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Platinum-Catalyzed Nucleophilic Addition of Vinylsilanes at the *β*-Position

Katsukiyo Miura,*,† Gen Inoue,‡ Hisashi Sasagawa,‡ Hidenori Kinoshita,† Junji Ichikawa,‡ and Akira Hosomi‡

Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University, Sakura-ku, Saitama 338-8570, Japan, and Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

kmiura@apc.saitama-u.ac.jp

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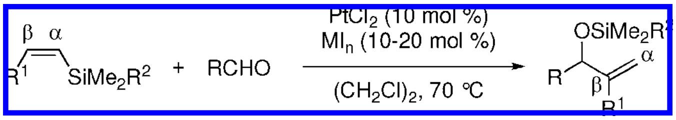
ABSTRACT



In the presence of catalytic amounts of PtCl$_2$ and metal iodides, *β*-substituted vinylsilanes reacted with aldehydes at the *β*-position to give allyl silyl ethers. The Pt-catalyzed addition to aromatic aldehydes proceeded efficiently in the presence of LiI. The combined use of PtCl$_2$ and MnI$_2$ was found to be effective in addition to aliphatic aldehydes.

Vinylsilanes have frequently been used as stable vinyl anion equivalents for efficient, stereospecific carbon−carbon bond-forming reactions promoted by Lewis acids and transition-metal catalysts.[1,2] They react with carbon electrophiles usually at the α-position, although there are a few exceptions.[3,4] We report here that Pt catalysis enables the addition of vinylsilanes to aldehydes at the position *β* to silicon.[5]

We have previously reported the Pt(II)-catalyzed annulation of hydroxyalkyl-substituted vinylsilanes with aldehydes, which involves alkene migration to the corresponding allylsilanes and subsequent Prins-type annulation with aldehydes.[6] On the basis of the previous work, our interest was focused on the Pt(II)-catalyzed intermolecular allylation of aldehydes with vinylsilanes. Initially, the reaction of benzaldehyde (**1a**) with vinylsilane **2a** was carried out in the presence of PtCl$_2$ (Scheme 1). As a result, the desired allylation product was not obtained. However, it was fortunate that we found the formation of a small quantity of allyl TMS ether **3aa**. The vinylation product indicates that **2a** reacted at the *β*-position. Thus, our interest was switched to this novel type of nucleophilic addition of vinylsilanes.

Screening of some Pt salts and complexes revealed that PtI$_2$ works as an effective catalyst of the addition of **2a** (Scheme 1).[7] Inspired by this result, we investigated the effects of alkali iodides (LiI, NaI, and KI) on the catalysis

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† Saitama University.

‡ University of Tsukuba.

[1] (a) Miura, K.; Hosomi, A. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, p 409. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000.

[2] (a) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; De Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; p 163. (b) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; p 421.

[3] (a) Blumenkopf, T. A.; Bratz, M.; Castaneda, A.; Look, G. C.; Overman, L. E.; Rodriguez, D.; Thompson, A. S. *J. Am. Chem. Soc*. **1990**, *112*, 4386. (b) Blumenkopf, T. A.; Look, G. C.; Overman, L. E. *J. Am. Chem. Soc*. **1990**, *112*, 4399.

[4] (a) Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1959. (b) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845.

[5] For the Pt(II)-catalyzed reaction of aldehydes with allylsilanes, see: Fürstner, A.; Voigtländer, D. *Synthesis* **2000**, 959.

[6] Miura, K.; Itaya, R.; Horiike, M.; Izumi, H.; Hosomi, A. *Synlett* **2005**, 3148.

[7] PtCl$_4$, PtBr$_2$, PtI$_4$, and PtCl$_2$L$_2$ (L$_2$ = 2,2′-bipyridine, COD, (PPh$_3$)$_2$, (PhCN)$_2$) were much less effective than PtI$_2$. Pt(0)L$_n$ (L$_n$ = (PPh$_3$)$_4$, (dba)$_2$, (CH$_2$=CHSiMe$_2$)$_2$O) showed no catalytic activity.

