

Copper-Catalyzed Regiodivergent Silacarboxylation of Allenes with Carbon Dioxide and a Silylborane

Yosuke Tani, Tetsuaki Fujihara, Jun Terao, and Yasushi Tsuji*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

S Supporting Information

ABSTRACT: A regiodivergent silacarboxylation of allenes under a CO₂ atmosphere with PhMe₂Si–B(pin) as a silicon source in the presence of a copper catalyst at 70 °C has been developed. The regioselectivity of the reaction is successfully reversed by the proper choice of ligand; carboxylated vinylsilanes are obtained with *rac*-Me-DuPhos as the ligand, whereas the use of PCy₃ affords carboxylated allylsilanes. Thus, two different carboxylated silanes can be selectively and regiodivergently synthesized from a single allene substrate.

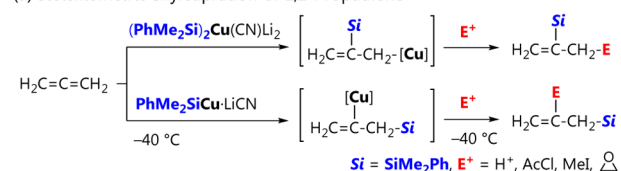
Silylcupration across C–C multiple bonds¹ is a reliable and powerful process that forms both C–Si and C–Cu bonds, with the latter amenable to further in situ C–C bond-forming events. Conventionally, a stoichiometric amount of a silylcuprate such as (PhMe₂Si)₂Cu(CN)Li₂ is used in the reaction.^{1a–e} Catalytic silylcuprations employing a silylborane² as a silicon source have been postulated in the Cu-catalyzed hydrosilylations of alkynes^{1f–i} and allenes.^{1j,k} However, utilization of the resulting C–Cu bonds in subsequent C–C bond formation has remained mostly unexplored.^{1k,l}

Among unsaturated substrates for silylcupration, allene derivatives are very versatile reaction partners. Addition reactions across allenes often provide many regio- and stereoisomers. Control of the selectivity is challenging, but once it is achieved, a structurally diverse array of products become accessible.³ Regioselective silylcuprations of allenes provide vinyl-⁴ or allylsilanes,^{4a,d,5} which are indispensable in organic synthesis. If a *regiodivergent*⁶ allene silylcupration followed by functionalization of the resulting Cu–C moiety could be realized, functionalized vinyl- and allylsilanes could be obtained selectively from a single substrate. Pioneering studies by Fleming and Pulido showed that the silylcupration of 1,2-propadiene (CH₂=C=CH₂) with a stoichiometric amount of a silylcyanocuprate proceeded in a regiodivergent manner (Scheme 1a).⁷ The higher-order silylcyanocuprate afforded vinylsilanes (Scheme 1a, top),^{7a–c} whereas the lower-order analogue provided allylsilanes (Scheme 1a, bottom).^{7d,e} Unfortunately, substituents on the 1,2-propadiene considerably disturbed the regioselectivity, and thus, the regiodivergence appeared only with CH₂=C=CH₂.^{7a–e} Furthermore, the reaction temperature also significantly affected the regiodivergence.^{7d,e}

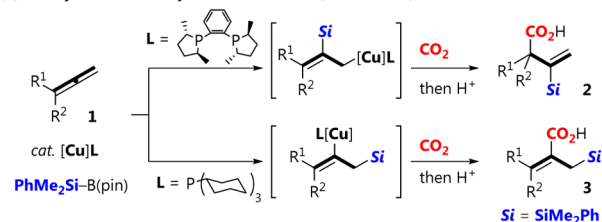
During studies on catalytic C–C bond-forming reactions using CO₂,^{8,9} we discovered the Cu-catalyzed silacarboxylation of alkynes with a silylborane.^{9c} The reaction is highly regioselective

