Chem. Rev. **2000,** *100,* 3221–3256

Transition-Metal-Catalyzed Additions of Silicon–Silicon and Silicon–Heteroatom Bonds to Unsaturated Organic Molecules

Michinori Suginome and Yoshihiko Ito*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Received January 11, 2000

Contents

I. Introduction

With the increasing demand for organosilicon compounds in organic synthesis as well as material sciences, development of new methodologies that offer efficient entries into a variety of organosilanes is eagerly desired. Transition-metal-catalyzed reactions of organosilanes are the most attractive strategy for the efficient synthesis of organosilicon compounds, since otherwise stable organosilanes can take part in the reaction with the aid of the catalysts. In fact, hydrosilanes, which are quite readily activated by the transition-metal catalysts, have been utilized for the synthesis of organosilicon compounds via transition-metal-catalyzed hydrosilylation reactions.

Silicon−silicon bonds are nonpolarized, thermally stable σ-bonds possessing the dissociation energy of 220−300 kJ/mol. The σ-bond features the high-lying HOMO and low-lying LUMO, whose energy levels are comparable to those for the carbon−carbon double bonds. The characteristic nature of the Si−Si bonds enables interaction with transition-metal complexes, which in turn leads to catalytic reactions involving the activation of the Si−Si bonds.

In 1972, Okinoshima, Yamamoto, and Kumada found that 1,2-dihydrotetramethyldisilane added to 1,3-dienes in a 1,4-fashion to give α,α'-bis(silyl)-alkenes in the presence of a nickel catalyst.[1] As suggested in the report, the reaction may proceed through the initial activation of the Si−H bond, which is followed by the formation of the bis(dimethylsilyl)nickel complex via silylene migration. Nevertheless, this was the first example of the transition-metal-catalyzed addition of the Si−Si bond of disilane across carbon−carbon multiple bonds. Since then, a variety of bis-silylation reactions of unsaturated organic compounds have been reported. Furthermore, catalytic addition reactions of other silicon-containing σ-bonds have been developed.

The principal aim of this review is to present a general overview of the transition-metal-catalyzed addition reaction of the silicon-containing σ-bond including Si−Si, Si−Ge, Si−Sn, Si−B, Si−C, Si−S, and Si−Se bonds. The authors also put emphasis on the application of these reactions to organic synthesis. The most well-investigated hydrosilylation will not be covered by this article.[2] This review describes those reactions where the activation of the silicon-containing σ-bond by transition-metal complexes leads to addition reactions. Stoichiometric reactions will not be mentioned unless it may be closely related to the catalytic processes. Since the mechanistic classification of the reactions is difficult in some cases, this review simply includes those reactions where the two elements forming the σ-bond are *both* incorporated into the product of major interest.

For the related chemistry which is not covered by this review, several review articles have appeared, focusing on the Si−Si bond activation,[3−5] the Pd-catalyzed reactions of silanes,[6] and the reactions

10.1021/cr9902805 CCC: $35.00

Michinori Suginome was born in 1966. He graduated from Kyoto University, where he received his Doctor Degree of Engineering under the supervision of Professor Y. Ito in 1993 with his thesis titled *Bis-Silylation of Unsaturated Compounds Catalyzed by Palladium-Isonitrile Complex*. Since 1993 he has worked as Assistant Professor of the Department of Synthetic Chemistry and Biological Chemistry, Kyoto University. Afterward, he carried out postdoctoral work in the United States with Professor Gregory C. Fu at Massachusetts Institute of Technology during 1998–1999. He has been the recipient of the Chemical Society of Japan Award for Young Chemists (1999). His research interests are currently in the catalytic, stereoselective synthesis of organic molecules, including organosilicon compounds and stereoregular macromolecules, by means of transition-metal catalysts.

Yoshihiko Ito was born in 1937. He graduated from Kyoto University, where he received his Doctor Degree of Engineering under the supervision of Professor R. Oda in 1966. His thesis was entitled *New Synthetic Reactions with Isonitriles, Ylides and Carbenes*. Afterward, he spent one year as a postdoctrate at the University of California, San Diego, working with the late Professor Teddy G. Traylor. He is now Full Professor of the Department of Synthetic Chemistry and Biological Chemistry, Kyoto University. His research group is involved in the study of a broad range of topics covering the general area of synthetic organic chemistry with emphasis on development of new synthetic methodologies by means of organometallic compounds. Synthesis and synthetic methods of new silicon compounds and functionally interesting molecules are also current topics in his group.

involving the silyl–transition-metal intermediates.[7] Moreover, some accounting articles have also been published.[8–14] Very recently, a review focusing on element–element addition to alkynes has appeared.[15]

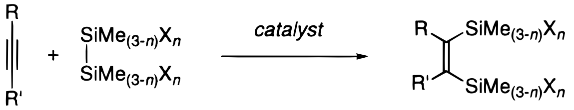
II. Silicon–Silicon Bond

A. Addition to Alkynes

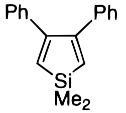
The bis-silylations of alkynes have been the most extensively studied. In addition to intermolecular bis-silylations with acyclic as well as cyclic disilanes, intramolecular variants have been developed in recent years, aiming at effective synthesis of organosilicon compounds which are otherwise inaccessible. In this section, bis-silylations with acyclic disilanes are dealt with first for understanding the basic factors governing the course of the reaction, followed by bis-silylation with cyclic disilane and intramolecular variants of bis-silylation.

1. Acyclic Disilanes

Representative results of bis-silylations of alkynes with symmetrical acyclic disilanes are summarized in Table 1 (eq 1). The addition of the Si–Si bond across the carbon–carbon triple bond was first realized by use of hydrodisilanes.[16] The Si–Si bond added to the electron-deficient alkyne in a cis-fashion in moderate yield (entry 1). The use of the hydrodisilane, however, accompanied the formation of a silole derivative **1**, which arose from a silylene palladium intermediate, along with the bis-silylation product obtained in low yield (entry 2). The silylene-mediated reaction was later modified for application to the convenient synthesis of the silole derivatives.[17] The silylene extrusion was suppressed by use of fluorodisilanes, resulting in the formation of bis-silylation products in better yields (entries 3–6).[18] Arylacetylenes such as diphenylacetylene and phenylacetylene showed higher reactivity than aliphatic internal alkynes such as 3-hexyne. Methoxy- and chlorodisilanes were also employed for bis-silylation reactions (entries 7–15).[19–21] Although no significant dependence of the yields on the number of the methoxy groups was observed, the stereoselectivity of the reaction with tetramethoxydimethyldisilane was higher than that with dimethoxytetramethyldisilane (entries 7, 8 vs 9, 11). Note that the platinum complex also catalyzed the bis-silylation reaction, albeit in low yield as well as low stereoselectivity (entry 10).[19]



(1)



1

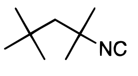
As long as the phosphine–palladium complexes are used, it has been difficult to achieve the bis-silylation with hexamethyldisilane, which is regarded as one of the least reactive disilanes. For instance, attempted reactions of hexamethyldisilane with dimethyl acetylenedicarboxylate,[22] phenylacetylene,[19] and 1-hexyne[21] provided the corresponding bis-silylation products in low yields (entries 16–18). Remarkable improvement in the bis-silylation reaction with hexamethyldisilane was made by modification of the ligand on the palladium catalysts. The combination of commercially available 1,1,3,3-tetramethylbutyl isonitrile (*t*-Oc-NC) and $Pd(OAc)_2$ was highly effective for the bis-silylation of terminal alkynes with hexamethyldisilane (entries 19 and 20).[23] A

Table 1. Bis-Silylation of Alkynes with Acyclic Symmetrical Disilanes ($X_nMe_{(3-n)}Si$-$SiMe_{(3-n)}X_n$)

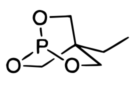
entry	*n*	X	R	R′	catalyst	conditions[a]	yield/%[b]	Z/E[c]	ref
1	1	H	CO_2Me	CO_2Me	$PdCl_2(PEt_3)_2$	PhH, reflux	40	*Z*	16
2	1	H	Ph	H	$PdCl_2(PEt_3)_2$	PhH, reflux	25	*Z*	16
3	2	F	Ph	Ph	$PdCl_2(PPh_3)_2$	100 °C	>60	*Z*	18
4	1	F	Ph	Ph	$PdCl_2(PPh_3)_2$	100 °C	>60	*Z*	18
5	1	F	Ph	H	$PdCl_2(PPh_3)_2$	100 °C	>60	*Z*	18
6	1	F	Et	Et	$PdCl_2(PPh_3)_2$	100 °C	<50	*Z*	18
7	2	OMe	Ph	H	$Pd(PPh_3)_4$	110 °C	(71)	96/4	19
8	2	OMe	*n*-Bu	H	$Pd(PPh_3)_4$	130 °C	(46)	100/0	20
9	1	OMe	Ph	H	$Pd(PPh_3)_4$	110 °C	(78)	92/8	19
10	1	OMe	Ph	H	$Pt(PPh_3)_4$	130 °C	(34)	65/35	19
11	1	OMe	*n*-Bu	H	$Pd(PPh_3)_4$	130 °C	(76)	84/16	20
12	1	OMe	Me_3Si	H	$Pd(PPh_3)_4$	100 °C	(33)	98/2	20
13	1	OMe	H	H	$Pd(PPh_3)_4$	toluene, 110 °C	32	95/5	20
14	2	Cl	H	H	$Pd(PPh_3)_4$	80 °C	(96)	79/21	20
15	1	Cl	H	H	$Pd(PPh_3)_4$	130 °C	(78)	89/11	20
16	0	−	CO_2Me	CO_2Me	$PdCl_2(PPh_3)_2$	PhH, reflux	3.4	*Z*	22
17	0	−	Ph	H	$Pd(PPh_3)_4$	110 °C	(26)	100/0	19
18	0	−	Bu	H	$Pd(PPh_3)_4$	130 °C	(7)	100/0	21
19	0	−	Ph	H	$Pd(OAc)_2$/*t*Oc−NC	toluene, reflux	82	96/4	23
20	0	−	*n*-Hex	H	$Pd(OAc)_2$/*t*Oc−NC	toluene, reflux	81	95/5	23
21	0	−	Ph	H	$Pd(dba)_2$/ETPO	120 °C	(91)	*Z*	25
22	1	Ph	*n*-Hex	H	$Pd(OAc)_2$/*t*Oc−NC	toluene, reflux	96	100/0	23
23	1	Ph	H	H	$Pd(OAc)_2$/*t*Oc−NC	toluene, reflux	98	97/3	23

[a] The reaction was carried out without solvent, unless the solvent is specified. [b] Isolated yield. The yields in parentheses are determined by GC. [c] The description "*Z*" stands for predominant or exclusive formation of the *Z* isomer.

palladium(0) complex with isonitrile ligands may be involved as the active species in the reactions. In fact, bis(*tert*-alkyl isonitrile)palladium(0) complex independently prepared served as a good precursor for the synthesis of bis(silyl)palladium(II) complexes.[24] The catalyst system was applied to the bis-silylation with 1,2-diphenyltetramethyldisilane, which may be slightly more reactive than hexamethyldisilane (entries 22 and 23).[23] Another reactive catalyst system, a combination of $Pd(dba)_2$ with a bicyclic phosphate, etpo (etpo = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane), was active for the bis-silylation of phenylacetylene with hexamethyldisilane (entry 21).[25]

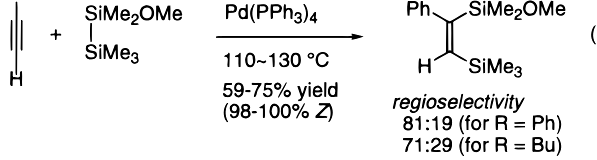


t-Oc-NC



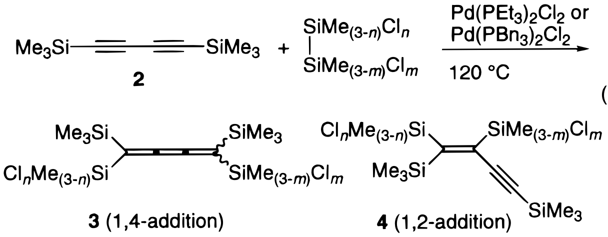
etpo

The bis-silylations with unsymmetrical disilanes were attempted to examine the regiochemical preference in the addition.[19] Unsymmetrical methoxydisilanes reacted with the terminal alkynes with the regiochemical preference for addition of the silyl group with the methoxy-substituted silyl group attached to the internal carbon atom (eq 2).



(2)

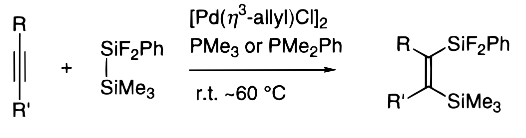
Bis-silylation of bis(trimethylsilyl)butadiyne (**2**) with chlorodisilanes proceeded in the presence of $Pd(PEt_3)_2Cl_2$ and $Pd(PBn_3)_2Cl_2$, which were more reactive than the corresponding PPh_3 and PMe_3 complexes, to give a mixture of a butatriene **3** and an enyne **4** derived from 1,4-addition and 1,2-addition of the Si−Si bond, respectively (eq 3).[26] The ratio of



(3)

3 to **4** varied with the number of the chlorine groups on the disilanes: highly chlorinated disilanes provided the 1,4-disilylation and less chlorinated disilanes prefer the 1,2-addition. For instance, $ClMe_2SiSiMe_2Cl$ afforded the 1,2-addition product **4** in 72% yield in the presence of the PEt_3 catalyst, whereas $Cl_2MeSiSiMeCl_2$ gave the 1,4-addition product **3** in 49% yield along with the 1,2-addition product **4** in 22% yield. 1,2-Difluoro- and 1,2-diisopropoxy-tetramethyldisilane afforded the corresponding 1,2-addition products selectively in 86% and 55% yield, respectively.

More recently, a highly effective catalytic system has been developed for bis-silylation with unsymmetrical fluorodisilanes (eq 4).[27] 1,1-Difluoro-1-phenyltrimethyldisilane added to a variety of alkynes in high yields in the presence of the catalyst prepared from $[Pd(\eta^3\text{-allyl})Cl]_2$ with trimethylphosphine or dimethylphenylphosphine (Table 2). Like the regioselectivity in the reactions with the methoxydisilanes, the difluorophenylsilyl group added exclusively to the



(4)

Table 2. Palladium-Catalyzed Bis-Silylation of Alkynes with $PhF_2SiSiMe_3$

	alkynes				
entry	R	R′	phosphine[d]	yield/%[e]	Z:E
1[a]	Ph	Ph	PMe_2Ph	95	>99:1
2[a]	Ph	Ph	PMe_3	95	>99:1
3[b]	Et	Et	PMe_3	76	>99:1
4[c]	Ph	Me	PMe_3	96	>99:1
5[b]	Ph	H	PMe_2Ph	94	89:11
6[a]	*n*-Hex	H	PMe_2Ph	94	87:13

[a] At room temperature. [b] At 60 °C. [c] At 40 °C. [d] 1.0–1.1 equiv to $[Pd(\eta^3\text{-allyl})Cl]_2$.

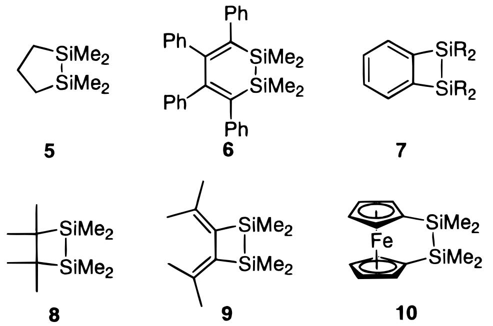
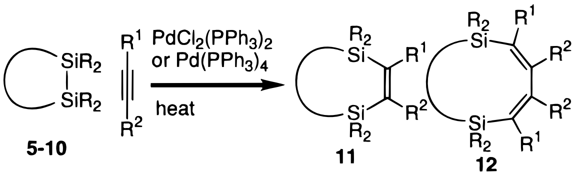


Figure 1. Cyclic disilanes used for bis-silylation of alkynes.

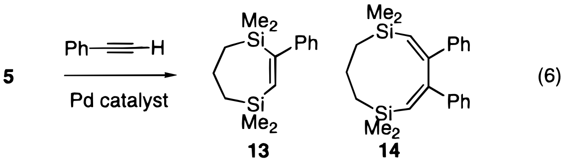
internal carbon atom of terminal alkynes (entries 5 and 6). In the case of 1-phenylpropyne, the addition reaction also proceeded regioselectively (85:15) to afford a product with the fluorinated silyl group α to the phenyl group (entry 4). It is interesting to note that the structural dissymmetry of disilane was highly desirable to accomplish the high reactivity; no bis-silylation of diphenylacetylene took place with symmetrical hexamethyldisilane and PhF_2SiSiF_2Ph, whereas an efficient bis-silylation (95% yield at room temperature) proceeded with the unsymmetrically substituted fluorinated disilanes under the identical reaction conditions (entries 1 and 2).

2. Cyclic Disilanes

A variety of cyclic disilanes **5**–**10**, listed in Figure 1, have been used for the reaction with alkynes.[22,28–32] They commonly underwent the insertion of alkynes into the Si–Si bond to give 1:1 adducts **11** in good yields in the presence of palladium–phosphine complexes (eq 5). However, the reactions of cyclic disilanes with alkynes were often accompanied by the formation of cyclic dienes **12**, which arose from successive insertion of alkynes into the silicon–silicon bond. The formation of **12** was favored by use of $PdCl_2(PhCN)_2$ as a catalyst. For instance, the reaction of **5** with phenylacetylene in the presence of $PdCl_2(PhCN)_2$ provided the double-insertion product **14** along with the single-insertion product **13**, whereas use of $PdCl_2(PPh_3)_2$ catalyst resulted in the formation of **13** exclusively in high yield (eq 6).[22] Note that the highly selective formation of the head-to-head regioisomer was observed in the bis-silylative dimerization.



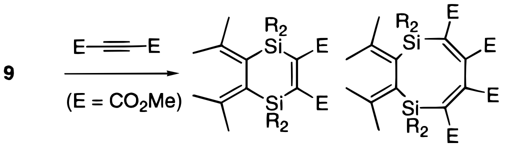
(5)



(6)

	13	14
$PdCl_2(PPh_3)_4$	85%	-
$PdCl_2(PhCN)_2$	19%	15%

The phosphine-free palladium catalyst $[PdCl_2(PhCN)_2]$ also favors the formation of the double-insertion product in the reaction of the four-membered cyclic disilane **9** (eq 7).[28,30] A platinum complex

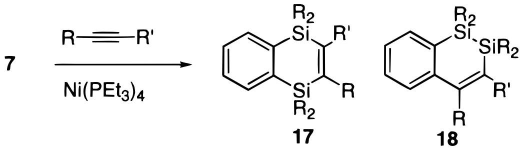


(7)

	15	16
R = Me		
$PdCl_2(PPh_3)_4$	68%	18%
$PdCl_2(PhCN)_2$	30%	47%
$Pt(CH_2CH_2)(PPh_3)_2$	71%	-
R = Et		
$PdCl_2(PPh_3)_4$	77%	-

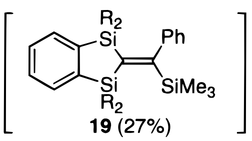
was found to catalyze the formation of the single-insertion product **15** in high yield. The substituents on the silicon atoms of **9** also affect the reaction course; a tetraethyl derivative exclusively afforded **15** in good yield without formation of **16**, which was formed in 18% yield in the reaction of the corresponding methyl derivative.

