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Platinum-Catalyzed One-Pot Alkenylation of Aldehydes Using Alkynes and Triethylsilane: Dual Catalysis by Platinum(II) Chloride

Hidenori Kinoshita, Ryousuke Uemura, Daiki Fukuda, and Katsukiyo Miura*

Department of Applied Chemistry, Graduate School of Science and Engineering,
Saitama University, Sakura-ku, Saitama 338-8570, Japan

kmiura@apc.saitama-u.ac.jp

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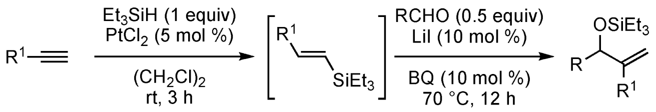
ABSTRACT



The $PtCl_2$-catalyzed hydrosilylation of terminal alkynes with triethylsilane and subsequent alkenylation of aldehydes with the resultant (*E*)-alkenylsilanes in a one-pot manner are described. By adding *p*-benzoquinone and LiI, the latter alkenylation step proceeds smoothly to give allyl silyl ethers in moderate to high yields. This one-pot alkenylation is tolerant to a reasonable range of functional groups. $PtCl_2$ plays a dual role as hydrosilylation and alkenylation catalysts.

Since allylic alcohols and their protected forms are very useful synthetic intermediates, various methods have been developed so far for efficient synthesis of this important class of compounds.[1] The transition-metal-mediated reductive coupling between carbonyls and alkynes, a kind of carbonyl alkenylation, provides a straightforward method for this end.[2−9] Particularly, the Ni-catalyzed reaction using Et_3B or a hydrosilane as a reducing agent has a wide scope of available alkynes.[2−4] In this context, intermolecular regiocontrol of the Ni-catalyzed alkenylation with unsymmetrical alkynes is an important issue and has been extensively studied by Montgomery's and Jamison's groups for the past decade. In general, the C−C bond formation with unsymmetrical alkynes occurs selectively at the sterically less hindered sp-carbon. Introduction of an alkene moiety[3a−c] or a TMS group[2c,d,3f] into alkynes or a proper choice of NHC ligands[2a,b] can reverse the sense of regioselection. However, complete regiocontrol toward the C−C bond formation at the internal sp-carbon of terminal alkynes remains as a subject of further study.[10] We herein report a Pt-catalyzed one-pot alkenylation of aldehydes

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(10) Takai and co-workers have reported that the Cr(II)-mediated reductive coupling between aldehydes and terminal alkynes proceeds at the internal sp-carbon with high regioselectivity. See refs 9a and 9b.

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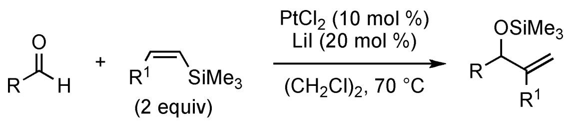
with terminal alkynes and triethylsilane (Et_3SiH), which solves a part of the problem of regiocontrol in carbonyl alkenylation.

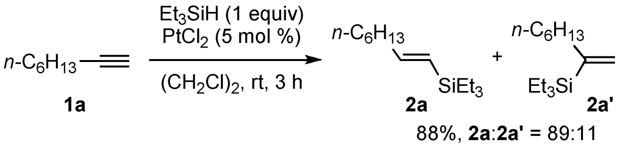
Recently we have reported the Pt(II)-catalyzed alkenylation of aldehydes with alkenylsilanes (Scheme 1).[11] Reactions of alkenylsilanes with carbon and heteroatom electrophiles take place usually at the position α to silicon,[12] while the alkenylation developed by us proceeds only at the β-position. Additionally, alkenylsilanes can be readily prepared by the Pt-catalyzed hydrosilylation of terminal alkynes with hydrosilanes.[13] Our interest was therefore focused on a one-pot hydrosilylation–alkenylation reaction utilizing dual catalysis by a single platinum catalyst to develop a more convenient method for aldehyde alkenylation.

