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Communication

Catalytic Decarboxylation of Silyl Alkynoates to Alkynylsilanes

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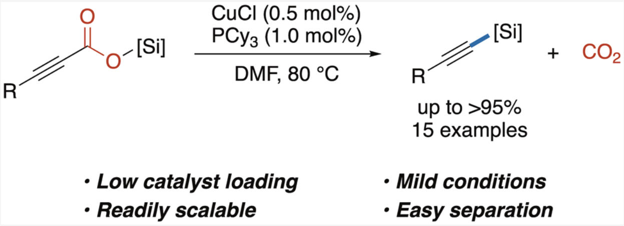
Cite This: https://dx.doi.org/10.1021/acs.organomet.0c00433

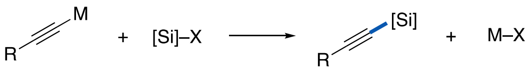
ABSTRACT: Herein, we describe a decarboxylative approach to the preparation of alkynylsilanes. Treatment of a silyl alkynoate in *N*,*N*-dimethylformamide (DMF) at 80 °C in the presence of catalytic amounts of CuCl and PCy_3 produced the corresponding alkynylsilane in excellent yield. The copper-catalyzed decarboxylation proceeded smoothly with low catalyst loadings (0.5 mol % of CuCl and 1.0 mol % of PCy_3) under mild reaction conditions and is easily scalable to gram quantities.



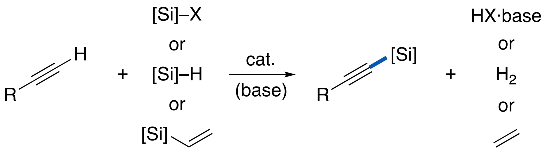
Alkynylsilanes are important building blocks used in transition-metal-catalyzed cross-coupling reactions and related transformations.[1] A conventional synthetic approach to an alkynylsilane involves the nucleophilic substitution of a halosilane with a metal acetylide, which is readily generated by the deprotonation of a terminal alkyne with a strong base, such as an alkyllithium or a Grignard reagent (Scheme 1a).[2]

Scheme 1. Synthetic Approaches to Alkynylsilanes

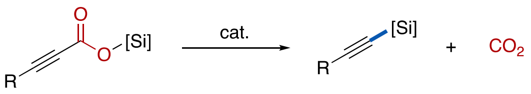
(a) Nucleophilic substitution with metal acetylide



(b) Cross-coupling approach



(c) Decarboxylation approach – ***THIS WORK***



However, the coproduction of stoichiometric amounts of metal-based wastes and the low functional-group tolerance associated with the highly reactive metal acetylide are sometimes problematic in terms of practicality and sustainability. Consequently, catalytic cross-coupling reactions involving terminal alkynes and silicon electrophiles have been developed as alternative synthesis routes to alkynylsilanes (Scheme 1b).[3−5] For example, Calas and co-workers reported that alkynylsilanes can be prepared by heating chlorosilanes and terminal alkynes at 150 °C in the presence of a catalytic amount of CuCl.[3a] Moreover, Yamaguchi and co-workers demonstrated that AgCl, $AgNO_3$, and CuCl promote the catalytic alkynylation of Me_3SiCl in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under mild reaction conditions.[3b] In addition, iodosilanes[4] and silyl triflates[5] are silicon electrophiles that can be alkynylated under $\{Ir(\mu\text{-}Cl)(CO)_2\}_2$ and $Zn(OTf)_2$ catalysis, respectively. Moreover, dehydrogenative alkynylations using terminal alkynes and hydrosilanes have been achieved,[6] and a unique alkynylation of vinylsilanes that includes elimination of ethylene was reported by Marciniec and co-workers.[7]

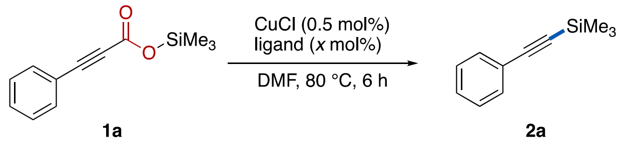
As discussed above, condensation reactions, such as nucleophilic substitutions and cross-coupling reactions, are general approaches for introducing carbon substituents onto silicon atoms, irrespective of alkynylation. On the other hand, another possible approach involves the decarboxylation of a silyl ester, as some kinds of silyl esters have been reported to undergo decarboxylation in the presence of a base; however, substrates that can be used under these decarboxylation conditions are highly limited to particular silyl esters, such as trichloroacetates and pentafluorobenzoates.[8−10] While bis(trimethylsilyl) acetylenedicarboxylate, a silyl alkynoate, also undergoes decarboxylation in the presence of an amine base, to our knowledge no other examples of silyl alkynoates suitable for such a decarboxylation have been reported in the literature.[11] In this communication, we apply transition-metal catalysis to decarboxylate various silyl alkynoates and produce the corresponding alkynylsilanes (Scheme 1c). We hypothe-

