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

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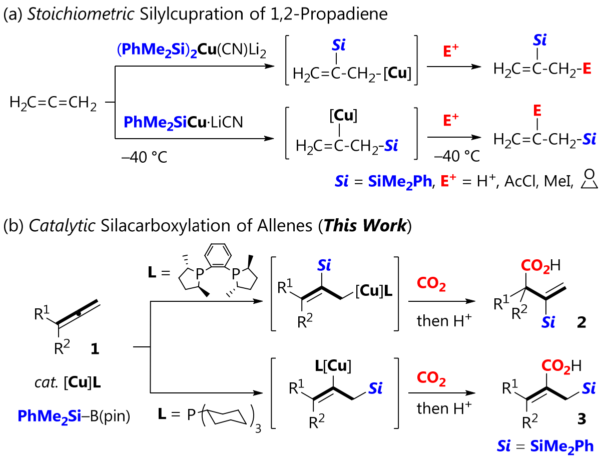
Supporting Information Placeholder

ABSTRACT: The regiodivergent silacarboxylation of allenes is developed under carbon dioxide atmosphere with $PhMe_2Si–B(pin)$ as a silicon source in the presence of a copper catalyst at 70 °C. 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 carboxylated allylsilanes are provided by employing PCy_3. Thus, two different carboxylated silanes can be selectively and regiodivergently synthesized from a single allene substrate.

Scheme 1. Regiodivergent Silylcupration of Allenes



Silylcupration across carbon–carbon multiple bonds[1] 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 $(PhMe_2Si)_2Cu(CN)Li_2$ is used in the reaction.[1a-e] Catalytic silylcuprations employing a silylborane[2] 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 remained mostly unexplored.[1k,l]

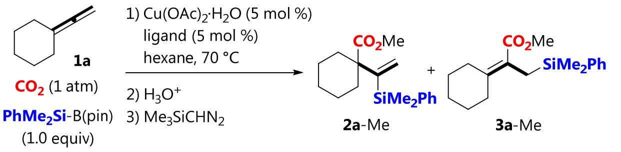
Among unsaturated substrates for silylcupration, allene derivatives are very versatile reaction partners. Frequently, addition reaction across allenes provides many regio- and stereoisomers. Controlling these selectivities is therefore challenging but once achieved, structurally diverse array of the products become accessible.[3] Regioselective silylcuprations of allenes provide vinyl-[4] or allylsilanes,[4a,d,5] which play indispensable roles in organic synthesis. If a *regiodivergent*[6] allene silylcupration followed by functionalization of the resulting Cu–C moiety could be realized, both the functionalized vinyl- and allylsilanes would be obtained selectively from a single substrate. Pioneering studies by Fleming and Pulido showed that the silylcupration of 1,2-propadiene ($CH_2=C=CH_2$: *unsubstituted* allene) 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, thus the regiodivergency appeared only with $CH_2=C=CH_2$.[7a-e] Furthermore, the reaction temperature also significantly affected the regiodivergency.[7d,e]

During studies on catalytic C–C bond-forming reactions using CO_2,[8,9] we discovered the Cu-catalyzed silacarboxylation of alkynes with a silylborane.[9c] The reaction was highly regioselective, but could not be made regiodivergent at all. Among the catalytic carboxylation of allenes using CO_2,[10] there are only two precedents of selective reaction.[11] Mori and Sato reported the selective Ni-catalyzed carboxylation of trimethylsilylallenes.[11a] 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 only one particular regioisomer was afforded. Herein, we report a *regiodivergent* silacarboxylation of allenes with CO_2 in the presence of a copper catalyst. The regioselectivity can be highly controlled and even reversed by the proper choice of ligand; both the carboxylated vinylsilanes (**2**) and allylsilanes (**3**) are synthesized regiodivergently from a single substrate (Scheme 1b). Notably, there are no reported precedents for the silacarboxylation of allenes nor the regiodivergent carboxylation.[12a,b]

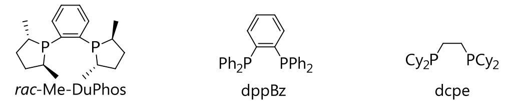
Initially, we examined the reaction of 1,1-pentamethyleneallene (**1a**) and $PhMe_3Si–B(pin)$ under CO_2 (1 atm, closed) with 5 mol % of $Cu(OAc)_2·H_2O$ and 5 mol % of a ligand at 70 °C (Table 1). The carboxylated vinylsilane (**2a**) and allylsilane (**3a**) were obtained, and their yields were determined by GC after conversion to the corresponding methyl esters (**2a**-Me and **3a**-Me) with Me_3SiCHN_2. The nature of the ligands successfully controlled the regioselectivity. The vinylsilane (**2a**) was regioselectively obtained with *rac*-Me-DuPhos[13] in 72% yield with 93% regioselectivity (i.e., isomeric ratio of **2a**-Me/**3a**-Me; entry 1). When we used Cu(OAc) as a catalyst precursor, the yield was 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 PPh$_3$ was employed as the ligand, the regioselectivity was switched, giving the allylsilane **3a** (**2a**-Me/**3a**-Me = 16/84) as the major product, albeit in 24% yield (entry 5). Gratifyingly, tricyclohexylphosphine (PCy$_3$) 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). A use of 10 mol % of PCy$_3$ decreased both the yield and the selectivity, suggesting the importance of a vacant coordination site on copper (entry 9). These results clearly indicate that regiodivergent silacarboxylation can be realized by simply tuning the catalyst system with the proper ligands.

