



Platinum-catalyzed allylation of carbon electrophiles with alkenylsilanes



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ARTICLE INFO

Article history:

Received 1 November 2014

Revised 5 December 2014

Accepted 14 December 2014

Available online 19 December 2014

Keywords:

Platinum(II) catalysis

Allylation

Alkenylsilane

Allylsilane

One-pot reaction

ABSTRACT

In the presence of catalytic amounts of PtCl₂ and AgSbF₆, (Z)-alkenylsilanes react with various carbon electrophiles at the γ -position to give allylation products. A plausible mechanism for the Pt-catalyzed allylation involves alkene migration of alkenylsilanes to allylsilanes and subsequent allylation of carbon electrophiles.

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Allylsilanes have frequently been used for regiospecific allylation of various carbon electrophiles.¹ Since they react with electrophiles only at the position γ to silicon, use of α - or γ -substituted allylsilanes gives allylation products as single regioisomers. Thus far a large number of methods for regio-controlled synthesis of α - or γ -substituted allylsilanes have been developed.^{2,3} However, convenient access to these allylsilanes from inexpensive commercially available compounds is rather limited. There is much room for development of regio-controlled allylation using more accessible reagents. We herein report that (Z)-alkenylsilanes serve as γ -substituted allylsilane equivalents for allylation of carbon electrophiles under catalysis by a cationic Pt(II) species.⁴

We have previously reported the Pt(II)-catalyzed annulation of hydroxyalkenylsilanes with aldehydes leading to 2,3-disubstituted THPs and THFs.⁵ The reaction mechanism involves alkene migration of the alkenylsilane, the formation of an oxocarbenium ion from the hydroxy group and an aldehyde, and intramolecular allylation of the electrophilic carbon by the allylsilane part formed. On the basis of the previous work, our interest was focused on the Pt(II)-catalyzed intermolecular allylation of carbon electrophiles with β -substituted alkenylsilanes.⁶ Initially the reaction of benzaldehyde with alkenylsilane **2a** was carried out in the presence of PtCl₂–2AgOTf; however, no allylation product was obtained.⁷ We

next tried the allylation of benzaldehyde dimethyl acetal (**1a**) (Table 1).⁸ As expected **1a** reacted with **2a** (2 equiv) under catalysis by PtCl₂–2AgOTf (10 mol % Pt) at room temperature to give an allylation product **3aa** in 78% yield (*syn/anti* = 63:37) (entry 1). AgSbF₆ as well as AgOTf served as an effective cocatalyst although AgBF₄ and AgPF₆ were not effective (entries 2–4). Without the cocatalyst, the allylation was not observed (entry 5). The reaction using AgSbF₆ at 40 °C gave **3aa** in high yields (entry 8). The use of AgSbF₆ at 70 °C achieved an efficient allylation with reduced amounts of **2a** (1.2 equiv) and PtCl₂ (5 mol %) (entry 9).⁹ Under the same conditions, the allylation with (E)-**2a** was rather slow and resulted in a low yield of **3aa** (entry 10).

The optimized conditions were applied to the allylation of various acetals (Table 2). Acetals **1b–d** derived from 4-substituted benzaldehydes efficiently underwent the Pt(II)-catalyzed allylation with **2a** to afford the corresponding homoallylic ethers **3ba–da** (entries 2–4). Under the same conditions, acetal **1e** derived from 4-methoxybenzaldehyde was converted into a complex mixture of products. This is probably due to the instability of the allylation product **3ea** under the Lewis acidic conditions. Shortening the reaction time enabled the isolation of **3ea** (entry 5). The allylation of acetal **1f** derived from cyclohexanecarbaldehyde proceeded in a moderate yield (entry 6).

