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Shinya Tanaka, Yuuki Tanaka, Masafumi Chiba, Tetsutaro Hattori

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Lewis Acid-Mediated β-Selective Hydrocarboxylation of α, α -Diaryl- and α -Arylalkenes with R ₃ SiH and CO ₂ Shinya Tanaka, ^{a, *} Yuuki Tanaka, ^a Masafumi Chiba, ^a and Tetsu Ph $\stackrel{R^1}{\underset{R^2}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{EtsSi(C_0H_3)[E(C_0F_5)_d]}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{CO_2}{\overset{EtsSiH}{\overset{EtsSi}{\overset{CO_2}{\overset{EtsSiH}{\overset{EtsSi}{\overset{CO_2}{\overset{EtsSiH}{\overset{EtsSi}{\overset{EtsSiH}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{\overset{Ets}{T$	Leave this area blank for abstract info. that Hattori ^{a.} * $Ph \xrightarrow{\mathbb{R}^1 \\ \mathbb{R}^2 \xrightarrow{\mathbb{R}^3 \\ \mathbb{R}^1}} \prod_{\mathbb{R}^1} \prod_{k=1}^{\infty} \prod_{k=1}^{$
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Lewis Acid-Mediated β -Selective Hydrocarboxylation of α , α -Diaryl- and α -Arylalkenes with R₃SiH and CO₂

Shinya Tanaka,^a,* Yuuki Tanaka,^a Masafumi Chiba,^a Tetsutaro Hattori^a,*

^aDepartment of Biomolecular Engineering, Graduate School of Engineering, Tohoku University, 6-6-11 Aramaki-Aoba, Aoba-ku, Sendai 980-8579, Japan

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ABSTRACT

Article history: Received Received in revised form Accepted Available online Keywords: Carbon dioxide Lewis acid Hydrocarboxylation Alkene Chlorosilane α, α -Diarylalkenes are successfully hydrocarboxylated with Et₃SiH and CO₂ with the aid of Et₃SiB(C₆F₅)₄ or EtAlCl₂/Ph₃SiCl to give carboxylic acids with a carboxy group at the β -position to the aryl groups. The EtAlCl₂/Ph₃SiCl-mediated reaction is also applicable to various α -arylalkenes. ¹H NMR analysis of a mixture of EtAlCl₂, Ph₃SiCl, and Et₃SiH strongly suggests the formation of a μ -H complex, [Ph₃Si-H–SiEt₃]⁺ AlEtCl₃⁻, which is an equivalent of R₃Si⁺ ions, while Et₃SiB(C₆F₅)₄ is an ion pair with a Et₃Si⁺ ion. Therefore, in these reaction systems, a siloxycarbonylium, R₃Si–O–C=O⁺, is considered to be a common electrophile, the addition of which to the substrate, followed by trapping of the resulting cationic species with Et₃SiH seems to afford the desired acid after aqueous workup.

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Carbon dioxide (CO₂) is an inexpensive and renewable carbon source and, therefore, the development of methods to use CO₂ as a C1 feedstock is highly demanded. In recent years, the development of transition metal-catalyzed carboxylation has advanced remarkably, which improved the substrate applicability of aromatic compounds.¹ However, successful examples for the carboxylation of alkenes are still limited,² except for specific alkenes such as allenes,³ dienes,⁴ bisdienes,⁵ and *o*hydroxystyrenes,⁶ because alkenes are readily decomposed, polymerized, and/or isomerized under the reaction conditions.⁷

