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Review

Stereoselective bis-silylations and silylborations of carbon–carbon multiple bonds catalyzed by palladium(0) *t*-alkyl isocyanide complex[☆]

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Abstract

Palladium(0) *t*-alkyl isocyanide complex, generated in situ by mixing palladium(II) acetate or palladium(II) acetylacetonate and an excess of *t*-alkyl isocyanide, is a novel and efficient catalyst for activation of the Si–Si bond of disilanes, which promotes bis-silylation of carbon–carbon double bonds as well as triple bonds. Intramolecular disilanyl ethers of propargyl alcohols underwent 4-*exo*-cyclization reactions in the presence of the palladium *t*-alkyl isocyanide catalyst, producing four membered cyclic oxasiletanes. The intramolecular disilanyl ethers of optically active secondary propargylic alcohols followed by treatment with *n*-BuLi provided optically active allenylsilanes with high stereoselectivity. The intramolecular bis-silylation of allylic alcohols proceeded with 4-*exo*-ring closure, giving four membered oxasilatanes, which were converted to allylsilanes stereoselectively via dimerization and subsequent disproportionation. Thus, highly enantio-enriched allylsilanes were prepared from the corresponding optically active secondary allylic alcohols with 1,3-chirality transfer. Related silylboration reactions of carbon–carbon multiple bonds were also described.

Keywords: Bis-silylations; Optically active allylsilanes; Palladium *t*-alkyl isocyanide complex; Silylborations

1. Introduction

Isocyanides, which are structurally isoelectronic to carbon monoxide, function as π-acid ligands for complexation with various transition metals. The complexation with transition metals causes activation of isocyanides which has made wide synthetic application of isocyanides possible. Thus, isocyanides have been used as a C_1 source in organic synthesis, which is the synthetic equivalent to carbon monoxide.

On the other hand, the catalytic activities of transition metals conferred by isocyanide coordination could lead to activation of any coordinating substrates on the metals, which have not been synthetically utilized. This paper describes bis-silylation and silylboration reactions of carbon–carbon multiple bonds catalyzed by the palladium(0) *t*-alkyl isocyanide complex. To our best knowledge, this provides the first example of a palladium isocyanide complex catalyst, in which isocyanide functions just as a ligand on the metal, a ‘spectator ligand’, but not a reagent.

Several years ago, we found that a catalyst generated in situ by mixing $Pd(OAc)_2$ and an excess of *t*-alkyl isocyanide promoted addition of the Si–Si bond of hexamethyldisilane, which had been known to be inert in the presence of palladium complexes, across the carbon–carbon triple bonds [1]. The palladium *t*-alkyl isocyanide complex has been successfully applied to intramolecular bis-silylation of carbon–carbon double bonds as well as triple bonds, leading to regio- and stereoselective syntheses of organosilicon compounds which are useful in organic synthesis.

[☆] Dedicated to Professor Jiro Tsuji for his great contributions to palladium chemistry in organic synthesis.

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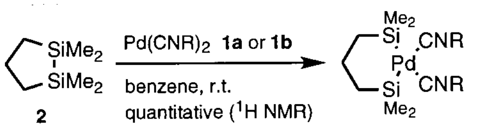
Concerning an active palladium species in the catalytic reactions, a bis(*t*-alkyl isocyanide)palladium(0) complex may be presumably generated from Pd(OAc)$_2$ and an excess of *t*-alkyl isocyanide. Indeed, bis(*t*-alkyl isocyanide)palladium(0), which is independently prepared by the reaction of the (cyclopentadienyl)(p-allyl)palladium(II) complex [2] with *t*-alkyl isocyanide, promoted an activation of the Si–Si bonds of disilanes.

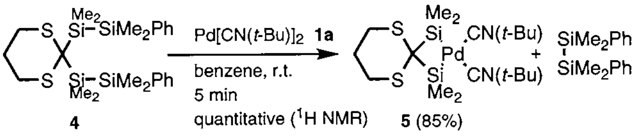
2. Formation of bis(organosilyl)bis(*t*-alkyl isocyanide)palladium(II) complexes

Oxidative addition of the silicon–silicon bond of 1,1,2,2-tetramethyl-1,2-disilacyclopentane onto bis(*t*-butyl isocyanide)palladium(0) took place instantaneously at room temperature in benzene, giving a six-membered cyclic bis(organosilyl)bis(*t*-butyl isocyanide)palladium(II) complex (**3a**), which was isolated by crystallization in high yield [3]. An X-ray analysis of the related six-membered cyclic bis(organosilyl)bis(1-adamantyl isocyanide) complex (**3b**) revealed a four coordinated square planar structure [4,5].

