]^{-1}$ , in which  $P = (F_o^2 + 2F_c^2)/3$ . [e]  $w = [q^2(F_o^2) + (0.0446P)^2 + 3.5959P]^{-1}$ , in which  $P = (F_o^2 + 2F_c^2)/3$ .

ic ligand. The copper is approximately linearly coordinated with bond length and angles comparable to the closely related complex [(*i*PrNHC)Cu–CH(2,4,6-trimethylphenyl)-(OBpin)] (adopted numbering scheme): Cu(1)–C(9) 1.898(2) Å, Cu(1)–C(1) 1.947(2) Å, C(9)–Cu(1)–C(1) 175.46(8)°.<sup>[28a]</sup> The slightly larger deviation from linearity

might be attributed to the increased steric encumbrance of the complex. The formation of **6a** seems to suggest a nucleophilic attack of the copper atom on the carbonyl carbon atom in **4a**. This regioselectivity would be more than surprising as **3** and related complexes are supposed to transfer the silicon nucleophile onto the electrophilic carbon atoms of  $\alpha,\beta$ -unsaturated carbonyl and carboxyl compounds,<sup>[2–4]</sup> and imines<sup>[5]</sup> under formation of a C–Si bond. On the other hand, the formation of an analogous benzyl complex is reported for the closely related reaction of complex [(*i*PrNHC)Cu–Bpin] with aldehydes.<sup>[28]</sup> A DFT study on this reaction substantiates the initial formation of the alcoholato complex [(*i*PrNHC)Cu–OCHR(Bpin)] followed by a [1,2]-Brook-like rearrangement to yield [(*i*PrNHC)Cu–CHR(OBpin)].<sup>[28]</sup> This suggests a similar pathway to **6a** and, hence, **5a** rearranges to isomeric **6a**, which is corroborated by the known [1,2]-Brook rearrangement of  $\alpha$ -silyl-substituted alkoxides.<sup>[29]</sup> To confirm the formation of **5a** as an intermediate, the reaction of **3** and **4a** (excess) was monitored by <sup>1</sup>H NMR spectroscopy (Figure 2). It is evident from the

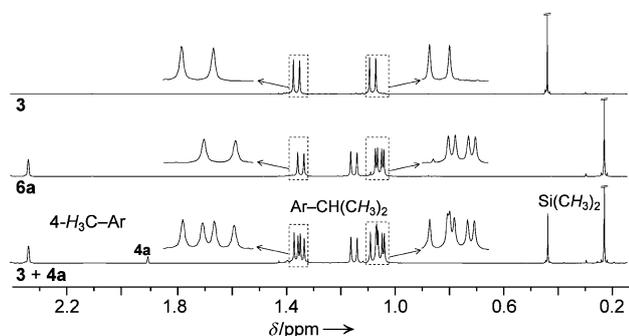
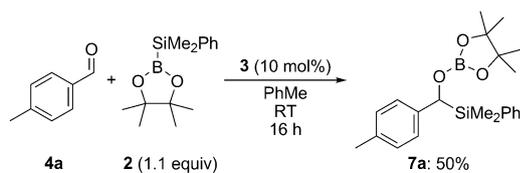


Figure 2. Relevant segments of the <sup>1</sup>H NMR spectra (300 MHz, C<sub>6</sub>D<sub>6</sub>, RT) of **3** and **6a**, as well as the reaction mixture of **3** and **4a** after 1 h at ambient temperature (+**6a** in bottom spectrum).

<sup>1</sup>H NMR data obtained that complex **6a** is formed as single product, whereas unreacted **3** and **4a** are still present after 1 h at ambient temperature. This clearly indicates that the rearrangement step **5a**→**6a** is considerably faster than the insertion step **4a**→**5a** (Scheme 1). The reaction of a catalytic amount of **3** (10 mol %) with **2** and **4a** at ambient temperature resulted in the formation of a new compound (Scheme 2), which was identified by NMR spectroscopy and single crystal X-ray diffraction analysis as *C*-silylated and *O*-borylated **7a** (Figure 3). This is strong evidence that com-



Scheme 2. Catalytic experiment: Isolation of the non-rearranged *O*-borylated  $\alpha$ -silyl alcohol.