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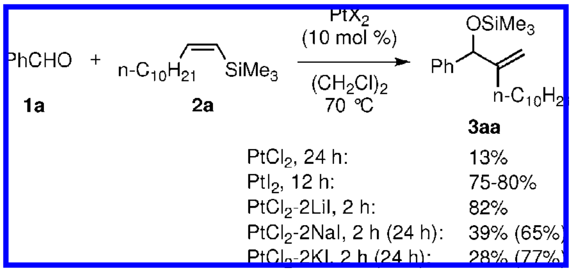
by $PtCl_2$. These iodides effectively promoted the Pt-catalyzed vinylation. In particular, the use of LiI completed the reaction within 2 h.[8]

Scheme 1



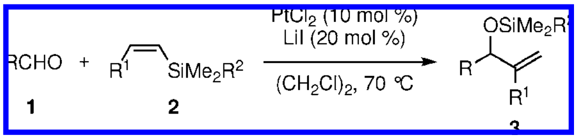
We next carried out the reaction of **2a** with various aldehydes **1** under the optimized conditions. 1-Naphthaldehyde (**1b**) and substituted benzaldehydes **1c**−**k** were smoothly converted into allyl TMS ethers **3ba**−**ka** (entries 1−10 in Table 1). C−I and C−Br bonds, which are reactive toward oxidative addition to Pt(0) species,[9] are compatible with the present vinylation. The reaction of 4-methoxybenzaldehyde (**1l**) gave **3la** in low yield due to the decomposition of **3la** (entry 11).

The addition of **2a** to aliphatic aldehydes **1m**−**o** resulted in low or no yield of **3ma**−**oa** under catalysis by $PtCl_2$−LiI. Self-aldol condensation of **1m** and silylation of **1n** to the corresponding TMS enolate were observed under these conditions. As the result of screening of other metal iodides, MnI_2 was found to serve as an effective cocatalyst of the vinylation of aliphatic aldehydes (entries 12−14).

Other vinylsilanes were applied to the Pt-catalyzed addition to **1a**. The *E*-isomer of **2a** was not as reactive as **2a** (entry 15). Vinylsilane **2b** as well as **2a** showed high reactivity (entries 16−17). As shown in the case of **2c**, the presence of a bulky alkyl group at the β-position largely reduced the reactivity to **1a** (entry 18). Phenyl-substituted vinylsilane **2d** was reactive enough; however, vinylsilane **2e**, bearing a 4-trifluoromethylphenyl group, reacted sluggishly (entries 19 and 20). Thus, the steric and electronic natures of the β-substituents strongly affected the reactivity of **2**. Use of the parent vinylsilane **2f** led to a complex mixture of products (entry 21). The replacement of the methyl group on silicon by a *tert*-butyl or phenyl group decelerated the vinylation of **1a** (entries 22 and 23).

The $PtCl_2$-catalyzed reaction of **2a** with benzaldehyde dimethyl acetal also proceeded at the β-position to give allyl methyl ether **4** but in low yield (Scheme 2).

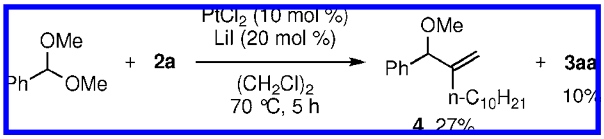
Table 1. Addition of Vinylsilanes to Aldehydes[a]