Scheme 1. Pt(II)-Catalyzed Alkenylation of Aldehydes with Alkenylsilanes



We initially examined the $PtCl_2$-catalyzed reaction of oct-1-yne (**1a**, 1 mmol) with Et_3SiH (1 mmol) in 1,2-dichloroethane (DCE, 1.5 mL) (Scheme 2). As expected, the desired hydrosilylation proceeded smoothly at room temperature in the presence of 5 mol % $PtCl_2$. Under these conditions, **1a** was completely consumed in 3 h, and a mixture of (*E*)-alkenylsilane **2a** and its regioisomer **2a′** (**2a**:**2a′** = 89:11) was obtained in 88% yield.[14]

Scheme 2. Hydrosilylation of Oct-1-yne with Et_3SiH



Our previous work on the Pt(II)-catalyzed alkenylation disclosed that an (*E*)-alkenylsilane showed lower reactivity than its (*Z*)-isomer.[11] To test the reactivity of (*E*)-alkenylsilane **2a**, the reaction of benzaldehyde (**3a**) with a pure sample of **2a** was carried out under the conditions shown in Scheme 1. As a result, the reaction carried out for 18 h gave the corresponding alkenylation product **4aa** in 75% yield. This result ensured sufficient reactivity of **2a**.

With these encouraging results, we next investigated the one-pot alkenylation of **3a** using the reaction mixture obtained from **1a** and Et_3SiH under catalysis by 5 mol % $PtCl_2$. After the hydrosilylation of **1a** (1 mmol) with Et_3SiH (1 mmol) in DCE was completed, LiI (0.1 mmol) and **3a** (0.5 mmol) were added to the reaction vessel.[15,16] The mixture was heated to 70 °C and stirred for 24 h. This one-pot operation afforded the desired product **4aa** but with low reproducibility (Table 1, entry 1). As described in our previous report, the present alkenylation is hardly catalyzed by Pt(0) and Pt(0) complexes.[11] Therefore, it seemed that the deactivation of the active Pt(II) species by the remaining Et_3SiH, that is, the generation of an inactive Pt(0) species, caused the low reproducibility. To avoid the reductive deactivation, excess amounts of **1a** were used for fast, complete conversion of Et_3SiH. The reaction with 1.5 mmol of **1a** gave **4aa** in moderate yield with good reproducibility (entry 2). Use of a small excess (1.2 mmol) of **1a** led to a successful result (entry 3). In entry 2, the remaining **1a** may retard the alkenylation step by competitive coordination to the active Pt(II) species. On the other hand, an excess of Et_3SiH completely inhibited the alkenylation (entry 4). In this case, the formation of platinum black was observed during the hydrosilylation step. These results obtained by variation of the reactant ratio support the deactivation of the Pt(II) catalyst by Et_3SiH.

Introduction of oxidizing agents (0.1 mmol) was also examined for more efficient alkenylation by conversion of the inactive Pt(0) species into the active Pt(II) species. When the crude **2a** obtained from an equimolar mixture of **1a** and Et_3SiH was used, *N*-methylmorpholine *N*-oxide (NMO), $CuCl_2$, and $K_2S_2O_8$ were not effective in promoting the alkenylation (entries 5–7). To our delight, the reaction using *p*-benzoquinone (BQ) proceeded efficiently with good reproducibility (entries 8 and 9). It was completed in 12 h, and the reaction for 12 h achieved a better yield of **4aa** than that for 24 h due to the suppression of side reactions. Alkenylsilane **2a′** was recovered from the reaction mixture, which indicates that the regioisomer does not participate in the alkenylation step.

With the optimized reaction conditions in hand (Table 1, entry 9),[17] our attention was turned to defining the scope and functional group compatibility of this one-pot

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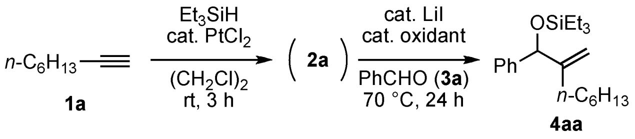
(14) The H_2PtCl_6-catalyzed reaction of 1-hexyne with Et_3SiH at 20 °C shows a similar regioselectivity (*E*:regio = 82:18). Pukhnarevich, V. B.; Kopylova, L. I.; Trofimov, B. A.; Voronkov, M. G. *J. Gen. Chem. USSR (Engl, Transl.)* **1975**, *45*, 2600.

(15) LiI is quite effective in promoting the Pt(II)-catalyzed alkenylation as described in ref 11. It likely serves to enhance the π-Lewis acidity of the postulated active catalyst, $Li[PtX_3]$ (X = Cl, I), by introduction of the iodide ion.

(16) It is necessary to add LiI after the hydrosilylation step. The combined use of $PtCl_2$ and LiI induced the dehydrogenative coupling between **1a** and Et_3SiH to give 1-triethylsilyloct-1-yne mainly. Voronkov, M. G.; Pukharevich, V. B.; Ushakova, N. I.; Tsykhanskaya, I. I.; Albanov, A. I.; Vitkovskii, V. Y. *J. Gen. Chem. USSR (Engl, Transl.)* **1985**, *55*, 80.