It is known that aromatic compounds are carboxylated with CO₂ in the presence of an aluminum-based Lewis acid to give aromatic carboxylic acids.⁸ The reaction is believed to proceed via the $S_{\rm F}$ Ar mechanism, in which CO₂ is activated by a Lewis acid and the resulting active CO₂ species serves as an electrophile.^{8d} However, the yields of carboxylic acids are generally poor because of the low electrophilicity of CO₂ and/or side reactions caused by the strong Lewis acidity of aluminumbased compounds.^{8d-f} In this respect, we previously reported that the combined use of AlBr₃ and R₃SiCl efficiently promotes the carboxylation.9 Mechanistic studies revealed that a silyl haloformate-like species is generated in situ from CO2 and R₃SiCl with the aid of AlBr₃. Therefore, a siloxycarbonylium, $R_3Si-O-C\equiv O^+$, is considered to be the actual electrophile in this reaction. This consideration led us to investigate the direct activation of CO₂ with silvlium ions, which resulted in the development of $R_3SiB(C_6F_5)_4$ -mediated carboxylation.¹⁰⁻¹² In this study, we investigated the application of these CO_2 activation

methods to functionalizing alkenes and succeeded in the hydrocarboxylation of α -aryl- and α , α -diarylalkenes, in which a carboxy group is introduced at the β -position to the aryl group(s). Although the α -selective hydrocarboxylation of α -arylalkenes has been reported, ^{2a,b} this is, to the best of our knowledge, the first example to achieve β -selectivity.

Initially, 1,1-diphenylpropene (1a) was hydrocarboxylated by treating with Et₃SiH under CO₂ pressure (3.0 MPa) in the presence of a benzene complex of $Et_3SiB(C_6F_5)_4^{13}$ in benzene at room temperature (entry 1 in Table 1).¹⁴ The reaction proceeded with complete regioselectivity to give 2-methyl-3,3diphenylpropanoic acid (2a) in a good yield (65%). Other trialkylsilyliums exhibited similar performances (entries 2 and 3), while triphenvlsilvlium was less effective (entry 4). Changing the solvent to hexane slightly improved the yield (entry 5). As for the reductant, i-Pr₃SiH could be used without appreciable loss of the acid yield (entry 6), while Ph₃SiH reduced the yield (entry 7). Lowering the temperature to 0 °C was effective (entry 8). Finally, the best yield (78%) was achieved by using a small excess of Et_3SiH over the triethylsilylium borate in hexane at 0 °C (entry 9). It has been reported that silvlium ions readily form μ -H complexes in the presence of hydrosilanes.¹⁵ We then prepared a μ -H complex beforehand and subjected it to the hydrocarboxylation using no external reductant. The reaction gave acid 2a although in a reduced yield (entry 10 as compared with entry 8).

The hydrocarboxylation of various α , α -diarylalkenes was conducted under the optimal conditions (Scheme 1). The reaction

^{*} Corresponding author. Tel./fax: +81-22-795-7263; e-mail: tanaka@orgsynth.che.tohoku.ac.jp

^{*} Corresponding author. Tel./fax: +81-22-795-7262; e-mail: hattori@orgsynth.che.tohoku.ac.jp

Tetrahedron

Table 1. Hydrocarboxylation of 1,1-diphenyl propene with the aid of silylium borates^a

Ph 人		F	R ₃ Si(C ₆ H ₆)B(C ₆ F ₅) ₄		Ph Д. солн	
Ph	1a ⁺	502 <u>so</u>	cO ₂ reductant solvent, temp. (°C), 1 h		2a	
entry	R	reductant	solvent	temp. (°C)	yield (%) ^b	
1	Et	Et ₃ SiH	benzene	r.t.	65	
2	i-Pr	Et ₃ SiH	benzene	r.t.	62	
3	Hex	Et ₃ SiH	benzene	r.t.	59	
4	Ph	Et ₃ SiH	benzene	r.t.	22	
5	Et	Et ₃ SiH	hexane	r.t.	71	
6	Et	i-Pr ₃ SiH	hexane	r.t.	69	
7	Et	Ph ₃ SiH	hexane	r.t.	56	
8	Et	Et ₃ SiH	hexane	0	73	
9°	Et	Et ₃ SiH	hexane	0	78	
$10^{d,e}$	-	-	hexane	0	51	

^a Reaction conditions: **1a** (0.30 mmol), silylium borate (0.20 mmol), reductant (0.20 mmol), CO₂ (3.0 MPa), solvent (1.0 mL).

^b Isolated yield based on the quantity of silylium borate.

^c Et₃SiH (0.24 mmol) was used.

