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Copper-catalyzed Twofold Silylmetalation of Alkynes

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Abstract The first twofold silylmetalation across a C-C bond is achieved. In the presence of a catalytic amount of copper cyanide, diarylacetylenes were converted to 1,2-dimetalated 1,2-disilyl-1,2-diarylethenes on treatment with silylpotassium species generated in situ from disilane and BuOK. The dimetalated species were protonated to yield a series of 1,2-disilyl-1,2-diarylethenes.

Key words silylmetalation, disilane, copper, ate complex, dianion

Organosilicon compounds have attracted much attention both as synthetic intermediates and functional materials. Development of methods for the formation of C-Si bonds is thus considered as an important research topic in organic chemistry. Among such methods, transition-metal-catalyzed silylations of C-C multiple bonds represent a straightforward method. Particularly, silylmetalation of alkynes is useful for the synthesis of highly functionalized alkenylsilanes and has hence been investigated well (Scheme 1a) with a combination of copper species and silylalkali metal species. All the reported silylmetalation reactions of alkynes occur only once to yield the corresponding silylmetalated alkenes. Thus, there are no reports about twofold addition of silylmetals across alkynes to yield doubly silylmetalated alkanes. Here we report the first twofold silylmetalation of alkynes with the aid of a copper catalyst and disilanes as a precursor of silylpotassium species (Scheme 1b). The doubly silylmetalated species thus obtained could be protonated to provide access to 1,2-disilylalkenes.

Scheme 1 Mono-silylmetalation and Twofold Silylmetalation of Alkyne

For devising the standard reaction conditions, an extensive screening of silicon sources, copper species, bases, and solvents were conducted. This optimization eventually revealed that treatment of diphenylacetylene (1a) with copper cyanide (20 mol%), 1,1,2,2-tetramethyl-1,2-diphenyldisilane (2, 3.0 equiv) and BuOK (3.2 equiv) in 1,2-dimethoxyethane (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% (66% isolated4) yield as a 1:1.2 diastereomeric mixture (Table 1, entry 1). In the absence of a copper catalyst, the reaction was more complicated and 3a was obtained in much lower yield (35%) (entry 2). Other copper species gave slightly reduced yields (entries 3, 4). The reaction did not proceed without any bases (entry 5). Lithium or sodium tert-butoxide did not mediate the reaction due to the inefficiency of deaving the Si–Si bond (entries 6, 7). These results underscore the importance of potassium alkoxide for in situ generation of silylpotassium species. This species would then mediate the formation of silylcopper species. This direct formation of silylcopper species from disilanes differentiates the current methodology from the past ones.1 KHMS was not effective, which indicates the importance of nucleophilic alkoxide for this reaction (entry 8). The reaction was relatively sluggish in THF, and no desired product was observed in 1,4-dioxane and toluene (entries 9–11).
With the optimized conditions in hand, we surveyed the scope of this double-silylation with respect to alkynes (Figure 1). Di-p-tolyl (3b), di-p-methoxyphenyl (3c), di-2-naphthyl (3d) adducts were obtained in good yields. Di-o-tolyl adducts 3e was not obtained, probably due to the steric effect of the o-methyl groups. Less symmetrical p-dimethylaminophenyl (3f), p-methoxyphenyl (3g), m-methoxyphenyl (3h) substituted products were obtained in high yields. While an electron-withdrawing m-fluorophenyl substituent was barely tolerated to give a 27% yield of the product 3l, no products 3j, 3k were formed when the para position was substituted with electron withdrawing groups. Alkyl acetylenes were not good substrates for this transformation and no desired products 3l and 3m were obtained. The reaction is not applicable to terminal alkynes to rapidly generate an unidentified precipitate probably through the formation of an acetylide.

Investigation on the effect of organosilicon source is shown in Figure 2. Hexamethyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenylsilane showed lower reactivity to yield 3n and 3o in 20% and 24% respective yields. The lower yield of 3n may be ascribed to the elevated temperature that is required for generating trimethylsilylcopper by cleaving the less reactive Si-Si bond. The formation of 3o may be hampered by the steric hindrance of Ph₃MeSi group.