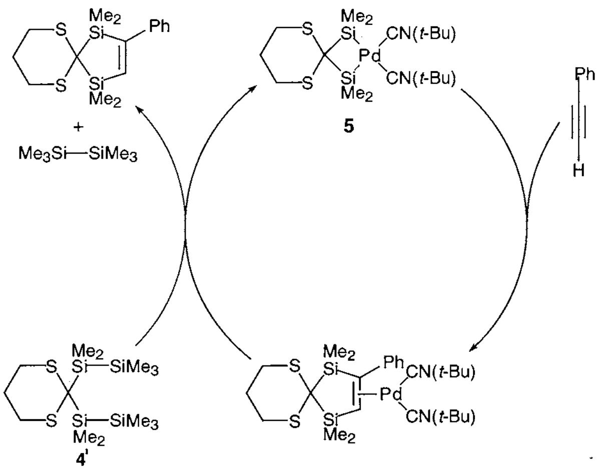


3a (R = *t*-Bu; 85%)
3b (R = 1-adamantyl (Ad); 97%)

Of interest is that reaction of bis(disilanyl)dithiane **4** with an equimolar amount of bis(*t*-butyl isocyanide)palladium(0) resulted in the formation of a four membered cyclic bis(organosilyl) palladium(II) bis(*t*-butyl isocyanide)complex together with 1,1,2,2-tetramethyl-1,2-diphenyldisilane. Presumably, the formation of **5** may have arisen from the simultaneous activation of the two Si–Si bonds on palladium, which led to intramolecular metathesis (disproportionation) [6].

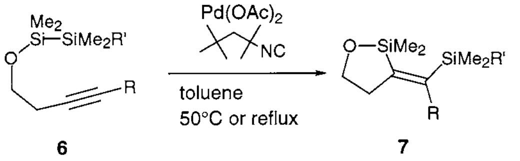


A stoichiometric reaction [5] of the bis(organosilyl)palladium(II) complex (**5**) with terminal alkynes or bis(methoxycarbonyl)acetylene proceeded smoothly at room temperature, giving the corresponding *spiro*-disilacyclopentene derivatives in high yields, as illustrated below. However, attempts at the reactions with dialkylacetylenes as well as unactivated alkenes have all failed even using forced conditions.



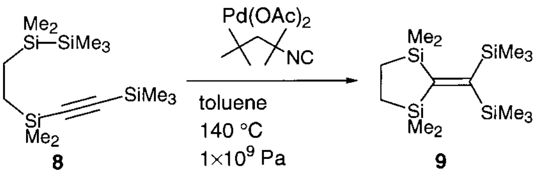
3. Bis-silylation of carbon–carbon multiple bonds catalyzed by palladium(0)(*t*-alkyl isocyanide) complex—intramolecular bis-silylation of alkynes

The palladium(0) *t*-alkyl isocyanide catalyst failed to promote the intermolecular bis-silylation of internal alkynes. However, disilanyl ethers **6** of homopropargylic alcohols having internal carbon–carbon triple bonds underwent intramolecular bis-silylation with 5-*exo*-ring-closure to give cyclic oxasilolanes **7** in good yields in the presence of a catalytic amount of palladium(II) acetate and an excess of *t*-octyl isocyanide [7,8].

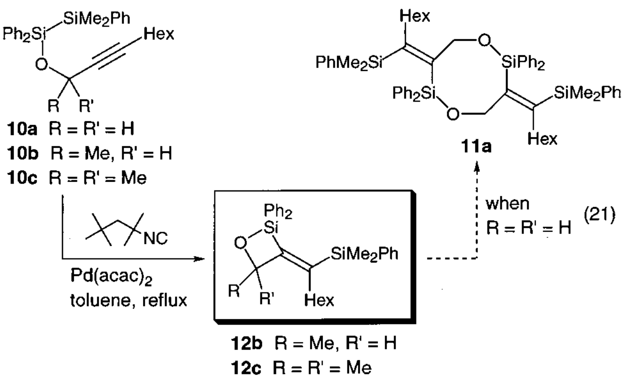


R = H, Me, Ph, SiMe$_3$, CO$_2$R, CH=CH$_2$, *etc.*
R' = Me, Ph

A highly sterically congested tetrakis(organosilyl)ethene **9** was successfully synthesized by intramolecular bis-silylation of **8** under high pressure [8].