^d (Et₃Si)₂(µ-H)B(C₆F₅)₄ was used as a silylium borate-cum-reductant.

^e Compound 1a (0.60 mmol) was used.

of terminal alkene **1b** resulted in the decomposition of the substrate, while internal alkenes bearing a phenyl group (**1c**) and two methyl groups (**1d**) at the β -position gave the corresponding acids **2c** and **2d**, respectively, although in poor yields. Better yields were obtained for cyclic α , α -diarylalkenes **1e**–**g**. The stereochemistries of the resulting acids **2e**–**g** were assigned to be *cis* by NOESY analysis. This is probably because the attack of the hydrosilane to a cationic intermediate, generated *in situ* by the addition of an active CO₂ species, *i.e.* a siloxycarbonylium (*vide infra*), to the substrate occurred from the opposite side to the ester group to avoid steric repulsion.



Scheme 1. Hydrocarboxylation of 1,1-diarylalkenes with the aid of $Et_3SiB(C_6F_5)_4$. Reaction conditions: **1** (0.30 mmol), $Et_3Si(C_6H_6)B(C_6F_5)_4$ (0.20 mmol), Et_3SiH (0.24 mmol), CO_2 (3.0 MPa), hexane (0.50 mL). Yields are based on the quantity of the silylium borate. ^{a 1}H NMR yield determined using CH_2Br_2 as an internal standard.

Next, we investigated the hydrocarboxylation of arylalkenes by combined use of an aluminum-based Lewis acid and $Ph_3SiCl.$ ¹⁶ Contrary to the silylium borate-mediated reaction, terminal alkene **1b** gave the corresponding acid **2b** (8%), when treated with Et₃SiH under CO₂ pressure (3.0 MPa) in the presence of AlBr₃ and Ph₃SiCl in toluene at 60 °C (entry 1 in Table 2). The reaction was accompanied by the formation of toluic acid, apparently due to the carboxylation of the solvent with the aid of AlBr₃ and Ph₃SiCl. Interestingly, EtAlCl₂ was most effective among the Lewis acids tested (entries 1–4). This shows a sharp contrast to the carboxylation of arenes,⁹ in which AlBr₃ with stronger Lewis acidity exhibited better performance than EtAlCl₂. Toluic acid was not obtained when Lewis acids other than AlBr₃ were employed. Changing the solvent to chlorobenzene–hexane and hexane did not affect much on the acid yield (entries 5 and 6). Increasing the temperature to 80 °C improved the yield (entry 7). The molar ratio of Ph₃SiCl to EtAlCl₂ (y/x) was varied within the range of 0–2.0, among which the ratio of 1.5 was most effective (entries 7–11). Finally, the best yield (80%) was achieved by increasing the molar equivalence of EtAlCl₂ to the substrate (x) to 2.5 with keeping the molar ratio y/x (entry 12).

Table 2. Hydrocarboxylation of 1,1-diphenylethylene by	combined	use	of
aluminum-based Lewis acids and Ph ₃ SiCl ^a			

	Ph	~~	Lewis A Ph ₃ Si	cid (x mol equiv) Cl (y mol equiv)	Ph	
Ph + CO_2 Et_3SiH Ph CO_2H 1b solvent, temp. (°C), 24 h 2b				-CO ₂ H		
entry	Lewis acid	х	y/x	Solvent	temp. (°C)	yield (%) ^b
1	AlBr ₃	1.25	1.5	toluene	60	8^{d}
2	AlCl ₃	1.25	1.5	toluene	60	43
3	$EtAlCl_2$	1.25	1.5	toluene-hexane ^c	60	53
4	Et ₂ AlCl	1.25	1.5	toluene-hexane ^c	60	10
5	Et ₂ AlCl	1.25	1.5	chlorobenzene- hexane ^c	60	50
6	Et ₂ AlCl	1.25	1.5	hexane ^c	60	50
7	EtAlCl ₂	1.25	1.5	toluene-hexane ^c	80	66
8	EtAlCl ₂	1.25	0	toluene-hexane ^c	80	54
9	EtAlCl ₂	1.25	0.5	toluene-hexane ^c	80	49
10	EtAlCl ₂	1.25	1.0	toluene-hexane ^c	80	53
11	EtAlCl ₂	1.25	2.0	toluene-hexane ^c	80	63
12	EtAlCl ₂	2.5	1.5	toluene-hexane ^c	80	80 (77)

