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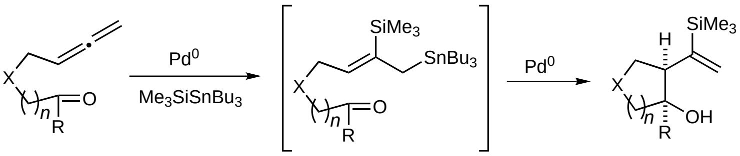
Palladium-Catalyzed Regio- and Diastereoselective Tandem Silastannylation/Allyl Addition of Allene Aldehydes and Allene Ketones: Synthesis of *cis* Cyclopentanols and Cyclohexanols**

Suk-Ku Kang,* Young-Hwan Ha, Byung-Soo Ko,
Yoongho Lim, and Jihyun Jung

To achieve economically useful transformations in organic synthesis it would be desirable if multistep bond formations and/or bond cleavages could be facilitated with a single catalyst in one pot at a constant temperature. Such a process would minimize the amount of chemicals, the production of waste, and the processing time.[1, 2] In this regard, Jeong et al.[3] reported allylation/Pauson–Khand reactions with two artificial catalysts in a one-pot procedure. Subsequently, Evans et al.[4] developed the allylation/Pauson–Khand reaction in a tandem sequence with a Rh complex as the only catalyst. Recently, Shibasaki and co-workers[5] reported a one-pot synthesis of β-cyanohydrin from olefins mediated by a Zr catalyst.

The palladium-catalyzed addition of silylstannanes to allenes is known[6] and the palladium- or platinum-catalyzed addition of allylstannanes to aldehydes was reported by Yamamoto et al.[7, 8] However, to the best of our knowledge, the transition metal catalyzed addition of allylstannanes to ketones has not yet been successful. Our ongoing studies into the use of allene substrates in organic synthesis[9] led us to believe that allene aldehydes and allene ketones are good substrates for palladium-catalyzed silastannylations. In a tandem reaction, the resulting allylstannanes would be good candidates for carbonyl allyl addition with a single palladium catalyst at a constant temperature (Scheme 1).

The results of the tandem silastannylation/carbonyl allyl addition of allene aldehydes and allene ketones to form *cis* cyclopentanols[10] are summarized in Table 1. In finding



Scheme 1. Tandem silastannylation/allyl addition of allene aldehydes and allene ketones ($n = 1, 2$; R = H, CH_3; X = NTs, O, $C(CO_2Et)_2$, etc.).

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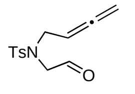
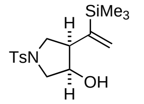
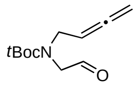
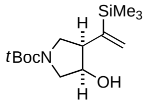
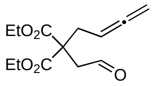
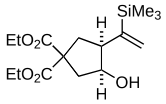
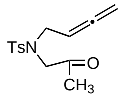
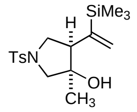
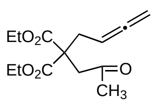
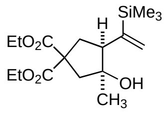
Table 1. The palladium-catalyzed silastannylation/allyl addition of allene aldehydes and allene ketones.[a]

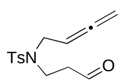
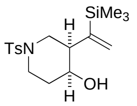
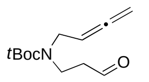
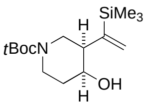
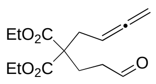
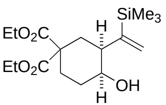
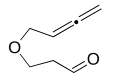
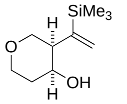
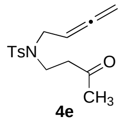
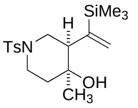
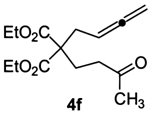
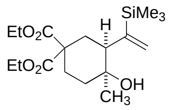
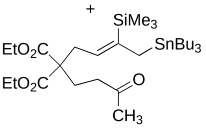
Entry	1	3	Yield [%]
1	 **1a**	 **3a**	71
2	 **1b**	 **3b**	66
3	 **1c**	 **3c**	63
4	 **1d**	 **3d**	67
5	 **1e**	 **3e**	66[b]

[a] The reaction was carried out with $(\pi\text{-allyl})_2\mathrm{Pd_2Cl_2}$ (5 mol %), $\mathrm{Me_3SiSnBu_3}$ (**2**) (1.1 equiv), and **1** (1.0 equiv) in THF at room temperature for 10 min. [b] The reaction was carried out at room temperature for 80 min.