Table 1. Effect of Ligands on Cu-Catalyzed Silacarboxylation of 1,1-Pentamethyleneallene (1a)[a]



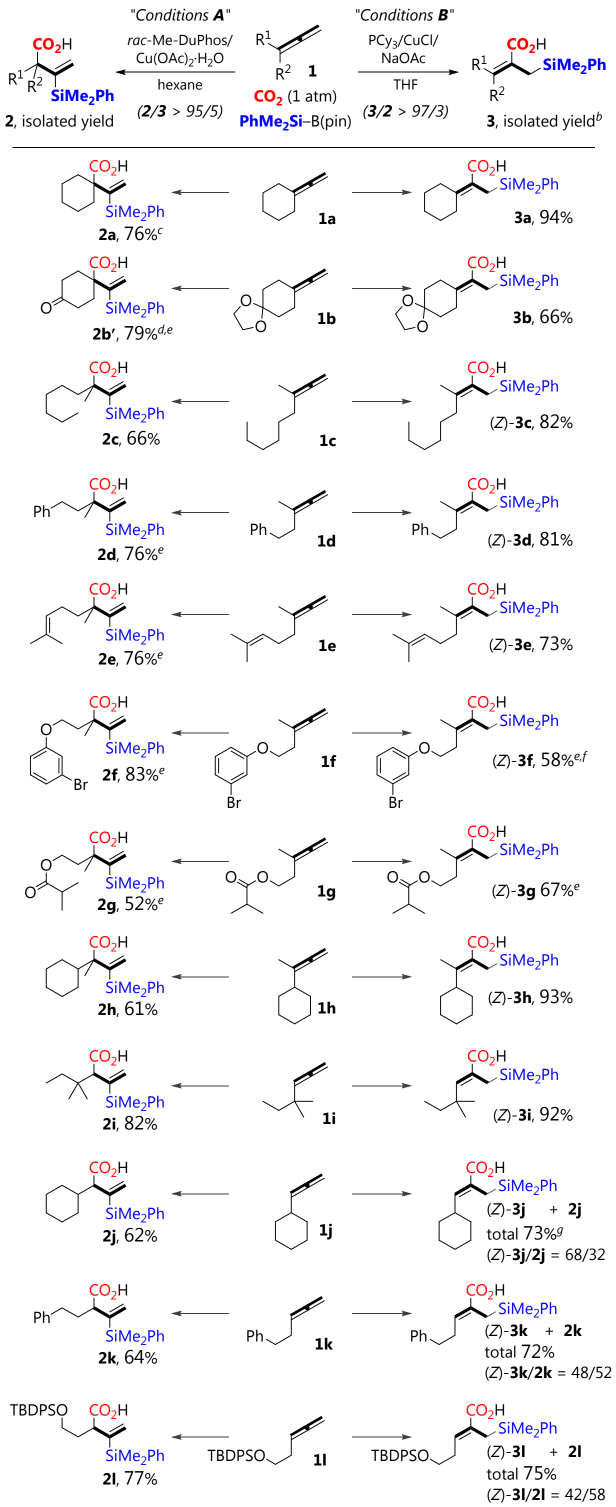
entry	ligand	yield (%)[b]	**2a**-Me/**3a**-Me[c]
1	*rac*-Me-DuPhos	72	93/7
2[d]	*rac*-Me-DuPhos	58	91/9
3	dppBz	75	83/17
4	dcpe	15	50/50
5	PPh$_3$	24	16/84
6	PCy$_3$	64	15/85
7[e]	PCy$_3$	70	6/94
8[e,f]	PCy$_3$	90	2/98
9[e,f]	PCy$_3$ (10 mol %)	59	11/89



[a]Reaction conditions: **1a** (0.20 mmol), PhMe$_2$Si–B(pin) (1.0 equiv), ligand (5 mol %) and Cu(OAc)$_2$·H$_2$O (5 mol %) in hexane (0.40 M) under CO$_2$ (1 atm, closed) at 70 °C for 16–18 h. [b]Combined yield of **2a**-Me and **3a**-Me determined by GC analysis after esterification using Me$_3$SiCHN$_2$. [c]Determined by GC analysis. [d]CuOAc (5 mol %) was used instead of Cu(OAc)$_2$·H$_2$O. [e]In THF. [f]5 mol % of CuCl and 15 mol % of NaOAc were used instead of Cu(OAc)$_2$·H$_2$O.