entry	aldehyde (R)	vinylsilane (R^1, R^2)	time (h)	product, yield[b] (%)
1	**1b** (1-naphthyl)	**2a** (n-$C_{10}H_{21}$, Me)	24	**3ba**, 84
2	**1c** (4-$O_2NC_6H_4$)	**2a**	24	**3ca**, 84
3	**1d** (4-$MeO_2CC_6H_4$)	**2a**	48	**3da**, 77
4	**1e** (4-FC_6H_4)	**2a**	24	**3ea**, 89
5	**1f** (4-ClC_6H_4)	**2a**	5	**3fa**, 90
6	**1g** (2-ClC_6H_4)	**2a**	48	**3ga**, 86
7	**1h** (4-BrC_6H_4)	**2a**	48	**3ha**, 91
8	**1i** (4-IC_6H_4)	**2a**	36	**3ia**, 71
9	**1j** (4-$AcOC_6H_4$)	**2a**	24	**3ja**, 69
10	**1k** (4-MeC_6H_4)	**2a**	5	**3ka**, 58
11	**1l** (4-$MeOC_6H_4$)	**2a**	2	**3la**, 18
12[c]	**1m** ($Ph(CH_2)_2$)	**2a**	4	**3ma**, 64
13[c]	**1n** (c-C_6H_{11})	**2a**	4	**3na**, 71
14[c]	**1o** (t-Bu)	**2a**	4	**3oa**, 52
15	**1a** (Ph)	(E)-**2a**	24	**3aa**, 60
16	**1a**	**2b** (Me, Me)	2	**3ab**, 78
17	**1f**	**2b**	24	**3fb**, 91
18	**1a**	**2c** (c-C_6H_{11}, Me)	24	**3ac**, 5
19	**1a**	**2d** (Ph, Me)	10	**3ad**, 69
20	**1a**	**2e** (4-$F_3CC_6H_4$, Me)	24	**3ae**, 6
21	**1a**	**2f** (H, Me)	2	−, 0
22	**1a**	**2g** (n-$C_{10}H_{21}$, t-Bu)	24	**3ag**, 29
23	**1a**	**2h** (n-$C_{10}H_{21}$, Ph)	10	**3ah**, 60

[a] All reactions were carried out with an aldehyde (0.50 mmol), a vinylsilane (1.00 mmol), $PtCl_2$ (0.05 mmol), and LiI (0.10 mmol) or MnI_2 (0.05 mmol) in 1,2-dichloroethane (1.5 mL) at 70 °C. [b] Isolated yield. [c] MnI_2 (10 mol %) was used instead of LiI.

Scheme 2



To gain mechanistic insight, we performed some experiments using D-labeled vinylsilanes **2a**-D and **2i**. The reaction of **1a** with **2a**-D revealed 1,2-shift of the deuterium atom (Scheme 3). Crossover experiments using a 1:1 mixture of **2i** and **2j** were conducted under different sets of reaction conditions (Table 2). Under the standard conditions, the reaction of **1a** with **2i** and **2j** gave non-crossover products **3ai** and **3aj** mainly (**3ai**/**3aa** = 94:6, **3aj**/**3ak** = 93:7, entry 1). Use of a 2-fold amount of the solvent hardly affected the ratios of non-crossover to crossover products (entry 2). In contrast, increased concentrations promoted the formation of crossover products **3aa** and **3ak** (entries 3 and 5). These results suggest that the catalytic cycle should involve the formation of a transient intermediate from a vinylsilane molecule by elimination of the silyl group. In subsequent reaction of the intermediate, incorporation of the original silyl

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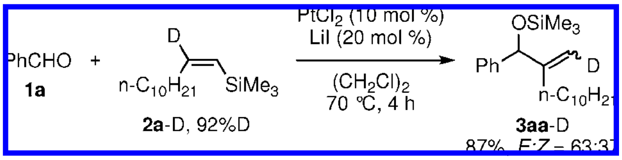
(8) PtI_2−2LiCl showed a catalytic activity similar to that of $PtCl_2$−2LiI. The activity of PtI_2−2LiI was lower than that of PtI_2. Use of LiCl as cocatalyst did not enhance the catalytic activity of $PtCl_2$.

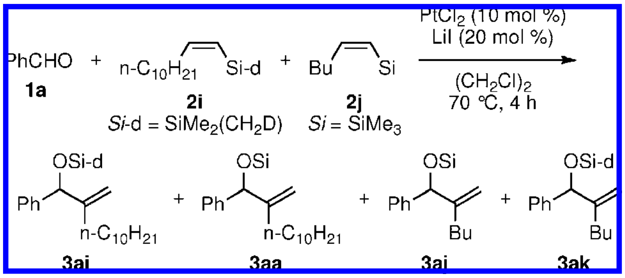
(9) (a) Hartley, F. R. In *Comprehensive Organometallic Chemistry I*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Elsevier: Oxford, 1982; Vol. 6, p 471. (b) Anderson G. K. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds; Elsevier: Oxford, 1995; Vol. 9, p 431.