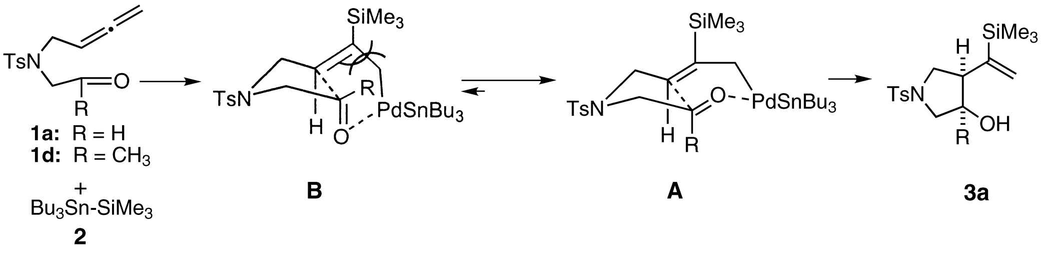
optimum conditions, it is critical to find an effective palladium catalyst for both silastannylation and carbonyl allyl addition. When allene aldehyde **1a** was treated with trimethylsilylstannane **2** in THF at room temperature in the presence of $(\pi\text{-allyl})_2\mathrm{Pd_2Cl_2}$ catalyst for 10 min, *cis* cyclopentanol **3a** was formed in 71 % yield (Table 1, entry 1). Of the palladium and platinum catalysts tested, $\mathrm{Pd(PPh_3)_4}$, $\mathrm{Pd_2(dba)_3 \cdot CHCl_3}$, $\mathrm{Pd_2(dba)_3}$, $\mathrm{PdCl_2(PPh_3)_2}$, $\mathrm{PtCl_2(PPh_3)_2}$, $\mathrm{PdCl_2}$, and $(\pi\text{-allyl})_2\mathrm{Pd_2Cl_2}$, only $(\pi\text{-allyl})_2\mathrm{Pd_2Cl_2}$ in THF at room temperature catalyzed this tandem reaction. At room temperature, the other catalysts did not give any of the cyclized product **3a**. However the reaction of **1a** with silylstannane **2** in the presence of catalytic $\mathrm{Pd(PPh_3)_4}$ in THF at reflux for 2 h afforded the cyclized *cis* cyclopentanol **3a** in 53 % yield. The reaction of **1a** with $\mathrm{Me_3SiSnBu_3}$ (**2**) in THF for 12 h at room temperature in the presence of $\mathrm{Pd_2(dba)_3 \cdot CHCl_3}$ catalyst gave the cyclized product **3a** (20 %) along with the uncyclized silastannylative addition product (45 %). The *cis* stereochemistry was confirmed by NOESY (nuclear Overhauser enhancement spectroscopy) experiments together with molecular modeling; the coupling constant ($J = 3.7$ Hz) implies a dihedral angle of 46° for the two protons on the ring junction (see Supporting Information). Under the same conditions, δ-allene aldehyde **1c** cyclized smoothly to give substituted cyclopentanol **3d** in 63 % yield (Table 1, entry 3). This tandem sequence was also applied to allene ketones. δ-Allene ketone **1d** was treated with $\mathrm{Me_3SiSnBu_3}$ (**2**) in the presence of $(\pi\text{-allyl})_2\mathrm{Pd_2Cl_2}$ catalyst under the same conditions to afford the methyl-substituted *cis* cyclopentanol **3d** in 67 % yield (Table 1, entry 4). To the best of our knowledge, this is the first example of a palladium-catalyzed allyl addition of organostannanes to ketones, although it is known for aldehydes.[7] The *cis* stereochemistry of **3d** was unambiguously determined by NOE interactions between the methyl protons and the proton at the ring junction (2.5 % enhancement). Under the same conditions, the malonate-substituted δ-allene ketone **1e** was converted into the *cis*-cyclopentanol **3e** (66 % yield) after a prolonged reaction time (Table 1, entry 5).

This silastannylation/allyl addition tandem reaction was extended to synthesize cyclohexanol derivatives **5** (Table 2). Allene aldehyde **4a** was treated with $\mathrm{Me_3SiSnBu_3}$ (**2**) in the presence of $(\pi\text{-allyl})_2\mathrm{Pd_2Cl_2}$ to afford *cis*-cyclohexanol **5a** in 62 % yield (Table 2, entry 1). Allene aldehyde **4c** was converted into diester-substituted cyclohexanol derivative **5c** (63 % yield) under the same conditions, but with a 2-h reaction time (Table 2, entry 3). Allene aldehyde **4d** was smoothly cyclized in a tandem reaction to provide pyranyl-substituted alcohol **5d** in 68 % yield (Table 2, entry 4). The *cis*

Table 2. The palladium-catalyzed silastannylation/allyl addition of allene aldehydes and allene ketones.[a]

Entry	4	Product	Yield [%]
1	 **4a**	 **5a**	62
2	 **4b**	 **5b**	64
3	 **4c**	 **5c**	63[b]
4	 **4d**	 **5d** **5d**	68
5	 **4e**	 **5e**	67
6	 **4f**	 **5f** (30%) +  **6** (35%)	65[c]

[a] The reaction was run with $(\pi\text{-allyl})_2\mathrm{Pd_2Cl_2}$ (5 mol %), $\mathrm{Me_3SiSnBu_3}$ (**2**) (1.1 equiv), and allene-aldehyde or ketone **4** (1.0 equiv) in THF at room temperature for 10 min. [b] The reaction was carried out at room temperature for 2 h. [c] The reaction was carried out at room temperature for 70 min.