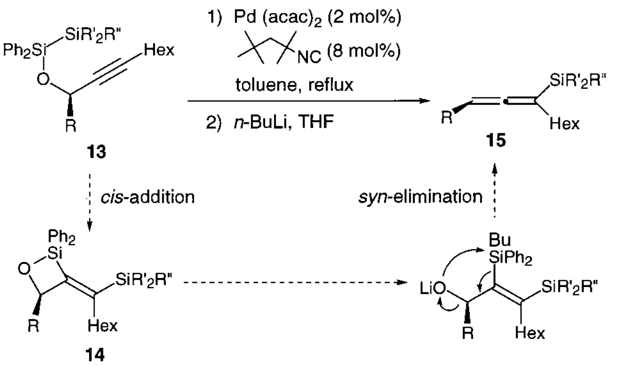


The intramolecuar bis-silylation of propargylic alcohols is noteworthy, since few examples have been known for 4-*exo*-cyclization reactions producing four-membered ring organosilicon compounds containing Si–O bonds. Reaction of disilanyl ether **10a** prepared from a primary propargylic alcohol gave the eight-membered ring compound **11a** in good yield [9]. The formation of **11a** may be rationalized by initial 4-*exo*-cyclization followed by dimerization of the unstable oxasiletane [10]. In fact, the four-membered cyclic compound **12b** was formed quantitatively in the reaction of **10b** prepared from the corresponding secondary alcohol, but was difficult to be isolated. Moreover, the reaction with tertiary **10c** afforded **12c**, which was chromatographically stable and was isolated in high yield.

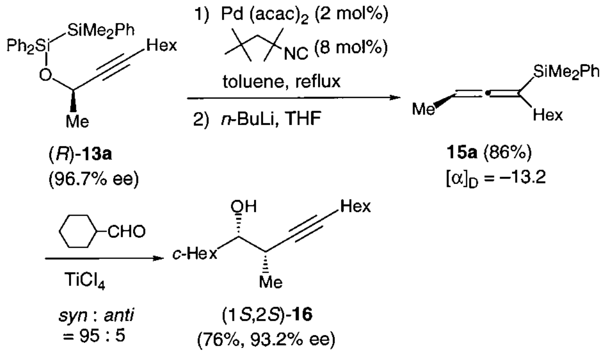


4. Stereospecific synthesis of chiral allenylsilanes

The intramolecular bis-silylation of **13** (R = Me, $R'_2R''Si = PhMe_2Si$), prepared from 3-decyn-2-ol, afforded the four-membered **14** in high yield under reflux in toluene, which was subsequently treated with *n*-butyllithium in THF, providing allenylsilane derivative **15** [11].

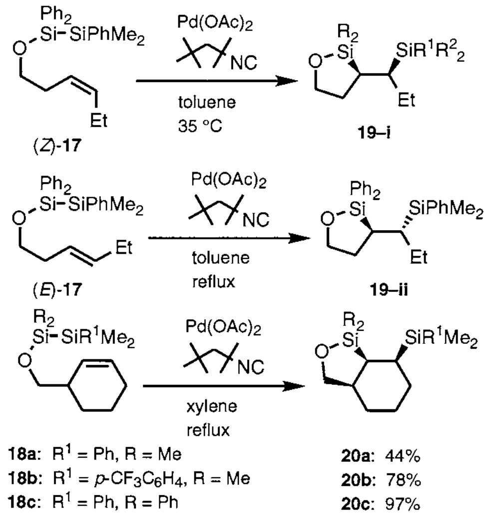


New preparative method of optically active allenylsilanes has been developed according to the procedure. Optically active allenylsilane (−)-**15a** ($[a]^{20}_{D}$ = −13.2 (c = 1.7, benzene)) prepared from (*R*)-**13a** of 96.7% enantiomeric excess (ee) was subjected to a $TiCl_4$ mediated reaction with cyclohexane-carboxaldehyde under the conditions reported by Danheiser et. al. providing *syn*-homopropargylic alcohol **16a** of 93.2% ee with (1*S*,2*S*) configuration stereoselectively. The stereochemical outcome indicates that allenylsilane **15a** with (*R*)-configuration was formed via the two stereospecific processes, i.e. *cis*-addition of the Si–Si bond to the carbon–carbon triple bond and *syn*-elimination of the resultant silanolate. Probably, the subsequent reaction of cyclohexane-carboxaldehyde with high stereoselectivity at the π-face anti to the silyl group to give (1*S*,2*S*)-**16a** with high ee [11].