(17) Other hydrosilanes, $BuMe_2SiH$ and $PhMe_2SiH$, were also used for the reaction of **3a** with **1a** under the optimized conditions. However, the alkenylation resulted in low yields of the corresponding silyl ethers (35% with $BuMe_2SiH$, 39% with $PhMe_2SiH$).

Table 1. Optimization for One-Pot Reaction among Oct-1-yne, Et_3SiH, and Benzaldehyde[a]

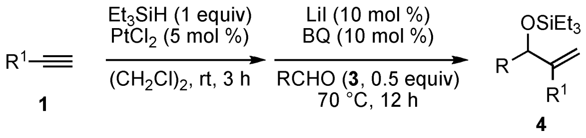


entry	**1a** (mmol)	Et_3SiH (mmol)	oxidant	isolated yield (%)
1	1	1	none	35–65
2	1.5	1	none	52
3	1.2	1	none	73
4	1	1.5	none	0
5	1	1	NMO	19
6	1	1	$CuCl_2$	trace
7	1	1	$K_2S_2O_8$	40
8	1	1	BQ	79[b]
9[c]	1	1	BQ	85

[a] All reactions were carried out with **1a** (1–1.5 mmol), Et_3SiH (1–1.5 mmol), $PtCl_2$ (0.05 mmol), LiI (0.1 mmol), an oxidant (0.1 mmol), and **3a** (0.5 mmol) in DCE (1.5 mL). [b] The desilylated alcohol was detected. [c] The alkenylation time is 12 h.

transformation (Table 2). Aromatic aldehydes bearing an electron-withdrawing group efficiently underwent the Pt-catalyzed alkenylation with **1a** (entries 1–4). Introduction of an electron-donating group into the aromatic ring decreased the yield of **4** (entries 5 and 6). 1-Naphthaldehyde (**3h**) gave the corresponding allyl silyl ether **4ah** in 73% yield (entry 7). These results roughly agree with our previous results using (*Z*)-1-(trimethylsilyl)dodec-1-ene (**5**), an isolated alkenylsilane.[11] The one-pot alkenylation of aliphatic aldehydes **3i** and **3j** proceeded smoothly under catalysis by $PtCl_2$–LiI (entries 8 and 9). In the previous work, the $PtCl_2$–LiI system was not effective in the alkenylation of **3i** and **3j** with **5** because of competitive α-deprotonation leading to the silyl enolate of **3i** or aldol products from **3j**. The reasonable results may come from the use of a triethylsilyl group although it is not clear at present.

Table 2. One-Pot Alkenylation of Aldehydes with Alkynes and Et_3SiH[a]



entry	R^1 in **1**	R in **3**	product	yield (%)[b]
1	n-C_6H_{13} (**1a**)	4-ClC_6H_4 (**3b**)	**4ab**	92
2	n-C_6H_{13}	4-BrC_6H_4 (**3c**)	**4ac**	85
3[c]	n-C_6H_{13}	4-$O_2NC_6H_4$ (**3d**)	**4ad**	80
4	n-C_6H_{13}	4-$MeO_2CC_6H_4$ (**3e**)	**4ae**	73
5	n-C_6H_{13}	4-MeC_6H_4 (**3f**)	**4af**	64
6	n-C_6H_{13}	4-$AcOC_6H_4$ (**3g**)	**4ag**	37
7	n-C_6H_{13}	1-naphthyl (**3h**)	**4ah**	73
8	n-C_6H_{13}	c-C_6H_{11} (**3i**)	**4ai**	78
9	n-C_6H_{13}	$Ph(CH_2)_2$ (**3j**)	**4aj**	63
10	c-C_6H_{11} (**1b**)	Ph (**3a**)	**4ba**	77
11	$Cl(CH_2)_3$ (**1c**)	Ph	**4ca**	90
12	$Cl(CH_2)_3$	c-C_6H_{11}	**4ci**	83
13[e]	Ph (**1d**)	Ph	**4da**	86
14[c,e]	Ph	$Ph(CH_2)_2$	**4dj**	73[d]
15[c]	$BnO(CH_2)_3$ (**1e**)	Ph	**4ea**	75[d]
16[c,f]	$PhCO_2(CH_2)_4$ (**1f**)	Ph	**4fa**	83[d]
17[f,g,h]	$PhCO_2(CH_2)_4$	c-C_6H_{11}	**4fi**	51[d]
18	$PI(CH_2)_4$ (**1g**)[i]	Ph	**4ga**	51[d]