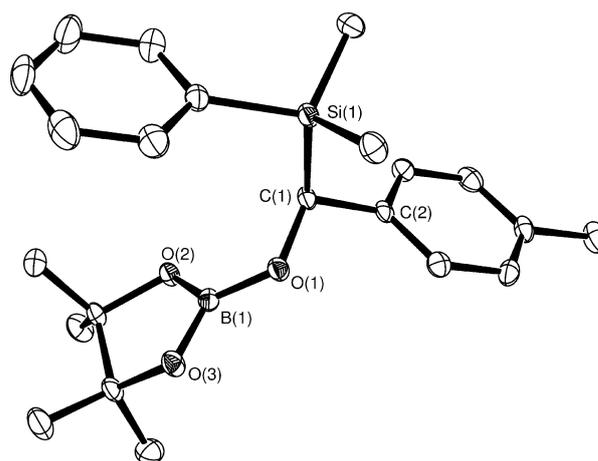


Figure 3. Molecular structure of **7a**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C(1)–O(1) 1.458(4); O(1)–B(1) 1.352(3); C(1)–C(2) 1.504(3); C(1)–Si(1) 1.909(3).

plex **5a** is indeed an intermediate in the formation of **6a** and likewise **7a**. Moreover, we also conclude that the transmetalation reaction of **5a** and **2** generating **7a** and **3** is significantly faster than the competing rearrangement of **5a** to **6a**. Compound **7a** was isolated in 50% yield by crystallization from the reaction mixture upon addition of *n*-pentane at –20 °C. It crystallized as racemate in the centrosymmetric monoclinic space group *P*2<sub>1</sub>/*c* with four molecules in the unit cell. The molecular structure (Figure 3 and Table 1, right column) is comparable to the closely related compound pinB–CH(2,4,6-trimethylphenyl)(OBpin) (adopted numbering scheme): C(1)–O(1) 1.456(2) Å, O(1)–B(1) 1.358(2) Å, C(1)–C(2) 1.518(2) Å.<sup>[28a]</sup> The formation of **7a** was also monitored by time-dependent <sup>1</sup>H NMR spectroscopy, using **3** (10 mol %), silyl boronic ester **2** (0.90 equiv), and excess aldehyde **4a** (1.0 equiv). Clean formation of **7a** from **4a** and **2** is seen at ambient temperature (Figure 4), the only identified copper complex is **3** until **2** is largely consumed. Complex **6a**, being the “dead-end” copper complex, is only formed from **5a** when **2** is essentially completely consumed. A reaction performed as described above (but in the absence of **3**) proved that no uncatalyzed background reaction

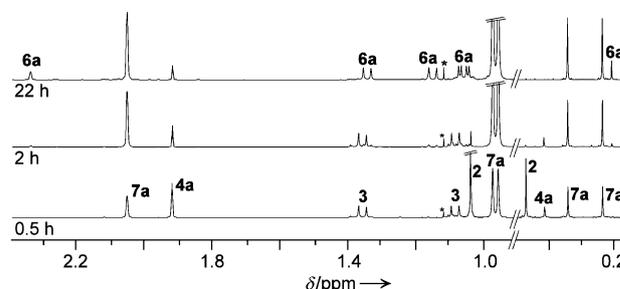
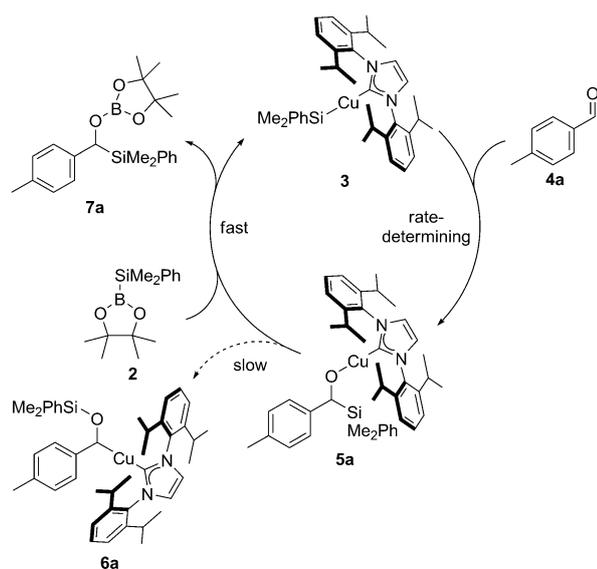


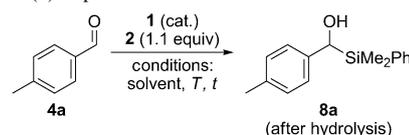
Figure 4. Relevant segments of the time-dependent <sup>1</sup>H NMR spectra (300 MHz, C<sub>6</sub>D<sub>6</sub>, RT) of the copper-catalyzed 1,2-addition of **4a** with **2** [**3** (10 mol %), **2** (0.90 equiv), and **4a** (1.0 equiv)]; \* denotes an unassigned signal].