Miscellaneous reactions with disilanes should also be mentioned. The four-membered cyclic disilane **7** reacted with some internal alkynes in the presence of $Ni(PEt_3)_4$ to give two isomeric 1:1 alkyne insertion products (eq 8). In addition to the product **17** derived from the insertion into the Si–Si bond, a product **18** arising from the insertion into the C–Si bond of the four-membered ring was obtained. The formation of **18** predominates in the reaction of **7** with diphenylacetylene, while reaction with 3-hexyne gave the corresponding C–Si insertion product as the minor product. Interestingly, reaction of phenyl(trimethylsilyl)ethyne afforded a silyl-migration product **19** along with the bis-silylation product **17**.



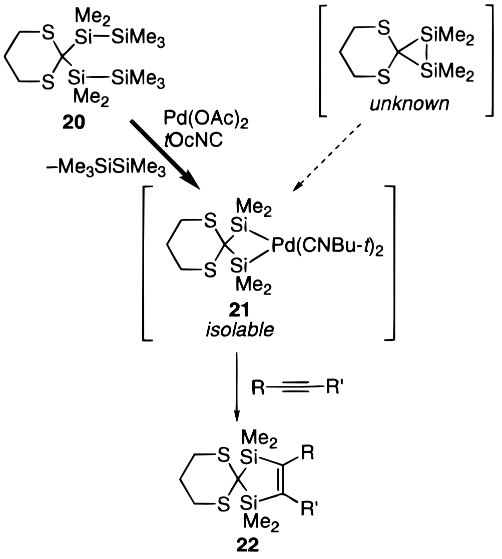
(8)

	17	18
R = R' = Et	36%	29%
R = R' = Ph	27%	72%
R = Ph, R' = $SiMe_3$	44%	-



19 (27%)

Scheme 1. Catalytic Bis-Silylation of Alkynes through Intramolecular σ-Bond Metathesis of Si−Si Bonds



The reactions of cyclic disilanes are a convenient methods for the preparation of the six- or higher-membered disilacycloalkenes. However, this approach is not applicable to the synthesis of five-membered cyclic alkenes due to the instability of three-membered cyclic disilanes. Alternatively, bis(disilanyl)dithiane **(20)** was used for the generation of the equivalent intermediates through intramolecular σ-bond metathesis of the silicon−silicon bonds (Scheme 1).[33] The facile intramolecular metathesis was catalyzed only by the palladium−isonitrile complex (2 mol%) to provide the palladacycle intermediate **21** selectively, which led to bis-silylation of alkynes. It is remarked that the intramolecular metathesis was not accompanied by direct insertion of alkyne into the Si−Si bond of **20**. The cyclization took place not only with the dithiane derivative **20**, but also with the related bis(disilanyl)methane derivatives. However, the efficiency of the intramolecular metathesis largely depended on the substitution at the methylene group connecting the two disilanyl groups. Thus, bis(disilanyl)methane afforded the corresponding five-membered ring product only in 4% yield with a mixture of regioisomers derived from the direct insertion. Substitution at the methylene tether with methyl, phenoxy, and phenylthio groups remarkably increased the yields for the cyclic products. An NMR mechanistic investigation of the intramolecular metathesis with **20** indicated that formation of the four-membered palladacycle intermediate **21** was followed by insertion of alkyne to give the bis-silylation product **22**, whose dissociation from the palladium complex may be involved as the rate-determining step.

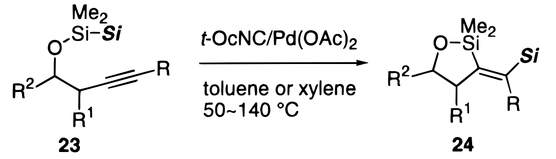
3. Intramolecular Bis-Silylation

Organodisilanes tethered to a carbon−carbon triple bond are easily accessible through the reaction of chlorodisilanes with alkynols and aminoalkynes as well as alkynyl organometallic reagents. An intramolecular version of the palladium-catalyzed bis-silylation was examined with alkyne-tethered disilanes thus prepared, aiming to gain enhanced reactivity as well as high regioselectivity.

Table 3. Intramolecular Bis-Silylation of Alkynes in the Presence of the Palladium−Isonitrile Catalyst

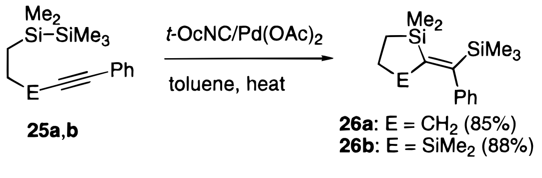
entry	R^1	R^2	R	***Si***	% yield of **24**
1	H	H	H	$SiMe_3$	**a** (91)
2	H	H	Me	$SiMe_3$	**b** (93)
3	H	H	Ph	$SiMe_3$	**c** (85)
4	H	H	$CH{=}CH_2$	$SiMe_3$	**d** (81)
5	H	H	$SiMe_3$	$SiMe_3$	**e** (81)
6	H	H	CO_2Et	$SiMe_3$	**f** (97)
7	OH	H	Bu	$SiMe_3$	**g** (96)
8	Me	H	H	$SiMe_2Ph$	**h** (56)
9	H	Et	H	$SiMe_2Ph$	**i** (96)
10	H	(*E*)-$CH{=}CHCH_3$	H	$SiMe_2Ph$	**j** (75)
11	H	Ph	Et	$SiMe_2Ph$	**k** (82)

A disilanyl ether of homopropargyl alcohol **23a** underwent the intramolecular bis-silylation in the presence of $Pd(OAc)_2$/*t*-OcNC in high yield (eq 9, Table 3; entry 1).[23,34] As expected, various internal alkynes bearing alkyl, aryl, alkenyl, and ethoxycarbonyl groups at the alkynyl carbon atoms underwent the intramolecular bis-silylation without difficulty. Of note is that the intramolecular bis-silylations always proceeded with high regioselectivity for 5-exo cyclization.



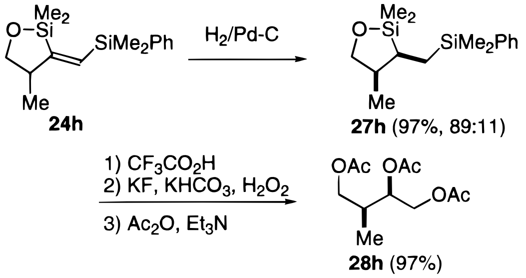
(9)

Disilanyl homopropargyl ether **23g** bearing free hydroxy group in the tether also afforded the corresponding five-membered cyclic product **24g** in good yield. Moreover, alkynes connected to the disilane by a $(CH_2)_3$ or a $-CH_2CH_2SiMe_2-$ chain (**25**) similarly underwent the intramolecular reaction in high yields (eq 10).



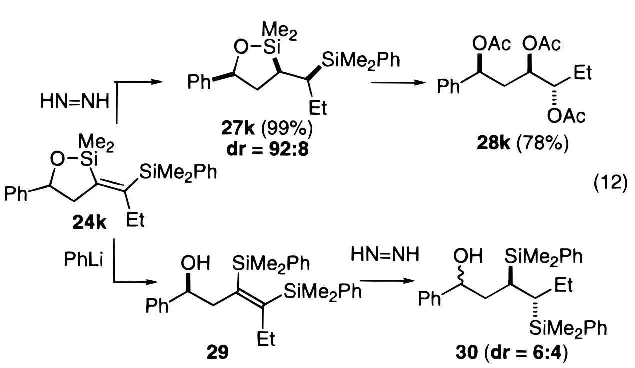
(10)

The intramolecular bis-silylation reactions of alkynes were applied to the stereoselective synthesis of 1,2,4-triols (eqs 11 and 12).[34] Thus, hydrogenation



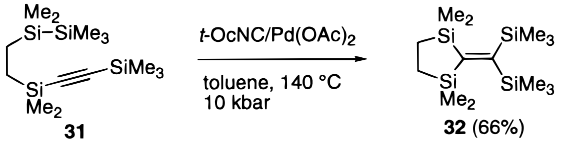
(11)

of **24h** and **24k** with H_2−Pd/C or diimide provided *cis*-**27h**,**k** diastereoselectively in high yield. Subsequent oxidative cleavage of the Si−C bonds[35] of **27h**,**k** and following acetylation furnished triacetate of stereodefined 1,2,4-triols **28h**,**k** in good yields. Note that the oxasilolane structure created by the intramolecular bis-silylation was crucial to attain high diastereoselectivity in the subsequent reaction step; the corresponding acyclic compounds **29** prepared by the reaction of **24k** with phenyllithium failed to give high diastereoselectivity (eq 12).

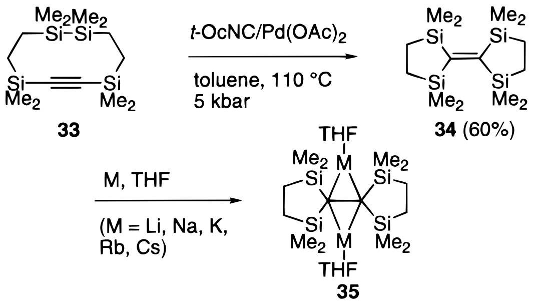


(12)

The intramolecular bis-silylation of sterically congested bis(silyl)alkynes **31** was only achieved under ultrahigh pressure (ca. 10 000 atm) in the presence of $Pd(OAc)_2$/*t*-OcNC (eq 13).[36] It is worth mentioning that the untwisted structure of the C=C bond thus formed, shown by an X-ray crystallographic analysis, was different from the twisted structure for tetrakis(trimethylsilyl)ethene. Of interest is that bicyclic tetrasilylethene **34**, whose synthesis was achieved by use of the palladium−isonitrile catalyst, gave dialkali metal dianions **35** on treatment with alkali metals (eq 14).[37,38]

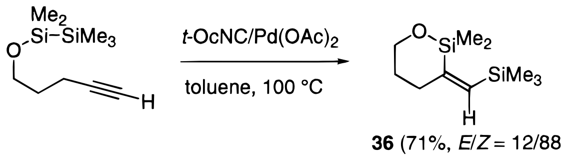


(13)



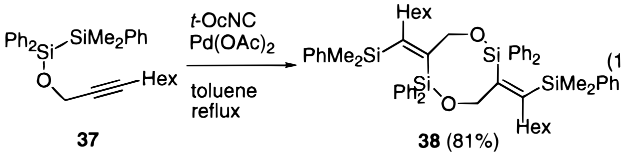
(14)

The corresponding six-membered ring formation by intramolecular bis-silylation reaction with alkynes, however, was not as successful from a synthetic viewpoint. A disilanyl ether of 4-pentyn-1-ol underwent the intramolecular bis-silylation only sluggishly in the presence of $Pd(OAc)_2$/*t*-OcNC to form an 88:12 mixture of the *Z* and *E* isomers **36** (eq 15).[34]

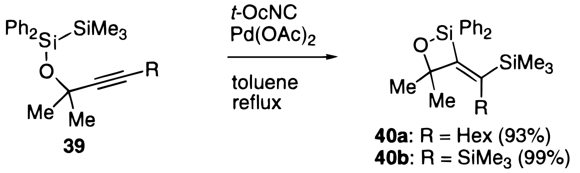


(15)

In contrast to the sluggish 6-exo cyclization of disilanyl ether of 4-pentyn-1-ol, the intramolecular bis-silylation of disilanyl ethers of propargylic alcohols proceeded smoothly with regioselective 4-exo cyclization. Subsequent dimerization of the four-membered cyclic silyl ether thus produced gave eight-membered disiladioxacyclooctane **38** in the reactions of a disilanyl ether of primary propargylic alcohol **37** (eq 16).[39] In contrast, intramolecular bis-silylation of *tert*-propargylic ethers **39** afforded the four-membered cyclic silyl ethers **40** in high yields without dimerization, which were isolable by silica gel chromatography (eq 17).[40] Formation of the four-membered cyclic silyl ethers has rarely been achieved by the intramolecular cyclization of the organosilicon compounds.[41]

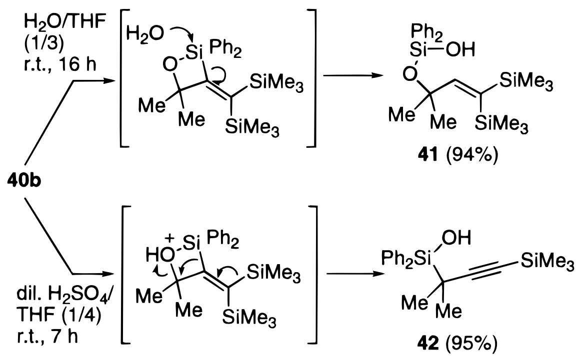


(16)



(17)

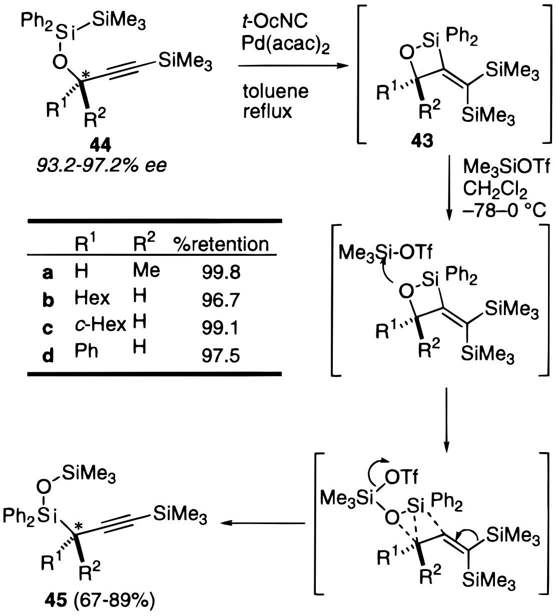
The isolated silaoxetane **40** underwent a novel solvolysis in aqueous media.[40] In the reaction of **40b** in aqueous THF at room temperature, **41** was obtained in high yield through hydrolysis of the silicon−carbon bond (eq 18). On the other hand, when the reaction was conducted in acidic aqueous THF, propargylic silane **42** was obtained in high yield without the formation of **41**. The reaction mechanism may involve intial acid-catalyzed cleavage of the C−O bond followed by 1,2-migration of the ring silicon atom with a concerted elimination of the terminal TMS group.



(18)

The mechanism of the rearrangement of **40** to **42** was investigated by using enantioenriched oxasiletanes **43** prepared from disilanyl ethers (**44**) of the corresponding enantioenriched *sec*-propargylic alco-

Scheme 2. Cationic Stereospecific Syn [1,2]-Silyl Shift of Enantioenriched 3-Alkylidene-1,2-oxasiletanes

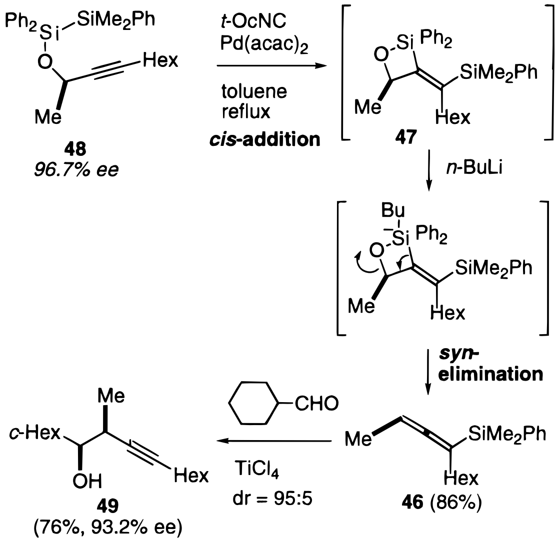


	R^1	R^2	%retention
a	H	Me	99.8
b	Hex	H	96.7
c	*c*-Hex	H	99.1
d	Ph	H	97.5

hols (Scheme 2). The intramolecular bis-silylation of the *sec*-propargylic ethers **44** proceeded also via a 4-exo cyclization to provide the corresponding oxasiletanes **43** in high yield without dimerization, although they were not stable on silica gel chromatography. Treatment of the in-situ-formed enantioenriched oxasiletanes **43** with TMSOTf induced the rearrangement reaction to afford propargylic silanes **45** in good yields. Notably, the propargylic silanes **45** were formed with nearly complete retention of configuration at the propargylic carbon atoms. For instance, reaction of an oxasiletane **43a** prepared from (*R*)-propargylic alcohol with 97.2% ee afforded (*R*)-propargylic silane **45a** of 97.0% ee. The mechanism of the migration was assumed to involve a cationic stereospecific *syn*-[1,2]-silyl shift, where the TMSOTf-catalyzed cleavage of the C—O bond and the formation of the C—Si bond occur in a concerted manner with a *syn*-periplaner orientation. Such retention of the configuration at the migration termini has never been reported for the related cationic silyl migration reactions or for the cationic alkyl migration reactions such as Wagner—Meerwein and pinacol rearrangements.

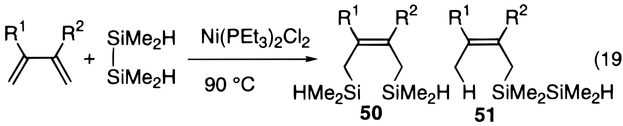
Another useful application of the oxasiletane chemistry is the stereoselective synthesis of enantioenriched allenylsilanes **46** (Scheme 3).[39] Treatment of the oxasiletane **47**, prepared from enantioenriched disilanyl propargylic ether **48** with 96.7% ee, with *n*-BuLi-induced Peterson-type elimination to give optically active allenylsilane **46** in good yield.[42,43] Although the enantiomeric excess of the allenylsilane **46** could not be determined at this stage, the ee was estimated to be higher than 93.2% by conversion to the *syn*-homopropargylic alcohol **49** by reaction with cyclohexanecarbоxaldehyde in the presence of $TiCl_4$. The absolute configuration of **49** evidenced that the electrophilic attack of the aldehyde took place on the π-face anti to the silyl group (*anti attack*) in the same manner as allylsilanes do.[44]

Scheme 3. Stereospecific Synthesis and Stereoselective Reaction of Enantioenriched Allenylsilane



B. Addition to 1,3-Dienes

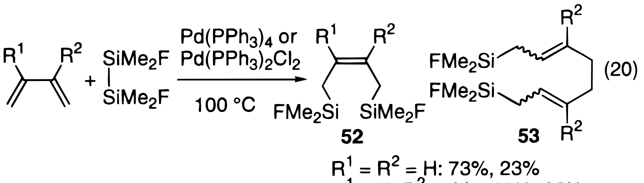
The 1,4-addition of a silicon—silicon bond across a 1,3-diene was first achieved with hydrodisilanes in the presence of a nickel—phosphine catalyst (eq 19).[1]



$R^1 = R^2 = H$: 69%, 0%
$R^1 = H, R^2 = Me$: 66%, 15%
$R^1 = R^2 = Me$: 20%, 50%

However, the bis-silylation with the hydrodisilanes to give **50** was accompanied by the formation of allylic disilane **51**, which arose from the addition of the H—Si bond across the diene.