As shown in entries 7–11, the Pt(II)-catalyzed reaction was also valuable for the allylation of aminals **4a–e** derived from aromatic aldehydes and methyl carbamate. With half amounts of PtCl₂

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Table 1
Optimization of reaction conditions^a

Entry	AgX	Temp (°C)	Time (h)	Yield ^b (%)	syn/anti ^c
1	AgOTf	rt	24	78	63:37
2	AgSbF ₆	rt	24	60	73:27
3	AgPF ₆	rt	24	28	72:28
4	AgBF ₄	rt	24	8	70:30
5	none	rt	24	0	—
6	AgOTf	40	12	71	64:36
7	AgOTf	70	1.5	72	61:39
8	AgSbF ₆	40	10	89	74:26
9 ^d	AgSbF ₆	70	4	84	63:37
10 ^{d,e}	AgSbF ₆	70	24	26 ^f	61:39

^a Reaction conditions: **1a** (0.50 mmol), **2a** (*Z/E* = >98:2, 1.00 mmol), PtCl₂ (0.05 mmol), AgX (0.10 mmol), and CH₂Cl₂ (1.5 mL, entries 1–5) or (CH₂Cl)₂ (1.5 mL, entries 6–9).

^b Isolated yield.

^c Determined by ¹H NMR analysis.

^d With **2a** (0.60 mmol), PtCl₂ (0.025 mmol), and AgSbF₆ (0.05 mmol).

^e The *E*-isomer of **2a** (*(E)*-**2a**, *Z/E* = 3:97) was used.

^f (*E*)-**2a** was recovered in 60% yield.

Table 2
Allylation of acetals **1** and amins **4**^a

Entry	1 or 4 : R ¹	Time (h)	Product	Yield ^b (%)	syn/anti ^c
1	1a : Ph	4	3aa	84	63:37
2	1b : 4-Br-C ₆ H ₄	10	3ba	93	70:30
3	1c : 4-O ₂ N-C ₆ H ₄	24	3ca	76	68:32
4 ^d	1d : 4-Me-C ₆ H ₄	4	3da	74	40:60
5	1e : 4-MeO-C ₆ H ₄	0.5	3ea	26	47:53
6	1f : Cy	2	3fa	65	75:25
7	4a : Ph	24	5aa	91	62:38
8	4b : 4-Br-C ₆ H ₄	24	5ba	93	62:38
9	4c : 4-O ₂ N-C ₆ H ₄	24	5ca	84	68:32
10	4d : 4-Me-C ₆ H ₄	24	5da	86	64:36
11	4e : 4-MeO-C ₆ H ₄	24	5ea	74	55:45
12	4f : Cy	24	5fa	0	—

^a Reaction conditions in entries 1–6: an acetal **1** (0.50 mmol), **2a** (0.60 mmol), PtCl₂ (0.025 mmol), AgSbF₆ (0.05 mmol), and (CH₂Cl)₂ (1.5 mL) at 70 °C. Reaction conditions in entries 7–12: an amins **4** (1.00 mmol), **2a** (1.20 mmol), PtCl₂ (0.025 mmol), AgSbF₆ (0.05 mmol), and (CH₂Cl)₂ (3.0 mL) at 70 °C.

^b Isolated yield.

^c Determined by ¹H NMR analysis.

^d With PtCl₂ (0.05 mmol) and AgSbF₆ (0.10 mmol).

(2.5 mol %) and AgSbF₆ (5 mol %), the amins allylation gave homoallylic amines **5aa–ea** in good to high yields. Unlike **1e**, amins **4e** underwent a successful allylation without a rapid decomposition of **5ea** (entry 11). Amins **4f** derived from cyclohexanecarbaldehyde did not react with **2a** at all (entry 12).

