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## Letter

# **Copper-Catalyzed Twofold Silylmetalation of Alkynes**

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**Abstract** The first twofold silylmetalation across a C=C triple bond was achieved. In the presence of a catalytic amount of copper cyanide, diarylacetylenes were converted into 1,2-dimetalated 1,2-disilyl-1,2-di-arylethanes on treatment with silylpotassium species generated in situ from disilane and t-BuOK. The dimetalated species were subsequently protonated to yield a series of 1,2-disilyl-1,2-diarylethanes.

Key words silylmetalation, disilane, copper catalysis, ate complex, disilyldiarylethanes

Organosilicon compounds have attracted much attention as both synthetic intermediates<sup>1</sup> and functional materials.<sup>2</sup> The development of methods for the formation of C-Si bonds is therefore considered to be an important research topic in organic chemistry. Among such methods, transition-metal-catalyzed silvlation of C-C multiple bonds represents a straightforward method. In particular, silylmetalation of alkynes is useful for the synthesis of highly functionalized alkenylsilanes (Scheme 1a)<sup>3</sup> and, consequently, has been thoroughly investigated by using various combinations of a copper species and a silvl alkali metal species. All the reported silvlmetalation reactions of alkynes occur only once to yield the corresponding monosilylmetalated alkenes. There are no previous reports of a twofold addition of silvlmetals across the triple bond of an alkyne to yield a doubly silylmetalated alkane. Here we report the first such twofold silvlmetalation of alkynes with the aid of a copper catalyst and a disilane as a precursor of a silylpotassium species (Scheme 1b). The resulting doubly silylmetalated species can be protonated to provide access to 1,2-disilylethanes.



To develop standard reaction conditions, we performed an extensive screening of various silicon sources, copper species, bases, and solvents. This optimization eventually revealed that treatment of diphenylacetylene (1a) with copper(I) cyanide (20 mol%), 1,1,2,2-tetramethyl-1,2-diphenyldisilane (2, 3.0 equiv), and t-BuOK (3.2 equiv) in 1,2dimethoxyethane (DME) as the solvent at 25 °C for 1.5 h, followed by aqueous workup, provided 1,2-disilyl-1,2-diphenylethane (**3a**) in 88% yield (66% isolated yield)<sup>4</sup> as an inseparable 1:1.2 diastereomeric mixture (Table 1, entry 1).<sup>5</sup> In the absence of a copper catalyst, the reaction was more complicated, and **3a** was obtained in a much lower yield (35%) (entry 2). Other copper species gave slightly reduced yields (entries 3 and 4). The reaction did not proceed in the absence of a base (entry 5). Lithium or sodium tertbutoxide did not mediate the reaction because they are inefficient in cleaving the Si-Si bond (entries 6 and 7). These results underscore the importance of using a potassium alkoxide to generate silvlpotassium species in situ:<sup>6</sup> these species then mediate the formation of silvlcopper species. This direct formation of silylcopper species from disilanes differentiates the current method from previous silvlmetalations of alkynes.<sup>3</sup> KHMDS was ineffective as a base (entry 8), indicating the importance of a nucleophilic alkoxide for

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this reaction. The reaction was relatively sluggish in THF, and none of the desired product was obtained in 1,4-diox-ane or toluene (entries 9–11).



<sup>a</sup> Determined by <sup>1</sup>H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

<sup>b</sup> Isolated yield; dr = 1:1.2.

With the optimized conditions in hand, we surveyed the scope of this double silylmetalation with respect to the alkyne (Figure 1). The di-p-tolyl, di-p-methoxyphenyl, and di-2-naphthyl adducts **3b-d**, respectively, were obtained in good yields. The di-o-tolyl adduct **3e** was not obtained, probably due to the steric effect of the o-methyl groups. Less-symmetrical *p*-(dimethylamino)phenyl-, *p*-methoxyphenyl-, and *m*-methoxyphenyl-substituted products **3f**-**h**, respectively, were obtained in high yields. Whereas an electron-withdrawing *m*-fluorophenyl substituent was barely tolerated to give a 27% yield of product **3i**, products **3j** and **3k** were not formed when the *para*-position was substituted with an electron-withdrawing group. Alkylacetylenes were not good substrates for this transformations; the desired products 31 and 3m were not obtained. With terminal alkynes, the reaction rapidly gave an unidentified precipitate, probably through the formation of an acetylide.

Next, we examined the effect of the organosilicon source (Figure 2). Hexamethyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane showed lower reactivities, yielding **3n** and **3o** in yields of 20 and 24%, respectively. The lower yield of **3n** might be due to the elevated temperature required to generate the trimethylsilylcopper species by cleaving the less-reactive Si–Si bond. The formation of **3o** 



Figure 1 Scope of the reaction with respect to the alkyne

might be hampered by steric hindrance by the  $Ph_2MeSi$  group.

To probe the reaction mechanism, the reaction mixture was treated with  $D_2O$  to afford the corresponding doubly deuterated 1,2-disilylated diphenylethane **4** in 85% yield with 91% deuterium incorporation (Scheme 2).<sup>7</sup> This confirmed that a dianionic intermediate **5** was generated in situ. This dianionic intermediate **5** could be oxidized in situ with iodine<sup>8</sup> to afford (*E*)-1,2-bis[dimethyl(phenyl)silyl]-



Figure 2 Scope of the reaction with respect to the disilane

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1,2-diphenylethene (**6**) selectively in 44% yield. Notably, the overall transformation represents a rare intermolecular *anti*-disilylation of an alkyne.<sup>9</sup> The reaction with other electrophiles such as BuCl or ClCH<sub>2</sub>OMe did not provide a doubly alkylated product, probably due to the bulkiness of the metalated species **5**.



