Palladium-Catalyzed Carbocyclization/ Silastannylation and Distannylation of Bis(allenes)

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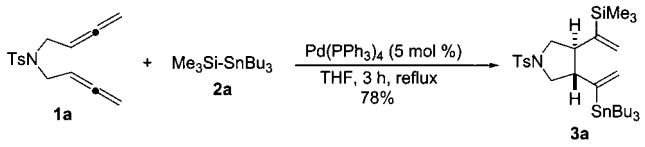
The transition metal-catalyzed intramolecular carbocyclization of enyne, diynes, and bis(dienes) is a versatile method for the construction of ring systems because this method offers a simple entry from acyclic substrates to cyclic compounds.[1] Along this line, the palladium-catalyzed addition−cyclization reaction of tethered diynes, enynes, or bis(dienes) with reagents having Sn−Si, Sn−Sn, and B−Sn σ-bonds etc. is particularly useful because the resulting heteroatom-containing cyclic compounds allow further numerous synthetic transformations.[2] To the best of our knowledge, however, the transition metal-catalyzed cyclization of bis(allenes) has not been known.[3−5] Here we wish to report carbocyclization via silastannylation and distannylation of bis(allenes) to form five-membered-ring systems with these Group-14 atom compounds involving silylstannanes, distannanes, and tributyltin hydride catalyzed by palladium complexes as illustrated in Scheme 1.

When bis(allene) **1a**[6] reacted with (trimethylsilyl)tributylstannane (**2a)** in the presence of a catalytic amount of $(Ph_3P)_4Pd$ (5 mol %) in refluxing THF for 3 h, the cyclization proceeded smoothly to afford the trans-fused cyclized product **3a** in 78% yield. The use of $(\pi\text{-allyl})_2Pd_2Cl_2$ (5 mol %) at room temperature in THF for 3 h afforded the same product **3a** in 76% yield (entry 1 in Table 1). The trans stereochemistry of the cyclized product **3a** was unambiguously confirmed by the coupling constant (J = 13.3 Hz) of the two protons (δ 2.79 and 2.97 ppm) at ring juncture in the ^{1}H NMR spectrum.[7] However, when bis(allene) **1a** was

Scheme 1



treated with $Bu_3SnSnBu_3$ (**2b**) in the presence of $Pd(PPh_3)_4$ (5 mol %) in THF at reflux for 3 h or $(\pi\text{−allyl})_2Pd_2Cl_2$ (5 mol %) at room temperature for 3 h, the cyclization proceeded smoothly to yield the cis-fused distannane **4a** (entry 2). The cis stereochemistry was deduced by the chemical shift (δ 2.93) of the two symmetrical protons in the ^{1}H NMR spectrum at ring junction and the numbers of carbon-13 in ^{13}C NMR for the symmetric structure of **4a**. To assign and determine the cis stereochemistry for distannyl compound **4a** more clearly, the cyclized distannane **4a** was converted into the alkynyl compound **7** via iodostannane **6** (Scheme 2). The cis relationship was confirmed by the examination of two-dimensional ^{1}H NMR proton homodecoupling experiments for compound **7** by the coupling constant (J = 9.0 Hz) for the two protons at ring junction (see Supporting Information). It is noteworthy that this result is in contrast to the palladium-catalyzed carbocyclization of bis(dienes) with distannane $Bu_3SnSnBu_3$ to give trans compound at ring junction reported by Obora et al.[2c] As indirect additional evidence for the formation of the cis-product **4a**, the reaction of bis(allene) **1a** with distannane **2b** at reflux for a prolonged period (12 h) gave the cis-fused bicyclic diene **5a** in 58% yield resulting from intramolecular palladium-catalyzed homocoupling of the intermediate distannyl compound **4a** (entry 3).[8] The exact mechanism of the palladium-catalyzed additions and cyclizations of allenes with two different substrates $Bu_3SnSiMe_3$ and $Bu_3SnSnBu_3$ for the striking reversal of stereochemistry in the cyclization remains to be elucidated. Our explanation for the formation of the trans product **3a** with $Bu_3SnSiMe_3$ and the cis product **4a** with $Bu_3SnSnBu_3$ is as follows based on the addition of **2a** and **2b** with allenes worked by Mitchell et al.[3,9] We believe that $Bu_3SnPdSiMe_3$ species are generated via oxidative addition and then add to the allene moiety and the trimethylsilyl group is attached irreversibly to the central carbon of the allene and the tributyltin on the Pd metal to form σ-allylpalladium complex **A** or π-allylpalladium complex which undergoes further reaction with the tethered another allenyl group. Intermediate **A′** must be favored over **A** in the cyclization to form the trans product **3a** probably due to the steric hindrance of the neighboring trimethylsilyl group. The key to this prediction of steric hindrance of the Me_3Si group compared to Bu_3Sn is the shorter Si−C bond length and thus a larger effective size.[3] On the other hand in the case of $Bu_3SnSnBu_3$ at first the intermediate *cis*-bis(allene)$Pd(SnBu_3)_2$ (**B**) is formed and/or the chelated σ-allylpalladium complex **B′** is formed probably reversibly. The fast carbocyclization of *cis*-bis(allene)$Pd(SnBu_3)_2$ directly or through **B′** would give the vinylpalladium complex **C′**, which then yields cis compound **4a** by reductive elimination and/or cis-bicyclic diene **5a** through σ-bond metathesis as a kinetically