To probe the reaction mechanism, the reaction mixture was treated with D₂O to afford the corresponding doubly deuterated 1,2-disilylated diphenylethane 4 in 85% yield with 91% deuterium incorporation (Scheme 2). We thus confirmed the formation of a dianionic intermediate 5 generated in situ. This dianionic intermediate 5 could also be oxidized in situ with iodine⁶ to selectively afford [Et]₂1,2-bis(dimethylphenylsilyl)]-1,2-diphenylethane 6 in 44% yield. Notably, the overall transformation represents a rare intermolecular anti-disilylation of alkynes.⁷ The reaction with other electrophiles such as nBuCl and chloromethyl methyl ether did not provide the doubly
alkylated product probably due to the bulkiness of the metalated species.

A plausible reaction mechanism is accordingly proposed as shown in Figure 3. Copper cyanide would react with two equivalents of silylpotassium species that is generated in situ from disilane and tBuOK.6,10 Copper-ate complex 7 thus formed would be susceptible to the silyl cyanation with diarylacetylene to form adduct 8.11 The remaining silyl group on the copper atom would migrate to the adjacent carbon to lead to carbaniom 9. With the aid of two equivalents of silylpotassium species, the copper atom in 9 would be replaced with potassium to afford 1,2-dimetalated species 5. The copper-ate species 7 would be concomitantly regenerated to close the catalytic cycle. The efficient double silylmethylation can be ascribed to smooth 1,2-migration from 8 with the aid of potassium as the counterion.12

![Figure 3 Proposed Reaction Mechanism](image)

In conclusion, we have developed the first twofold silylmethylation across a C-C triple bond. The reaction is in the presence of copper cyanide catalyst and silylpotassium species generated from disilane and tBuOK. Protonation of the 1,2-dimetalated species provided a series of 1,2-disilyl-1,2-diarylethenes. Further applications of cuprate species and detailed mechanistic study will be reported in due course.

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**Supporting Information**

Supporting information for this article is available online.

**References and Notes**


(4) The reduced isolated yield is due to difficulty in chromatographically separating the product from tBuOSiMe3Ph that is generated during the formation of silyl potassium species.

(5) **Twofold Silylmethylation of Alkynes.** An oven-dried Schlenk tube was charged with diphenylacetylene (1a, 53.5 mg, 0.300 mmol), CuCN (5.4 mg, 0.060 mmol) and potassium tert-butoxide (108 mg, 0.960 mmol). DME (2.0 mL) and diethyl ether (0.2 mL) were sequentially added to the mixture to give a white solid. Data for 1,2-dimethylated derivative (1b): [M+]: 450.2194, found: 450.2197.

(6) This work was supported by JSPS KAKENHI Grant Numbers JP15H05641, JP16H04109, JP18H04254, JP18H04469, and JP19H00895. H.Y. thanks The Asahi Glass Foundation for financial support.

(9) The oxidation of dianionic species 5 with iodine probably proceeds through the formation of a radical intermediate that would lose the stereochemical information. Thus, the less stereochemically congested 6 was selectively obtained. Garst, J. F.; Roberts, R. D.; Pacifici, J. *J. Am. Chem. Soc.* 1977, **99**, 3528.

(10) Even though a free silylpotassium species seems to function in the reaction, the formation of the silicate species generated from disilane and tert-butoxide could not be excluded.

(11) In ref. 3b, an example of mono-silylcupration of (R3Si)2Cu(CN)Li to a C–C triple bond was reported. However, no report of any type of addition of (R3Si)2Cu(CN)K2 is known.

(12) In the presence of smaller amounts of disilane (1.0 equiv) and tBuOK (1.2 equiv), we observed recovered alkynone 1a (32%) and disilylated product 3a (19%) as well as the monosilylated alkene (25%) after protic workup. This result suggests the formation of monosilylated copper species just before consuming up the silylpotassium species. The monosilylated copper species may also add to the alkynone to eventually provide the monosilylated alkene.