Received: June 25, 2020

sized that a metal alkynoate generated from a silyl alkynoate would undergo decarboxylation to afford a metal acetylide intermediate, after which the metal acetylide would react with the silyl alkynoate to give the desired alkynylsilane, with regeneration of the metal alkynoate.

As CuCl was reported to be an effective catalyst for the decarboxylation of 2-alkynoic acids,[12−14] and copper acetylides are potentially nucleophilic,[3,15] we initially examined the decarboxylation of trimethylsilyl 3-phenylpropiolate (**1a**) in the presence of a catalytic amount of CuCl (Table 1). As expected, decarboxylation occurred to give the desired alkynylsilane **2a** when 0.5 mol % of CuCl was used as the catalyst, albeit in low yield (23%, entry 1). Since the addition of 0.5 mol % of PPh_3 improved the yield slightly to 30% (entry 2), other phosphine ligands were briefly screened. While PCy_3 displayed superior catalytic performance to give alkynylsilane **2a** in 64% yield (entry 3), the bulkier P*t*Bu_3 gave an inferior yield (40%, entry 4). Dramatic improvement was observed when PCy_3 was loaded at twice the level of CuCl, to afford **2a** in quantitative yield within 6 h (entry 5). A comparable yield was obtained in the reaction with the isolated $[CuCl(PCy_3)_2]$ complex.[16]

Table 1. Ligand Optimization

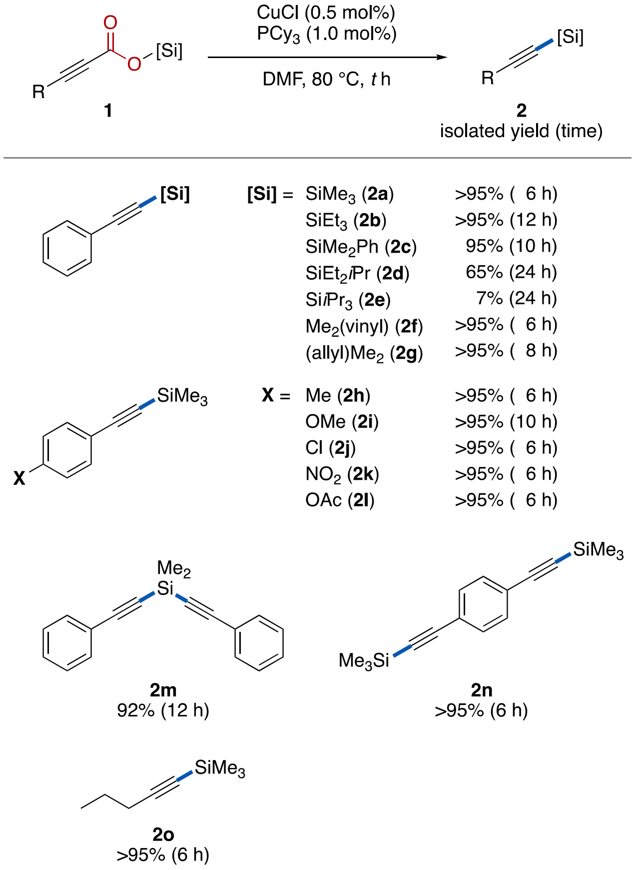


entry	ligand	*x* (mol %)	yield (%)[a]
1	none	–	23
2	PPh_3	0.5	30
3	PCy_3	0.5	64 (65)[b]
4	P*t*Bu_3	0.5	40
5	PCy_3	1.0	>95 (>95)[c]

[a]Isolated yield. [b]With 0.25 mol % of $[CuCl(PCy_3)]_2$. [c]With 0.5 mol % of $[CuCl(PCy_3)_2]$.