Other alkenylsilanes also served as allylating agents under the Pt(II) catalysis (Table 3). The reaction of **1a** with alkenylsilanes **2b** (R = Ph) gave the corresponding homoallylic ethers **3ab** in good yields (entry 1). Alkenylsilanes **2c** and **2d** bearing an oxygen functionality showed lower reactivity than **2a** (entries 2 and 3). It may be due to deactivation of the Pt(II) species by coordination of the functional group. Amins **4a** as well as **1a** reacted with

Table 3
Allylation with other alkenylsilanes **2**^a

1a : X = OMe 4a : X = NHCO ₂ Me					
Entry	1a or 4a	2 : R	Product	Yield ^b (%)	syn/anti ^c
1 ^d	1a	2b : Ph	3ab	76	70:30
2	1a	2c : PhCO ₂ (CH ₂) ₃	3ac	65	68:32
3	1a	2d : MeO(CH ₂) ₃	3ad	61	70:30
4	4a	2b : Ph	5ab	60	50:50
5	4a	2e : TIPSO(CH ₂) ₃	5ae	62	60:40
6	4a	2f : Me	5af	86	67:33

^{a–c} See footnotes a–c in Table 2.

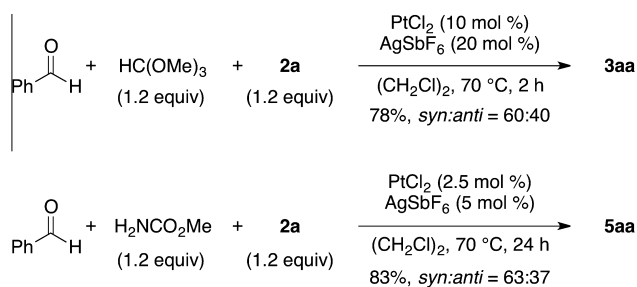
^d The reaction time was 4 h.

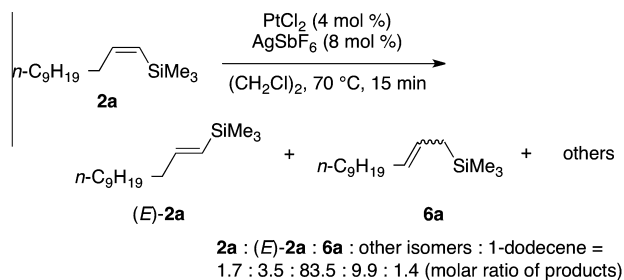
alkenylsilanes **2b**, **2e**, and **2f** to afford the corresponding homoallylic amines **5ab**, **5ae**, and **5af**, respectively (entries 4–6).

The Lewis or Brønsted acid-catalyzed three-component coupling of aldehydes, oxygen or nitrogen donors, and allylsilanes is valuable as a direct approach to homoallylic ethers or amines.^{10,11} The Pt(II)-catalyzed allylation using alkenylsilanes is applicable to the three-component coupling. As shown in Scheme 1, when a mixture of benzaldehyde, trimethyl orthoformate, and **2a** was treated with catalytic amounts of PtCl₂ and AgSbF₆, homoallylic ether **3aa** was formed in good yields. The three-component coupling reaction using methyl carbamate, a nitrogen donor, also proceeded successfully.

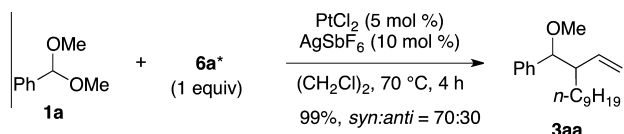
In the Pt(II)-catalyzed allylation of **1a** with **2a**, the formation of allylsilane **6a** was observed. This implies that the allylation proceeds by alkene migration of **2a** and subsequent allylation of **1a** with **6a**. To ascertain the postulated mechanism, we first examined alkene migration of **2a**. When only **2a** was treated with a catalytic amount of PtCl₂ or AgSbF₆, the isomerization of **2a** to **6a** did not occur in each case. The combined use of PtCl₂ and AgSbF₆ effectively promoted the isomerization to give **6a** (*E/Z* = ca. 7:1) mainly with (*E*)-**2a** and other isomers (Scheme 2).^{12,13} We next examined the allylation of **1a** with **6a**. A catalytic amount of PtCl₂ or AgSbF₆ did not serve for the allylation of **1a**. In contrast, the combination of PtCl₂ with AgSbF₆ achieved an efficient allylation of **1a** (Scheme 3).⁸ Judging from these results, the allylation mechanism involves a consecutive isomerization-allylation process, in which a Lewis acidic, cationic Pt(II) species generated from PtCl₂ and AgSbF₆ promotes both steps by activation of the C–C double bond and the acetal C–O bond.¹⁴