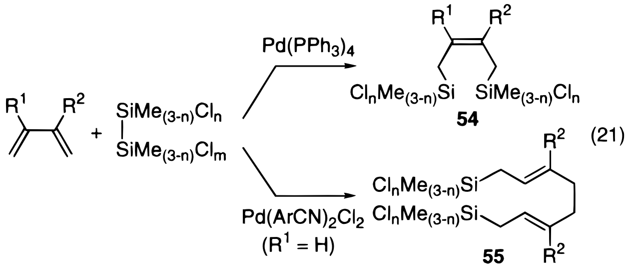
The formation of **51** could be avoided by use of chloro-, fluoro-, and methoxydisilanes in the presence of the palladium catalysts. Depending on the reaction conditions employed, the reaction of the disilanes with 1,3-dienes proceeded, giving competitively 1,4-addition products with bis-silylative products arising from successive insertion of the dienes into the Si—Si bond. 1,2-Difluorotetramethyldisilane reacted with 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene in the presence of a catalytic amount of $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$,[45] giving the corresponding 1,4-addition products **52** as major products (66—97% yield) along with varing amounts of the corresponding bis-silylative dimerization products **53** (25—0% yield) (eq 20). The 1,4-addition reaction proceeded with *cis*-stereochemistry, while the dimerization



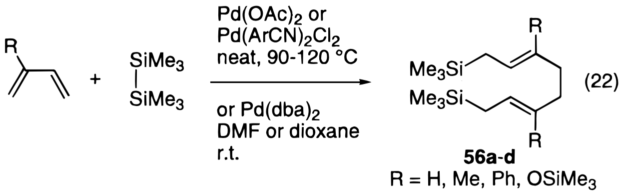
$R^1 = R^2 = H$: 73%, 23%
$R^1 = H, R^2 = Me$: 66%, 25%
$R^1 = R^2 = Me$: 97%, 0%

reactions took place with high regioselectivity but with low stereoselectivity to give mixtures of the geometric isomers of the head-to-head dimers.

Chlorodisilanes similarly added to the 1,3-dienes in a 1,4-fashion in moderate-to-good yields in the presence of $Pd(PPh_3)_4$ without formation of dimerization products (eq 21).[46] In contrast, use of phosphine-free palladium catalysts such as $Pd(OAc)_2$ and $Pd(ArCN)_2Cl_2$ resulted in the exclusive formation of the bis-silylative dimerization products **55** in good yields with high regio- and stereoselectivity.[47,48]

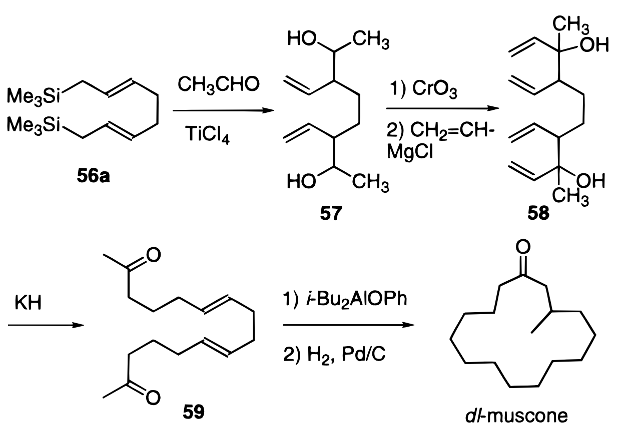


The bis-silylative dimerization proceeded even with hexamethyldisilane in the presence of the phosphine-free palladium catalysts without solvent at 90−120 °C (eq 22).[47] More recently, use of $Pd(dba)_2$ in DMF or dioxane was found to catalyze the reaction even at room temperature.[49] In addition to the ordinary dienes, 2-trimethylsiloxy-1,3-butadiene also afforded the corresponding dimerization product **56** in good yield under the modified reaction conditions.



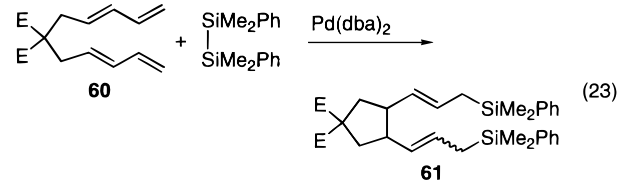
Starting from the bis-silylative dimerization of 1,3-butadiene, DL-muscone was synthesized (Scheme 4).

Scheme 4. Synthesis of dl-Muscone from (*E*,*E*)-1,8-Bis(trimethylsilyl)octa-2,6-diene

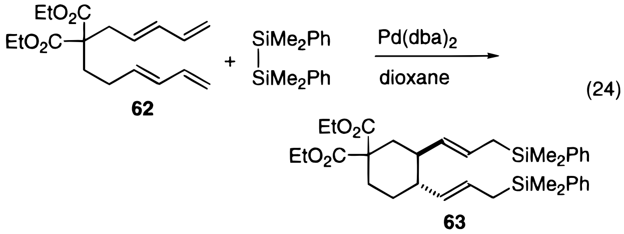


A $TiCl_4$-catalyzed reaction of **56a** with acetaldehyde gave the branched diol **57**, which was then oxidized to the corresponding diketone. Reaction of the ketone with vinyl Grignard reagent gave **58**, which was subjected to oxy-Cope rearrangement to provide the key dienedione **59** in high yield. Subsequent cyclization followed by hydrogenation of the C=C bonds afforded DL-muscone.

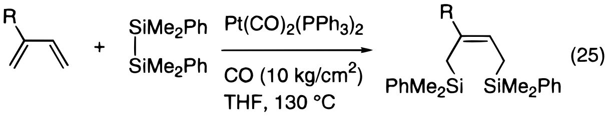
Bis-silylative cyclization of bis-diene **60** with 1,2-diphenyltetramethyldisilane proceeded in good yields in the presence of $Pd(dba)_2$ (eq 23).[50] The cyclization was applicable to five- and six-membered ring formation. The stereoselectivity of the reactions largely depended on the structure of the tethers linking the two diene moieties. A malononitrile derivative **60c** underwent the bis-silylative cyclization to give 1,2-*trans*-disubstituted cyclopentane **61c** as a single *E*,*Z* isomer in good yield. On the other hand, a malonate derivative **62** afforded the corresponding 1,2-*trans*-disubstituted cyclohexane **63** as a single *E*,*E* isomer (eq 24).



a: E = CO_2Et (82%, *trans*-(*E*,*E*): *trans*-(*E*,*Z*): *cis*-(*E*,*E*) = 25:70:5)
b: E = SO_2-*p*-Tol (98%, *trans*-(*E*,*E*): *trans*-(*E*,*Z*): *cis*-(*E*,*E*) = 36:59:5)
c: E = CN (74%, *trans*-(*E*,*Z*) only)

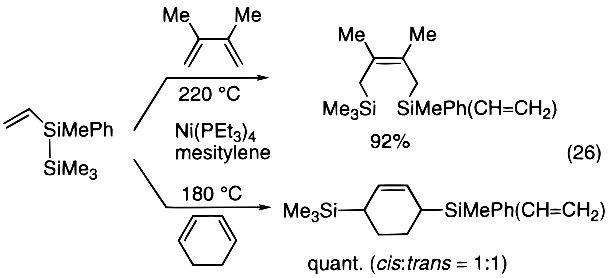


Platinum-catalyzed reaction of 1,3-dienes with aryldisilanes provided the 1,4-addition products in high yields (eq 25). Unlike the palladium-catalyzed reactions, however, E/Z ratios ranged from 0.5 to 4.6 depending on the substituents of the disilanes as well as the dienes.[51]



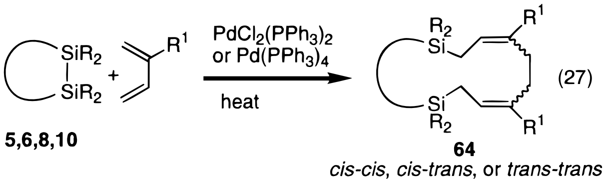
R = H (98%, *E*/*Z* = 3.0)
R = Me (91%, *E*/*Z* = 2.1)
R = Ph (51%, *E*/*Z* = 0.5)

Bis-silylation of a cyclic diene has only been achieved with use of a vinyldisilane in the presence of $Ni(PEt_3)_4$ at 180 °C to form a 1:1 mixture of the cis and trans addition products (eq 26).[52] The disilane



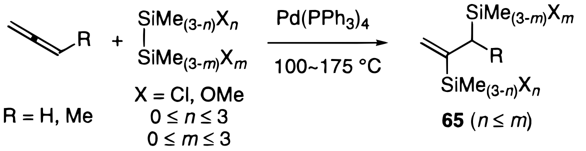
also reacted with 2,3-dimethylbutadiene at 220 °C to give the (*Z*)-adduct in high yield.

Palladium-catalyzed reactions of cyclic disilanes with 1,3-dienes were reported to give bis-silylative dimerization products **64** even in the presence of phosphine ligands, which gave monoinsertion products in the reactions of acyclic disilanes (eq 27). Two aspects of the bis-silylative dimerization reaction should be mentioned. First, isoprene underwent regioselective bis-silylative head-to-head dimerization. Second, the stereoselectivity of the C=C double bonds formed was dependent on the disilanes used, e.g., selective formation of the cis–cis products for the reaction of **5** and **6**,[47] 7:3 formation of the trans–trans and cis–trans isomer for **10**,[31] and formation of a complex stereoisomeric mixture for **8**.[28] A simple monoinsertion reaction of 2,3-dimethyl-1,3-butadiene with cyclic disilane **9** proceeded in the presence of a platinum catalyst.[29]



C. Addition to Allenes

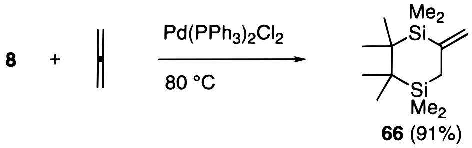
Bis-silylation of 1,2-propadiene (allene, R = H) gave 2,3-bis(organosilyl)propene **65**, which beared silyl groups both at the vinylic and allylic positions (eq 28).[53] Among the triphenylphosphine complexes of Pd, Pt, Ni, and Rh, tetrakis(triphenylphosphine)palladium was found to be most active. In addition to the disilanes bearing electron-withdrawing groups, hexamethyldisilane ($n = m = 0$) added to the carbon–carbon double bond in the presence of the palladium catalyst.

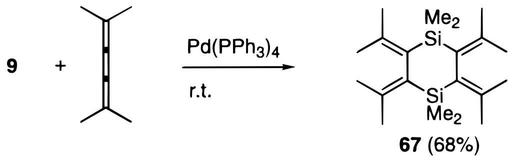


It is noteworthy that the bis-silylation of 1,2-butadiene (R = Me) proceeded with high regioselectivity; the addition of the silicon–silicon bond occurred only at the internal C=C bond to give 2,3-bis(organosilyl)-1-butene exclusively. Moreover, the bis-silylation of allenes with unsymmetrical methyldisilanes bearing methoxy or chloro groups ($n < m$) selectively afforded a single regioisomer in which the silicon atom carrying more electron-withdrawing groups was attached at the allylic position. The observed high regioselectivity has not been mechanistically clarified.

The four-membered cyclic disilane **8** reacted with allene in the presence of $Pd(PPh_3)_2Cl_2$ to give a six-membered ring product **66** in high yield (eq 29).[28]

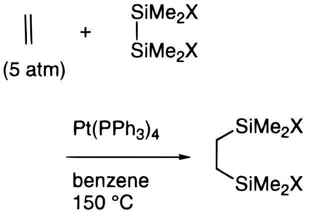
A tetrasubstituted 1,2,3-butatriene reacted with the four-membered cyclic disilane **9** in the presence of $Pd(PPh_3)_4$ to give tetrakis(alkylidene)-1,4-disilacyclohexane **67** as a 3:1 mixture of twist and chair conformers (eq 30).[30]





D. Addition to Alkenes

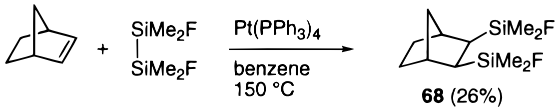
Reactions of various disilanes with ethylene were investigated in the presence of $Pt(PPh_3)_4$ (eq 31).[54]



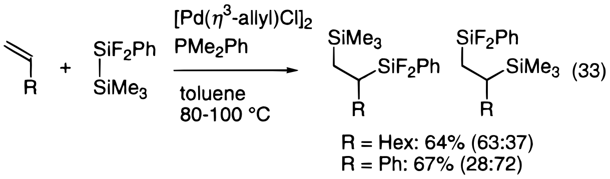
X	yield
F	95%
MeO	53%
Cl	49%
CH_3	18%
p-$CF_3C_6H_4$	16%
C_6H_5	4.3%
p-$CH_3C_6H_4$	3.8%

(31)

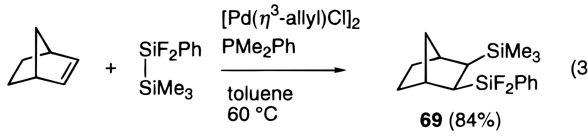
Among the disilanes examined, flurodisilane was most reactive. Methoxy- as well as chlorodisilanes gave the corresponding bis-silylation products in moderate yields. Hexamethyldisilane and 1,2-diphenyltetramethyldisilane also afforded the corresponding products in low yields. Use of $Pt(PMe_3)_4$ as a catalyst improved the yield for the reaction of 1,2-diphenyltetramethyldisilane with ethylene (33% yield). The platinum complex $Pt(PPh_3)_4$ catalyzed the bis-silylation of norbornene to give the *exo,exo*-product **68** (eq 32).



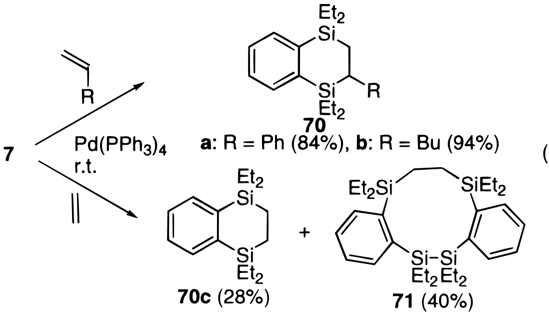
Simple alkenes such as 1-octene and styrene underwent intermolecular bis-silylation with the unsymmetrical fluorodisilane in the presence of "Pd$(PPhMe_2)_2$" (eq 33).[27] The opposite regiochemical preference was observed for the bis-silylations of octene and styrene, although the selectivities were modest. The bis-silylation of norbornene gave an *exo,exo*-2,3-bis(silyl)norbornane **69** stereoselectively in high yield (eq 34).



The four-membered cyclic disilane **7** underwent addition to of styrene and 1-hexene in high yields in the presence of $Pd(PPh_3)_4$ (eq 35). In the reaction with



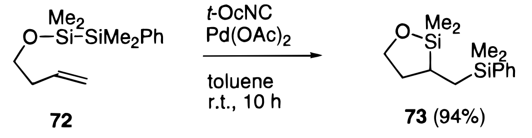
(34)



(35)

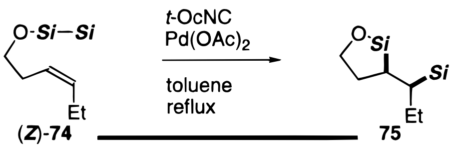
ethylene, however, a 10-membered ring product **71** was obtained as the major product along with the simple insertion product **70c**.[32]

In sharp contrast to the intermolecular additions, intramolecular bis-silylation of alkenes proceeded under very mild reaction conditions in the presence of the palladium−isonitrile catalyst (eq 36).[55] For instance, a disilanyl ether of homoallylic alcohol (**72**) afforded a five-membered ring silyl ether **73** in high yield at room temperature. The reaction was not catalyzed by $Pd(OAc)_2$, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, or $Pd_2(dba)_3CHCl_3/P(OEt)_3$ under comparable conditions.[56]



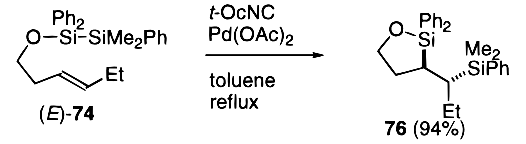
(36)

Intramolecular bis-silylation of the geminally disubstituted C=C bond also proceeded at elevated temperature (ca. 80 °C). For the bis-silylation of vicinally disubstituted (internal) alkenes, appropriate choice of the disilanyl group was essential to attain high yield (eq 37). Attempted bis-silylations with various disilanyl ethers of (*Z*)-3-hexen-1-ol (*Z*)-**74** revealed that phenyl substituents at the silicon atom proximal to the ether oxygen atom significantly increased the rate of the reaction and yield of the intramolecular bis-silylation product **75**.[57] The bis-silylation reactions of internal alkenes proceeded with the stereospecific cis-addition of the silicon−silicon bond across the carbon−carbon double bond (eq 38).



(37)

disilanyl group	yield/%
$-SiMe_2SiMe_3$	0
$-SiMe_2SiMe_2Ph$	56
$-SiMe_2SiPh_3$	66
$-SiPh_2SiMe_3$	91
$-SiPh_2SiMe_2Ph$	91

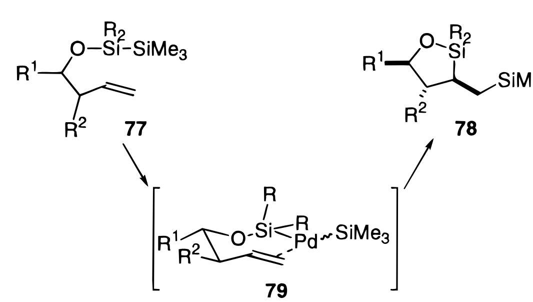


(38)

High diastereoselectivity was observed for the intramolecular bis-silylation of homoallylic alcohols with allylic and/or homoallylic substituents (Table 4). The homoallylic ethers **77** with a substituent at the allylic position underwent the intramolecular bis-silylation with high diastereoselectivity for the formation of *trans*-3,4-disubstituted oxasilolanes **78** (Table 4, entry 1). Higher stereoselectivity was observed for the intramolecular bis-silylation of disilanyl ethers with phenyl groups at the silicon proximal to the oxygen than for the disilany ethers with the corresponding methyl substitution (entry 2). Intramolecular bis-silylation of *cis*- and *trans*-internal alkenes with an allylic substituent proceeded with complete *cis*-addition of the Si−Si bond across the C=C bond, giving *trans*-3,4-disubstituted oxasilolanes (entries 3 and 4). For the cyclic alkene, the addition of the Si−Si bond to the C=C bond exclusively occurred at the π-face syn to the disilanyloxymethyl group (entry 5).

