

Intramolecular bis-silylation of alkenes catalyzed by palladium(0) *tert*-alkyl isocyanide complex. Stereoselective synthesis of polyols

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Abstract. The intramolecular bis-silylation of alkenes promoted by a palladium / *tert*-alkyl isocyanide is described. With disilanyl ethers derived from homoallylic alcohols, intramolecular bis-silylation proceeded with stereospecific *cis*-addition to give 5 *exo*-ring closure products. It is noteworthy that the bis-silylation of an alkene having an asymmetric center in the tether took place with high diastereoselection. Stereoselective synthesis of triols was carried out by oxidative cleavage of the Si-C bond thus formed. The reaction mechanism and synthetic application of the present bis-silylation will be discussed.

Organosilicon compounds have attracted much interest from view-points of organic synthesis as well as new functional materials. This trend of organometallic chemistry has prompted us to develop new methodologies for stereoselective formation of silicon-carbon bonds.

The addition of organosilicon compounds to unsaturated organic substrates is a fundamental process in organosilicon chemistry. The utility of hydrosilylation as a synthetic tool has even been extended into the area of enantioselective reactions. Although less attention has been paid to bis-silylation than to hydrosilylation, the addition of Si-Si bonds across C-C multiple bonds to give 1,2-bis(organosilyl)alkane (or -alkene), i.e., bis-silylation is a particularly attractive transformation in that two Si-C bonds are created at once. The bis-silylation of C-C triple bonds with disilanes has been achieved by palladium catalyst. In contrast, difficulties were encountered with C-C double bonds. While the catalytic bis-silylation of ethene using platinum complex was recently reported, the synthetic utilities were limited.

Recently we disclosed that a bis-silylation of C-C triple bonds was catalyzed by a new catalyst system, palladium(II) acetate-*tert*-alkyl isocyanide. Although this new catalyst failed to promote the intermolecular bis-silylation of alkenes, application to the intramolecular variant found wide synthetic usefulness. The present paper describes the stereoselective intramolecular bis-silylation of C-C double bonds which provides a new method for polyol synthesis.

Activation of Silicon-Silicon Bond of Disilanes with Palladium *tert*-Alkyl Isocyanide Complex

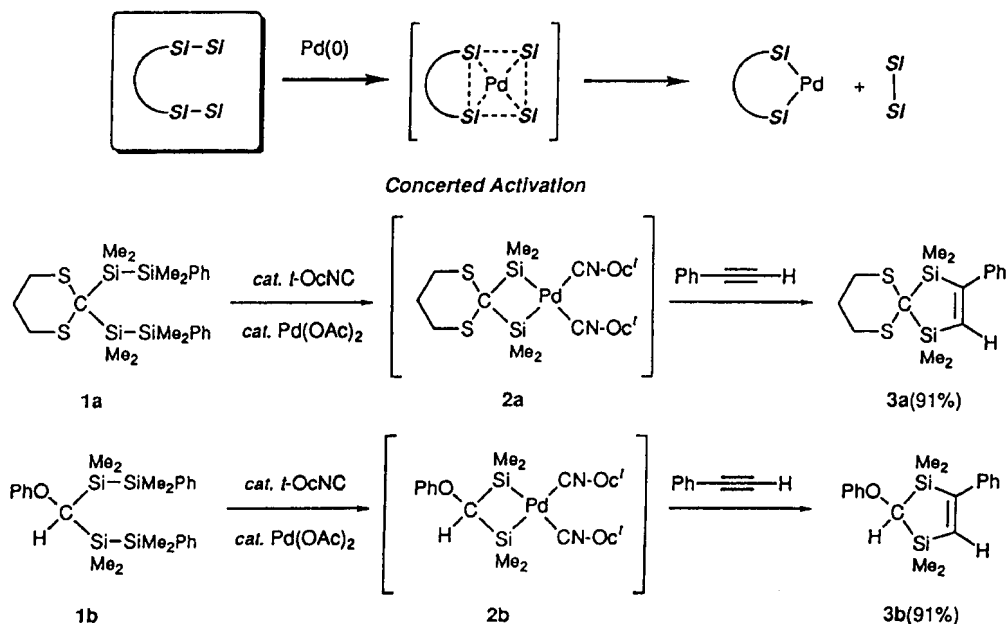
Some palladium and platinum complexes have been so far reported for activation of disilanes, which is utilized for the reactions with unsaturated carbon compounds. Recently, we found a remarkably efficient and versatile palladium complex catalyst, which is *in situ* generated by mixing a catalytic amount of Pd(II)(OAc)₂ and an excess (6-15 molar equivalent) of *tert*-alkyl isocyanide, for bis-silylation reactions of carbon-carbon double bonds and triple bonds.