Scheme 1. Regiodivergent Silylcupration of Allenes

(a) Stoichiometric Silylcupration of 1,2-Propadiene



(b) Catalytic Silacarboxylation of Allenes (*This Work*)

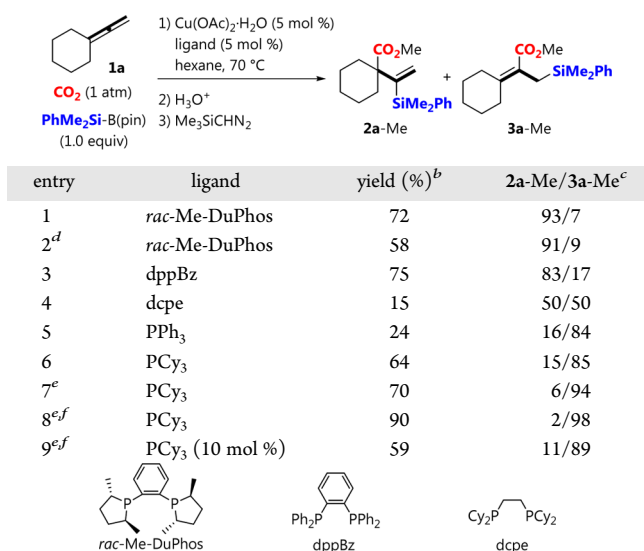


but could not be made regiodivergent at all. Among the catalytic carboxylations of allenes using CO₂,¹⁰ there are only two precedents of selective reaction:¹¹ Mori and Sato reported the selective Ni-catalyzed carboxylation of trimethylsilylallenes,^{11a} and Iwasawa demonstrated the hydrocarboxylation of allenes in the presence of a Pd catalyst bearing a PSiP pincer ligand.^{11b} These reactions proceeded with good selectivity but afforded only one particular regioisomer. Herein we report a regiodivergent silacarboxylation of allenes with CO₂ in the presence of a copper catalyst. The regioselectivity can be highly controlled and even reversed by the proper choice of ligand; both carboxylated vinylsilanes (**2**) and allylsilanes (**3**) can be synthesized regiodivergently from a single substrate (Scheme 1b). Notably, there are no reported precedents for the silacarboxylation of allenes or the regiodivergent carboxylation.¹²

We initially examined the reaction of 1,1-pentamethyleneallene (**1a**) and PhMe₂Si–B(pin) under CO₂ (1 atm, closed) with 5 mol % Cu(OAc)₂·H₂O and 5 mol % ligand at 70 °C (Table 1). The carboxylated vinylsilane **2a** and allylsilane **3a** were obtained, and their yields were determined by GC after conversion to the corresponding methyl esters **2a-Me** and **3a-Me** with Me₃SiCHN₂. The nature of the ligand successfully controlled the regioselectivity. Vinylsilane **2a** was regioselectively obtained with *rac*-Me-DuPhos¹³ in 72% yield with 93% regioselectivity (i.e., **2a-Me**/**3a-Me** isomeric ratio = 93:7; entry 1). When we used Cu(OAc) as the catalyst precursor, the yield