On the other hand, the disilanyl ethers bearing a substituent at the homoallylic position afforded the *cis*-3,5-disubstituted oxasilolanes stereoselectively (entries 6−10). The intramolecular bis-silylation of the geminally disubstituted C=C bond took place with higher diastereoselectivity than that for the terminal C=C bond (entries 6 and 7). The phenyl groups on the proximal silicon improved the stereoselectivity (entry 8). Unlike the substrate having an allylic substituent, internal alkenes with a homoallylic substituent underwent the cyclization with lower stereoselectivities than that for the corresponding terminal alkenes (entries 9 and 10).

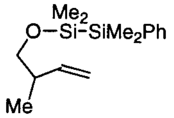
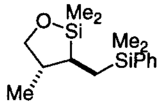
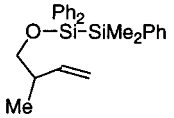
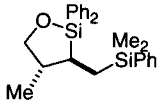
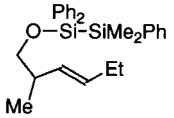
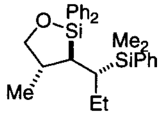
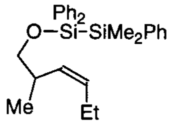
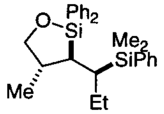
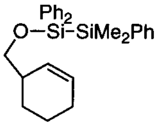
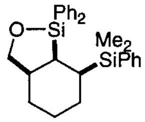
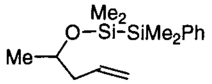
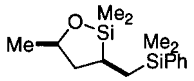
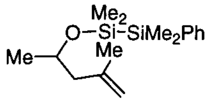
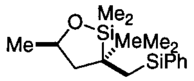
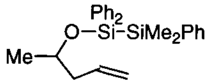
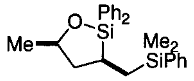
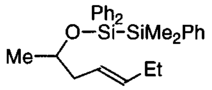
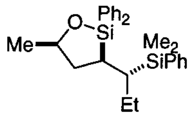
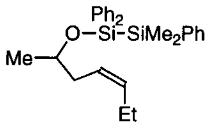
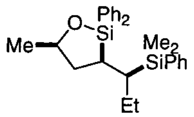
On the basis of the stereochemical outcome in the conversion of **77** to **78**, a pseudo-six-membered chair-like transition state was proposed for the stereoselective intramolecular bis-silylation of homoallylic alcohols (eq 39). The reaction may proceed through the bis(silyl)palladium intermediate **79**, in which the allylic or homoallylic substituent occupies the equatorial positions of the chair conformation, to give the *trans*-3,4- or *cis*-3,5-oxasilolanes in high selectivity.



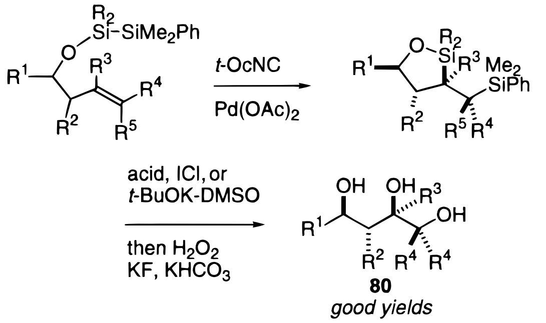
(39)

The mechanism shown in eq 39 may be in accord with the stereochemical outcome of the intramolecular bis-silylation of both diastereomers of homoallylic alcohols substituted at the allylic and homoallylic

Table 4. Intramolecular Bis-Silylation of Homoallylic Alcohols with a Substituent Either at the Allylic or Homoallylic Position

entry	disilanyl ether **77**	conditions	product **78**	yield/%	cis/trans
1		r.t.		95	7:93
2		r.t.		84	3:97
3		110 °C		97	<1:>99
4		110 °C		92	<1:>99
5		140 °C		97	100:0
6		r.t.		90	93:7
7		80		97	96:4
8		r.t.		90	96:4
9		110		99	90:10
10		110		99	86:14

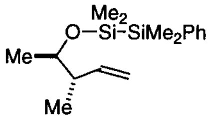
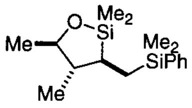
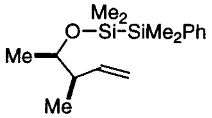
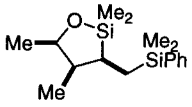
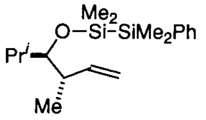
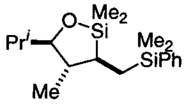
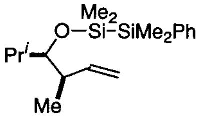
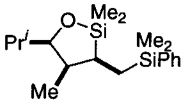
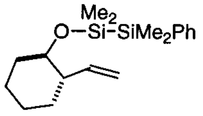
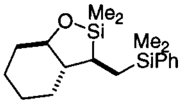
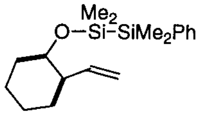
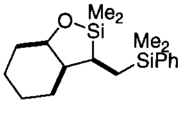
positions (Table 5).[58] Indeed, the generally high diastereoselectivities for the reactions of (R^*,S^*)-diastereomers (entries 1,3,5) can be attributed to the fact that the both substituents can occupy the equatorial positions in the chair conformation. In contrast, the other (R^*,R^*)-isomers underwent the reaction only in moderate stereoselectivities (entries 2,4,6). However, it may be noted that the homoallylic substituent played a decisive role in determining the diastereochemical preference. Thus, in any case, the reaction selectively proceeded through the bis(silyl)-palladium species in which the homoallylic substituent might occupy the equatorial position of the chair conformation.



(40)

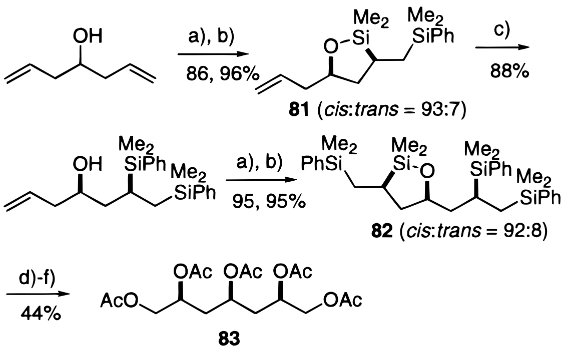
The highly stereoselective intramolecular bis-silylation has been applied to the stereoselective synthesis of polyols, including 1,2,4-triols **80**, through the oxidative cleavage of the Si−C bond of the resultant oxasilolanes under the Tamao conditions (eq 40). For this synthetic application, the terminal silicon atom of the disilanyl group must carry at least one phenyl group which is able to be substituted to an electronegative group requisite for the oxidative cleavage of the Si−C bond formed by the bis-silylation. The substitution was carried out under acidic (CF_3CO_2H), electrophilic (ICl), or nucleophilic (*t*-BuOK/DMSO) reaction conditions, which were compatible with functionalities present in the substrate.

Table 5. Intramolecular Bis-Silylation of Homoallylic Alcohols with Substituents Both at the Allylic and Homoallylic Positions

entry	disilanyl ether	product	yield/%	cis:trans
1			94	96:4
2			96	82:18
3			93	97:3
4			91	91:9
5			99	100:0
6			99	82:18

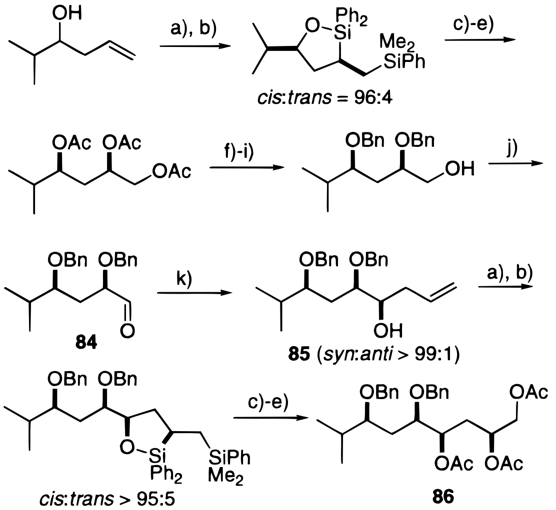
Stereodefined pentaols were successfully prepared by sequential bis-silylation.[58] Intramolecular bis-silylation of 1,6-heptadien-4-ol gave the oxasilolane **81** in high stereoselectivity (Scheme 5). After cleavage of the Si–O bond by PhLi, the disilanyl group was introduced again. The second intramolecular bis-silylation stereoselectively produced an oxasilolane **82**, from which triacetate of heptane-1,2,4,6,7-pentaol **83** was obtained. In another example, the bis-silylation was employed in combination with stereoselective elongation of the carbon chain (Scheme 6). Thus, the stereodefined triol, which was obtained via the first bis-silylation, was transformed into aldehyde **84**. The stereoselective allylation of the aldehyde with allylstannane in the presence of magnesium bromide afforded the *syn*-homoallylic alcohol **85**. Subsequent bis-silylation followed by the Si–C bond cleavage afforded the protected pentaol **86** stereoselectively.

Scheme 5. Stereoselective Synthesis of Heptane-1,2,4,6,7-pentaol[a]



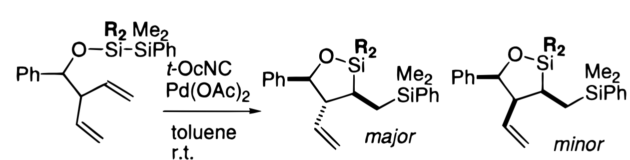
[a] Reagents: (a) $ClMe_2SiSiMe_2Ph$, Et_3N, cat. DMAP, THF; (b) *t*-OcNC, $Pd(OAc)_2$; (c) PhLi, Et_2O; (d) CF_3CO_2H; (e) H_2O_2, KF, $KHCO_3$, MeOH, THF; (f) Ac_2O, Et_3N, DMAP.

Scheme 6. Stereoselective Synthesis of 8-Methylnonane-1,2,4,5,7-pentaol[a]



[a] Reagents: (a) $ClPh_2SiSiMe_2Ph$, Et_3N, cat. DMAP, THF; (b) *t*-OcNC, $Pd(OAc)_2$; (c) KO-*t*-Bu, DMSO; (d) H_2O_2, TBAF, $KHCO_3$, THF, MeOH; (e) Ac_2O, Et_3N, cat. DMAP; (f) NaOMe, MeOH; (g) TBSCl, imidazole; (h) BuLi, THF, then BnBr, HMPA; (i) TBAF, THF; (j) DMSO, ClCOCOCl, Et_3N; (k) allyltributyltin, $MgBr_2$.

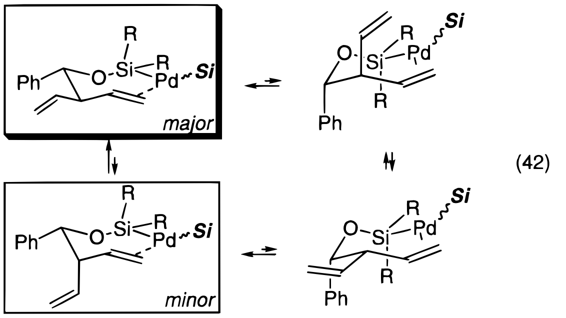
Intramolecular bis-silylation of the disilanyl ethers (**87**) of a dienol, which creates two new stereogenic centers stereoselectively, may be synthetically useful (eq 41).[59] The reaction provided two of the four possible diastereomers, whose ratios depended remarkably upon the substituent at the proximal silicon atom of the disilanyl group. Although a substituent such as an isobutyl group gave high diastereoselectivity, larger substituents such as an isopropyl group resulted in low yield.



(41)

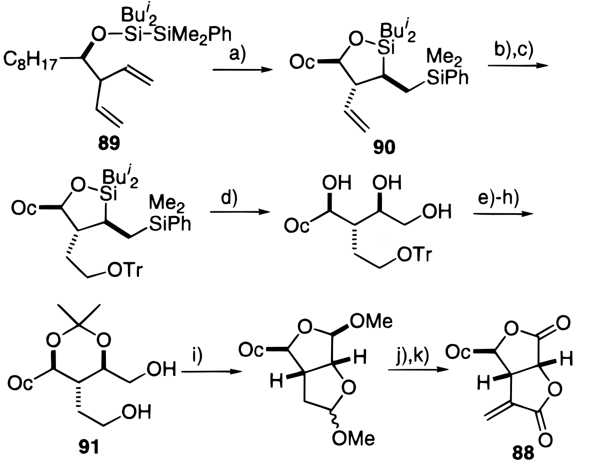
R	yield/%	ratio
Me	98	59:41
Et	82	75:25
i-Pr	27	92:8
Ph	87	83:17
i-Bu	90	88:12

The observed stereoselection was also attributed to the chairlike transition state in which both the phenyl group at the homoallylic position and the vinyl group which was not coordinated to palladium occupy the equatorial positions (eq 42).



This highly diastereoselective process was involved in the total synthesis of (−)-avenaciolide **88** (Scheme 7).[59] The intramolecular bis-silylation of enantioenriched disilanyl ether (**89**) of a dienol, which was prepared enantioselectively, proceeded with high diastereoselectivity. Use of the diisobutyl-substituted disilanyl ether was essential to attain the high stereoselectivity (90:10) and yield. The major isomer **90** can be readily separated from the minor one and used for further steps.

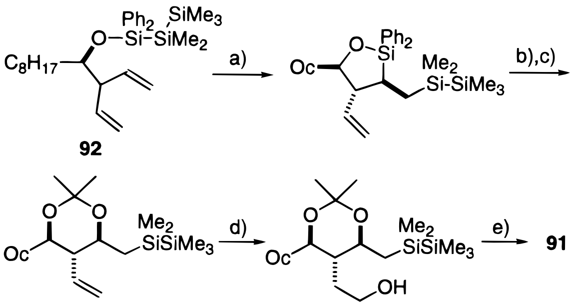
Scheme 7. Total Synthesis of (−)-Avenaciolide[a]



[a] Reagents: (a) *t*-OcNC, $Pd(OAc)_2$, toluene, room temperature, 86%; (b) catecholborane, $RhCl(PPh_3)_3$, then H_2O_2, NaOAc, 94%; (c) TrCl, DMAP, Et_3N, 86%; (d) *t*-BuOK, DMSO, then H_2O_2, TBAF, $KHCO_3$, MeOH, THF, 75%; (e) TBDPSCl, imidazole, 76%; (f) $CH_2{=}CMe(OMe)$, cat. PPTS, acetone, 93%; (g) TBAF, THF, 97%; (h) Ca, liquid NH_3, 87%; (i) DMSO, ClCOCOCl, Et_3N, then HCl, MeOH, 97%; (j) mCPBA, BF_3OEt_2, 68%; (k) $MeOCO_2MgOMe$, then formaldehyde, Et_2NH, 63%.

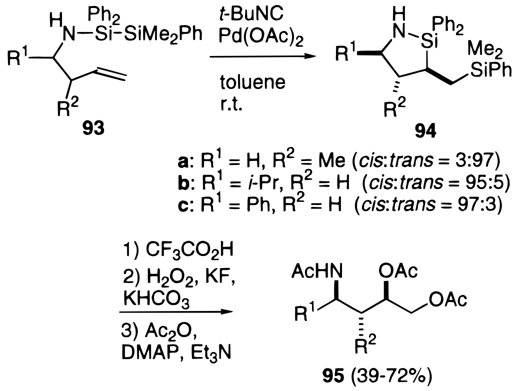
The tedious protection−deprotection sequence with the trityl and TBDMS groups was skipped by using trisilanyl ether **92**, which underwent selective 5-exo ring closure at the internal Si−Si bond in the presence of the palladium−isonitrile catalyst (Scheme 8).[60] The key synthetic intermediate **91** for (−)-avenaciolide **88** was successfully available via selective oxidation at the silyl group in the oxasilolane ring, followed by hydroboration−oxidation and subsequent oxidation at the disilanyl group, which was a synthetic equivalent to the hydroxy group that does not require the pretreatment with acid or base prior to the oxidation.[61]

Scheme 8. Formal Total Synthesis of (−)-Avenaciolide[a]



[a] Reagents: (a) *t*-OcNC, $Pd(OAc)_2$, toluene, room temperature., 86% (4:1); (b) H_2O_2, KF, $KHCO_3$, EtOH, MeOH, 75%; (c) 2-methoxypropene, CSA, 90%; (d) $HBCy_2$, then H_2O_2, NaOAc, 94%; (e) TBAF, THF, then H_2O_2, $KHCO_3$, MeOH, 99%.

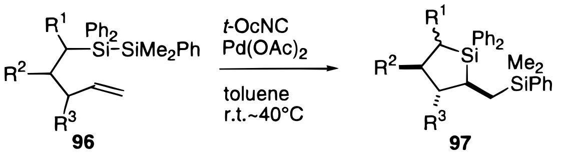
Intramolecular bis-silylation of (disilanyl)homoallylamines **93** was also reported (eq 43).[58] In the same manner as the corresponding homoallyl alcohols so far mentioned, homoallylamines underwent the stereoselective intramolecular bis-silylation with 5-exo cyclization. *N*-Disilanylhomoallylamines bearing a substituent at the allylic carbon gave *trans*-3,4-disubstituted 2-silapyrrolidines **94**, while those with a homoallylic substituent gave 3,5-*cis* products **94** with high diastereoselectivities. Oxidation of the Si−C bond of **94** provided stereodefined aminodiols **95** stereoselectively.



a: R^1 = H, R^2 = Me (*cis*:*trans* = 3:97)
b: R^1 = *i*-Pr, R^2 = H (*cis*:*trans* = 95:5)
c: R^1 = Ph, R^2 = H (*cis*:*trans* = 97:3)

(43)

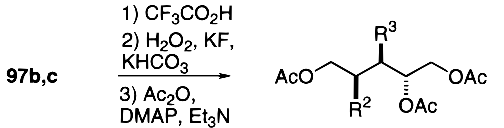
4-Pentenyldisilanes **96**, in which the Si−Si moiety was connected to the C=C bond by a three-carbon chain, successfully underwent intramolecular bis-silylation in the presence of $Pd(OAc)_2$/*t*-OcNC (eq 44).[58] For alkenes with a substituent at either an



96 → **97** (44)

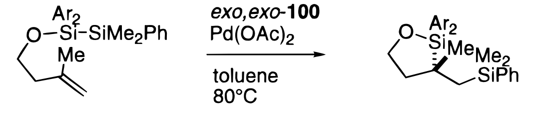
a: R^1 = Me, R^2 = R^3 = H (89%, *cis*:*trans* = 40:60)
b: R^2 = Me, R^1 = R^3 = H (92%, *cis*:*trans* = 96:4)
c: R^3 = Me, R^1 = R^2 = H (99%, *cis*:*trans* = 1:>99)

allylic (**96c**) or a homoallylic (**96b**) carbon, high diastereoselectivity was observed as expected. However, for the alkene **96a** with a substituent α to the disilanyl group, almost no selectivity was found. Oxidation of **97** afforded the corresponding 1,2,5-triols **98** with defined stereochemistry (eq 45).