With the optimized reaction conditions in hand, the scope and limitations of the silyl alkynoate were explored (Table 2). Triethylsilyl 3-phenylpropiolate (**1b**) and dimethylphenylsilyl 3-phenylpropiolate (**1c**) underwent smooth decarboxylation to give the corresponding alkynylsilanes **2b** (>95%) and **2c** (95%), respectively. However, decarboxylation hardly proceeded with the more sterically demanding triisopropylsilyl group (**2e**). Vinyl and allyl substituents on the silicon atom were tolerated under the decarboxylation conditions to give the corresponding alkynylsilanes **2f,g** in excellent yields. Adding a substituent to the benzene ring of **1a** had little effect on the product yield. ((Trimethylsilyl)ethynyl)benzene derivatives with electron-donating methyl (**2h**) and methoxy (**2i**) groups and electron-withdrawing chloro (**2j**) and nitro (**2k**) groups at the *para* position were obtained in quantitative yields in all cases. A normal ester group (OAc) was tolerated under the reaction conditions, to afford **2l** in >95% yield. Dimethylsilanediyl bis(3-phenylpropiolate) (**1m**) underwent 2-fold decarboxylation efficiently to give dialkynylsilane **2m** in high yield (92%). Bis((trimethylsilyl)ethynyl)benzene (**2n**) was also obtained in quantitative yield by 2-fold decarboxylation. Aliphatic alkynoates were also examined, with the propyl-bearing alkynylsilane **2o** obtained in >95% yield. Other silyl esters, such as benzoate and cinnamate, gave no decarboxylation products under the optimized conditions.

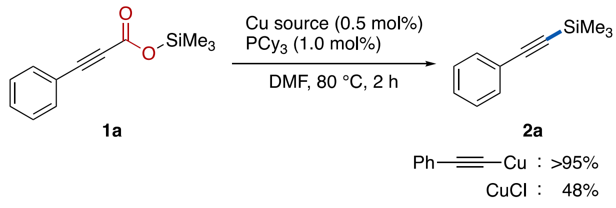
Table 2. Silyl Alkynoate Scope and Limitations



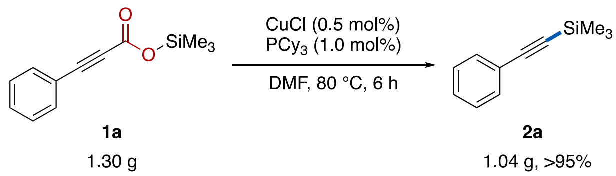
Since we hypothesized that copper acetylides are active intermediates in the catalytic cycle, we next investigated the catalytic activity of copper(I) phenylacetylide in the decarboxylation of silyl alkynoate **1a** (Scheme 2a); the reaction with copper acetylide was observed to proceed more quickly than that with CuCl and was complete within 2 h. While the details are unclear at present, this study suggests that copper acetylide is an active intermediate or precatalyst of the decarboxylation.

Scheme 2. (a) Decarboxylation with Copper Acetylide and (b) Decarboxylation on the Gram Scale

(a) Decarboxylation with Copper Acetylide



(b) Gram-Scale Decarboxylation



The copper-catalyzed decarboxylation was readily scaled up without difficulty (Scheme 2b); 1.04 g of highly pure alkynylsilane **2a** (>95% yield) was isolated by simply passing the reaction mixture through a short silica gel pad.

In summary, we developed a facile method for the preparation of alkynylsilanes through the decarboxylation of silyl alkynoates. The CuCl/2PCy$_3$ system effectively catalyzed the decarboxylation of an array of silyl alkynoates with low catalyst loadings under mild reaction conditions to afford the corresponding alkynylsilanes in quantitative yields in most cases. The copper-catalyzed decarboxylation is scalable to the gram scale without any loss of efficiency. In addition, the alkynylsilane products are easily purified because gaseous carbon dioxide is the sole byproduct of decarboxylation. Experimental studies suggested that copper acetylide is an active intermediate or precatalyst in the decarboxylation process. Our laboratory is further investigating catalytic systems for decarboxylating silyl esters other than alkynoates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00433.

> Experimental procedures, characterization data, and NMR spectra (^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H}) of the alkynylsilane products (PDF)

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Author Contributions

[†]T.K. and K.A. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the "Development of Innovative Catalytic Processes for Organosilicon Functional Materials" project (Project Leader: K.S.) from the New Energy and Industrial Technology Development Organization (NEDO).

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