After these optimization, regioselective syntheses of the carboxylated vinylsilanes **2** were performed under Conditions A, using the same catalyst system as in Table 1, entry 1, and employing *rac*-Me-DuPhos as the ligand (Table 2, left column). From 1,1-disubstituted allenes (**1a**–**h**), the corresponding vinylsilanes (**2a**–**h**) were afforded 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. As for monosubstituted allenes (**1i**–**l**), the regioselectivity was perfect giving vinylsilane **2i**–**l** exclusively in good to high yields.

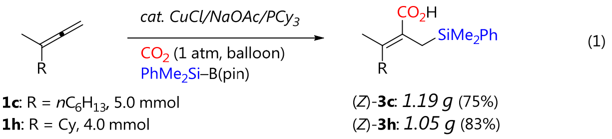
Table 2. Regiodivergent Silacarboxylation of Allenes to Carboxylated Vinylsilanes (2) and Allylsilanes (3)[a]

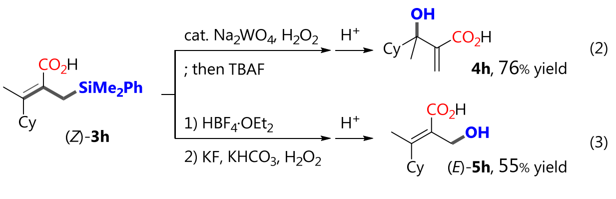


[a]Conditions **A**: *rac*-Me-DuPhos (5 mol %) and Cu(OAc)$_2$·H$_2$O (5 mol %) in hexane (0.40 M); Conditions **B**: PCy$_3$ (5 mol %), CuCl (5 mol %) and NaOAc (15 mol %) in THF (0.40 M). In both conditions, **1** (0.20 mmol) and PhMe$_2$Si–B(pin) (1.1 equiv) were reacted under CO$_2$ (1 atm, closed) at 70 °C for 16–18 h. [b]*Z*/*E* > 96/4 if any. [c]**2a**/**3a** = 93/7. [d]Isolated after acidic work-up.[14] [e]PhMe$_2$Si–B(pin) (1.5 equiv). [f](*Z*)-**3f**/(*E*)-**3f**/**2f** = 90/3/7. [g]PCy$_2$(*o*-tol) was used instead of PCy$_3$. TBDPS = *tert*-butyldiphenylsilyl.

The regioselectivity switch observed for **1a** in Table 1 (entry 1 vs. 8) was quite general for 1,1-disubstituted allenes (**1a**–**h**) under Conditions B, using the same catalyst system as entry 8 in Table1, and utilizing PCy_3 as the ligand (Table 2, right column). The reactions now provided the corresponding allylsilanes (**3a**–**h**) with excellent 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 (*Z*)-isomers preferentially (*Z*/*E* > 80/20) in the crude mixtures. The *Z*/*E* ratios of **3h** was much higher (95/5). Gratifyingly, (*Z*)-**3c**–**h** were easily isolated by silica-gel column chromatography in good yields with high (*Z*) ratios (*Z*/*E* > 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 in 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 would be 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 regiodivergent.

The preparation of **3** can 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 cascade[17] furnished the tertiary allylic alcohol **4h** in 76% isolated yield (eq 2). On the other hand, α-oxidation using the Tamao-Fleming protocol[18] led to the corresponding 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 Tamao-Fleming protocol is unreliable, since allylic C–Si bonds are preferentially cleaved over Ph–Si bonds.[19] The α-oxidation of **3h** proceeded smoothly, possibly owing to a deactivation of the allylic moiety by conjugation with the carboxylic acid functionality.[19b] Thus, the regiodivergent oxidations (eqs 2 and 3) and the regiodivergent silacarboxylation (Scheme 1b) can provide a wide range of products (**2**, **3**, **4**, and **5**) from a single allene substrate (**1**).