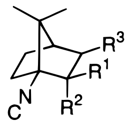
97b,c → **98** (70-88%) (45)

Enantioselective intramolecular bis-silylation with 3-methyl-3-butenyl disilanyl ether catalyzed by chiral *tert*-alkyl isonitrile–palladium complex was also reported (eq 46).[62] Chiral *tert*-alkyl isonitriles **99** and **100** with the rigid skeleton which was derived from D-camphor provide moderate enantioselectivities for the intramolecular bis-silylation. Noteworthy is that the isonitrile *exo*-**99** bearing an *exo*-siloxy group on the camphor structure provided higher enantioselectivity than *endo*-**99** bearing an *endo*-siloxy group, which showed the opposite enantioselection. The best ee was achieved by the ligand **100** with the two *exo*-siloxy groups.



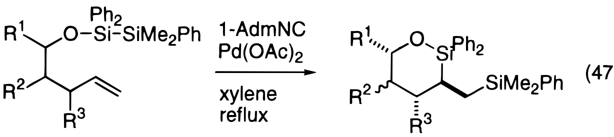
Ar = *o*-Tol

78% ee (59%) (46)



exo-**99** (R^1 = $OSiMe_3$, R^2 = R^3 = H)
endo-**99** (R^2 = $OSiMe_3$, R^1 = R^3 = H)
exo,exo-**100** (R^1 = R^3 = $OSiMe_3$, R^2 = H)

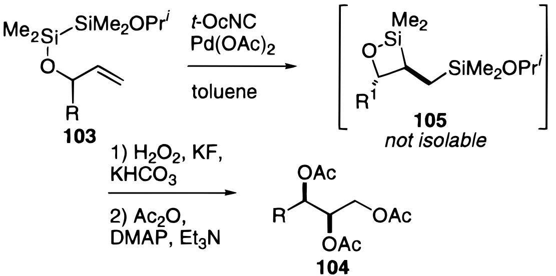
Intramolecular bis-silylation with a 6-exo cyclization mode was also possible for disilanyl ethers of bishomoallylic alcohols **101**, although a rather harsh condition was needed even for the reactions of terminal alkenes (eq 47).[63] Diastereoselective 6-exo cyclization was achieved with 4-pentenyl disilanyl ether **101d** having an allylic substituent, which gave the corresponding *trans*-1,2-disubstituted oxasilin **102d**.



101 → **102** (47)

a: R^1 = R^2 = R^3 = H (84%)
b: R^1 = Me, R^2 = R^3 = H (99%, *cis*:*trans* = 30:70)
c: R^2 = Me, R^1 = R^3 = H (92%, *cis*:*trans* = 1:1)
d: R^3 = Me, R^1 = R^2 = H (56%, *cis*:*trans* = 10:90)

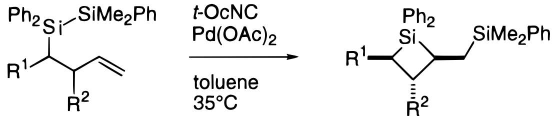
Unlike the intramolecular bis-silylation of homoallylic and bishomoallylic alcohols shown thus far, the corresponding bis-silylation reaction of allylic alcohols did not permit isolation of the cyclized product, presumably due to instability of the formed four-membered cyclic silyl ethers. For instance, no product was identified in the reactions with some disilanyl ethers of allylic alcohols **103** (eq 48). However, oxidation of the reaction mixture after the removal of the palladium catalyst afforded the corresponding 1,2,3-triols **104** in good yields stereoselectively. The result may indicate that stereoselective 4-exo cyclization takes place initially, giving the unstable four-membered cyclic silyl ether **105**, which may undergo oligomerization under the reaction conditions.



103 → [**105** *not isolable*] → **104** (48)

a: R = Me (75%, *syn*:*anti* = 80:20)
b: R = Ph (70%, *syn*:*anti* = 88:12)

In fact, 4-exo cyclization was unambiguously confirmed by the reaction of 4-disilanyl-1-butenes **106** tethered by the two-carbon chain (eq 49). From the disilanylbutenes **106** with a methyl group either at the allylic or homoallylic positions, *trans*- and *cis*-silacyclobutane **107** were stereoselectively obtained, respectively.

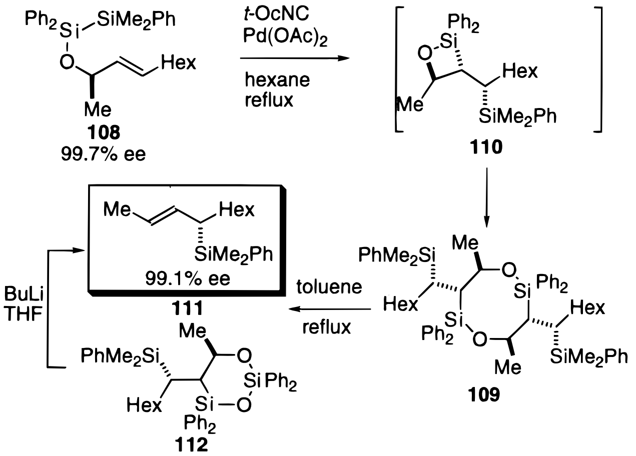


106 → **107** (49)

a: R^1 = Me, R^2 = H (91%, *cis*:*trans* = 85:15)
b: R^1 =H, R^2 =Me (76%, *cis*:*trans* = 16:84)

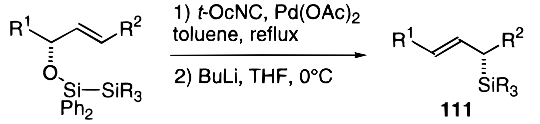
The successful application of the 4-exo cyclization was demonstrated by the stereoselective synthesis of highly enantioenriched allylsilanes.[64–66] The synthesis involved stereoselective intramolecular bis-silylation of enantioenriched allyl alcohols, which were easily available by asymmetric syntheses such as Sharpless kinetic resolution as well as Noyori enantioselective hydrogenation. For instance, the intramolecular bis-silylation of disilanyl ether (**108**) of enantiopure (*R*)–(*E*)-3-decen-1-ol (99.7% ee) in refluxing hexanes initially produced the eight-membered ring **109** with extremely high diastereoselectivity, which may be derived from cyclodimerization of the 4-exo cyclization product **110** (Scheme 9). Subsequent heating of **109** under reflux in toluene promoted a thermal disproportionation reaction to give the (*E*)-allylsilane **111** along with the six-membered ring disiladioxane **112** in high total yield

Scheme 9. Synthesis of Highly Enantioenriched Allylsilanes through the Intramolecular Bis-Silylation of Enantioenriched Allyl Alcohols

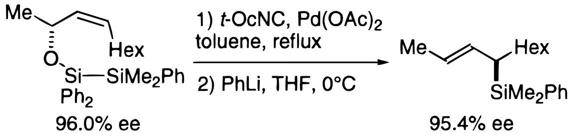


(1:1). The disiladioxane **112** was transformed into the allylsilane **111** through Peterson-type elimination by the treatment with BuLi. Note that the allylsilane **111** was produced with 99.1% enantiomeric excess and exclusive (*E*) geometry of the C=C bond.

The three steps, i.e., bis-silylation, thermal disproportionation, and Peterson elimination, can be conveniently carried out in one-pot (eq 50). Thus, the intramolecular bis-silylation in refluxing toluene followed by the treatment of the reaction mixture with BuLi in THF at 0 °C afforded the (*E*)-allylsilane **111** in high yield. As exemplified in Table 6, a variety of enantioenriched allylsilanes **111** with different silyl groups are prepared by the protocol. In all cases, the enantiomeric excesses of the starting allylic alcohols were nearly completely conserved in the enantioenriched allylsilanes. It is noted that application of the protocol to a (*Z*)-allyl alcohol produced the enantioenriched allylsilane with the absolute configuration opposite to that derived from the corresponding (*E*)-allyl alcohol (eq 51).

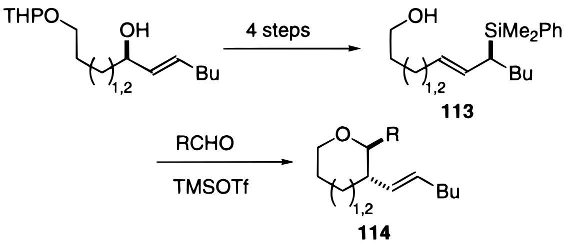


(50)



(51)

The new allylsilane synthesis features (1) applicability to a wide range of allylic alcohols, (2) formation of a highly enantioenriched product with 100% *E* geometry, and (3) manipulative simplicity. The method was applied to the synthesis of functionalized enantioenriched allylsilanes **113**, which served as new chiral synthons for the preparation of enantioenriched six- and seven-membered cyclic ethers **114** through the acid-catalyzed *acetalization–intramolecular allylsilane cyclization* protocol (eq 52).[67,68]

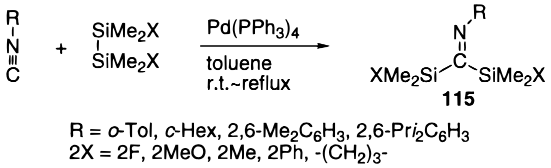


(52)

>96% stereoconservation

E. Addition to Isonitriles

Insertion of isonitriles into the silicon–silicon bond, i.e., 1,1-bis-silylation of isonitrile, was catalyzed by palladium complexes,[69] although the insertion of isonitrile into the Si–Si bond of highly strained cyclic disilanes can proceed in the absence of the catalyst (eq 53).[70] Disilanes with a fluorine substituent reacted exothermically with isonitriles in the presence of the palladium catalyst even at room temperature to give the corresponding N-substituted bis(silyl)iminomethanes **115** in moderate yields. Alkoxydisilanes, hexaalkyldisilanes, and disilacyclopentane underwent the isonitrile insertion on heating. Aryl as well as *sec*-alkyl isonitriles afforded the corresponding imines in the reactions with 1,2-diphenyltetramethyldisilane. In particular, *N*-(2,6-disubstituted phenyl) bis(silyl)iminomethanes were stable in air.[71,72] It is, however, noted that no reaction took place with *tert*-alkyl isonitriles, which served as spectator ligands in the palladium-catalyzed bis-silylation reactions described above. The insertion reaction of isonitriles was extended to oligosilanes as described later.



(53)

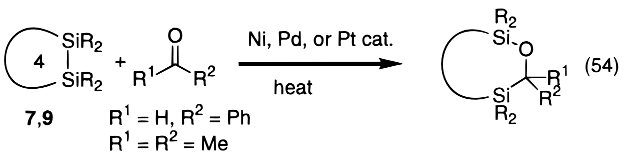
R = *o*-Tol, *c*-Hex, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$
2X = 2F, 2MeO, 2Me, 2Ph, -$(CH_2)_3$-

Table 6. Stereoselective Synthesis of Enantioenriched (*E*)-Allylsilanes 111 via Intramolecular Bis-Silylation of Allylic Alcohols

entry	% ee	R^1	R^2	R_3Si	% yield of **111**	% ee	% stereoconservation
1	99.7	Me	Hex	$PhMe_2Si$	90	99.1	99
2	>99.0	Ph	Hex	$PhMe_2Si$	99	98.7	99
3	99.8	*c*-Hex	Hex	$PhMe_2Si$	96	99.0	99
4	98.2	Me	Ph	$PhMe_2Si$	92	98.1	100
5	99.6	Me	Hex	Me_3Si	81	99.1	99
6	99.6	Me	Hex	*t*-$BuMe_2Si$	82	99.4	100
7	99.6	Me	Hex	Et_3Si	94	99.2	100
8	99.6	Me	Hex	*i*-Pr_3Si	62	98.8	99

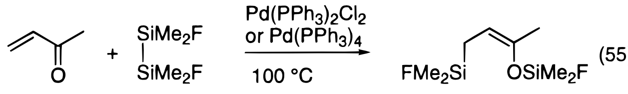
F. Addition to Carbonyl Compounds

Although an addition of the Si−Si bond of acyclic disilanes across the carbon−oxygen double bond has not been reported, four-membered cyclic disilanes **7** and **9** reacted with carbonyl compounds in the presence of nickel, palladium, and platinum catalysts (eq 54).[28,30,32]



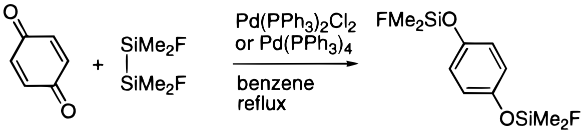
(54)

On the other hand, α,*β*-unsaturated carbonyl compounds underwent the bis-silylation in a 1,4-fashion in the presence of palladium catalysts. 1,2-Difluorotetramethyldisilane added to methyl vinyl ketone in the presence of a PPh_3 complex of palladium at 100 °C to give a silyl enol ether **116**, which possibly had a *Z* configuration, in high yield (eq 55).[45] Under similar reaction conditions, *p*-benzoquinone afforded *p*-bis(siloxy)benzene **117**, i.e., a 1,6-addition product (eq 56).



(55)

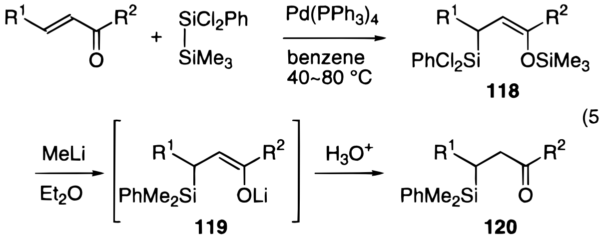
116 (81%)



(56)

117 (41%)

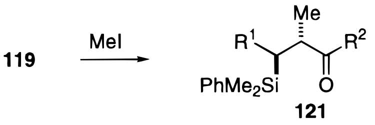
In general, 1,4-bis-silylation of enones is best carried out by use of unsymmetrical disilane, $PhCl_2SiSiMe_3$, in the presence of $Pd(PPh_3)_4$ (eq 57).[73] A variety of enones underwent the bis-silylation at 40−80 °C in a highly regioselective manner, where the trimethylsilyl group was attached to the oxygen atom and the phenyldichlorosilyl group was attached at the *β*-carbon. 2-Cyclohexenone similarly underwent the 1,4-addition of the disilane in moderate yield. In contrast to the high reactivity of $PhCl_2SiSiMe_3$ as well as $Cl_3SiSiMe_3$, no reaction took place with $MeX_2SiSiMe_3$ (X = Cl, F), $(MeO)_3SiSiMe_3$, and symmetrical disilanes $XMe_2SiSiMe_2X$ (X = F, Cl, Ph) under otherwise identical reaction conditions.



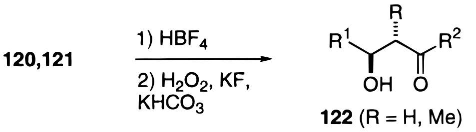
(57)

a: R^1 = Ph, R^2 = Me (78%); **b**: R^1 = Me, R^2 = Ph (68%); **c**: $R^1 = R^2$ = Ph (80%); **d**: $R^1 = R^2$ = Me (64%)

The 1,4-addition products **118** were treated with methyllithium to generate the corresponding lithium enolates **119** bearing a $PhMe_2Si$ group at the *β*-position, which were reacted with methyl iodide to provide stereoselectively anti α-methyl-*β*-silyl ketones **121** (eq 58). *β*-Hydroxy ketones **122** were synthesized in good yield by the Tamao method from the *β*-silyl ketones **120** and **121** (eq 59).



(58)

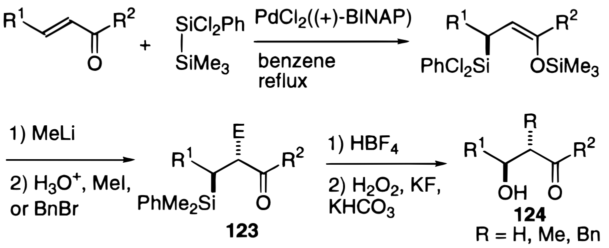


(59)

122 (R = H, Me)

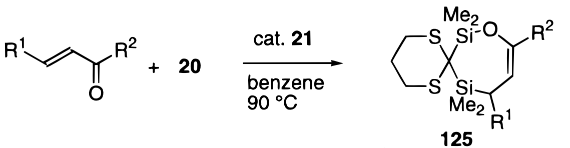
A highly enantioselective version of the 1,4-bis-silylation of enones was developed using BINAP as a ligand for the palladium catalyst (Scheme 10).[74] The enantiomeric excesses ranged from 74% to 92%, depending on the substrates used. The silyl ketones **123** were isolated in moderate-to-good yields after the treatment of the bis-silylation product with methyllithium followed by reaction with electrophiles. By oxidation of the Si−C bond, the corresponding enantioenriched *β*-hydroxy ketones **124** were obtained in good yields.

Scheme 10. Enantioselective Bis-Silylation of Conjugated Enones in the Presence of BINAP−Pd Complex



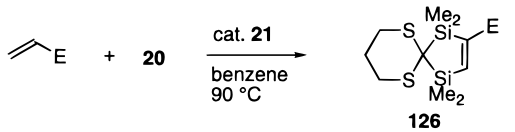
R^1	R^2	%ee
Ph	Me	78
Me	Ph	85-87
Me	*p*-Anis	92
i-Pr	Ph	86
Me	Me	74

Bis(disilanyl)dithiane **20** reacted with some conjugated enones in a 1,4-fashion to give seven-membered cyclic silyl enol ethers **125** in high yield (eq 60). In contrast, α,*β*-unsaturated esters and nitriles exclusively gave the corresponding 3,4-addition products **126** in high yield (eq 61).



(60)

125
a: R^1 = H, R^2 = Me (96%)
b: R^1 = H, R^2 = Ph (82%);
c: $R^1 = R^2$ = Me (99%)



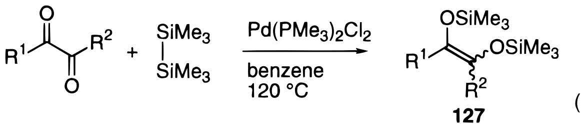
126

a: E = CO_2Me (88%)

b:E = CN (86%)

(61)

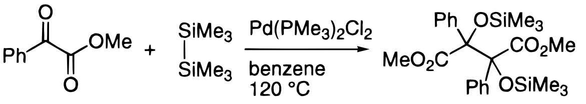
α-Diketones underwent bis-silylation with hexamethyldisilane in the presence of palladium and platinum catalysts to give 1,2-bis(siloxy)ethylene derivatives **127** in high yields (eq 62).[75] The bis-silylation reactions of benzil (**a**) were carried out in the presence of $Pd(PR_3)_2Cl_2$ complexes, in which the catalytic activity decreased in the order of PMe_3 (99%) > $P(i\text{-}Bu)_3$ (22%) > PPh_3 (1%). The $Pt_2(dba)_3$-etpo complex was also effective (86%) for the 1,4-bis-silylation of benzil. On the other hand, an α-keto ester such as methyl benzoylformate underwent bis-silylative dimerization in the presence of $Pd(PMe_3)_2Cl_2$ (eq 63).



