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Preliminary communication

Palladium-*tert*-alkyl isocyanide catalyzed intramolecular bis-silylation of vicinally disubstituted alkenes ☆

Michinori Suginome, Akira Matsumoto, Koichi Nagata, Yoshihiko Ito *

Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

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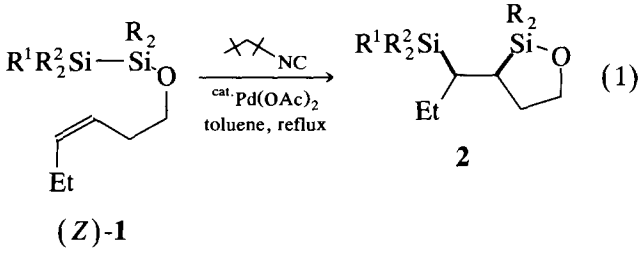
Abstract

Intramolecular bis-silylation of (*Z*)- and (*E*)-alkenes tethered to disilanyl groups by ether linkage $-CH_2CH_2O-$ proceeded with stereospecific *cis*-addition to give 5-exo ring-closure products. Phenyl substituents on the silicon atom proximal to the ether oxygen were crucial for the successful bis-silylation reaction. NMR study of a stoichiometric reaction of disilanyl alkenes with bis(*tert*-alkyl isocyanide)palladium(0) complex showed that facile formation of an intermediate of bis(silyl)palladium(II) complexes may determine on the observed high reactivity in the catalytic reaction. Disilanyl ethers derived from (*Z*)- and (*E*)-2-methyl-3-hexen-1-ol gave *trans*-3,4-disubstituted 2-silatetrahydrofurans and those derived from (*Z*)- and (*E*)-4-hepten-2-ol gave *cis*-3,5-disubstituted 2-silatetrahydrofurans selectively. Application to stereoselective synthesis of triols was demonstrated by H_2O_2 oxidation of the cyclic products with retention of stereochemistry at the silicon substituted carbons.

Keywords: Bis-silylation; Palladium; Isocyanide; Alkene; Triol; Silicon

Stereo- and regioselective formation of Si–C bonds is important from the viewpoint of synthesis of functional molecules as well as application for selective organic synthesis. The transition metal-catalyzed addition of Si–Si bond across C–C multiple bond, i.e. bis-silylation, is attractive transformation in that two Si–C bonds are stereoselectively created at once [1]. Recently, we have found that intramolecular bis-silylation of *terminal* alkenes was effectively promoted by a palladium–*tert*-alkyl isocyanide catalyst to lead to stereoselective synthesis of polyols [2]. In this paper, we describe intramolecular bis-silylation of *internal* alkenes, which have been reluctant to react under the conditions so far reported.

Various disilanyl ethers of (*Z*)-3-hexen-1-ol were subjected to intramolecular bis-silylation in the presence of 0.03 equivalents of $Pd(OAc)_2$ and 0.45 eq. of 1,1,3,3-tetramethylbutyl isocyanide in refluxing toluene (Eq. 1, Table 1). Though disilanyl ethers **1a,b** with only alkyl substituents on the disilanyl groups did not react at all, **1c–f** with aryl groups on the silicon atom distal to the ether oxygen gave the corresponding cyclized prod-



(1)

Table 1
Effect of substituents of disilanyl group

entry	disilanyl group		% yield of **2**
	(*Z*)−**1**	$R^1R^2_2Si-SiR_2$	
1	**a**	$Me_3Si-SiMe_2$	no reaction
2	**b**	$^tBuMe_2Si-SiMe_2$	no reaction
3	**c**	(*p*-MeOPh)$Me_2Si-SiMe_2$	low conversion
4	**d**	$PhMe_2Si-SiMe_2$	56
5	**e**	(*p*-CF_3Ph)$Me_2Si-SiMe_2$	64
6	**f**	$Ph_3Si-SiMe_2$	66
7	**g**	$PhMe_2Si-SiMePh$	75
8	**h**	$Me_3Si-SiPh_2$	91
9	**i**	$PhMe_2Si-SiPh_2$	91

☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University, Japan.