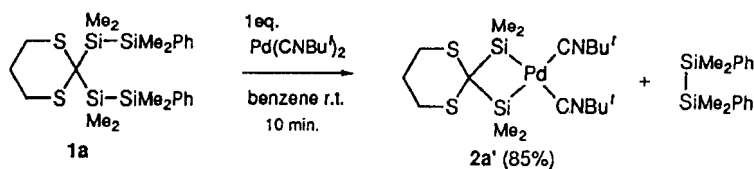
A catalyst prepared from Pd(acac)₂ and *tert*-alkyl isocyanide exhibited similar catalytic activity. In the absence of *tert*-alkyl isocyanide, none of the palladium compounds examined [Pd(OAc)₂, Pd(PPh₃)₄, PdCl₂(PPh₃)₂, Pd(OAc)₂ / PPh₃ (1 : 2), Pd₂(dba)₃·CHCl₃ / PPh₃ (1 : 4), Pd₂(dba)₃·CHCl₃ / P(OEt)₃ (1 : 4), and Pd₂(dba)₃·CHCl₃ / 2,2'-bipyridine (1 : 4)] induced the intramolecular bis-silylation of olefins at all.

As for the true active palladium catalyst, we assume that palladium(II) acetate is initially reduced by *tert*-alkyl isocyanide to form the palladium(0) species ligated by *tert*-alkyl isocyanide. It is noted that Pd(CN-Bu-*tert*)₂ complex prepared according to the reported procedure provided an efficient catalyst for silicon-silicon bond activation as described below.

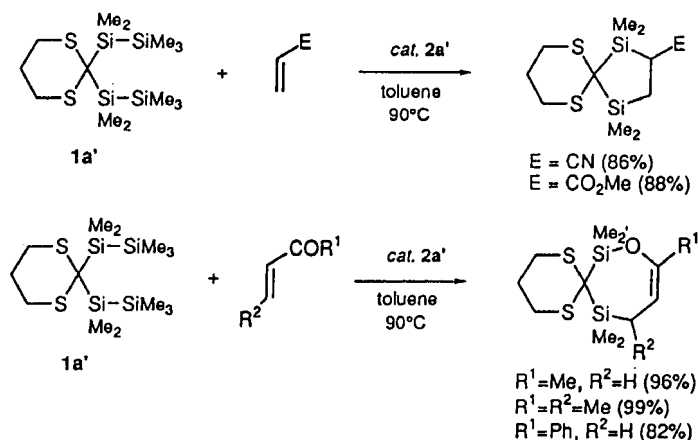
An interesting activation of silicon-silicon bond of disilanes was observed in the reaction of bis(disilanyl)alkanes with a catalytic amount of $\text{Pd}(\text{OAc})_2$ and 1,1,3,3-tetramethylbutyl isocyanide in the presence of phenylacetylene. The reactions with bis(disilanyl)methanes **1a** and **1b** provided the corresponding 5-membered cyclic products **3** and **3**, respectively, in high yields with sym-diphenyltetramethyldisilane. The formation of **3** may suggest that two Si-Si bonds of **1** were simultaneously activated by the palladium catalyst to generate a 4-membered cyclic bis(silyl)palladium(II) intermediates **2**, which was subsequently trapped with phenylacetylene.¹⁾



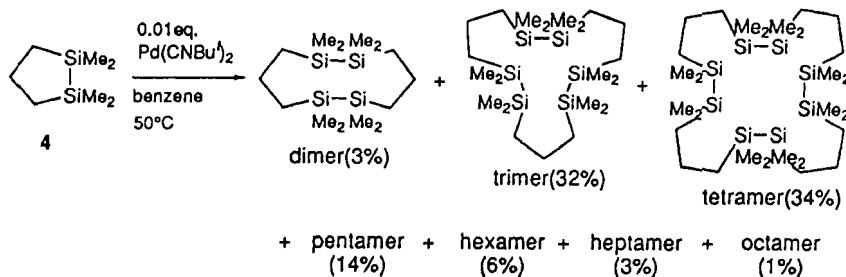
In the reaction of **1a** with a stoichiometric amount of $\text{Pd}(\text{CN-Bu-tert})_2$ in benzene at room temperature for 10 min, 4-membered cyclic bis(silyl) palladium(II) bis(*tert*-butyl isocyanide) **2a'** was isolated, which was characterized by X-ray analysis. The *tert*-butyl isocyanide ligands are essential for the simultaneous activation of the two Si-Si bonds. The bis(silyl)palladium(II) complex thus isolated reacted immediately with phenylacetylene to give **3a** in an almost quantitative yield.¹⁾



Furthermore, use of **2a'** as a catalyst promoted a bis-silylation of electron-deficient olefins with 1,1-bis(disilanyl)dithiane **1a'**. Without excess isocyanide, the electron-deficient olefins underwent bis-silylation exclusively. α,β -Unsaturated ketones provided 1,4-bis-silylation adducts, whereas the corresponding ester and nitrile gave 3,4-adducts.