127

(62)

a: $R^1 = R^2$ =Ph (99%, *cis*:*trans* = 85:15)
b: R^1 = Me, R^2 = Ph: (64%, *cis*:*trans* = 62:38)
c: $R^1 = R^2$ = naphthalene-1,8-diyl (65%)
d: $R^1 = R^2$ = 1,2,2-trimethylcyclopentane-1,3-diyl (42%)

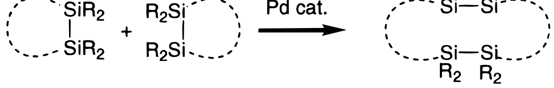


(63)

89% (*dl*:*meso* = 63:37)

G. Cyclodimerization and Oligomerization

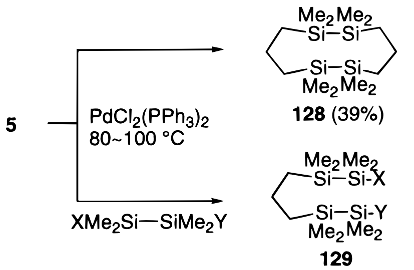
σ-Bond metathesis of the Si−Si bond is catalyzed by transition-metal complexes. While the metathesis of acyclic disilanes results in a disproportionation reaction, cyclic disilanes provide an efficient way to synthesize macrocyclic organosilicon compounds which are otherwise inasccessible (eq 64). The Si−Si σ-bond metathesis can be regarded as an addition of the Si−Si bond across the Si−Si bond.



(64)

The five-membered cyclic disilane **5** underwent cyclodimerization to afford 10-membered tetrasilacycloalkane **128** in moderate yield in the presence of $Pd(PPh_3)_2Cl_2$ (eq 65).[18] Reaction of **5** with linear disilane gave acyclic cross-metathesis product **129** under similar conditions.[76]

The four membered cyclic disilanes **7**[32] and **9**[30] also provided the corresponding dimers in the presence of the palladium catalyst. However, it is noted that the tetraethyl derivative of **7** afforded a dimer **130** formed via a mechanism involving silylene migration,[77] whereas the corresponding teramethyl derivative of **7** formed an "ordinary" dimer **131** at room temperature (eq 66).



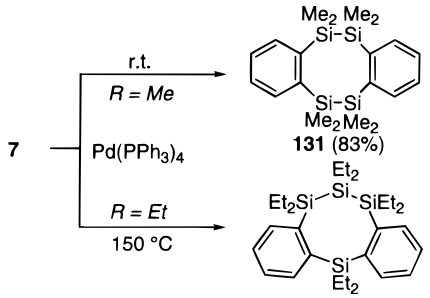
128 (39%)

129

X = Y = F (85%)

X = Me, Y = C≡CH (33%)

(65)

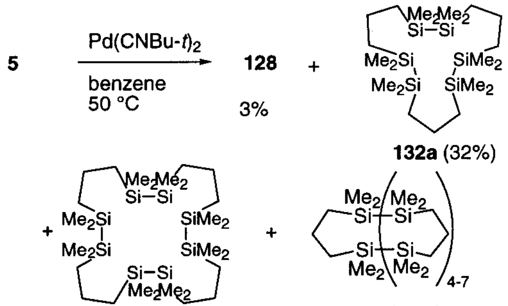


131 (83%)

130 (79%)

(66)

In sharp contrast to the cyclodimerization catalyzed by the phosphine−palladium complex, the five-membered cyclic disilane **5** underwent cyclooligomerization in the presence of bis(*tert*-butyl isonitrile)-palladium(0) (eq 67).[78] Macrocyclic oligomers **132** up to the 40-membered octamer were isolated in high total yield. The reactions with each isolated oligomer under the oligomerization conditions revealed that the cyclooligomerization proceeded with a stepwise ring enlargement in which a 1,1,5,5-tetramethyl-1,5-disilapentane-1,5-diyl moiety on the cyclic bis(silyl)-palladium(II) intermediate was transferred to the Si−Si bond of the oligomers through an oxidative addition−reductive elimination mechanism.[79]



132a (32%)

132b (34%)

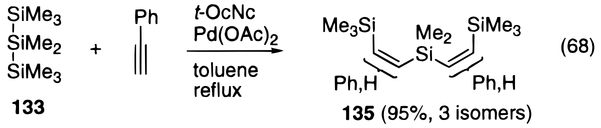
132c (24%)

(67)

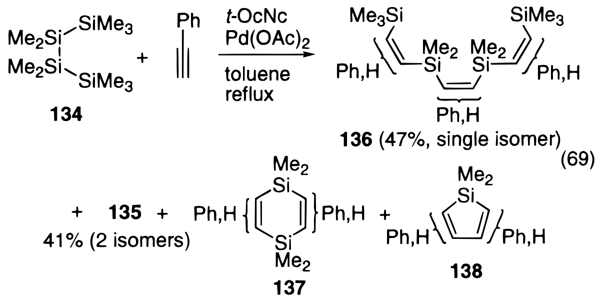
H. Polysilanes

The ability to form stable catenate makes silicon a highly distinguished element. The catenate of silicon, i.e., polysilane, attracts much attention due to its intriguing physical and chemical properties. Hence, new reactions of polysilanes catalyzed by transition-metal complexes have been studied, aiming at the development of new functional materials.

Although the Si−Si bond of polysilanes shows reactivity similar to that in disilanes, transition-metal-catalyzed reactions of polysilanes may encounter some uncontrollable difficulties. An example was given in the reactions of permethyltrisilane **133** and -tetrasilanes **134** with phenylacetylene in the presence of $Pd(OAc)_2$/*t*-OcNC (eqs 68 and 69).[23] While the trisilane **133** cleanly reacted with phenylacetylene to provide a mixture of three regioisomers of the double-insertion products **135** in high total yield, tetrasilane **134** gave the corresponding triple-insertion products **136** only in moderate yield along with **135**. Indeed, a silylene extrusion occurred during the bis-silylation reaction, and the generated silylene species reacted with phenylacetylene to give silacyclic dienes **137** and **138**. This silylene generation may be closely related to the generation of silylenes from hydrodisilanes in the presence of a platinum catalyst.[80]

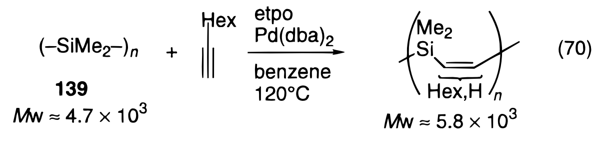


(68)



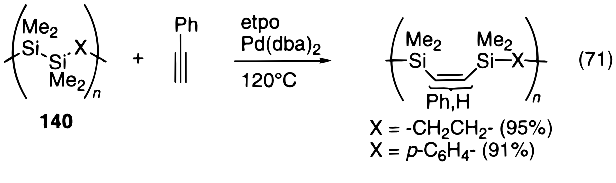
(69)

Despite the possibility of silylene extrusion, a proper choice of catalyst enabled exhaustive insertion of 1-octyne into poly(dimethylsilylene) **139** (eq 70).[25]



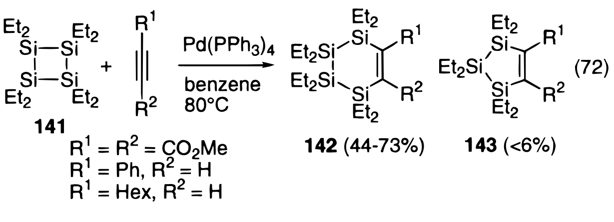
(70)

Much more promising application of the bis-silylations was demonstrated by the reaction of poly[(disilanylene)organylene]s **140**, in which each disilanyl group was linked by an ethylene or a phenylene group (eq 71).[81]

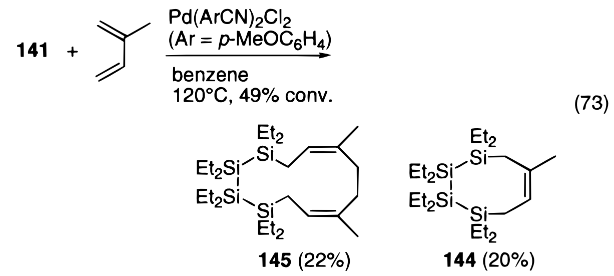


(71)

Alkyne insertion with cyclic oligosilanes has also been investigated. Octaethylcyclotetrasilane **141** gave a tetrasilacyclohexene derivative **142** in the reaction with alkyne (eq 72).[82] No further insertion took place due to the release of the ring strain during the first insertion. The reactions were accompanied by the extrusion of silylene species, resulting in the formation of the five-membered cyclic insertion products **143** and the 1,4-disilacyclohexadienes. Although an insertion of isoprene was also attempted, a mixture of a 1:1 adduct **144** and a bis-silylative dimerization product **145** was obtained in low total yield (eq 73).



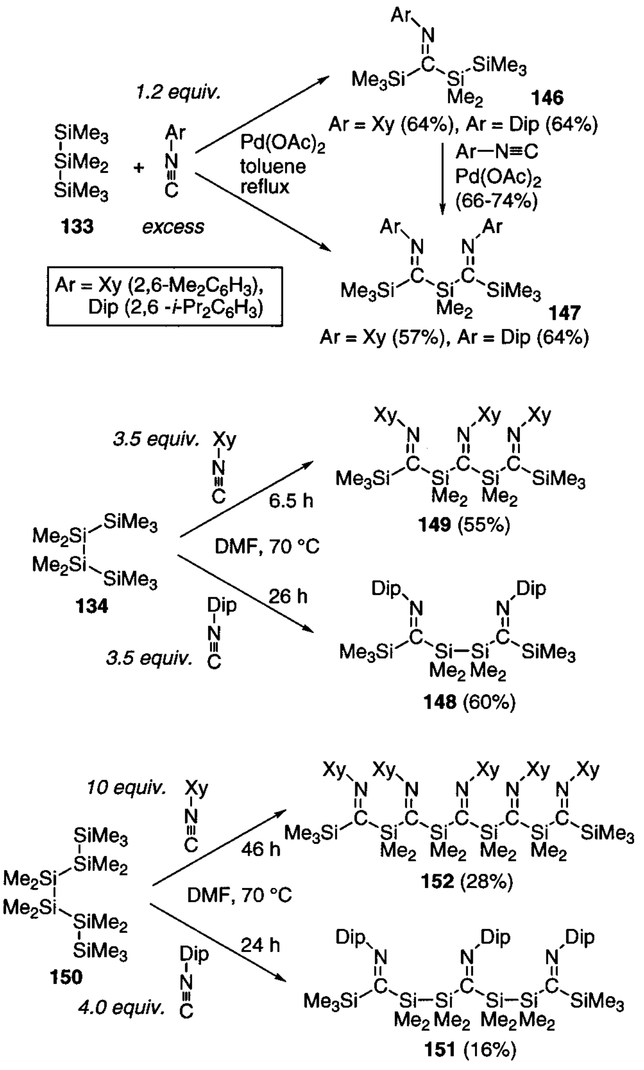
(72)



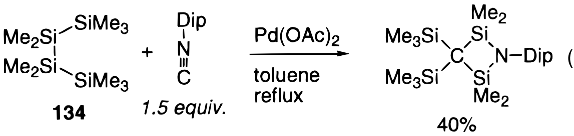
(73)

Palladium-catalyzed insertion of isonitriles into the Si–Si linkages of oligosilanes has been investigated.[71,72] A linear permethyltrisilane **133** reacted with 2,6-disubstituted aryl isocyanides in the presence of $Pd(OAc)_2$ to give imine derivatives in good yields (Scheme 11). When nearly 1 equiv of the

Scheme 11. Palladium-Catalyzed Insertion of Isonitriles into the Si–Si Linkages of Oligosilanes



isonitrile was used, monoinsertion product **146** was obtained selectively. On the other hand, use of an excess amount of the isonitrile afforded double-insertion products **147** in high yield. The isolated monoimine **146** underwent further insertion of isonitrile to give **147**. Reaction of permethyltetrasilane **134** with the isonitriles proceeded through selective insertion into the terminal Si–Si bonds. Thus, reaction with sterically bulky 2,6-diisopropylphenyl isocyanide gave the double-insertion product **148** selectively. No further insertion occurred even by use of a larger amount of isonitriles or by prolonged reaction time. In contrast, use of 2,6-xylyl isonitriles allowed isolation of the corresponding triple-insertion product **149** in good yield. Note that use of DMF (70 °C) as solvent resulted in better yields than use of toluene (110 °C) for the reactions of oligosilanes larger than tetrasilane. The alternating insertion of Dip-NC (2,6-diisopropylphenyl isocyanide) into the Si–Si bond of permethylhexasilane **150** provided triimine **151** albeit in low isolated yield. Exhaustive insertion of Xy-NC into the hexasilane **150** was also achieved, giving pentaimine **152**. Interesting skeletal rearrangement of tetrasilane was observed in the reaction with 1.5 equiv of Dip-NC, giving a four-membered cyclic product (eq 74).[83]



(74)

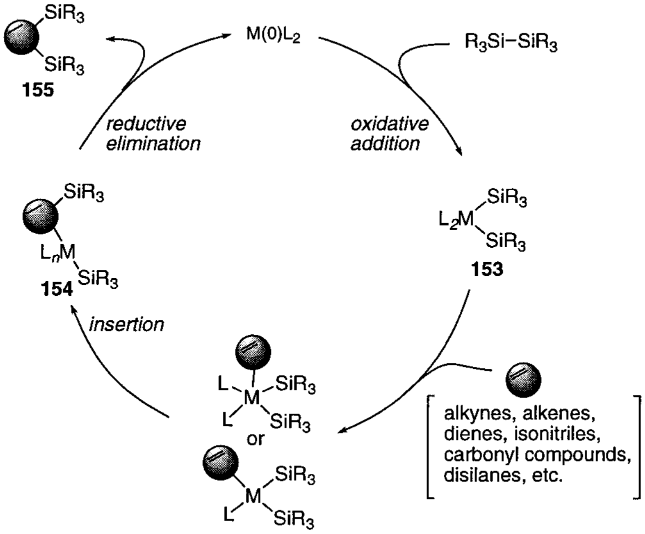
Isonitrile insertions with cyclic oligosilanes were also reported. Although the reaction of hexa-*tert*-butylcyclotrisilane did not require any catalyst,[84] octaphenylcyclotetrasilane[70] and decamethylcyclopentasilane[72] underwent the insertion of isonitrile in the presence of the palladium catalyst to give monoinsertion product selectively.

I. Mechanism

It is widely accepted that catalytic bis-silylation proceeds through oxidative addition of the Si–Si σ-bond onto the group 10 metal complexes to give bis(silyl) complexes of transition-metals **153** (Scheme 12). Subsequent insertion of alkynes into the silicon–transition-metal bond produces a (alkenyl)(silyl)metal intermediate **154**, followed by reductive elimination, leading to the bis-silylation products **155** with regeneration of the catalyst.

Successful formation and isolation of the bis(silyl)palladium,[24,27,28,85–87] -platinum,[88–90] and -nickel[91,92] complexes via oxidative addition of the Si–Si bond were reported. Use of disilanes with electron-withdrawing substituents or strained cyclic disilanes is crucial for the formation of bis(silyl)complexes of palladium, because the oxidative addition of the Si–Si bond onto palladium is reversible as unambiguously demonstrated by the bis(silyl)-exchange reaction for the cyclic bis(silyl)bis(isonitrile)palladium complexes.[24] On the other hand, use of the sterically small ligands such as isonitriles, carbon monoxide, and organodimethylphosphines is generally preferable for the high-yield formation of the bis(silyl)palladium complexes. However, the favorable formation of the bis(silyl)palladium intermediate in the oxidative addition equilibrium is not always required for the efficient catalytic bis-silylations. In fact, hexamethyldisilane, the least reactive disilane, successfully undergoes the palladium-catalyzed bis-silylation reactions, while no corresponding bis(silyl)palladium complex is detected in a stoichiometric reaction with palladium(0) complexes.

Scheme 12. General Mechanism of the Transition-Metal-Catalyzed Bis-Silylation of Unsaturated Organic Compound (indicated by the circle)[a]



[a] The change of the unsaturation is indicated by the numbers of lines in the circle.

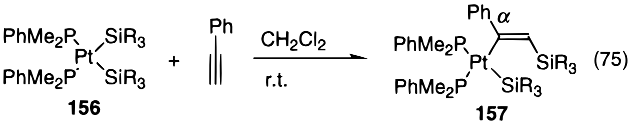
The oxidative addition step has been theoretically investigated for reactions of H_3SiSiH_3 with $Pd(PH_3)_2$ or $Pt(PH_3)_2$.[93–95] It was demonstrated that oxidative addition to the palladium complex was much less exothermic than the corresponding reaction onto the platinum complex, while the former proceeds with smaller activation energy than that for the latter. A comparison of the oxidative additions of Si–Si, Si–C, and C–C bonds onto those complexes revealed that the activation energies increased in the order of Si–Si, Si–C, and C–C and the exothermicity decreases in the same order. It was suggested that the reaction of the Si–Si bond with $Pt(PH_3)_2$, which is formally regarded as “oxidative addition”, can be considered as “rearrangement of covalent bonds”, since the electronically positive silyl groups do not significantly lower the Pt d-orbital population.[93]

The insertion process seems to be most important, since the regiochemistry as well as stereochemistry of the bis-silylations is determined at this step. However, the insertion of unsaturated carbon compounds into the Si–Pd bond of the bis(silyl)palladium complex has rarely been investigated separately from the subsequent reductive elimination, because the insertion may be involved as the rate-determining step in the palladium-catalyzed reactions and, therefore, the (silyl)(organyl)palladium **154** intermediates formed may immediately undergo the reductive elimination. It was reported that bis(organosilyl)bis(dimethylphenylphosphine)platinum complexes **156**,

Table 7. Silastannation of Terminal Alkynes in the Presence of $Pd(PPh_3)_4$ at 60−70 °C

entry	alkyne (R)	silylstannane	% yield	comment
1	Ph	Me_3Sn-$SiMe_2Bu$-*t*	89	ref 101
2	Ph	$Bu_3Sn-SiMe_3$	91	ref 101
3	Ph	$Ph_3Sn-SiMe_3$	66	ref 101
4	Bu	Me_3Sn-$SiMe_2Bu$-*t*	87	ref 101
5	Bu	$Bu_3Sn-SiMe_3$	52	ref 102
6	*i*-Pr	Me_3Sn-$SiMe_2Bu$-*t*	65	ref 101
7	*t*-Bu	Me_3Sn-$SiMe_2Bu$-*t*	<10	ref 101
8	*t*-Bu	$Bu_3Sn-SiMe_3$	46	ref 102, 20 °C/240 h
9	$Ph(CH_2)_3$	$Bu_3Sn-SiMe_3$	92	ref 107
10	$NC(CH_2)_3$	$Bu_3Sn-SiMe_3$	90	ref 101
11	Me_3Si	$Bu_3Sn-SiMe_3$	85	ref 101
12	H	$Bu_3Sn-SiMe_2Ph$	85	ref 101, $Z/E = 1/4$
13	$Cl(CH_2)_3$	$Me_3Sn-SiMe_2Bu$	87	ref 101
14	$HO(CH_2)_3$	$Bu_3Sn-SiMe_3$	87	ref 101
15	$HO(CH_2)_2$	Me_3Sn-$SiMe_2Bu-t$	77	ref 110
16	Me_2NCH_2	$Bu_3Sn-SiMe_3$	57	ref 102
17	$PhMeNCH_2$	$Bu_3Sn-SiMe_3$	64	ref 107
18	$HOCH_2$	$Me_3Sn-SiMe_3$	51	ref 102
19	$HO(CH_3)_2C$	$Me_3Sn-SiMe_3$	89	ref 102
20	$BnOCH_2$	$Bu_3Sn-SiMe_3$	68	ref 107
21	$(EtO)_2CH$	$Bu_3Sn-SiMe_3$	65	ref 103
22	EtO_2C	$Me_3Sn-SiMe_3$	75	ref 102
23	$AcO(CH_3)_2C$	$Bu_3Sn-SiMe_3$	0	ref 101
24	$BrCH_2$	$Bu_3Sn-SiMe_3$	0	ref 101

which were prepared by methods other than oxidative addition, underwent the stoichiometric insertion reaction of phenylacetylene to result in the formation of the corresponding organoplatinum complexes **157** in good yields (eq 75).[96] The insertion product was

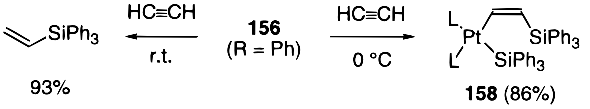


(75)

reactivity order: $SiPh_3 > SiMe_2Ph > SiMePh_2 > SiFPh_2$

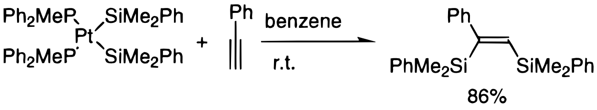
obtained as a single regioisomer with *cis*-configuration, in which the Pt−C bond was formed at the internal carbon of the alkyne. The reactivity with phenylacetylene decreased in the order of $Ph_3Si- > PhMe_2Si- > Ph_2MeSi- > Ph_2FSi$ complexes. The low reactivity of the fluorine derivative was rationalized by the strong $Ph_2FSi-Pt$ bond due to the electron-withdrawing group on the silicon. For the remaining three complexes, the difference in reactivity was proposed to be governed by the ease of dissociation of the PMe_2Ph ligand.