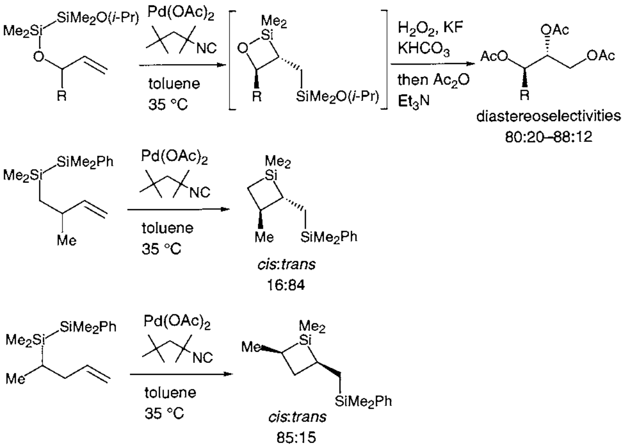
5. Intramolecular bis-silylation of alkenes catalyzed by palladium(0)(*t*-alkyl isocyanide) complex

In the intramolecular bis-silylation reactions [12] of homoallylic alcohols, the reactivities of the carbon–carbon double bonds decreased in the following order, i.e., monosubstituted > geminally disubstituted > vicinally disubstituted double bonds. The vicinally disubstituted alkenes failed to give cyclization products, while the monosubstituted alkenes underwent the intramolecular bis-silylation even at room temperature in high yields. However, the intramolecular bis-silylation of vicinally disubstituted carbon–carbon double bonds was achieved by a choice of the disilanyl group. Employment of disilanyl groups having aryl substituents on the silicon atom adjacent to the oxygen remarkably enhanced the reactivities for the bis-silylation reactions as manifested in the bis-silylations of **17** and **18**. The intramolecular bis-silylation proceeded with complete *cis*-addition.



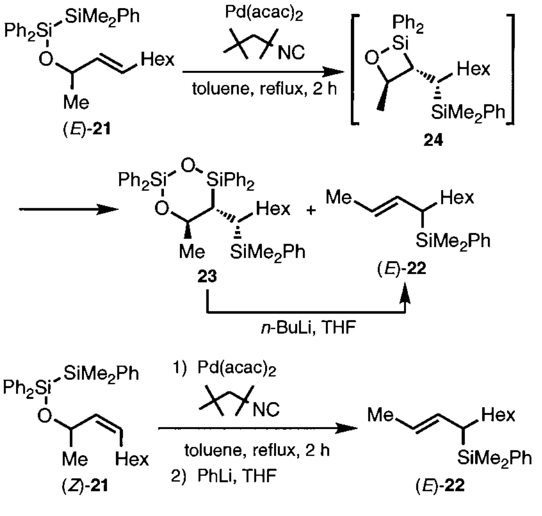
6. Stereoselective synthesis of highly enantio-enriched allylsilanes

The intramolecular bis-silylation of terminal allylic alcohols [13,14] proceeded under mild condition, although the expected bis-silylation products were not isolated. The reaction mixture was directly subjected to the oxidation with H_2O_2 to afford 1,2,3-triols in moderate stereoselectivities. The bis-silylation with the related 4-disilanyl-1-butenes underwent the stereoselective 4-*exo*-cyclization to give the corresponding silacyclobutanes in moderate stereoselectivities.

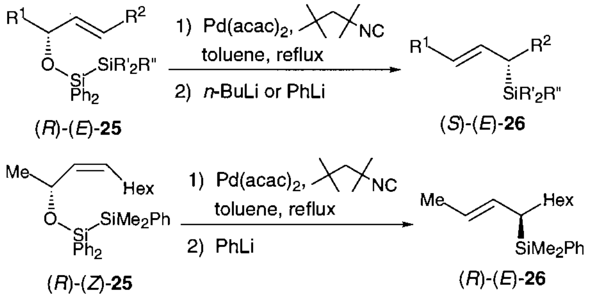


Disilanyl ether (*E*)-**21**, which was prepared from the corresponding allylic alcohol and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane, was heated for 2 h in the presence of $Pd(acac)_2$ (2 mol%) and 1,1,3,3-tetramethylbutyl isocyanide (8 mol%) under reflux in toluene. Unexpectedly, the reaction gave (*E*)-allylsilane **22** (49%) and six-membered cyclic siloxane **23** (46%), which were separated and isolated by column chromatography, through disproportionation of the four-membered oxasiletane intermediate **24**. Treatment of **23** with *n*-butyllithium in THF at 0°C led to the formation of (*E*)-**22** in high yield [15]. Noteworthy is that the relative stereochemistry of the three consecutive stereocenters in **23** as well as the *trans* geometry of the carbon–carbon double bond in **22** was completely controlled. The result obviously indicates the intramolecular bis-silylation of allyl alcohols takes place with highly stereoselective 4-*exo*-cyclization to give *trans*-oxasiletane **24**. It is noted that (*E*)-allylsilane **22** was obtained also from (*Z*)-**21** in high yield.