* Corresponding author.

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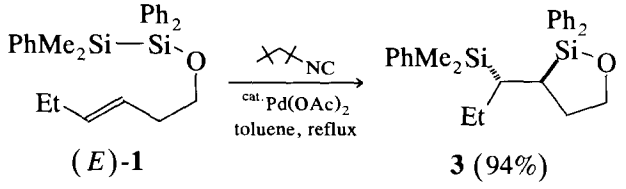
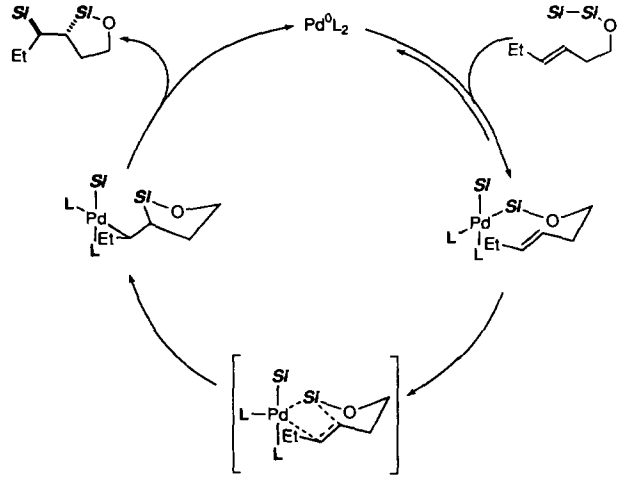
uct **2c–f** in low to moderate yields. We have found that employment of disilanyl groups having aryl substituents on the silicon atom adjacent to the oxygen remarkably enhanced the reactivities for satisfactory bis-silylation reactions (entries 8 and 9). The effect of the disilanyl groups were manifested in the bis-silylation of (*E*)-3-hexen-1-ol to give **3** in high yields (Eq. 2). As expected, intramolecular reaction of the disilanes with the (Z)- and (*E*)-double bonds occurred with complete cis-addition to afford (*R**,*S**)-**2** and (*R**,*R**)-**3**, respectively, in a stereospecific manner [3].



(*E*)-**1** **3** (94%) (2)

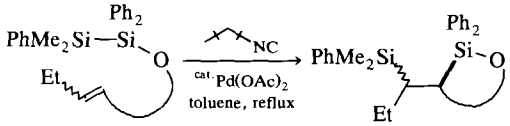
A stoichiometric reaction of (*E*)-**1i** with bis(1,1,2,2-tetramethylpropyl isocyanide)-palladium(0) in C_6D_6 was monitored at 10–20°C by ^1H NMR, being suggestive of a possible generation of the bis(silyl)palladium(II) complex [4], which was slowly converted to the cyclized product at room temperature. The formation of the complex was evidenced by the significant low-field shift of ^1H resonances of the substituents on silicon atoms (0.50 ppm for Si–*Me*), as observed for some cyclic bis(silyl)palladium bis(*tert*-alkyl isocyanide) complexes so far isolated [5]. On the other hand, **1a,b** failed to give the corresponding palladium complexes [6]. These results suggest that the catalytic cycle of bis-silylation involves bis(silyl)palladium intermediate, whose formation may be accelerated by the phenyl groups on the silicon atom (Scheme 1).

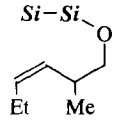
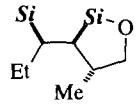
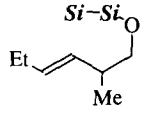
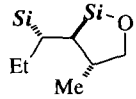
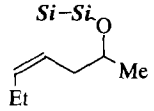
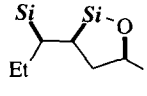
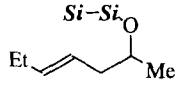
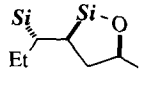
The homoallylic ethers having methyl substituent on the tether also underwent the bis-silylation to give cy-



Scheme 1. Possible catalytic cycle of intramolecular bis-silylatation of alkenes (substituents on the silicon atoms are omitted for clarity).