Ethyne also reacted with the bis(triphenylsilyl)platinum complex **156** (R = Ph) to give a (silyl)(2-silylvinyl)platinum complex **158** in good yield at 0 °C, while $CH_2{=}CHSiPh_3$ was obtained exclusively at room temperature (eq 76).



(76)

These results were in sharp contrast to those obtained previously for the reaction of *cis*-$(PhMe_2Si)_2Pt(PPh_2Me)_2$ with phenylacetylene, which only provided the bis-silylation product, *cis*-$(PhMe_2Si)PhC{=}CH(SiMe_2Ph)$, in high yield at room temperature (eq 77).[97]



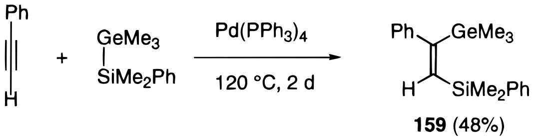
(77)

III. Silicon–Germanium and Silicon–Tin Bonds

Silylgermanes and silylstannanes usually show higher reactivity than the structurally related disilanes in the transition-metal-catalyzed addition reactions with carbon−carbon multiple bonds, although little is known about the reaction of silylgermanes.

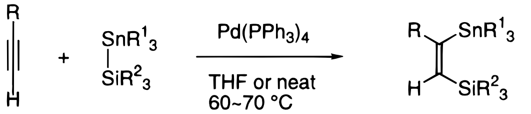
A. Addition to Alkynes

A catalytic addition of the Si−Ge bond of silylgermane across the carbon−carbon triple bond of phenylacetylene proceeded in a *cis*-fashion in the presence of a palladium catalyst (eq 78).[98] Although the yield of the adduct **159** was moderate, the addition took place with remarkably high regioselectivity, in which the silyl group was attached to the terminal carbon of the alkyne.



(78)

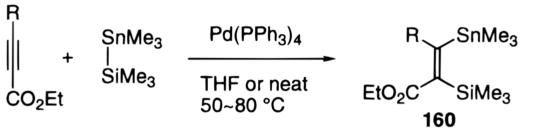
Much work has been done for the addition reactions of silylstannanes. Reactions of silylstannanes with a variety of terminal alkynes cleanly proceeded in the presence of $Pd(PPh_3)_4$ to give addition products in moderate-to-good isolated yields (eq 79).[99,100] In general, the addition reactions were carried out without solvent or in THF at 60−70 °C. The representative results are shown in Table 7.[101,102]



(79)

It is remarked that complete regio- and stereoselectivity was observed: cis-adducts with the silyl group at the terminal carbon were selectively obtained. Exceptional examples were given by the reactions of acetylene and trimethylsilylacetylene, which afforded a mixture of cis and trans alkenes (entries 11 and 12). In the former case, trans isomer predominated in a ratio of 4/1 over the cis isomer. A terminal alkyne with sterically bulky group underwent the silastannation sluggishly: a long reaction time at lower temperature was found to be better to attain reasonable yield (entries 7 and 8). Many functionalities including cyano, chloro, hydroxy, amino, and ester groups were tolerated in the reaction conditions (entries 13−17 and 22). In contrast to the success of the silastannation of propargylic alcohols, ether, and acetal[103] (entries 18−21), alkynes bearing acetoxy as well as bromine groups at the propargylic position completely failed to give the corresponding adducts (entries 23 and 24). Stannation of unreactive alkynes with $Me_3SiSnMe_3$ led to a disproportionation reaction to form $Me_3SnSnMe_3$ and $Me_3SiSiMe_3$. The former may react with alkynes to give byproducts arising from bis-stannylation. This disproportionation could be avoided by use of the higher alkyl homologues of the silylstannanes.

Internal alkynes with an ester group at the triple bond reacted with hexamethylsilylstannane (eq 80).[102]

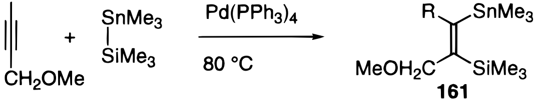


(80)

160
a: R = CO_2Et (17%)
b: R = Ph (84%)
c: R = Bu (E/Z = 1/1)

In the reaction of ethyl phenylpropiolate with permethylsilylstannane, only the *Z* isomer **160b** was formed in high yield. Use of the corresponding phenyl ester instead of the ethyl ester, however, did not give the corresponding adduct.

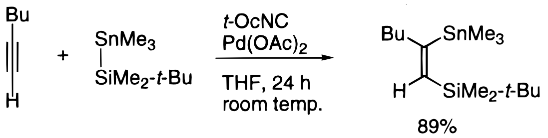
The presence of a propargylic ether functionality enhanced the reactivity of the internal triple bonds toward the silastannation (eq 81).[102] Thus, 1,4-dimethoxy-2-butyne reacted with the silylstannane at 80 °C to produce (*Z*)-alkene **161a** in 48% isolated yield. Replacement of one of the two ether groups by an alkyl group decreased the reactivity greatly: under essentially the same reaction conditions, only 12% yield of a mixture of the *E* and *Z* isomers **161b** was obtained.



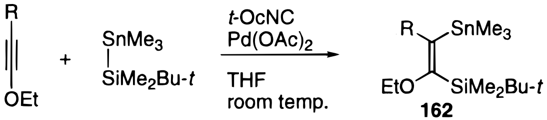
(81)

161
a: R =CH_2OMe (48%)
b: R = Me (12%, E + Z)

Remarkable improvement of catalytic activity was realized by using the palladium−isonitrile catalyst system, which was highly effective for the bis-silylations as mentioned above. The catalyst system could complete the reaction of 1-hexyne with $Me_3Sn-SiMe_2-t\text{-}Bu$ within 24 h at room temperature, while the conventional $Pd(PPh_3)_4$ catalyst required heating at 70 °C for completion of the reaction (eq 82).[104] The palladium−isonitrile catalyst was best applied to the silastannation of 1-alkoxyalkynes, which readily decompose on heating due to their thermal instabitity (eq 83). Thus, ethoxyacetylene underwent the silastannation reaction at room temperature to give a single product **162a** in which the silyl group was attached α to the alkoxy substituent in high yield. The corresponding reaction using $Pd(PPh_3)_4$ resulted in the formation of polymeric material due to the decomposition of the alkyne. Similarly, 1-ethoxy-1-propyne provided the silastannation product **162b** with high regio- and stereoselectivity, while the corresponding reaction with $Pd(PPh_3)_4$ afforded a regioisomeric mixture (35:65) at higher temperature.



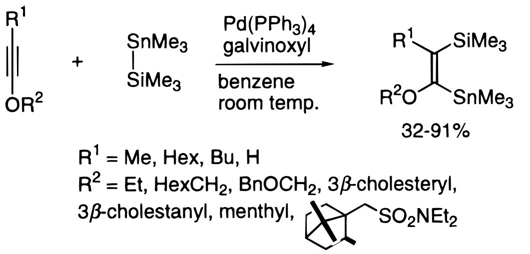
(82)



(83)

162
a: R = H (92%)
b: R = Me (99%)

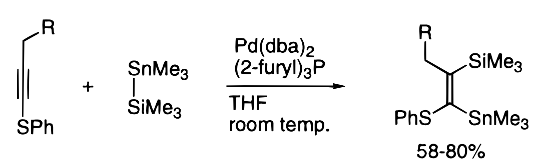
The silastannation of alkoxyacetylenes has been investigated in detail.[105] A variety of 1-alkoxy-1-alkynes underwent the regioselective silastannation with $Me_3Si-SnMe_3$ in the presence of $Pd(PPh_3)_4$ with galvinoxyl at room temperature, in which the stannyl group was attached at the vinylic carbon α to the alkoxy substituent (eq 84). Regioselectivity opposite to the silastannation of the ethoxyacetylene with the palladium−isonitrile catalyst was observed for the reactions. The high regioselectivity was found to be insensitive to the steric demand of the alkoxy moieties.



(84)

R^1 = Me, Hex, Bu, H
R^2 = Et, $HexCH_2$, $BnOCH_2$, 3*β*-cholesteryl, 3*β*-cholestanyl, menthyl,

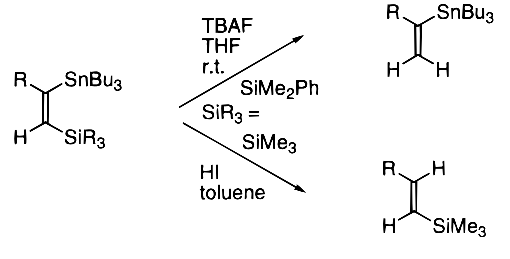
Silastannation of 1-phenylthioalkynes catalyzed by palladium−phosphine complex proceeded with high regioselectivity, which is similar to that observed in the silastannation of the alkoxyalkynes (eq 85).[105] Interestingly, a combination of $Pd(dba)_2$ with tri(2-furyl)phosphine was found to give better yields than the conventional triphenylphosphine complex.



(85)

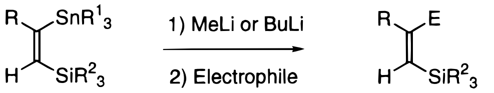
R = OTHP, OH, $(CH_2)_2OH$, OMe, *n*-Pr, *p*-$PhC_6H_4CO_2$

Selective protodesilylation and protodestannylation of the silastannation products were achieved by treatment either with tetrabutylammonium fluoride or hydriodic acid (eq 86). The TBAF treatment induced the cleavage of the Si–C bond to lead to the formation of 2-stannylalkenes, although the reaction was limited to the $PhMe_2Si$ derivatives.[106] On the other hand, treatment with hydriodic acid afforded the corresponding (*E*)-1-silylalkenes in high yields through cleavage of the Sn–C bond.[107]



(86)

Some synthetic applications of the silastannation products have been examined. Various β-silylvinyllithiums were generated by treatment of the stannanes with alkyllithium reagents at low temperature (eq 87).[101,102] Subsequent trapping with electrophiles afforded a variety of vinylsilanes. Although the vinyllithium reagents with a phenyl group α to the lithium were configurationally unstable, resulting in the formation of *trans*-vinylsilanes, those bearing only alkyl groups were successfully converted to vinylsilanes with complete retention of the geometry of the C=C bonds.

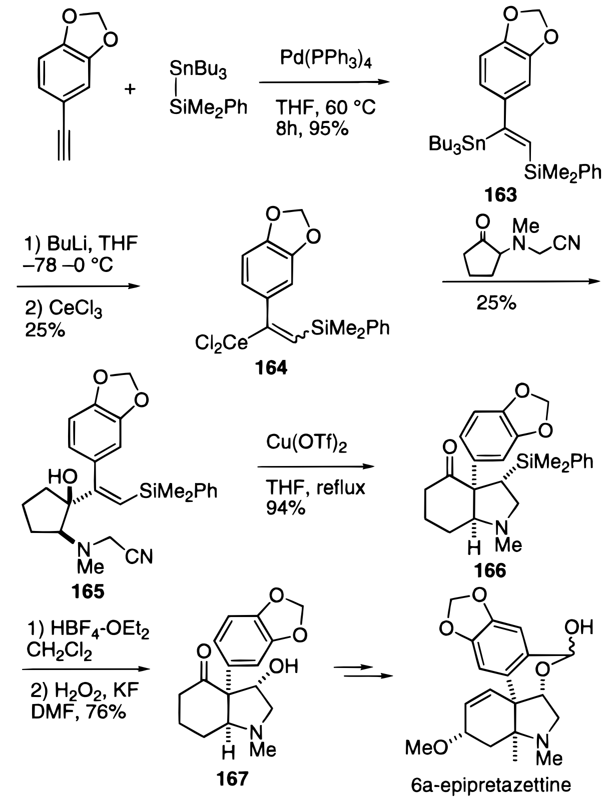


(87)

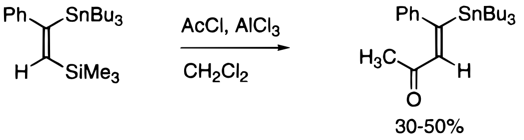
E = H, Me, CHO, HOCH(Et)
$SiMe_3$, $GeMe_3$, $PbMe_3$ etc.

Silastannation of (3,4-methylenedioxy)phenylacetylene was involved in the formal total synthesis of 6a-epipretazettine via the Sn–Li transmetalation strategy with the β-silylalkenylstannane **163** formed by the silastannation (Scheme 13).[108] Further transmetalation to Ce after *E*–*Z* equilibration at 0 °C provided a β-silylalkenylcerium **164** as an *E*,*Z* mixture. Only the (*E*)-cerium reagent was reacted with aminocyclopentanone to give **165** as a single stereoisomer. Treatment of **165** with copper(II) triflate in refluxing THF induced a rearrangement reaction to give the silylhydroindolone **166** in 94% yield. Final oxidative cleavage of the Si–C bond afforded a hydroxylated hydroindolone **167**, which is a key intermediate of 6a-epipretazettine.

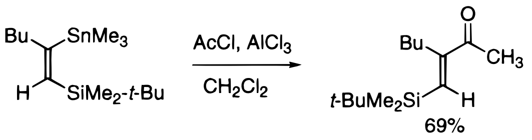
Scheme 13. Stereoselective Formal Total Synthesis of 6a-Epipretazettine



Lewis-acid-catalyzed reactions of the silastannation adducts with acyl chlorides took two reaction courses.[101] Acetylation of a silastannylation adduct derived from phenylacetylene predominantly afforded a trans α,β-unsaturated ketone where the silyl group was replaced (eq 88), while the acetylation of the 1-hexyne-derived adduct underwent replacement of the stannyl group with the acyl group (eq 89). The preferencial replacement of the silyl group in the former case may be explained by the cation-stabilizing effect of the phenyl group.

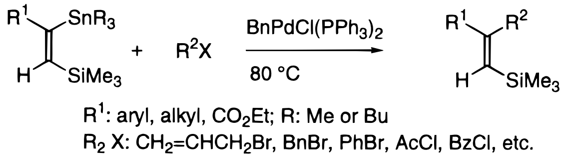


(88)



(89)

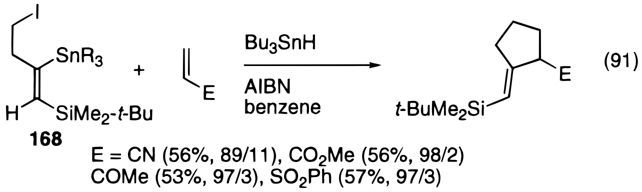
Various alkenylsilanes have been synthesized from the silastannation adducts by Migita–Stille coupling (eq 90).[109] Allyl bromide, benzyl bromide, bromobenzene, and some acyl chlorides were successfully coupled with the silastannation adducts in the presence of benzylchlorobis(triphenylphosphine)palladium.[102]



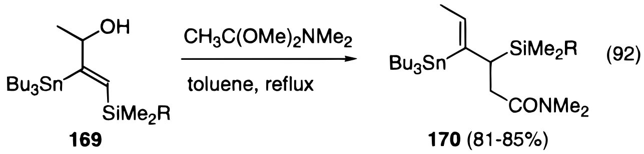
(90)

R^1: aryl, alkyl, CO_2Et; R: Me or Bu
R_2 X: CH_2=$CHCH_2Br$, BnBr, PhBr, AcCl, BzCl, etc.

1-Silyl-2-stannyl-4-iodo-1-butene **168** prepared via silastannation of homopropargylic alcohol served as an effective C3 component in cyclization with activated alkenes in the presence of Bu_3SnH/AIBN (eq 91).[110] The five-membered ring formation may proceed through stepwise radical reactions involving the elimination of a stannyl radical at the final step.