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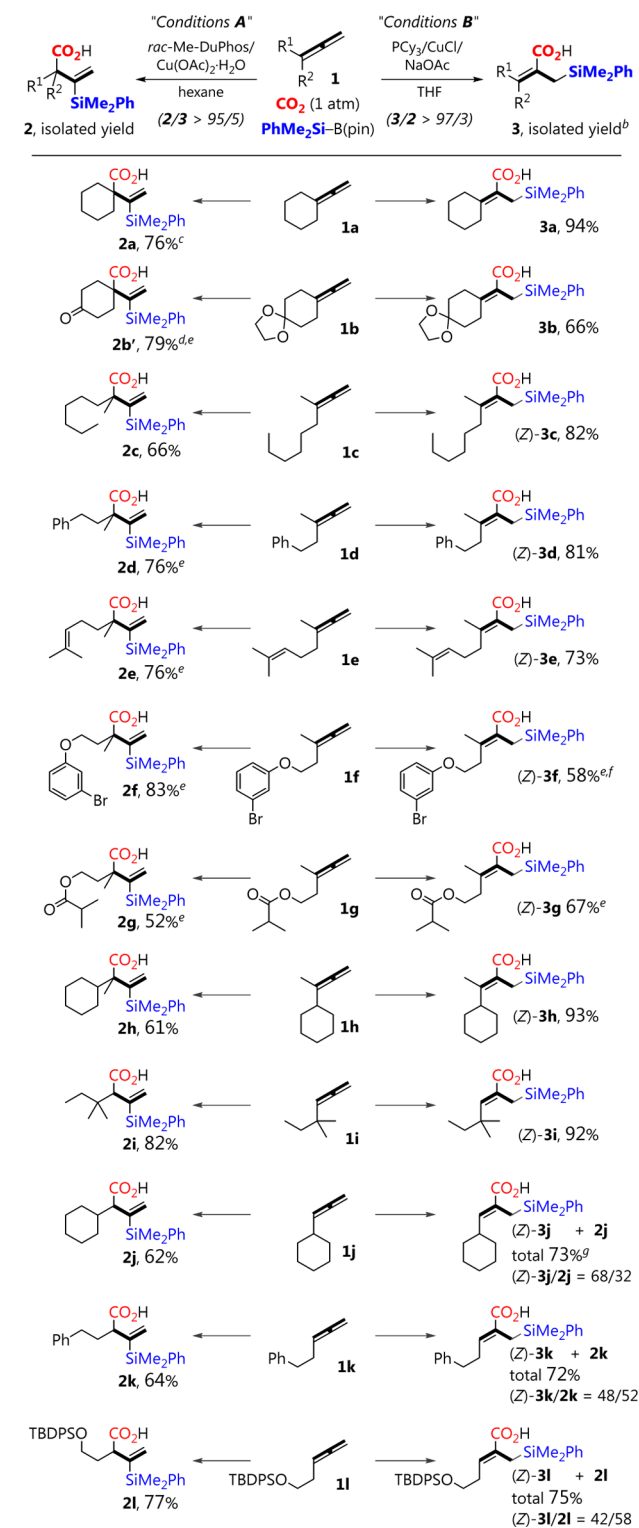
Table 1. Effect of the Ligand on Cu-Catalyzed Silacarboxylation of 1,1-Pentamethyleneallene (1a)^a


^aReaction conditions: **1a** (0.20 mmol), PhMe₂Si-B(pin) (1.0 equiv), ligand (5 mol %), and Cu(OAc)₂·H₂O (5 mol %) in hexane (0.40 M) under CO₂ (1 atm, closed) at 70 °C for 16–18 h. ^bCombined yields of **2a-Me** and **3a-Me** as determined by GC analysis after esterification using Me₃SiCHN₂. ^cDetermined by GC analysis. ^dCuOAc (5 mol %) was used instead of Cu(OAc)₂·H₂O. ^eIn THF. ^f5 mol % CuCl and 15 mol % NaOAc were used instead of Cu(OAc)₂·H₂O.

slightly decreased to 58% while the regioselectivity remained high (91%) (entry 2). Another chelating ligand, dppBz, produced **2a** in good yield (75%) but with slightly decreased regioselectivity (83%) (entry 3). dcpe was not effective at all in terms of yield and regioselectivity (entry 4). In contrast, when the monodentate phosphine PPh₃ was employed as the ligand, the regioselectivity was switched, giving allylsilane **3a** as the major product (**2a-Me**/**3a-Me** = 16/84), albeit in 24% yield (entry 5). Gratifyingly, using tricyclohexylphosphine (PCy₃) as the ligand increased the yield to 64% while maintaining 85% regioselectivity (entry 6). Finally, both the yield and the regioselectivity were significantly improved to 90% and 98%, respectively, with THF as the solvent and a mixture of CuCl/NaOAc as the Cu precursor (entry 8). Using 10 mol % PCy₃ decreased both the yield and regioselectivity, suggesting the importance of a vacant coordination site on copper (entry 9). These results clearly indicate that regiodivergent silacarboxylation can be realized simply by tuning the catalyst system with the proper ligand.