Scheme 2.

stereochemistry of **5d** was deduced clearly by means of X-ray crystallography. This tandem cyclization was also applied to allene ketones. Thus allene ketone **4e** was cyclized to give piperidyl-substituted alcohol **5e** in 67% yield (Table 2, entry 5). However, the malonate substrate **4f** gave rise to *cis*-cyclohexanol **5f** (30%) as well as the simple addition product **6** (35%) (Table 2, entry 6).

The exact mechanism of this *cis*-stereoselective tandem reaction has yet to be elucidated. It is presumed that Me$_3$SiPdSnBu$_3$ adds initially to the allene moiety to give σ- or π-allyl palladium complexes, which undergo intramolecular carbonyl allyl addition to afford *cis*-cycloalkanols. The *cis* selectivity of the reaction can be ascribed to the fact that intermediate **A**, which leads to the *cis*-cyclopentanol, is energetically more stable than **B**, presumably because of the steric hindrance between TMS and R (R = H, Me) groups (Scheme 2).[11]

In summary, the palladium-catalyzed regio- and diastereoselective tandem silastannylation/carbonyl allyl addition of allene aldehydes and ketones gives rise to *cis*-cycloalkanols. The process requires a single catalyst and is carried out at constant temperature.

Experimetal Section

Typical procedure: trimethyl(tributylstannyl)silane **2** (150 mg, 0.41 mmol) was added to a stirred solution of **1a** (100 mg, 0.38 mmol) and (π-allyl)$_2$Pd$_2$Cl$_2$ (6.9 mg, 5 mol%) in THF (3 mL). The reaction mixture was stirred room temperature for 10 min, and the THF solvent was evaporated *in vacuo*. The crude product was separated by means of column chromatography (EtOAc/hexane 1:2) to afford the cyclized product **3a** (91 mg, 71%) as a white solid. M.p. 95°C; $R_f = 0.41$ (EtOAc/hexane 1:2); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.00$ (s, 9H), 2.35 (s, 3H), 2.89 (m, 1H), 3.29 (dd, 1H, $J = 9.3$, 11.3 Hz), 3.35 (d, 1H, $J = 11.5$ Hz), 3.40 (dd, 1H, $J = 7.2$, 9.3 Hz), 4.05 (m, 1H), 5.59 (d, 2H, $J = 1.3$ Hz), 7.25 (d, 2H, $J = 8.0$ Hz), 7.68 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 147.9$, 145.0, 135.7, 131.2, 129.7, 129.1, 72.2, 57.7, 50.1, 49.8, 23.1, 0.0; HR-MS: calcd for C$_{16}$H$_{25}$NO$_3$SSi: 339.1324, found: 339.1366.

Typical experimental procedures for the preparation of **1a**, **1c**–**1e**, **4c**–**4f**, **3a**, spectroscopic and analytical data for **1a**–**1e**, **4a**–**4f**, **3a**–**3e**, **5a**–**5f**, **6**, and X-ray crystallographic data of **5d** can be found in the Supporting Information.

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[11] The palladium-catalyzed carbonyl allyl addition was reported by Stille et al. and Trost et al. They suggested that palladium(II) complexes might act as Lewis acids, or nucleophilic π-allylpalladium complexes might be involved; see: a) J. W. Labadie, D. Tueting, J. K. Stille, *J. Org. Chem.* **1983**, *48*, 4634–4642; b) B. M. Trost, S. A. King, *J. Am. Chem. Soc.* **1990**, *112*, 408–422.

IAN-Amines: Direct Entry to a Chiral C_2-Symmetric Zirconium(IV) β-Diketimine Complex**

Sarah B. Cortright and Jeffrey N. Johnston*

The immense utility of metallocene-based catalysts for synthesis[1] has stimulated the development of non-metallocene complexes that conserve metallocene topographies but offer a greater degree of accessibility and/or improved performance.[2] A number of recent publications have demonstrated that amidinate ligands,[3, 4] β-diketimines,[5–7] and other variations on the [1,*n*]-bisimine template are promising in this regard for group IV metals. In general, ligands used as the basis for a non-metallocene complex must 1) bind to the

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.