The plausible reaction mechanism shown in Figure 3 was accordingly proposed. Copper cyanide reacts with two equivalents of the silylpotassium species generated in situ from disilane and *t*-BuOK.<sup>6,10</sup> The resulting copper–ate complex **7** should be susceptible to silylcupration with the diarylacetylene to form adduct **8**.<sup>11</sup> The remaining silyl group on the copper atom migrates to the adjacent carbon to give carbanion **9**. With the aid of two equivalents of the silylpotassium species, the copper atom in **9** is replaced with potassium to afford 1,2-dimetalated species **5**. The copper–ate species **7** is concomitantly regenerated to close the catalytic cycle. The efficient double silylmetalation might be ascribed to smooth 1,2-silyl migration from **8** with the aid of potassium as the countercation.<sup>12</sup>



Figure 3 Proposed reaction mechanism

In conclusion, we have developed the first twofold silylmetalation across a C=C triple bond. The reaction is conducted in the presence of a copper cyanide catalyst and a silylpotassium species generated from a disilane and *t*-BuOK. Protonation of the 1,2-dimetalated species provided a series of 1,2-disilyl-1,2-diarylethanes. Further applica-

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study will be reported in due course.

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tions of the cuprate species and a detailed mechanistic

## **Supporting Information**

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611869.

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- (4) The reduction in the isolated yield is due to the difficulty in chromatographically separating the product from the *t*-BuO-SiMe<sub>2</sub>Ph generated during the formation of the silyl potassium species.

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## (5) **1,2-Bis[dimethyl(phenyl)silyl]-1,2-diphenylethane** (3a); Typical Procedure

An oven-dried Schlenk tube was charged with diphenylacetylene (**1a**; 53.5 mg, 0.300 mmol), CuCN (5.4 mg, 0.060 mmol), and *t*-BuOK (108 mg, 0.960 mmol). DME (2.0 mL) and 1,1,2,2tetramethyl-1,2-diphenyldisilane (**2**, 244 mg, 0.900 mmol) were added sequentially to the mixture, which was then stirred at 25 °C for 1.5 h. H<sub>2</sub>O (30 mL) was added at 0 °C, and the resulting biphasic solution was extracted with Et<sub>2</sub>O (3 × 15 mL). The combined organic layer was washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure. The resulting residue was purified by column chromatography (silica gel, hexane) and then by GPC (CHCl<sub>3</sub> eluent) to give a white solid; yield: 89.2 mg (0.198 mmol, 66%) (minor/major = 1:1.2 as an inseparable mixture).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.38–7.36 (m, 2 H × 0.55), 7.34–7.30 (m, 8 H × 0.55), 7.22 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 2 H × 0.45), 7.14–7.11 (m, 6 H × 0.55 + 4 H × 0.45), 7.07–7.01 (m, 6 H × 0.45), 6.98 (dd, *J* = 7.2, 1.2 Hz, 4 H × 0.45), 6.92 (d, *J* = 7.2 Hz, 4 H × 0.45), 6.84–6.83 (m, 4 H × 0.55), 2.88 (s, 2 H × 0.45), 2.75 (s, 2 H × 0.55), 0.10 (s, 6 H × 0.55), -0.17 (s, 6 H), -0.22 (s, 6 H × 0.45). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 142.5, 141.6, 138.5, 138.4, 134.1, 134.0, 131.5, 129.5, 128.8, 128.2, 127.7, 127.6, 127.3, 127.0, 125.1, 125.1, 38.5, 36.8, -2.36, -2.42, -3.36, -4.04. HRMS: *m/z* [M<sup>+</sup>] calcd for C<sub>30</sub>H<sub>34</sub>Si<sub>2</sub>: 450.2194; found: 450.2197.

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- (7) A different isomeric ratio was observed when intermediate **5** was quenched with D<sub>2</sub>O. So far, the reason for this phenomenon is unclear.
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- (9) The oxidation of dianionic species 5 with iodine probably proceeds through the formation of a radical intermediate, resulting in loss of stereochemical information. Thus, the less stereochemically congested 6 is selectively obtained. See: Garst, J. F.; Roberts, R. D.; Pacifici, J. A. J. Am. Chem. Soc. 1977, 99, 3528.
- (10) Even though a free silylpotassium species seems to function in the reaction, the formation of a silicate species generated from disilane and *tert*-butoxide cannot be excluded.
- (11) Ref. 3b reports an example of monosilylcupration by  $(R_3Si)_2Cu(CN)Li_2$  of a C=C triple bond however, no report of any type of addition of  $(R_3Si)_2Cu(CN)K_2$  is known.
- (12) In the presence of smaller amounts of disilane (1.0 equiv) and t-BuOK (1.2 equiv), we obtained recovered alkyne 1a (32%) and disilylated product 3a (19%), as well as the monosilylated alkene (25%), after protic workup. This suggests that a monosilylated copper species is formed just before the the silylpotassium species is consumed. The monosilylated copper species might also add to the alkyne to provide the monosilylated alkene eventually.