The present Pt(II)-catalyzed one-step reaction is not useful for stereoselective synthesis of homoallylic ethers and amines. The low stereoselectivity observed is probably due to relatively high reaction temperature at the allylation step. Therefore, to improve the stereoselectivity, we attempted a one-pot allylation by a

**Scheme 1.** Three-component coupling reaction.



Scheme 2. Pt-catalyzed alkene migration.



*80 wt% pure. **2a** : (*E*)-**2a** : **6a** : other isomers : 1-dodecene =
4.1 : 3.2 : 78 : 7.1 : 7.7 (molar ratio).

Scheme 3. Pt-catalyzed allylation.

two-step method using an additional Lewis acid (Scheme 4). The former step is the Pt(II)-catalyzed alkene migration of an alkenylsilane at 70 °C and the latter step is the Lewis acid-promoted allylation of a carbon electrophile with the resultant allylsilane at lower temperatures. When the latter step was conducted with $\text{BF}_3 \cdot \text{OEt}_2$ in MeCN at -30°C , the allylation of acetal **1a** with **2a** gave **3aa** in 96% yield with 87% *syn* selectivity. Without solvent displacement from CH_2Cl_2 to MeCN, the *syn* selectivity dropped to 81%. The stepwise allylation of **1f** also showed much better stereoselectivity than the one-step reaction. A similar stereochemical outcome was obtained in the allylation of aminal **4a**. Although **4f** did not undergo the one-step allylation with **2a** (Table 2, entry 12), the stepwise method using $\text{BF}_3 \cdot \text{OEt}_2$ efficiently converted **4f** into the allylation product **5fa** with high *syn* selectivity.

The Pt(II)-catalyzed allylation with alkenylsilanes is applicable to other carbon electrophiles (Table 4). Ether **7a** and ester **7b** underwent the one-step allylation (method A) with **2a** to afford the product **8a** (entries 1 and 2). As expected from the leaving groups, **7b** showed higher reactivity than **7a**. Adding **7b** after the isomerization of **2a**, that is, a stepwise method (method B) promoted the allylation more efficiently. Interestingly, method A

Table 4

Allylation of other carbon electrophiles^a

Entry	7: E-Y	Product	Isolated yield (%)	
			Method A ^b	Method B ^b
1	7a : $\text{Ph}_2\text{CH-OMe}$	8a	60, 81 ^{c,d}	43
2	7b : $\text{Ph}_2\text{CH-OAc}$	8a	84	94
3	7c : $\text{Ph}_2\text{CH-Cl}$	8a	0	77, 98 ^c
4	7d : <i>p</i> - $\text{AnCH}_2\text{-OAc}$	8d	0 ^e	Trace ^e , 79 ^f
5	7e : <i>p</i> - $\text{AnCH}_2\text{-Cl}$	8d	0	71 ^g
6	7f : $\text{MeOCH}_2\text{-Cl}$	8f	0	74
7	7g : Ac-OAc	8g	65, 74 ^h	56
8	7h : Bz-OBz	8h	41	Trace, 85 ⁱ
9	7i : Piv-OPiv	8i	60	51, 93 ^j

^a Reaction conditions: **7** (1.00 mmol), **2a** (1.40 mmol), PtCl_2 (0.025 mmol), AgSbF_6 (0.050 mmol) and $(\text{CH}_2\text{Cl})_2$ (3 mL).