After this optimization, regioselective syntheses of carboxylated vinylsilanes **2** were performed using the same catalyst system as in Table 1, entry 1, and employing *rac*-Me-DuPhos as the ligand (conditions A; Table 2, left column). From 1,1-disubstituted allenes (**1a–h**), the corresponding vinylsilanes (**2a–h**) were obtained regioselectively (**2/3** > 95/5) in good yields after silica-gel column chromatography. Functionalities such as ketal (**2b**),¹⁴ alkenyl (**2e**), bromo (**2f**), and ester (**2g**) groups were tolerated during the catalytic reaction. For monosubstituted allenes (**1i–l**), the regioselectivity was perfect, giving vinylsilanes **2i–l** exclusively in good to high yields.

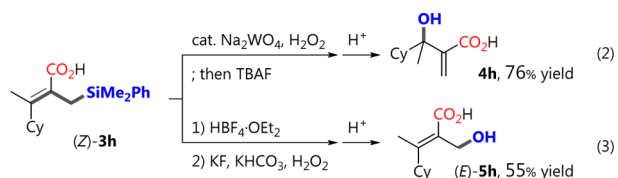
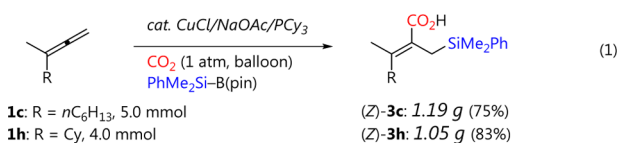
The regioselectivity switch observed for **1a** in Table 1 (entry 1 vs 8) was quite general for 1,1-disubstituted allenes **1a–h** using the same catalyst system as in Table 1, entry 8 with PCy₃ as the ligand (conditions B; Table 2, right column). These reactions provided the corresponding allylsilanes **3a–h** with excellent

Table 2. Regiodivergent Silacarboxylation of Allenes to Carboxylated Vinylsilanes (2**) or Allylsilanes (**3**)^a**


^aConditions A: *rac*-Me-DuPhos (5 mol %) and Cu(OAc)₂·H₂O (5 mol %) in hexane (0.40 M). Conditions B: PCy₃ (5 mol %), CuCl (5 mol %), and NaOAc (15 mol %) in THF (0.40 M). Under both conditions, **1** (0.20 mmol) and PhMe₂Si-B(pin) (1.1 equiv) were reacted under CO₂ (1 atm, closed) at 70 °C for 16–18 h. ^bZ/E > 96/4 if any. ^c**2a**/**3a** = 93/7. ^dIsolated after acidic workup.¹⁴ ^ePhMe₂Si-B(pin) (1.5 equiv). ^f(Z)-**3f**/(E)-**3f**/**2f** = 90/3/7. ^gPCy₂(*o*-tol) was used instead of PCy₃. TBDPS = *tert*-butyldiphenylsilyl.