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Trost, B. M.; Krische, M. J. *Synlett* **1988**, 1−16. (c) Negishi, E.; Coperet, C.; Ma. S.; Liou, S.-Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365−393. (d) Ojima, I.; Tzamarioudak, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635−662.

(2) For the silastannylation, distannylation, and silaboration of diynes, enynes, or bis(dienes) in cyclization, see: (a) Onozawa, S-y.; Hatanaka, Y.; Choi, N.; Tanaka, M. *Organometallics* **1997**, *16*, 5389−5391. (b) Onozawa, S-y.; Hatanaka, Y.; Tanaka, M. *J. Chem. Soc., Chem. Commun*. **1997**, 1229−1230. (c) Obora, Y.; Tsuji, Y.; Kakehi, T.; Kobayashi, M.; Shinkai, Y.; Ebihara, M.; Kawamura, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 599−608.

(3) Mitchell et al. studied the systematic and pioneering work on the palladium-catalyzed silastannylation and distannylation of the allenes and it is notable that the addition of hexa(*n*-butyl)distannane to allenes is reversible and that of trimethylsilyltributylstannane is irreversible and the trimethylsilyl group exclusively goes to the central position of the allenes. For the silastannylation and distannylation of allenes, see: Mitchell, T. N.; Schneider, U. *J. Organomet. Chem*. **1991**, 407, 319−327.

(4) The palladium-catalyzed dimerization of allene followed by cyclization is known; see: (a) Hegedus, L. S.; Kambe, N.; Tamaru, R.; Woodgate, P. D. *Organometallics* **1983**, *2*, 1658−1661. (b) Hegedus, L. S.; Kambe, N.; Ishii, Y.; Mori, A. *J. Org. Chem*. **1980**, *50*, 2240−2243. (c) It is well-known that palladium complex catalyzes dimerization and addition of propa-1, 2-diene in the presence of amines to give 2-methylene-3-methyl-3-butene-1-ylamines. See: Coulson, D. R. *J. Org. Chem*. **1973**, *38*, 1483−1490.

(5) In the Pd(0)-catalyzed intermolecular cyclization low yields are due to dimerization of allenes; see: (a) Shier, G. D. *J. Organomet. Chem*. **1967**, *10*, 15−17. (b) Reference 4c.

(6) Bis(allene) **1a** was readily prepared from *p*-toluenesulfonamide by propargylation followed by Crabbe reaction (see Supporting Information).

(7) The proton signals of doublet of doublet of doublet because of neighboring protons (J = 13.3, 12.1, and 7.8 Hz), which have two trans and one cis relationships, confirm the trans configuration (see Supporting Information).