[a] All reactions were carried out with **1** (1 mmol), Et_3SiH (1 mmol), $PtCl_2$ (0.05 mmol), LiI (0.1 mmol), BQ (0.1 mmol), and **3** (0.5 mmol) in DCE (1.5 mL). [b] Isolated yield based on **3**. [c] The alkenylation time was 24 h. [d] For ease of isolation, the product was converted into the corresponding allylic alcohol by desilylation with TBAF. [e] The alkenylation step was carried out at 100 °C. [f] The hydrosilylation time was 5 h. [g] MnI_2 (0.05 mmol) was used instead of LiI. [h] The alkenylation time is 15 h. [i] PI stands for phthalimide.

Other terminal alkynes **1b**–**g** also served in the alkenylation. Under the standard conditions, the reactions of cyclohexylacetylene (**1b**) and 5-chloropent-1-yne (**1c**) afforded alkenylation products **4** in good to high yields (entries 10–12). The sp^3-C–Cl bond did not suffer from any possible side reactions such as reduction and elimination. The alkenylsilane derived from phenylacetylene (**1d**) showed low reactivity and required severe conditions (entries 13 and 14). Pent-4-yn-1-ol could not be used for the alkenylation while the protected form **1e** served the purpose (entry 15). Ester and imide functionalities are also compatible with the Pt(II)-catalyzed alkenylation (entries 16–18). However, these alkynes **1f** and **1g** are inferior to **1a** in reactivity. In the reaction of **1f** with **3i**, MnI_2 was more effective than LiI in suppressing the formation of the silyl enolate of **3i** (entry 17). Oct-4-yne, an internal alkyne, was also subjected to the successive reaction with Et_3SiH and **3a**. Although the hydrosilylation with Et_3SiH proceeded, no alkenylation of **3a** was observed.

To ascertain the role of BQ as a catalyst activator, the reaction of **3a** with **2a** in the presence of Pt(0)-supporting $CaCO_3$ and LiI was investigated. Without any other additives, it afforded **4aa** in low yield (Table 3, entry 1). Use of LiCl as an additive led to a similar result (entry 2). In contrast, adding BQ was effective in promoting the alkenylation (enrty 3). The combined use of BQ and LiCl achieved an efficient conversion of **3a** into **4aa** (entry 4).[18]

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(18) As described in the previous report, the presence of a chloride ion is important for enhancing the activity of the Pt catalyst although the reason is not clear. See ref 11.

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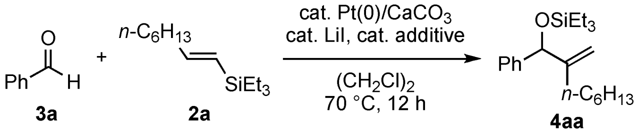
Table 3. Pt(0)-Catalyzed Alkenylation[a]



entry	additive	isolated yield (%)
1	none	12
2	LiCl	16
3	BQ	50
4	BQ + LiCl	73

[a] All reactions were carried out with **2a** (1 mmol), **3a** (0.5 mmol), 5% Pt(0)/$CaCO_3$ (0.05 mmol of Pt), LiI (0.1 mmol), and an additive(s) (0.1 mmol) in DCE (1.5 mL).

Although we do not have any direct evidence of the formation of a Pt(II) species by oxidation with BQ, these results suggest that the inactive Pt(0) species is changed into an active Pt(II) species by the action of BQ.

In conclusion, we have developed a new one-pot method for the alkenylation of aldehydes with terminal alkynes and a hydrosilane. The Pt(II)-catalyzed alkenylation takes place only at the internal sp-carbon to give single regioisomers of allyl silyl ethers and shows reasonable compatibility with polar functionalities including C–Cl and C–Br bonds. It is complementary to the Ni-catalyzed reductive coupling between aldehydes and alkynes. This one-pot Pt(II)-catalyzed reaction is valuable and intriguing not only from the synthetic point of view but also from the viewpoint of catalytic action. Several successive reactions involving two different catalytic cycles driven by a single Pt catalyst have been developed so far.[19,20] In most cases, however, the Pt catalyst functions as a π-Lewis acid or Lewis acid for electrophilic activation of C–C multiple bonds and C–heteroatom bonds. The present study on dual catalysis by $PtCl_2$ provides a rare example of Pt-catalyzed successive reaction.[21] We are now studying the alkenylation of other carbon electrophiles by this one-pot method.

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Supporting Information Available. Experimental details and characterization data (^{1}H NMR, ^{13}C NMR, IR, MS). This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.