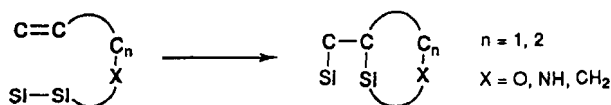


As the related metathesis reaction of disilanes, 5-membered 1,1,2,2-tetramethyl-1,2-disilacyclopentane **4** underwent a ring enlargement oligomerization in the presence of bis(*tert*-butyl isocyanide)palladium(0), giving cyclic oligomers up to the 40-membered octamer. The oligomerization is formally an insertion of $-\text{Me}_2\text{Si}(\text{CH}_2)_3\text{SiMe}_2-$ unit of **4** into the Si-Si bonds of oligomers produced.²⁾



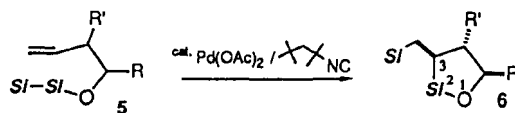
Intramolecular Bis-silylation of Olefins

No bis-silylation of simple olefins has been catalyzed with the present palladium(II) acetate / *tert*-alkyl isocyanide complex. However, some disilanyl alkenes, in which olefin and disilane moieties are tethered with chains of 2 and 3 atoms, underwent the exo ring closure giving the corresponding 4 and 5-membered cyclic silicon containing products. Herein, we describe an intramolecular bis-silylation of olefins tethered to a disilanyl group by a chain of 3 atoms through ether linkage, which leads to a stereoselective synthesis of polyols.³⁾



Disilanyl alkenes **2** were prepared in good yield by the reaction of homoallylic alcohols with chlorodisilanes in the presence of an amine. The bis-silylation reaction of **5** was carried out in the presence of a catalytic amount of palladium(II) acetate (0.01-0.05 equiv) and *tert*-alkyl isocyanide (0.15-0.75 equiv) in toluene. Intramolecular regioselective addition of the Si-Si linkage across the C=C bond took place to furnish the exo-ring closure product, i.e., 2-silatetrahydrofuran **6** in good yield. Tertiary alkyl carbon-silicon bonds were readily formed by the bis-silylation of geminally disubstituted olefins, although heating at 80°C was required. Ester and allylic benzyloxy groups did not encumber the desired bis-silylation reaction.

It is noteworthy that the bis-silylation of an alkene having an asymmetric center in the tether proceeds with high diastereoselection. Alkenes having substituents in allylic positions, i.e., α to the C=C bond, gave *trans*-3,4-disubstituted **6**. On the other hand, the *cis*-3,5-disubstituted **6** were favored in the reaction of β -substituted alkenes. Very similar selectivities in the vicinity of 92 : 8 - 93 : 7 were observed with β -substituents of varying bulkiness ranging from methyl to *tert*-butyl groups. Geminal disubstitution of the C=C bond improved the selectivity slightly. The reaction at reflux in toluene resulted in only a little decrease in the selectivity.



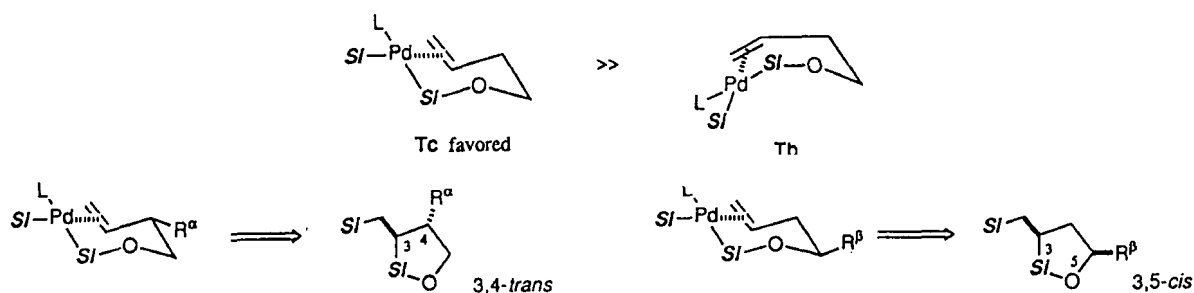
| entry | 5 | 6 | yield | cis : trans |
|-------|---|---|-------|-------------|
| 1 | | | 91 | 92 : 8 |
| 2 | | | 88 | 92 : 8 |
| 3 | | | 97 | 93 : 7 |
| 4 | | | 92 | 93 : 7 |