^a Reaction conditions: **1a** (0.40 mmol), Lewis acid (x mol equiv), Ph₃SiCl (y mol equiv), Et₃SiH (0.60 mmol), CO₂ (3.0 MPa), solvent (1.5–2.5 mL).

 b_1 H NMR yield determined using CH₂Br₂ as an internal standard. Isolated yield is shown in the parenthesis.

^c Lewis acid was used as a hexane solution and, therefore, hexane was included in the reaction mixture.

^d Toluic acid (0.032 mmol, o - : p - = 1:4) was also obtained.

The hydrocarboxylation of various arylalkenes was then conducted under the optimized conditions (Scheme 2). Acyclic α, α -diarylalkene **1a** with a methyl group at the β -position and cyclic α, α -diarylalkenes 1e-1g with no substituent at the β position gave the corresponding acids 2a and 2e-2g, respectively, in good yields; the stereochemistries of the cyclic acids 2e-2g were determined to be cis by NOESY analysis. On the other hand, acid yields were considerably reduced for more bulky α , α diarylalkenes with a phenyl group (1c) and two methyl groups (1d) at the β -position. It should be noted that both acyclic (1j) and cyclic alkenes 1h and 1i with only one aryl substituent at the α -position could be hydrocarboxylated in good yields; each of acids 2h and 2i was obtained as a *cis/trans* mixture containing the cis isomer as the major component. It seems that in the reaction of compounds 1h-1j, the attack of the hydrosilane to a cationic intermediate, generated in situ by the addition of an active CO_2 species or EtAlCl₂ to the substrate (vide infra), occurred rather unselectively from both sides of the alkene plane due to the low stability of the cationic intermediate bearing an alkyl group at the α position instead of a phenyl group. As mentioned the EtAlCl₂/Ph₃SiCl-mediated above, hydrocarboxylation exhibited wide applicability toward not only α, α -diarylalkenes but also α -aryllalkenes.

A feasible mechanism for the silylium borate-mediated hydrocarboxylation is illustrated in Scheme 3 as represented by the reaction using $Et_3Si(C_6H_6)B(C_6F_5)_4$ and Et_3SiH . As in the case of the carboxylation of aromatic compounds,^{10,12} the

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benzene complex of $Et_3SiB(C_6F_5)_4$ or the μ -H complex generated *in situ* from the benzene complex and Et_3SiH activates CO_2 to form siloxycarbonylium **A**. This active species electrophilically adds to an alkene, and the resulting dibenzyl cation is trapped by Et_3SiH to afford a silyl ester, which is decomposed by aqueous workup to give the corresponding carboxylic acid. The formation of the stable dibenzyl cation intermediate determines the regiochemistry of the reaction.



Scheme 2. Hydrocarboxylation of alkenes with the aid of EtAlCl₂ and Ph₃SiCl. Reaction conditions: **1** (0.40 mmol), EtAlCl₂ (1.0 mmol), Ph₃SiCl (1.5 mmol), Et₃SiH (0.60 mmol), CO₂ (3.0 MPa), toluene (1.5 mL). Yields are based on the quantity of substrate. ^a **1**J (E: Z = 95:5) was used. ^b¹H NMR yield determined using CH₂Br₂ as an internal standard. ^c (2*RS*₃*SR*):(2*RS*₃*SR*) = 17:83. ^d *cis* : *trans* = 70:30. ^c *cis* : *trans* = 77:23.



Scheme 3. Feasible mechanism for the $Et_3SiB(C_6F_5)_4$ -mediated hydrocarboxylation.