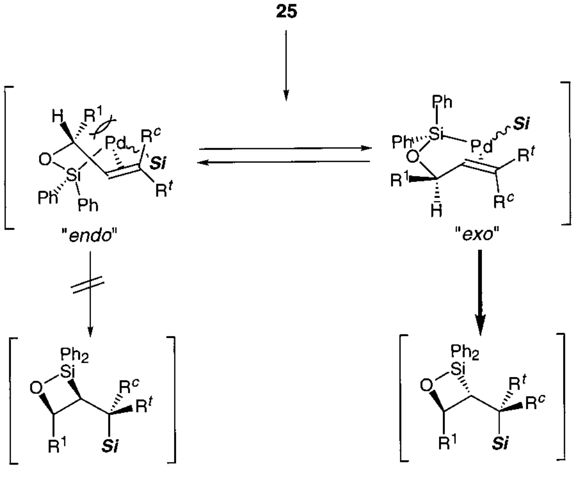
The present palladium-catalyzed bis-silylation of allylic alcohols followed by treatment with *n*-butyllithium provides a convenient and general one pot synthesis of (*E*)-allylsilanes [15].



The highly selective formation of (*E*)-allylsilanes prompted us to enantio-enriched allylic alcohols as the starting materials, which are readily available by asymmetric synthesis, e.g. Sharpless kinetic resolution. The palladium-catalyzed reaction of (*R*)-(*E*)-**25** (99.7–99.9% ee) followed by the treatment with *n*-butyllithium gave (*S*)-(*E*)-**26** in 90% yield. On the basis of the stereoselective bis-silylation followed by Peterson-type *syn*-elimination, highly enantio-enriched (*E*)-allylsilanes were prepared from optically active allylic alcohols with 1,3-chirality transfer.

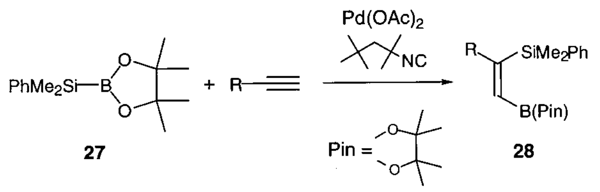


The stereoselective 1,3-chirality transfer may be explained by diastereoface-selective intramolecular bis-silylation, leading to the exclusive formation of 3,4-*trans*-oxasilatane intermediate, as illustrated below.



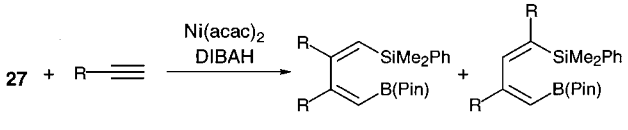
7. Silylboration of carbon–carbon multiple bonds

An addition of a silicon–boron bond of (dimethylphenylsilyl)pinacolborane (**27**) to alkynes took place stereoselectively and regioselectively at reflux in toluene in the presence of palladium(0) *t*-alkyl isocyanide catalyst, giving the corresponding (*Z*)-1-boryl-2-silylalkenes (**28**) [16].



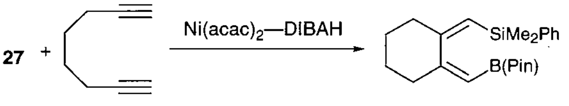
27 **28**

Double insertion of alkynes into the Si–B bond of **27** was catalyzed by nickel(0) catalyst, generated in situ from nickel(II) acetylacetonate and di(*i*-butyl)aluminum hydride, providing cis, *cis*-1-silyl-4-boryl-1,3-butadiene derivatives stereoselectively [17].



29 (major) (minor)

An application of the silaborative dimerization to 1,7-octyne provided the 1,2-dimethylenecyclohexane derivative in moderate yield [17].



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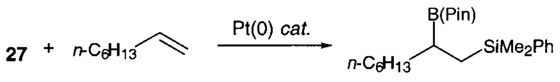
Unlike the silylboration of alkynes, alkenes underwent the insertion reaction into the silicon–boron bond of (dimethylphenylsilyl)pinacolborane (**27**) catalyzed by $Pt(CH_2{=}CH_2)(PPh_3)_2$ complex catalyst but not by palladium *t*-alkyl isocyanide. It is remarked that the regiochemistry of the silaborations with alkenes was opposite to that with alkynes, in which the silicon group is stereoselectively introduced at the less substituted terminal carbon [18].



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