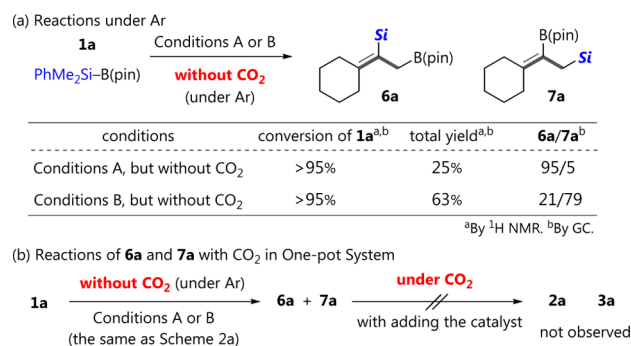
regioselectivities (3/2 > 98/2, except for 3f/2f = 93/7). Unsymmetrically substituted allenes such as **1c–h** may afford *E/Z* mixtures. The present catalyst system distinguished even subtle differences such as between the methyl and the primary alkyl substituents of **1c–g**, affording the *Z* isomers preferentially (*Z/E* > 80/20) in the crude mixtures. The *Z/E* ratio for **3h** was much higher (95/5). Gratifyingly, (*Z*)-**3c–h** were easily isolated by silica-gel column chromatography in good yields with high *Z/E* ratios (>96/4). The structure of (*Z*)-**3h** was further confirmed by X-ray crystallography.¹⁵ Under conditions B, ketal (**3b**),¹⁴ alkenyl (**3e**), bromo (**3f**), and ester (**3g**) groups remained intact.¹⁶ The monosubstituted allene bearing a tertiary alkyl substituent (**1i**) afforded the corresponding (*Z*)-allylsilane ((*Z*)-**3i**) with 97% regioselectivity in 92% yield. However, **1j** bearing a secondary alkyl substituent gave (*Z*)-**3j** only preferentially: (*Z*)-**3j**/**2j** = 68/32 in 73% total yield. Furthermore, allenes having a primary alkyl substituent (**1k** and **1l**) afforded the two regioisomers with low selectivities: (*Z*)-**3k**/**2k** = 48/52 in 72% total yield and (*Z*)-**3l**/**2l** = 42/58 in 75% total yield. Thus, steric hindrance at the 1-position of allenes is essential to provide **3** regioselectively. Unfortunately, the reactions using 1-methyl-1-phenylallene, 1-*tert*-butyl-3-(*p*-tolyl)allene, and 1,3-dimethyl-1-(2-phenethyl)allene were not regioselective.

The preparation of **3** could be carried out on gram scale: 1.19 g of (*Z*)-**3c** and 1.05 g of (*Z*)-**3h** were synthesized from **1c** (0.691 g, 5.0 mmol) and **1h** (0.548 g, 4.0 mmol), respectively (eq 1). γ -Oxidation of (*Z*)-**3h** through an epoxidation/desilylative ring opening cascade¹⁷ gave tertiary allylic alcohol **4h** in 76% isolated yield (eq 2). On the other hand, α -oxidation using the Tamao–Fleming (TF) protocol¹⁸ gave primary allylic alcohol (*E*)-**5h** in 55% yield with retention of the olefin configuration (eq 3). Usually, the α -oxidation of allylic phenylsilanes by the TF protocol is unreliable, since allylic C–Si bonds are preferentially cleaved over Ph–Si bonds.¹⁹ The α -oxidation of **3h** proceeded smoothly, possibly as a result of deactivation of the allylic moiety by conjugation with the carboxylic acid functionality.^{19b} Thus, the regioselective oxidations (eqs 2 and 3) and silacarboxylation (Scheme 1b) can provide a wide range of products (**2–5**) from a single allene substrate (**1**).