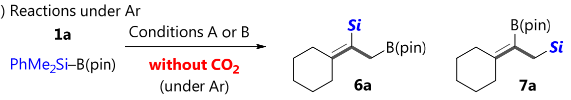




To gain insight into the reaction mechanism, several control experiments were carried out (Scheme 2). When the reactions were run in the absence of CO_2 (i.e., under Ar), using the same Conditions A or B as in Table 2, the reactions were less clean: the $PhMe_2Si$–B(pin) adducts with **1a** (**6a** and **7a**) were obtained in 25% and 63% yields, 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 CO_2 did not convert most **6a** and **7a**, and **2a** and **3a** were not detected at all (Scheme 2b).[15] These observations, therefore, clearly indicate that **2** and **3** are not generated via **6** and **7**.[20]

Scheme 2. Control Experiments in the Absence of CO_2

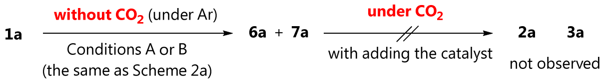
(a) Reactions under Ar



conditions	conversion of **1a**[a,b]	total yield[a,b]	**6a**/**7a**[b]
Conditions A, but without CO_2	>95%	25%	95/5
Conditions B, but without CO_2	>95%	63%	21/79

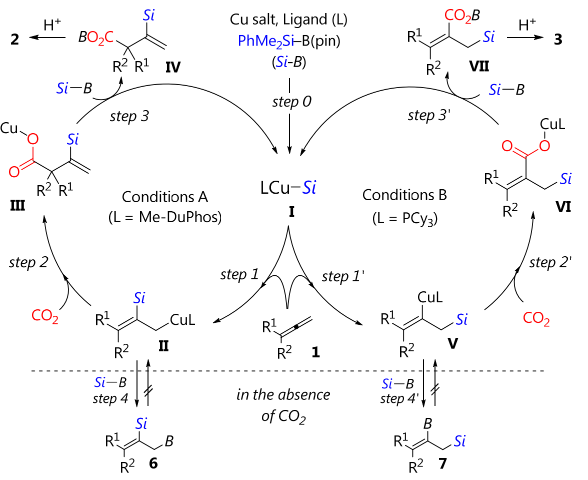
[a]By ^{1}H NMR. [b]By GC.

(b) Reactions of **6a** and **7a** with CO_2 in One-pot System



A possible catalytic cycle is shown in Scheme 3. The silylcopper species (**I**) is generated *in situ* by the reaction of $PhMe_2Si$–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 the allylcopper intermediate (**II**). Then, CO_2 inserts at the γ-position of **II** to provide the copper carboxylate species (**III**), possibly via a six-membered ring transition state (step 2). Finally, σ-bond metathesis of **III** with $PhMe_2Si$–B(pin) affords the boron carboxylate (**IV**) and regenerates **I** (step 3). In sharp contrast, under Conditions B using PCy_3 as the ligand, the regioselectivity of the silylcupration is reversed, providing the vinyl copper intermediate (**V**) (step 1'). The regioselectivity reversal in steps 1 and 1' might be attributed to the difference in relative steric bulk between the CuL (L = Me-DuPhos or PCy_3) and $SiMe_2Ph$ moieties. The insertion of CO_2 to **V** (step 2') followed by the σ-bond metathesis of **VI** with $PhMe_2Si$–B(pin) provides the boron carboxylate (**VII**) and regenerates **I** (step 3'). In the absence of CO_2, some **II** and **V** could be trapped as **6** and **7** (steps 4 and 4'), suggesting that the regiodivergency occurs at the silylcupration stage (steps 1 and 1').

Scheme 3. A Possible Reaction Mechanism



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

In conclusion, we have developed a regiodivergent silacarboxylation of allenes using PhMe$_2$Si–B(pin) under CO$_2$ atmosphere in the presence of a copper catalyst. The regioselectivity is highly controlled by the proper choice of ligand; both the carboxylated vinylsilanes (**2**) and allylsilanes (**3**) can be synthesized regiodivergently from a single substrate. Further studies on the reaction mechanism and optimization of the enantioselective reaction are now in progress.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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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 work-up. To our delight, the acetal moiety of **3b** was robust to a similar work-up procedure.

(15) See the Supporting Information for details.

(16) Besides entries in Tables 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.[15]

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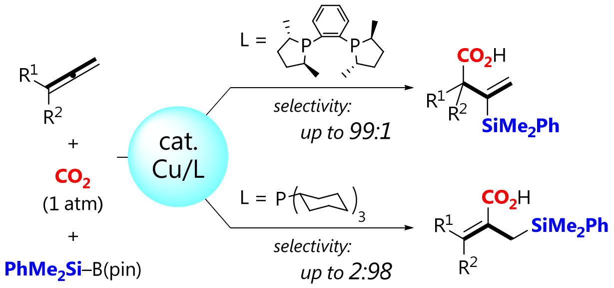
R1
R2
+
CO2
(1 atm)
+
PhMe2Si–B(pin)
cat.
Cu/L
L =
P
P
selectivity:
up to 99:1
CO2H
R1
R2
SiMe2Ph
L = P
3
selectivity:
up to 2:98
CO2H
R1
SiMe2Ph
R2