(8) In our hands, the reaction of bis(allene) (**1a**) without using hexa(*n*-butyl)distannane in the presence of $Pd(Ph_3P)_4$ under the same conditions did not give the bicyclic diene **5a**, which mechanistically eliminate [2+2] cyclization. The product **4a** isolated was subjected to reaction in the presence of $Pd(PPh_3)_4$ (5 mol %) in THF at reflux for 8 h to afford **5a**.

(9) An alternative mechanism proposed by one of the reviewers is as follows. For the formation of the trans product **3a** it is suggested that the insertion of $Bu_3SnPdSiMe_3$ to the bis(allene) moiety forms the (1-Bu_3Sn-vinyl)-(allene)$PdSiMe_3$ complex and the carbocyclization occurs after isomerization to the more thermodynamically stable *trans*-π-allyl(allene)$PdSiMe_3$ complex.

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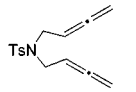
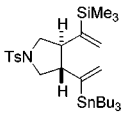
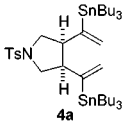
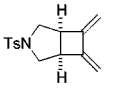
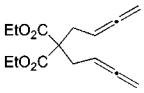
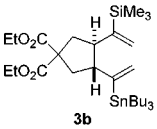
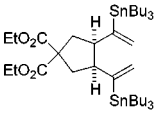
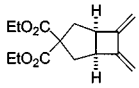
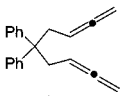
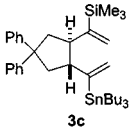
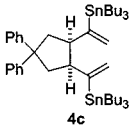
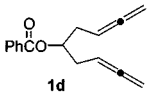
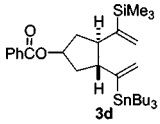
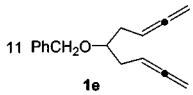
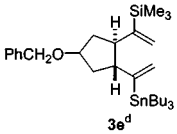
Table 1. Palladium-Catalyzed Carbocyclization-Silastannylation and Distannylation of Bis(allenes)

Entry	Bisallenes	Silylstannanes and Distannanes	Product	Reaction Conditions [a]	Isolated Yield (%)
1	 **1a**	$Me_3SiSnBu_3$ **2a**	 **3a**	A	78
				B	76
2	**1a**	$Bu_3SnSnBu_3$ **2b**	 **4a**	A	73
				B	80
3	**1a**	**2b**	 **5a**	A[b]	58
				B[c]	62
4	**1a**	nBu_3SnH **2c**	**5a**	A[b]	54
				B[c]	57
5	 **1b**	**2a**	 **3b**	A	72
				B	74
6	**1b**	**2b**	 **4b**	A	61
				B	53
7	**1b**	**2c**	 **5b**	A	48
				B	54
8	 **1c**	**2a**	 **3c**	A	71
				B	73
9	**1c**	**2b**	 **4c**	A	61
				B	54
10	 **1d**	**2a**	 **3d**	A[b]	74
				B[c]	73
11	 **1e**	**2a**	 **3e**[d]	A[b]	76
				B[c]	71

[a] Method A: $Pd(PPh_3)_4$ (5 mol %), THF, reflux, 3 h. Method B: $(\pi\text{-allyl})_2Pd_2Cl_2$ (5 mol %), THF, room temperature, 3 h. [b] $Pd(PPh_3)_4$ (5 mol %), THF, reflux, 12 h. [c] $(\pi\text{-allyl})_2Pd_2Cl_2$ (5 mol %), THF, room temperature, 12 h. [d] A mixture of isomers.