On the other hand, in the EtAlCl₂/Ph₃SiCl-mediated hydrocarboxylation, a beneficial effect of Ph₃SiCl was observed (entries 7 and 9-11 as compared with entry 8 in Table 2). This indicates that CO₂ was activated with the aid of Ph₃SiCl. In order to obtain better insight into the activation process, ¹H NMR analysis was carried out. Figure 1a shows ¹H NMR spectrum of a mixture of EtAlCl₂, Ph₃SiCl, and Et₃SiH (1.0:1.5:0.6) measured after stirring for 3 h at room temperature. The spectrum exhibited two singlets at 5.50 and 4.92 ppm, which are assignable to hydrogen atoms on silicon. The former and latter signals are different from the Si-H signal of Et₃SiH in both chemical shift and splitting pattern (Figure 1b), but are very close to the Si-H signals of Ph₃SiH and Ph₂SiH₂, respectively (Figure 1c and 1d). Moreover, stirring the solution for a further 9 h gave Ph₄Si as a colorless precipitate. These observations strongly suggests that μ -H complex **B** was generated from Ph₂SiCl. Et₂SiH. and EtAlCl₂ through a five-coordinated transition state, and was fragmented into Ph₃SiH, Et₃SiCl, and EtAlCl₂ through a similar transition state; the overall reaction results in the ligand exchange between the chlorine of Ph₃SiCl and the hydrogen of Et₃SiH (Scheme 4).¹⁵ The resulting Ph₃SiH was disproportionated into Ph₄Si and Ph_2SiH_2 through μ -H complexes C and D with the aid of Ph₃SiCl.¹⁷ In contrast, ¹H NMR spectrum of a mixture of Ph₃SiCl and Et₃SiH after stirring for 3 h at room temperature showed only the signal of Et₃SiH as the Si-H signal (Figure 1e), indicating that EtAlCl₂ is indispensable for the ligand exchange. Interestingly, ¹H NMR spectrum of a mixture of EtAlCl₂, Et₃SiCl, and Ph₃SiH measured after stirring for 1 h at room temperature (Figure 1f) exhibited the Si-H signals of Et₃SiH and Ph₂SiH₂, indicating the formation of Et₃SiH and Ph₃SiCl by the ligand exchange between Et₃SiCl and Ph₃SiH. Indeed, the hydrocarboxylation of compound 1b conducted under the same conditions as employed in entry 12 (Table 2), except Et₃SiCl and Ph₃SiH were used instead of Ph₃SiCl and Et₃SiH, afforded acid **2b** in a comparable yield (72%) to that achieved in entry 12. On the other hand, under the same conditions, the combined use of Et₃SiCl and Et₃SiH gave 54% yield, which is lower than the yield obtained only by using Et₃SiH (63%), that is, no beneficial effect of Et₃SiCl was observed. On the basis of these results, a feasible mechanism for the EtAlCl₂/R₃SiCl- mediated hydrocarboxylation is proposed as follows: When either the chlorosilane or



Figure 1. Expanded ¹H NMR spectra of (a) a mixture of EtAlCl₂, Ph₃SiCl, and Et₃SiH (1.0:1.5:0.6), (b) Et₃SiH, (c) Ph₃SiH, (d) Ph₂SiH₂, (e) a mixture of Ph₃SiCl, and Et₃SiH, and (f) a mixture of EtAlCl₂, Et₃SiCl, and Ph₃SiH (1.0:1.5:0.6) in toluene- d_8 -hexane (3:2).



Scheme 4. Feasible mechanism for the ligand exchange between Ph₃SiCl and Et₃SiH and the disproportionation of Ph₃SiH.

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hydrosilane has a Ph_3Si group, the relevant Si-X bond (X = Cl or H) is highly polarized, so that a μ -H complex such as **B** can be formed. However, not only the electronic effects but also the steric effects of the substituents on silicon seem to affect the efficiency of producing a μ -H complex, as indicated by the fact that the combined use of Ph₃SiCl/Ph₃SiH and Ph₃SiCl/i-Pr₃SiH gave 67% and 41% yields, respectively. The resulting μ -H complex activates CO_2 to form siloxycarbonylium E (path a in Scheme 5), as in the case of the $Et_3SiB(C_6F_5)_4$ -mediated hydrocarboxylation. The active CO₂ species adds to the substrate and the resulting dibenzyl cation is trapped with a hydrosilane to deliver the hydrocarboxylated product after aqueous workup. In the reaction conducted in the absence of a chlorosilane (entry 8 in Table 2), EtAlCl₂ seems to activate CO₂ instead of the μ -H complex (path b). An alternative mechanism is that an alkene is electrophilically metalated with EtAlCl₂ and the resulting cationic species is reduced by Et₃SiH to give an organoaluminum, which is carbonated to afford a carboxylic acid (path c).¹⁸ The latter two paths may be involved also in the reaction conducted in the presence of Ph₃SiCl.