Scheme 3. Catalytic cycle of a typical 1,2-addition of nucleophilic silicon using a preformed (NHC)Cu-Si complex.

is present.<sup>[30]</sup> Although no quantitative kinetic data have been obtained, the data available allows a catalytic cycle to be proposed for the copper-catalyzed addition of silicon nucleophiles to aldehydes (Scheme 3). It is particularly noteworthy that during the catalytic process complex **3** is identified in the reaction mixture, thereby indicating that **3** is the copper complex with the longest lifetime. We therefore conclude that the insertion of the aldehyde into the Cu-Si bond is the rate-determining step. The regeneration of **3** by transmetalation of **5a** and **2** accompanied by the release of the **7a** is supposed to be faster. The same step must also be considerably faster than the competing rearrangement of **5a** to **6a**, which is not formed until **2** is not available for the regeneration of **3**. Moreover, the reaction of isolated **6a** with **2** does not lead to the formation of **7a** and, for that reason, we are convinced that **6a** is not involved in the catalysis, and that **5a** and **6a** are not in rapid equilibrium.<sup>[30]</sup> All these data amount to the catalytic cycle depicted in Scheme 3. It must be emphasized that the outlined catalytic cycle is remarkably similar to the catalytic cycle proposed for the copper-catalyzed 1,2-bisboration of aldehydes on basis of DFT calculations, indicating a closely related mechanism for the 1,2-bisboration and C-silyl-O-boration of aldehydes.<sup>[28b]</sup> The reaction leading to **7a** represents a procedure for the chemoselective preparation of pinacol boric esters of  $\alpha$ -silyl alcohols (see Scheme 2). To make it synthetically useful, these primary products must be hydrolyzed to the  $\alpha$ -silyl alcohols. An exemplary experiment showed that **7a** hydrolyzes readily in the presence of D<sub>2</sub>O.<sup>[30]</sup> The hydrolysis also occurs readily during the purification by flash chromatography on silica gel. After these mechanistic investigations using stoichiometric and catalytic amounts of preformed complex [(*i*PrNHC)Cu-SiMe<sub>2</sub>Ph] (**3**), we turned toward the elaboration of a general procedure employing [(*i*PrNHC)-CuOtBu] (**1**) as the catalyst precursor. To establish suitable

Table 2. Copper-catalyzed 1,2-addition to aldehydes employing (NHC)CuOtBu (**1**): Optimization of the reaction conditions.

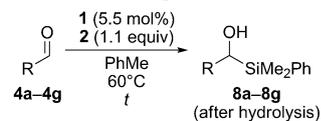


Entry	Catalyst <b>1</b> [mol %]	Solvent	<i>T</i> [°C]	<i>t</i> [h] <sup>[a]</sup>	Yield [%] <sup>[b]</sup>
1	10	PhMe	RT	32	75
2	5.5	PhMe	RT	74	81
3	5.5	PhMe	60	16	80
4	5.5	PhMe	90	16	54
5	5.5	THF	60	16	85

[a] Full consumption of aldehyde as monitored by GLC analysis. [b] Isolated product yield after flash chromatography on silica gel.

reaction conditions, we screened catalyst loading, reaction temperature, and solvent in the reaction of test substrate **4a** (Table 2 with selected data): 5.5 mol % of **1** and 60°C in toluene were found to be the optimal conditions (Table 2, entries 1–3). At higher reaction temperature (90°C), unidentified by-products were detected by GLC analysis (Table 2, entry 4). The catalysis worked equally well in THF (Table 2, entry 5). This reaction setup was then applied to a series of aromatic and aliphatic aldehydes **4** (Table 3). With respect

Table 3. Copper-catalyzed 1,2-addition to aldehydes employing (*i*PrNHC)CuOtBu (**1**): Substrate scope.



Entry	Aldehyde	R	<i>t</i> [h] <sup>[a]</sup>	$\alpha$ -Silyl alcohol	Yield [%] <sup>[b]</sup>
1	<b>4a</b>	4-MeC <sub>6</sub> H <sub>4</sub>	16	<b>8a</b>	80
2	<b>4b</b>	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	120	<b>8b</b>	78
3	<b>4c</b>	4-(MeO)C <sub>6</sub> H <sub>4</sub>	84	<b>8c</b>	74
4	<b>4d</b>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	16	<b>8d</b>	85
5	<b>4e</b>	(CH <sub>3</sub> ) <sub>2</sub> CH	16	<b>8e</b>	86 <sup>[c]</sup>
6	<b>4f</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	16	<b>8f</b>	68
7	<b>4g</b>	4-(CN)C <sub>6</sub> H <sub>4</sub>	16	<b>8g</b>	50