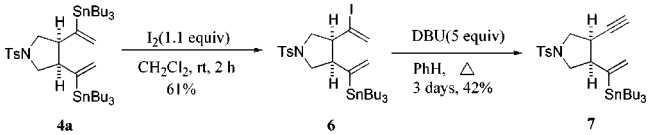
controlled product. The oxidative insertion of Pd(0) into the Sn−C bond in **4a** followed by σ-bond metathesis with the Sn−C bond also affords the bicyclic compound **5a** with liberation of $Bu_3SnSnBu_3$. Alternatively, for the same substrate **1a** the reaction with distannane **2b** in the presence of $(\pi\text{-allyl})_2Pd_2Cl_2$ (5 mol %) in THF at room temperature for 12 h provided the bicyclic compound **5a** in 62% yield (entry 3).

Treatment of bis(allene) **1a** with 2 equiv of nBu$_3$SnH (**2c**) with $Pd(PPh_3)_4$ (5 mol %) in THF at reflux for 12 h or $(\pi\text{-allyl})_2Pd_2Cl_2$ (5 mol %) in THF at room temperature for 12 h provided the bicyclic diene **5a** in 54 and 57% yield, respectively (entry 4 in Table 1). It is notable that the use of 1 equiv of nBu$_3$SnH resulted in the formation of **5a** in comparable yield. Moreover, the formation of **5a** can be realized by reacting a subcatalytic amount of nBu$_3$SnH (0.5 equiv, 25 mol %) under the same conditions in 49% yield. In considering a plausible mechanism for the formation of the bicyclic diene **5a** with a subcatalytic amount of nBu$_3$SnH, it is presumed that at first the intermediate *cis*-bis(allene)Pd(H)-$SnBu_3$ is formed followed by dehydrocoupling with nBu$_3$SnH to afford *cis*-bis(allene)Pd$(SnBu_3)_2$ or the formation of the intermediate **B′** to afford the cyclized product **5a** liberating $Bu_3SnSnBu_3$ (Scheme 4).[10]

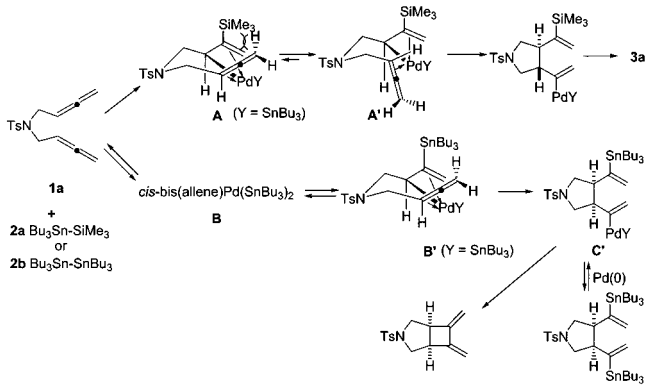
We have applied this method to a variety of bis(allenes) **1b**, **1c**, **1d**, and **1e** and the results are summarized in Table 1.

In summary, we have demonstrated the first palladium-catalyzed carbocyclization reaction of tethered bis(allene) substrates with Group 14 atom compounds to form the substituted five-membered rings.

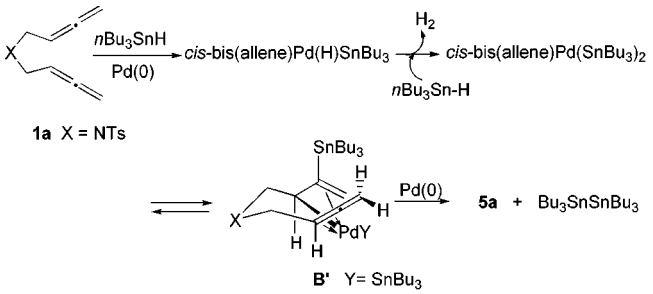
Scheme 2



Scheme 3



Scheme 4



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Supporting Information Available: Typical experimental procedures for the preparation of **1a** and **3a**−**5a,** spectroscopic and analytical data for **1a**, **3a**−**5a**, **3b**−**5b**, **3c**−**5b**, **3d**, **3e**, **6**, and **7**, and X-ray crystallographic data of **5a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001597L

(10) Elimination of PdH_2 from vinylpalladium complex has been reported in the palladium-catalyzed addition of nBu$_3$SnH to allenes. See: Ichinose, Y.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2693−2695.