Table 2
Diastereoselective intramolecular bis-silylation of internal alkenes

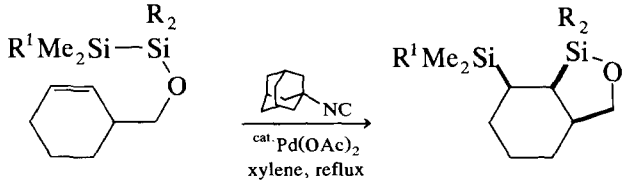


entry	substrate	product	yield/ %	*cis*:*trans* [a,b]
1	 (*Z*)-**4**	 **5**	92	1: > 99
2	 (*E*)-**4**	 **6**	97	1: > 99
3	 (*Z*)-**7**	 **8**	99	86:14
4	 (*E*)-**7**	 **9**	99	90:10

[a] stereochemistry in the 5-membered ring, [b] Determined by HPLC and ^1H NMR.

clized products in high yields (Table 2). The reaction proceeded to give the corresponding disubstituted 5-membered cyclic products with high diastereoselection. Thus, (*Z*)-**4** and (*E*)-**4** derived from 2-methyl-3-hexen-1-ol exclusively afforded *trans*-substituted **5** and **6**, respectively (entries 1,2), while (*Z*)-**7** and (*E*)-**7** derived from 4-hepten-2-ol selectively afforded *cis*-substituted **8** and **9**, respectively (entries 3,4).

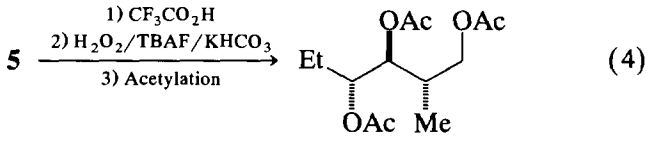
Cyclic alkenes **10a–c** also underwent intramolecular bis-silylation under rather forced conditions to give bicyclic products **11a–c** having all cis configuration in the cyclohexane ring (Eq. 3).



10a: R^1 = Ph, R = Me **11a**: 44%
b: R^1 = *p*-CF_3Ph, R = Me **b**: 78% (3)
c: R^1 = Ph, R = Ph **c**: 97%

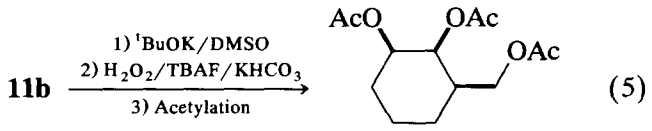
Stereoselective synthesis of triols was carried out by oxidative cleavage of Si–C bond in the presence of

fluoride anion [7]. For instance, treatment of **5** and **11b** with ^{t}BuOK in DMSO or CF_3CO_2H, followed by hydrogen peroxide oxidation gave triols which was isolated in the form of triacetate **12** and **13** in 74 and 72% yield, respectively (Eqs. 4 and 5).



(4)

12 (74%)



(5)

13 (72%)

Acknowledgments

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[4] ^{1}H NMR (200 MHz, C_6D_6) δ 0.64 (s, 18 H), 0.79 (s, 12 H), 0.92 (t, $J = 7.6$ Hz, 3 H), 0.99 (s, 6 H), 1.86–2.02 (m, 2 H), 2.36–2.48 (m, 2 H), 3.87 (t, $J = 7.1$ Hz, 2 H), 5.42–5.51 (m, 2 H), 6.98–7.37 (m, 13 H), 8.10 (d, $J = 6.5$ Hz, 2 H)

[5] (a) M. Suginome, H. Oike and Y. Ito, *Organometallics*, *13* (1994) 4148; (b) M. Suginome, H. Oike and Y. Ito, *J. Am. Chem. Soc.*, *117* (1995) 1665.

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