| entry | 5 | 6 | yield | cis : trans |
|-------|---|---|-------|-------------|
| 5 | | | 95 | 7 : 93 |
| 6 | | | 92 | 3 : 97 |
| 7 | | | 85 | 1 : >99 |

The influence of the silicon substituents on stereoselectivity was examined; no significant difference in selectivity was observed among pentamethyldisilanyl, 2-phenyl-1,1,2,2-tetramethyldisilanyl, and 2-isopropoxy-1,1,2,2-tetramethyldisilanyl groups, indicating that the stereochemical outcome was not affected by the substituents on the silicon atom distal to the ether oxygen. And, the two phenyl groups on the silicon atom proximal to the ether oxygen increased the selectivity slightly. However, it is noted that the employment of 1,1,2-triphenyldimethyldisilanyl group in disilanyl alkenes remarkably improved the intramolecular bis-silylation of internal alkenes. The intramolecular bis-silylation of the disilanes with (*Z*)- and (*E*)- carbon-carbon double bonds proceeded stereospecifically with complete cis-addition.⁴⁾



The stereoselectivity trends observed are formulated as arising from a preference for the chair-like transition state **Tc** over the boat-like one **Tb**. In the chair-like transition state **Tc**, a substituent, either α or β to the C=C bond, prefers the equatorial position. Consequently, the α -substitution of the C=C bond leads to *trans*-3,4-disubstituted 2-silatetrahydrofuran and β -substitution to *cis*-3,5-disubstituted 2-silatetrahydrofuran.

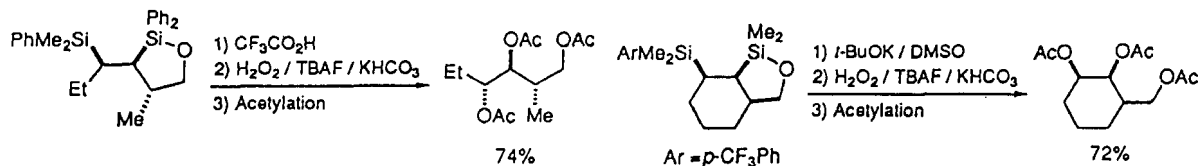


The stereochemical outcome of the bis-silylation reaction with erythro- and threo- disilanyl alkenes is also rationalized by assuming the chair-like transition state.

Oxidative Transformations of the 2-Silatetrahydrofuran into 1,2,4-Triols

It has been reported that the oxidative cleavage of a Si-C bond furnishing a hydroxyl group proceeds with retention of configuration at the cleaved carbon atom and that at least one functional group bound to the silicon such as an alkoxy group or a halogen is required for the oxidation to proceed. A phenyl-substituted silicon also undergoes oxidation via prior cleavage of the Ph-Si bond. The Si-Ph bond cleavage is conventionally carried out by treatment with an acid as reported. An alternative method for cleavage of the Si-Ph bond of the 2-silatetrahydrofuran has also been devised.

Treatment of the 2-silatetrahydrofuran derivatives with potassium tert-butoxide in dimethyl sulfoxide successfully cleaved the Si-Ph bond presumably via ring opening reaction. The oxidative transformation of the bis-silylation products into 1,2,4-triols has been exemplified as below.



References and Notes

1. M. Suginome, H. Oike, and Y. Ito, *Organometallics*, **13**, 4148 (1994).
2. M. Suginome, H. Oike, and Y. Ito, Submitted to *J. Am. Chem. Soc.*
3. a) M. Murakami, P. G. Andersson, M. Suginome, and Y. Ito, *J. Am. Chem. Soc.*, **113**, 3987 (1991). b) M. Murakami, M. Suginome, K. Fujimoto, H. Nakamura, P. G. Andersson, and Y. Ito, *J. Am. Chem. Soc.*, **115**, 6487 (1993).
4. M. Suginome, A. Matsumoto, K. Nagata, and Y. Ito, unpublished results.