



Platinum-catalyzed allylation of carbon electrophiles with alkenylsilanes



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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 regioselective 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 aminal **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 aminal allylation gave homoallylic amines **5aa–ea** in good to high yields. Unlike **1e**, aminal **4e** underwent a successful allylation without a rapid decomposition of **5ea** (entry 11). Aminal **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. Aminal **4a** as well as **1a** reacted with

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

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.

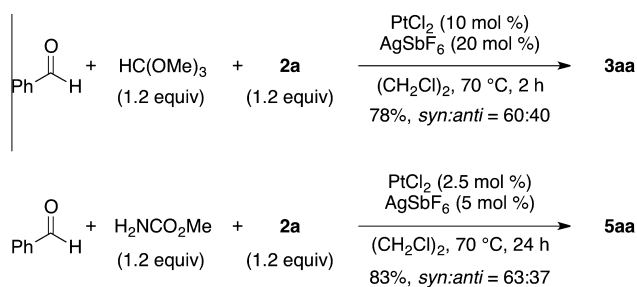
^d The reaction time was 4 h.

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.

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