Scheme 3



group would be faster than that of the silyl group from other vinylsilane molecules, although the latter crossover path is facilitated by an increase in concentration. As shown in entries 3 and 4, the product ratio did not depend on the reaction time. This fact indicates that the interconversion between non-crossover and crossover products does not occur under the reaction conditions.

Table 2. Crossover Experiments Using Vinylsilanes **2i** and **2j**[a]

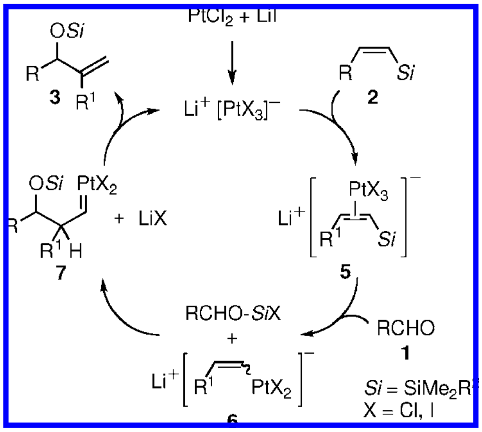


entry	volume of solvent (mL)	time (h)	yield of **3ai** + **3aa** (%), **3ai**:**3aa**[b]	yield of **3aj** + **3ak** (%), **3aj**:**3ak**[b]
1	1.5	4	48, 94:6	48, 93:7
2	3.0	4	21, 92:8	21, 93:7
3	0.75	4	43, 87:13	45, 86:14
4	0.75	2	14, 86:14	14, 86:14
5[c]	0.40	4	13, 79:21	17, 81:19

[a] All reactions were carried out with **1a** (0.50 mmol), **2i** (0.50 mmol), **2j** (0.50 mmol), $PtCl_2$ (0.05 mmol), and LiI (0.10 mmol) in 1,2-dichloroethane (0.4−3 mL) at 70 °C. [b] The yield and ratio were determined by GC−MS analysis of the mixture of products. [c] The reaction stopped before complete consumption of **1a**.

Pt(0) complexes showed no catalytic activity in the reaction of **1a** with **2a**.[6] Judging from this result and the high compatibility of C−X bonds, the participation of Pt(0) species in the catalytic cycle is not likely. A possible mechanism for the $PtCl_2$−LiI-catalyzed vinylation of aldehydes is as follows (Scheme 4): (1) Li[PtX_3] (X = Cl, I), a monomeric, coordinatively unsaturated Pt(II) species, is formed from $PtCl_2$ and LiI, (2) coordination of a vinylsilane to Li[PtX_3] affords alkene complex **5**,[10] (3) **5** reacts with an aldehyde **1** to give vinylplatinum **6** and a halosilane−aldehyde complex (Si−Pt transmetalation),[11] (4) addition of **6** to the activated aldehyde proceeds rapidly at the position β to platinum to form carbene complex **7**,[12] and (5) **7** undergoes 1,2-H-shift and elimination of PtX_2 to give allyl silyl ether **3**.[13] LiI likely serves to enhance the π-Lewis acidity of Li[PtX_3] by introduction of the iodide ion, which is a soft anion. In addition, the LiI-induced formation of anionic complexes **5** and **6** may accelerate the transmetalation and β-addition steps.

Scheme 4



The low reactivity of **2c** and **2g** is probably because the cyclohexyl and TBS groups suppress the coordination step by steric repulsion. The sluggish addition of **2e** is attributable to deceleration of the same step by the electron-withdrawing ability of the CF_3 group.

To ascertain the proposed mechanism, the reaction of **2a** with MeOH was performed under catalysis by $PtCl_2$−LiI (Scheme 5). We predicted methyl ether **8** would be formed by protonation of vinylplatinum **6a** to platinum carbene complex **9** and its insertion into the O−H bond.[14,15] Indeed, **8** was obtained as a minor product, although the desilylation

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(10) K[$PtCl_3CH_2$=$CHSiMe_3$], a vinylsilane−Pt(II) complex, can be prepared from CH_2=$CHSiMe_3$ and Zeise's salt (K[$PtCl_3CH_2$=CH_2]). Haschke, E. M.; Fitch, J. W. *J. Organomet. Chem*. **1973**, *57*, C93.