[a] Full consumption of aldehyde as monitored by GLC analysis. [b] Isolated product yield after flash chromatography on silica gel. [c] Reaction at ambient temperature.

to aromatic aldehydes, both electron-donating as well as electron-withdrawing groups were tolerated and isolated product yields were generally good (Table 3, entries 1–4). Reaction times were, however, much longer with a sterically bulky (Table 3, entry 2) or an electron-rich aryl group (entry 3). Conversely, an activated, electron-deficient aldehyde reacted in shorter reaction time (Table 3, entry 4). These results reflect the importance of the electrophilicity of the carbonyl carbon atom in the rate-determining silyl transfer. To our delight, we found that also aliphatic (that is, enolizable) aldehydes performed well (Table 3, entries 5 and 6). Functionalized aromatic aldehydes with reactive func-

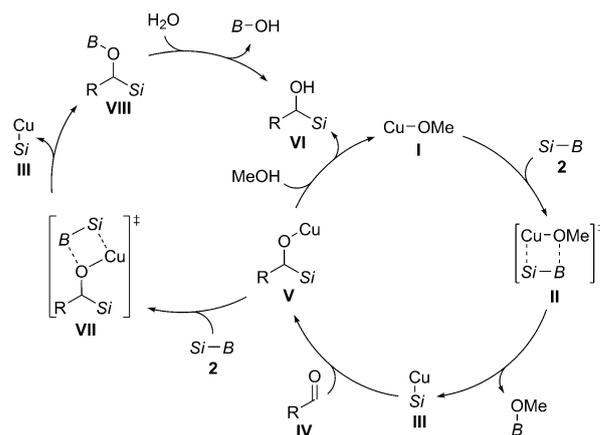
tional groups in the *para*-position (NO<sub>2</sub> and OH groups) or pyridine-4-carboxaldehyde did not yield the desired  $\alpha$ -silyl alcohols but only unidentified products (not shown). The related CN-substituted aldehyde afforded the product in moderate yield (Table 3, entry 7). Based on our recent imine addition,<sup>[5]</sup> we anticipated that a more reactive catalytic system might be generated from CuCN–NaOMe without added ligand. As shown in Table 4, aromatic and aliphatic alde-

Table 4. Copper-catalyzed 1,2-addition to aldehydes employing CuCN–NaOMe without added ligand: Substrate scope.

Entry	Aldehyde	R	<i>t</i> [h] <sup>[a]</sup>	$\alpha$ -Silyl alcohol	Yield [%] <sup>[b]</sup>
1	<b>4b</b>	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	<b>8b</b>	58 <sup>[c]</sup>
2	<b>4c</b>	4-(MeO)C <sub>6</sub> H <sub>4</sub>	2	<b>8c</b>	83
3	<b>4d</b>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	<b>8d</b>	89
4	<b>4e</b>	(CH <sub>3</sub> ) <sub>2</sub> CH	2	<b>8e</b>	73 <sup>[d]</sup>
5	<b>4h</b>	cyclohexyl	2	<b>8h</b>	50 <sup>[d]</sup>
6	<b>4i</b>	1-naphthyl	2	<b>8i</b>	82
7	<b>4j</b>	C <sub>6</sub> H <sub>5</sub>	2	<b>8j</b>	87
8	<b>4k</b>	4-ClC <sub>6</sub> H <sub>4</sub>	2	<b>8k</b>	93
9	<b>4l</b>	4-BrC <sub>6</sub> H <sub>4</sub>	2	<b>8l</b>	87

[a] Full consumption of aldehyde as monitored by GLC analysis. [b] Isolated product yield after flash chromatography on silica gel. [c] CuCN (10 mol%) and NaOMe (20 mol%) were used. [d] **2** (2.0 equiv) was used.