^b Method A: a mixture of all the listed compounds was stirred at 70 °C for 24 h. Method B: first, a mixture of **2a**, PtCl_2 , and AgSbF_6 in $(\text{CH}_2\text{Cl})_2$ was stirred at 70 °C for 2 h. Then, **7** was added. The resultant mixture was stirred at 70 °C for 24 h.

^c With **2a** (1.60 mmol).

^d With PtCl_2 (0.10 mmol) and AgSbF_6 (0.20 mmol).

^e With recovery of **7d**.

^f Allylation with $\text{BF}_3 \cdot \text{OEt}_2$ (1.00 mmol) at 30 °C for 2 h.

^g Allylation at 30 °C for 18 h.

^h Allylation for 4 h.

ⁱ Allylation with $\text{BF}_3 \cdot \text{OEt}_2$ (0.50 mmol).

^j Allylation with $\text{BF}_3 \cdot \text{OEt}_2$ (0.40 mmol) for 20 h.

completely suppressed the allylation of chloride **7c**, while the reaction by method B formed **8a** in good yields (entry 3). Similar results were observed in the reaction of chlorides **7e** and **7f** (entries 5 and 6). In these cases using method A, the chlorides **7** were decomposed and the isomerization of **2a** to **6a** hardly proceeded. This is probably due to fast chloride abstraction from **7** by AgSbF_6 . Allylation of ester **7d** resulted in failure even by method B. However, it was successfully achieved by a modified method using $\text{BF}_3 \cdot \text{OEt}_2$ (entry 4). Carboxylic anhydrides were also allylated under the Pt(II) catalysis (entries 7–9). The use of $\text{BF}_3 \cdot \text{OEt}_2$ was effective in the allylation of carboxylic anhydrides **7h** and **7i**.

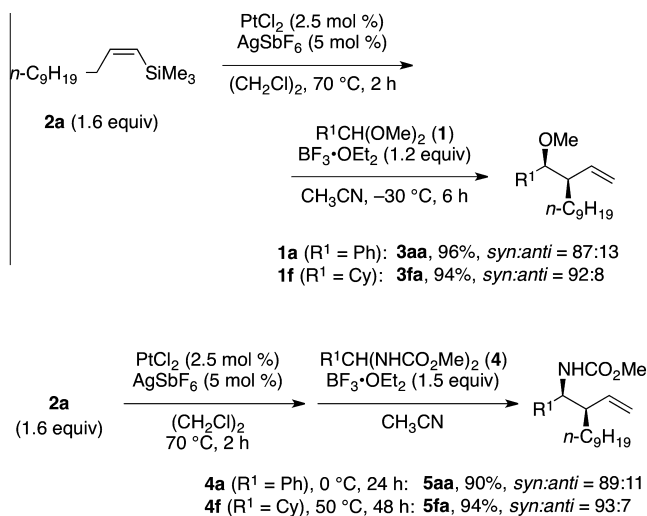
In conclusion, we have developed novel allylation reactions of carbon electrophiles with (*Z*)-alkenylsilanes, which serve as precursors of γ -substituted allylsilanes under catalysis by PtCl_2 and AgSbF_6 . It is noteworthy that the Pt(II) catalysis promotes both alkene migration of alkenylsilanes and subsequent allylation.¹⁴ Although the one-step allylation of acetals and aminals does not show good stereoselectivities, the stepwise allylation using an additional Lewis acid is useful for stereoselective synthesis of homoallylic ethers and amines. The reasonable compatibility with functional groups, a wide range of carbon electrophiles and easy access to (*Z*)-alkenylsilanes make these allylation reactions synthetically useful.⁴

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area 'Synergistic Effects for Creation of Functional Molecules' (No. 20036010) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supplementary data

Supplementary data (experimental details and characterization data ¹H NMR, ¹³C NMR, IR, elemental analysis) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2014.12.077>.



Scheme 4. Diastereoselective allylation.

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