(11) For activation of the sp^2-C−Si bond in vinylsilanes by Pt(II) complexes, see ref 9 and the following references: (a) Mansuy, D.; Pusset, J.; Chottard, J. C. *J. Organomet. Chem*. **1976**, *110*, 139. (b) Poist, J. E.; Kraihanzel, C. S. *Chem. Commun*. **1968**, 607.

(12) Some vinyl-transition metals are known to react with carbon electrophiles at the β-position to give carbene complexes. Kusama, H.; Yamabe, H.; Onizawa, Y.; Hoshino, T.; Iwasawa, N. *Angew. Chem., Int. Ed*. **2005**, *44*, 468, and references cited therein.

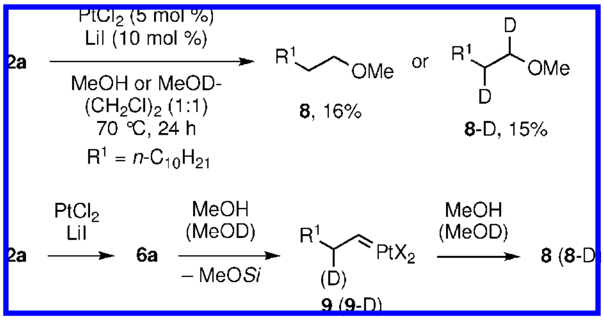
(13) The transformation of Pt−carbene complexes into alkenes has been proposed as a key step of the Pt(II)-catalyzed cycloisomerization of 1,6-enynes. (a) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc*. **2000**, *122*, 6785. (b) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704. (c) Echavarren, A. M.; Méndez, M.; Muñoz, M. P.; Nevado, C.; Martín-Matute, B.; Nieto-Oberhuber, C.; Cárdenas, D. *J. Pure Appl. Chem*. **2004**, *76*, 453.

(14) For protonation of vinylplatinum complexes to carbene complexes, see: Bell, R. A.; Chisholm, M. H.; Couch, D. A.; Rankel, L. A. *Inorg. Chem*. **1977**, *16*, 677.

(15) The Pt(II)-catalyzed reaction of diazo compounds with alcohols is known to give ethers by insertion into the O−H bond, which proceeds probably via Pt−carbene complexes. (a) Bertani, R.; Biasiolo, M.; Darini, K.; Michelin, R. A.; Mozzon, M.; Visentin, F.; Zanotto, L. *J. Organomet. Chem*. **2002**, *642*, 32. (b) Schils, R.; Simal, F.; Demonceau, A.; Noels, A. F.; Eremenko, I. L.; Sidorov, A. A.; Nefedov, S. E. *Tetrahedron Lett*. **1998**, *39*, 7849.

to 1-dodecene occurred mainly. As expected from the postulated mechanism, use of MeOD gave α,β-dideuterated ether **8**-D in a similar yield.[16] These results support the validity of the presence of intermediates **6** and **7** in the Pt-catalyzed vinylation.

Scheme 5



In conclusion, we have developed a novel type of nucleophilic addition of vinylsilanes, which occurs at the position β to silicon. Besides the novelty in regiochemistry, the reasonable applicability and easy access to vinylsilanes make it synthetically useful. It is also noteworthy that the Pt(II) catalysis efficiently activated the sp^2-C−Si bond of TMS-protected vinyl donors without any stoichiometric activators.[17] The applicability of the present vinylation and its detailed mechanism are now under further investigation.

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

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(16) Approximately one of two methylene hydrogens was displaced by deuterium in both the α- and β-positions.

(17) The Hiyama cross-coupling reactions of vinylsilanes generally requires a heteroatom-substituted silyl group (or its precursor) and a stoichiometric activator such as a fluoride ion. See ref 2. Narasaka and co-workers have recently reported an example of the catalytic C−C bond-forming reaction of the TMS-protected vinyl donor without any stoichiometric activators. Yamane, M.; Uera, K.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 477.