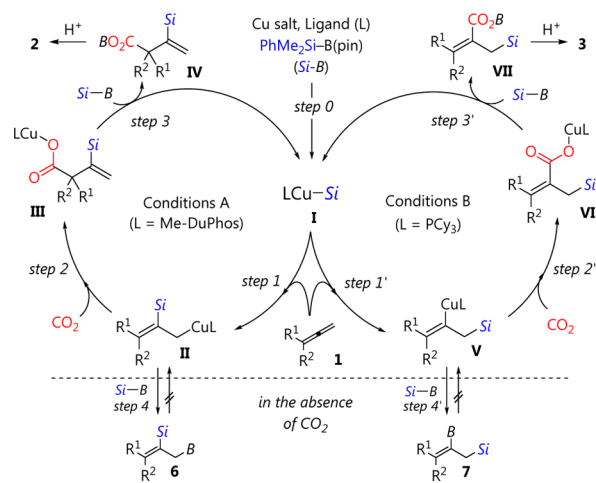


To gain insight into the reaction mechanism, several control experiments were carried out (Scheme 2). When the reactions were run in the absence of CO₂ (i.e., under Ar), using the same conditions A or B as in Table 2, the reactions were less clean: the PhMe₂Si–B(pin) adducts with **1a** (**6a** and **7a**) were obtained in 25% and 63% yield, respectively, with different regioselectivities (Scheme 2a). Conditions A led to the formation of **6a** with excellent regioselectivity (**6a**/**7a** = 95/5), while conditions B preferentially afforded **7a** (**6a**/**7a** = 21/79). Subsequent reactions with exchange of the atmosphere in the flask containing **6a** and **7a** from Ar to CO₂ did not convert most of the **6a** and **7a**, and **2a** and

Scheme 2. Control Experiments in the Absence of CO₂



Scheme 3. A Possible Reaction Mechanism



3a were not detected at all (Scheme 2b).¹⁵ These observations show that **2** and **3** are not generated via **6** and **7**.²⁰

A possible catalytic cycle is shown in Scheme 3. The silylcopper species **I** is generated in situ by the reaction of PhMe₂Si–B(pin) with a Cu precursor (step 0).²¹ Next, **I** adds across a terminal double bond of the allene **1** (step 1). Under conditions A with Me-DuPhos as the ligand, the Cu atom adds at the terminal carbon of **1**, generating allylcopper intermediate **II**. Then CO₂ inserts at the γ -position of **II** to provide copper carboxylate species **III**, possibly via a six-membered-ring transition state (step 2). Finally, σ -bond metathesis of **III** with PhMe₂Si–B(pin) affords boron carboxylate **IV** and regenerates **I** (step 3). In sharp contrast, under conditions B with PCy₃ as the ligand, the regioselectivity of the silylcupration is reversed, providing vinylcopper intermediate **V** (step 1'). The regioselectivity reversal in steps 1 and 1' might be attributed to the difference in relative steric bulk of the CuL (L = Me-DuPhos or PCy₃) and SiMe₂Ph moieties. The insertion of CO₂ into **V** (step 2') followed by the σ -bond metathesis of **VI** with PhMe₂Si–B(pin) provides boron carboxylate **VII** and regenerates **I** (step 3'). In the absence of CO₂, some **II** and **V** could be trapped as **6** and **7** (steps 4 and 4'), suggesting that the regioselectivity occurs at the silylcupration stage (steps 1 and 1').

Preliminarily, an enantioselective silacarboxylation of **1d** was carried out with (*R,R*)-Me-DuPhos under conditions A, and **2d** was obtained in 18% ee (unoptimized).

In conclusion, we have developed a regioselective silacarboxylation of allenes using PhMe₂Si–B(pin) under a CO₂ atmosphere in the presence of a copper catalyst. The regioselectivity is highly controlled by the proper choice of ligand, and

both carboxylated vinylsilanes (2) and allylsilanes (3) can be synthesized regiodivergently from a single substrate. Further studies of the reaction mechanism and optimization of the enantioselective reaction are now in progress.

■ ASSOCIATED CONTENT

Supporting Information

Procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

ytsuji@scl.kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

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- (14) The acetal moiety of **2b** was intact during the catalytic reaction but was mostly converted to the corresponding ketone (**2b'**) through the workup. To our delight, the acetal moiety of **3b** was robust toward a similar workup procedure.
- (15) See the Supporting Information for details.
- (16) Besides the entries in Table 2, four allenes **1m–p**, including those bearing silyl ether (**1m**) and ester (**1n**) groups, also provided the corresponding allylsilanes **3m–p** selectively in high yields under conditions B.
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