dehydes **4** are efficiently transformed into  $\alpha$ -silyl alcohols **8** under these reaction conditions (MeOH–THF). Reaction times are short, even at 0°C. A trend similar to that found for the NHC-based catalyst is observed. Steric hindrance is detrimental, and double the amount of catalyst is required to obtain a reasonable yield (Table 4, entry 1). Electron-deficient, non-hindered aldehydes perform best (Table 4, entries 2, 8, and 9). Aliphatic aldehydes afforded only decent yields when using excess **2** (Table 4, entries 4 and 5). It is important to note that the order of reagent is crucial (see general procedure 2 (GP2) in the Experimental Section). Any changes to that led to inconsistent results. Compared with the NHC-based system, the present setup is superior in terms of practicability and reactivity as no pre-prepared copper complex and no heating are required. The latter aspect might be beneficial for sensitive substrates. The catalytic cycle for the CuCN–NaOMe–MeOH system (Scheme 4) is likely to be similar to the one investigated in detail for [(*i*PrNHC)Cu–O*t*Bu] (**1**) and [(*i*PrNHC)Cu–SiMe<sub>2</sub>Ph] (**3**), respectively, (see Scheme 3). It begins with the boron-to-copper transmetalation of in situ-formed Cu–OMe and **2** (**I**→**III**), the formal  $\sigma$ -bond metathesis through **II**. Thus formed Cu–Si reagent **III** adds to aldehyde **IV** to arrive at intermediate **V** (**IV**→**V**) but we do not know whether the 1,2-addition is rate-determining as with the NHC ligand (see Scheme 3). With added MeOH, **V** is likely



Scheme 4. General catalytic cycle of the 1,2-addition of nucleophilic silicon using a CuCN–NaOMe as the pre-catalyst.

to be immediately protonated (**V**→**VI**). The catalysis also works without added MeOH, presumably through another  $\sigma$ -bond metathesis of intermediate **V** with **2** resulting in the formation of **VIII** and Cu–Si reagent **III** (**V**→**VII**→**VIII**). Final hydrolysis during the aqueous work-up affords the  $\alpha$ -silyl alcohols **VI** (**VIII**→**VI**).

## Conclusion

Stoichiometric experiments on the insertion of aldehydes into the Cu–Si bond of a well-defined NHC–copper silyl complex led to the development of a catalytic system for the  $\alpha$ -silylation of aldehydes. On the basis of experimental data and NMR spectroscopy, we propose a catalytic cycle and relative reaction rates of the reactions involved. Another protocol for the  $\alpha$ -silylation of aldehydes, employing a not yet characterized catalyst prepared in situ from CuCN and NaOMe, shows comparable performance at a significantly lower temperature. Both protocols are well-suited for the  $\alpha$ -silylation of aromatic and aliphatic aldehydes under mild conditions. Although the NHC-based catalytic system is synthetically more elaborate, it provides valuable mechanistic insight into copper-catalyzed transfer reactions of nucleophilic silicon. In turn, the CuCN–NaOMe-based system is preparatively straightforward and performs exceedingly well under mild conditions. However, functionalized aldehydes remain challenging substrates for both catalytic systems. Further combined computational and kinetic investigations to gain a deeper insight into the mechanism of the  $\alpha$ -silylation of aldehydes are subject of ongoing research.

## Experimental Section

**General:** Detailed experimental procedures (**6a** and **7a**), detailed characterization and experimental data (**6a**, **7a**, and **8a–8l**), and crystallographic data are provided in the Supporting Information.

**General procedure for the  $\alpha$ -silylation of aldehydes employing [(iPrNHC)CuOtBu] (**1**) as precatalyst (GP1 for Table 3):** In a glove box, a Schlenk tube was charged with **1** (11 mg, 0.021 mmol, 5.5 mol%) and the indicated dried and degassed solvent (5 mL). After addition of the indicated aldehyde **4** (0.38 mmol, 1.0 equiv) and Me<sub>2</sub>PhSiBpin (**2**, 110 mg, 0.42 mmol, 1.1 equiv) under inert conditions, the reaction was maintained at 60 °C until full conversion (GLC monitoring). After removal of solvent in vacuo, the residue was subjected to flash column chromatography on silica gel using *n*-hexane/diethyl ether as eluent affording analytically pure **8**.

**General procedure for the  $\alpha$ -silylation of aldehydes employing CuCN-NaOMe as precatalyst (GP2 for Table 4):** A flame-dried Schlenk tube was successively charged with CuCN (0.020 mmol, 5.0 mol%), and NaOMe (0.040 mmol, 10 mol%) under an inert atmosphere. After addition of THF (1 mL), the reaction mixture is maintained at RT for 1 h. At 0 °C, the indicated aldehyde **4** (0.40 mmol, 1.0 equiv), Me<sub>2</sub>PhSiBpin (**2**, 0.48 mmol, 1.2 equiv), MeOH (1.6 mmol, 4.0 equiv), and THF (1 mL) were added in this order. The reaction was subsequently maintained at 0 °C until full conversion (TLC and GLC monitoring). Filtration through a small pad of silica gel using *tert*-butyl methyl ether (10 mL) and evaporation of the solvents under reduced pressure afforded the corresponding  $\alpha$ -silyl alcohol **8** as the crude product. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether as the eluent affords analytically pure **8**.

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