In conclusion, we have shown that arylalkenes are hydrocarboxylated with Et₃SiH and CO₂ in the presence of Et₃SiB(C₆F₅)₄ or EtAlCl₂/Ph₃SiCl. The present methods provide the first example for the β -selective hydrocarboxylation of arylalkenes. It is expected that the method to activate CO₂ with EtAlCl₂, Ph₃SiCl, and Et₃SiH is applicable to the carboxylation of other unsaturated compounds, which are intolerant of strong Lewis acids such as AlBr₃. Further investigation along this line is in progress.

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- At nearly the same time as we reported the R₃SiB(C₆F₅)₄-mediated carboxylation, Müller *et al.* also reported the carboxylation of benzene in the presence of Ph₃CB(C₆F₅)₄ and Et₃SiH: Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 2981–2984.
- 12. In our previous report on the carboxylation of aromatic compounds,¹⁰ Et₃SiB(C₆F₅)₄ was prepared from Et₃SiH and Ph₂CB(C₆F₅)₄, according to Lambert's method.^{13b} Later on, we realized that it was a μ -H complex.^{15b} We then prepared Et₃Si(C₆H₆)B(C₆F₅)₄ according to Müller's method,¹¹ and confirmed that it mediates the carboxylation of aromatic compounds.
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- Et₃SiB(C₆F₅)₄-mediated 14. Typical procedure for the hydrocarboxylation of alkenes (entry 9 in Table 1): In a 50 mL autoclave equipped with a glass inner tube and a magnetic stirring bar were charged freshly prepared Et₃Si(C₆H₆)B(C₆F₅)₄ (175 mg, 0.20 mmol), dry hexane (1.0 mL), compound 1a (58.0 mg, 0.30 mmol), and Et₃SiH (d 0.73; 38 µL, 0.24 mmol) under nitrogen, and the apparatus was purged with CO2 by repeated pressurization and subsequent expansion; the final pressure was adjusted to 3.0 MPa. After the mixture was stirred at 0 °C for 1 h, the reactor was depressurized, and the mixture was quenched with 2 M HCl (10 mL) and extracted with ethyl acetate. The organic layer was extracted with 0.5 M Na₂CO₃ and the extract was acidified with concentrated HCl to liberate the free acid, which was extracted with ethyl acetate. The extract was dried over MgSO4 and evaporated to leave a residue, which was purified by column chromatography with chloroform/methanol (10:1) containing 1 vol% of acetic acid as an eluent to afford acid **2a** (37.8 mg, 78%).
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- EtAlCl₂/Ph₃SiCl-mediated 16. Typical procedure for the hydrocarboxylation of alkenes (entry 12 in Table 2): In a 50 mL autoclave equipped with a glass inner tube and a magnetic stirring bar were charged Ph₃SiCl (442 mg, 1.50 mmol), toluene (1.5 mL), Et₃SiH (d 0.73; 96 μL, 0.60 mmol), compound 1b (d 1.03; 70 μL, 0.40 mmol), and EtAlCl₂ (1.0 M solution in hexane; 1.0 mL, 1.00 mmol) in this order under nitrogen. The apparatus was purged with CO₂ by repeated pressurization and subsequent expansion; the final pressure was adjusted to 3.0 MPa. After the mixture was stirred at 80 °C for 24 h, the reactor was depressurized and the mixture was quenched with 2 M HCl (10 mL). The mixture was worked up and purified as mentioned above to afford acid 2b (70.0 mg, 77%).

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