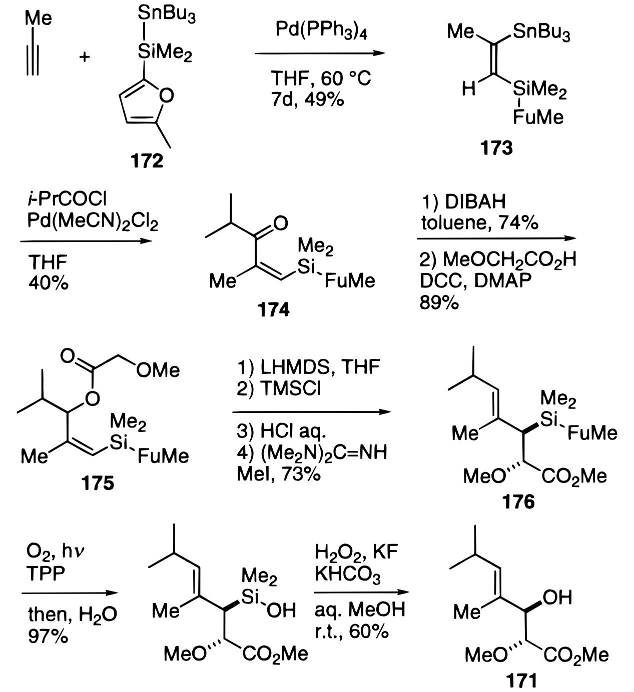


Claisen rearrangement of (*Z*)-4-stannyl-3-silyl-3-buten-2-ol **169** with *N*,*N*-dimethylacetamide dimethyl acetal was carried out to form β-silyl-γ-stannyl-γ,δ-unsaturated amide **170** in good yield (eq 92).[111]

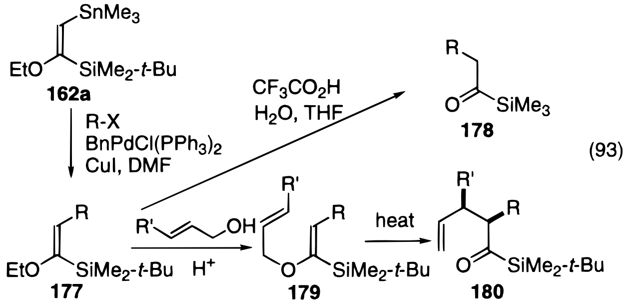


A model (**171**) for the C26–C32 fragment of rapamycin was synthesized by a sequence of reactions including silastannation and subsequent cross-coupling as key steps (Scheme 14).[112] For the oxidative cleavage of the Si–C bond at the final step, the silylstannane **172** with a 5-methylfur-2-yl group on the silicon was employed for the synthesis. The silastannation of propyne afforded the vinylstannane **173** in moderate yield, which was reacted with isobutyryl chloride to give β-silyl-α,β-unsaturated ketone **174**. Reduction of the carbonyl group followed by acylation with methoxyacetic acid gave the methoxyacetate **175**, whose silyl enol ether underwent Ireland–Claisen rearrangement to provide the α-methoxy-β-silyl ester **176** stereoselectively. The final oxidation of the Si–C bond was effected by photooxidation of the furan ring followed by treatment with hydrogen peroxide in the presence of fluorine source.

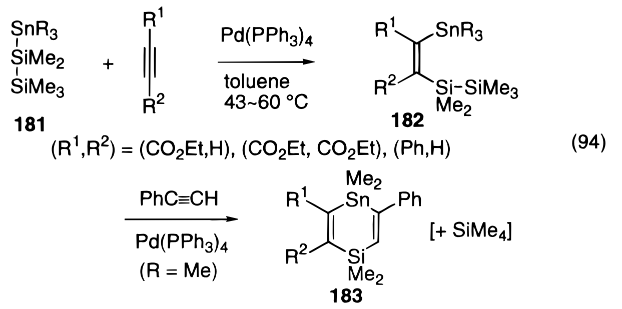
Scheme 14. Stereoselective Synthesis of a Model of the C26–C32 Fragment of Rapamycin via Palladium-Catalyzed Silastannation



A convenient method for the preparation of acylsilanes was developed on the basis of the alkoxyacetylene-derived silastannation adducts **162a** (eq 93). The α-ethoxyalkenylsilanes **177** were obtained by the cross-coupling reaction of **162a** with organic halides in the presence of $BnPdCl(PPh_3)_2$ and CuI.[113] Subsequent hydrolysis in the presence of acid afforded the corresponding acylsilanes **178** in good yields. Another synthetic route to acylsilanes was established via Claisen rearrangement. Ether exchange of the α-ethoxyalkenylsilanes with allyl alcohol afforded allyl vinyl ethers **179**, whose Claisen rearrangement gave γ,δ-unsaturated acylsilanes **180**. Use of *trans*-crotyl alcohol allowed for the preparation of stereodefined α,β-disubstituted γ,δ-unsaturated acylsilanes.

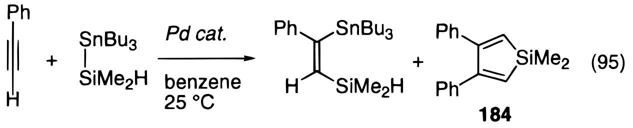


Reaction of disilanylstannane **181**, which has both Si–Si and Si–Sn bonds, with alkynes was also investigated in the presence of $Pd(PPh_3)_4$ (eq 94).[114]



The insertion of the alkyne took place exclusively at the Si–Sn bond in a regioselective fashion to produce β-disilanylalkenylstannanes in moderate isolated yields. Note that the disilanylalkenylstannanes **182** underwent further reaction with phenylacetylene to give 1-sila-4-stannacyclohexa-2,5-dienes **183** in high yields regioselectively.

Silylstannanes with a hydride on the silicon atom reacted with alkynes in the presence of palladium catalysts (eq 95).[115] However, in the reaction with $Pd(PPh_3)_4$, the formation of the silole derivatives **184** predominated, probably through the generation of a silylene–palladium intermediate.

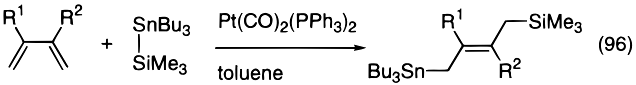


184

with $Pd(PPh_3)_4$: 3% and 58%
with $PdCl_2(PhCN)_2 + 2P(OEt)_3$: 49% and 13%

B. Addtion to 1,3-Dienes

1,4-Silastannation of 1,3-dienes was achieved by use of platinum catalysts.[116] Reaction of (trimethylsilyl)tributylstannane with 1,3-butadiene in the presence of $Pt(CO)_2(PPh_3)_2$ afforded *trans*-1-stannyl-4-silyl-2-butene **185a** as a single isomer in high yield (eq 96). However, other platinum catalysts such as $Pt(PPh_3)_4$ (trace), $Pt(C_2H_4)(PPh_3)_2$ (13%), $PtCl_2(PPh_3)_2$ (trace), $Pt(dba)_2$ (none), and $Pt(dba)_2 + 2PPh_3$ (12%) were not effective for 1,4-silastannation. The corresponding palladium complexes such as $Pd(PPh_3)_4$ and $Pd(CO)(PPh_3)_2$ failed to catalyze the reaction (<2%). 2,3-Dimethyl-1,3-butadiene was also reactive in the presence of $Pt(CO)_2(PPh_3)_2$ to give the corresponding 1,4-adduct **185b** in good yield. It is noted that 2-substituted 1,3-dienes afforded the corresponding *trans*-1,4-silastannation adducts **185c** and **185d** with excellent regioselectivity, in which the stannyl group was attached to the 1-position. Use of sterically more demanding silylstannanes such as $Me_3Sn{-}SiMe_2$-*t*-Bu (26%), $Me_3Sn{-}SiMe_2Ph$ (35%), and $Bu_3Sn{-}SiMe_2$-*t*-Bu (0%) with 1,3-butadiene resulted in much lower yields for the 1,4-adducts.

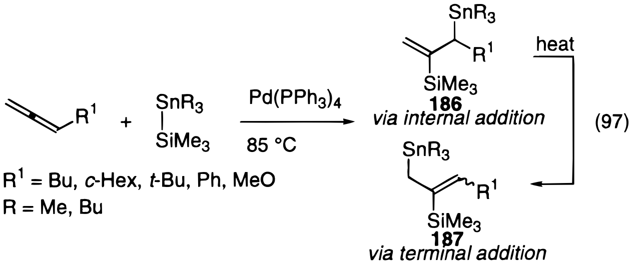


185

a: $R^1 = R^2 = H$ (93%), **b**: $R^1 = R^2 = Me$ (70%);
c: $R^1 = Me$, $R^2 = H$ (84%), **d**; $R^1 = Ph$, $R^2 = H$ (85%)

C. Addition to Allenes

Reaction of the silylstannanes with allenes proceeded in the presence of a palladium catalyst (eq 97).[99,117] An interesting regiochemical preference was observed in the reaction of monosubstituted allenes, where the silyl group was exclusively attached to the central sp-carbon of the allene. Furthermore, the position to which the stannyl group was attached depends remarkably upon the substituents on the allene as well as the silylstannane. Larger alkyl substituent on the allene increased the formation of internal addition product **186**, while a larger substituent on the tin atom of the silylstannanes increased the formation of the terminal addition product **187** (*E* and/or *Z*). Phenylallene and methoxyallene produced the terminal addition products **187** selectively. Isomerization of **186** to the thermodynamically more stable **187** occurred on heating.

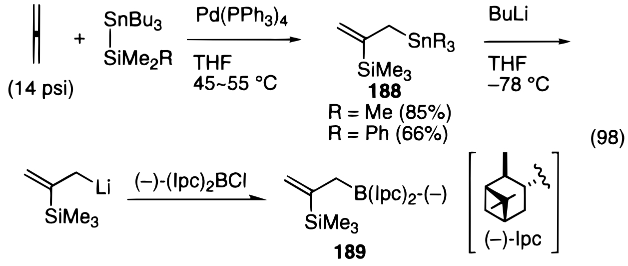


186
via internal addition

187
via terminal addition

R^1 = Bu, *c*-Hex, *t*-Bu, Ph, MeO
R = Me, Bu

2-Silyl-3-stannyl-1-propene **188** was synthesized by silastannation of 1,2-propadiene in the presence of $Pd(PPh_3)_4$ (eq 98).[118] Treatment of **188** with BuLi provided *β*-silylallyllithium, which was trapped with (−)-*β*-chlorodiisopinochanpheylborane to afford an optically active allylborane reagent **189** with a silyl group at the *β*-position. Reactions of these allylboranes **189** with aldehydes provided the corresponding homoallylic alcohols in good yields with moderate enantiomeric excesses.

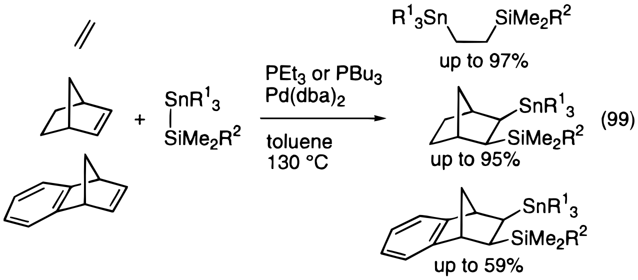


188
R = Me (85%)
R = Ph (66%)

189

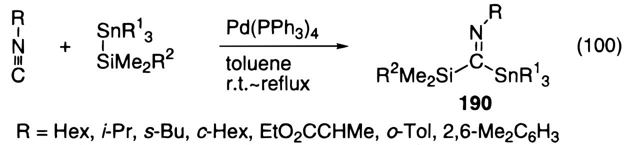
D. Addition to Alkenes

Silylstannanes added to the carbon−carbon double bond of alkenes in the presence of a palladium catalyst (eq 99).[119] The reaction was limited to ethylene, norbornene, and benzonorbornadiene, and use of PEt_3 or PBu_3 with $Pd(dba)_2$ was crucial for the reaction to proceed. Other ligands [PMe_3 (11%), PCy_3 (0%), PPh_3 (7%), $P(OPh)_3$ (7%), $P(i\text{-}Pr)_3$ (22%), and etpo (9%)] in combination with $Pd(dba)_2$ were not effective for the addition reaction to norbornene. In the reactions with the bicyclic alkenes such as norbornene and benzonorbornene, only exo,exo stereoisomers were formed, indicating the addition took place with stereospecific *cis*-addition. No reaction occurred with 1-hexene, styrene, cyclohexene, and cyclopentene.



E. Addition to Isonitriles

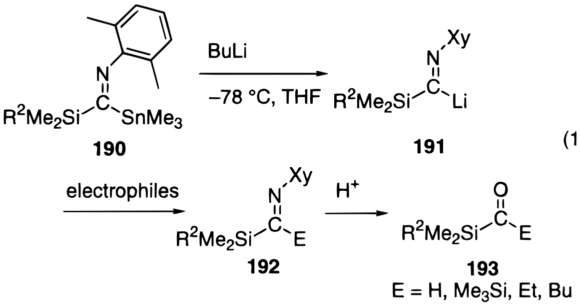
Synthetically useful (silyl)(stannyl)iminomethanes **190** were prepared by palladium-catalyzed 1,1-silastannation of isonitriles (eq 100).[120] Alkyl- and aryl-



190

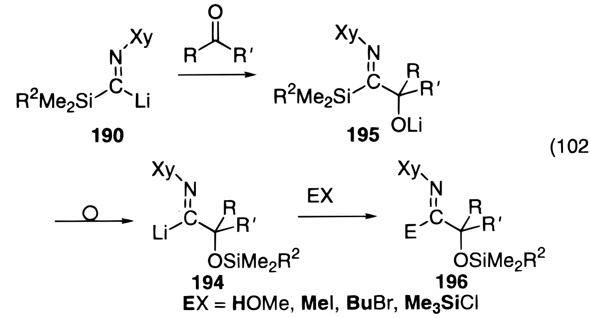
R = Hex, *i*-Pr, *s*-Bu, *c*-Hex, EtO_2CCHMe, *o*-Tol, 2,6-$Me_2C_6H_3$
$R^1 = R^2 = Me$; $R^1 = Bu$, $R^2 = Me$; $R^1 = Me$, $R^2 = Bu$-t

isocyanides were reactive with exception of sterically bulky *tert*-alkyl isonitrile. The imines **190** were useful precursors for the generation of *N*-substituted-imino(organosilyl)methyllithiums (**191**), which served as a synthetic equivalent of organosilylcarbonyl anion or carbonyl dianion (eq 101).[121] Thus, treatment of the *N*-(2,6-dimethylphenyl)(silyl)(stannyl)iminomethane **190** with BuLi at −78 °C generated the corresponding imino(silyl)methyllithium **191** through transmetalation. The imino(silyl)methyllithium reacted with a variety of electrophiles including alkyl bromides to afford the corresponding 1-imino-1-(organosilyl)alkanes **192** in good yields. Subsequent acidic hydrolysis gave the corresponding acylsilanes **193** in good yield.



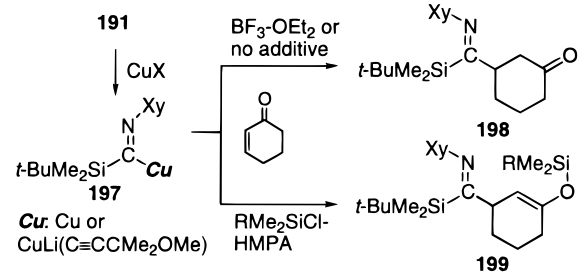
(101)

In the reaction with carbonyl compounds, the imino(silyl)methyllithium **191** afforded imino(α-siloxyalkyl)methyllithium **194** via Brook rearrangement of the primarily generated lithium alkoxide **195** (eq 102). The newly formed imidoyllithium species reacted with electrophiles to give various α-siloxyimines **196**, which were hydrolyzed to the corresponding α-hydroxyketones. In the sequence of the reactions, the imino(silyl)methyllithium **191** served as a synthetic equivalent of carbonyl dianion.

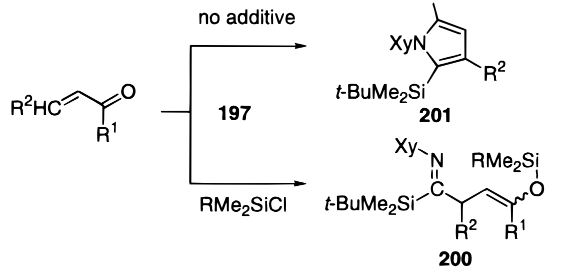


(102)

Imidoyl−copper or −cuprate reagents **197** were generated from the imino(silyl)methyllithium species **191** via transmetalation with CuBr−SMe$_2$ or CuC≡CCMe$_2$OMe) (eqs 103 and 104).[122] The copper species reacted with α,β-unsaturated ketones and aldehydes in a 1,4-fashion in the presence of additives such as BF$_3$−OEt$_2$ and chlorosilane-HMPA. Cyclic enones afforded 3-(iminomethyl)ketone **198** or the corresponding silyl enol ether **199** in the presence of the additives (eq 103). Acyclic enone and enals such as 3-penten-2-one, crotonaldehyde, and acrolein similarly underwent the conjugate addition in the presence of the chlorosilanes to give the corresponding silyl enol ethers **200** in good yields (eq 104). In the absence of the chlorosilanes, however, the acyclic α,β-unsaturated carbonyl compounds underwent cyclization to give pyrrole derivatives **201**.



(103)



(104)

F. Mechanistic Interpretation

A mechanism for silastannation may be closely related to the transition-metal-catalyzed bis-silylation of unsaturated organic compounds, involving oxidative addition of the Si−Sn bond onto the transition-metal complex and subsequent insertion of the unsaturated molecule into the resultant (silyl)(stannyl)-metal intermediate, which is followed by reductive elimination of the silastannation product. A theoretical study using ab initio Hartree−Fock calculations indicated that reaction of H$_3$Sn−SiH$_3$ with alkynes

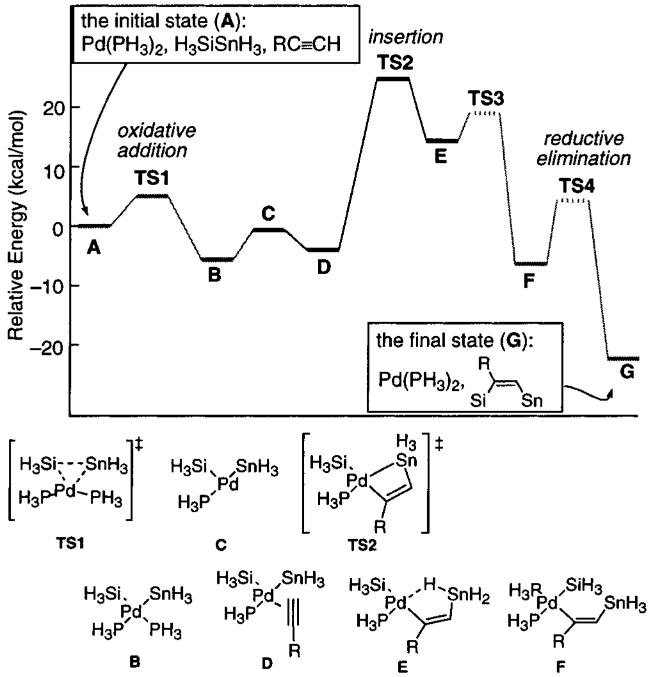
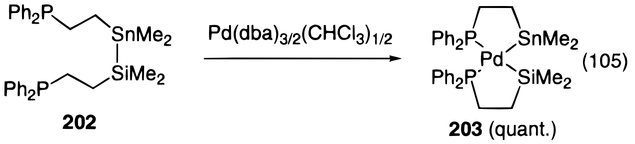


Figure 2. Energy diagram for silastannation of propyne (R = Me). A reaction pathway whose activation energy for the rate-determining step (**D**-**TS2**-**E**) is smallest among four possible pathways is depicted. The energy levels for **TS3** and **TS4** are calculated by the estimated geometries.

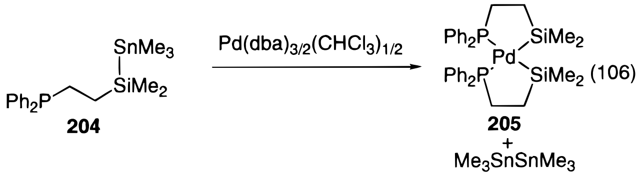
in the presence of $Pd(PH_3)_2$ proceeded via the assumed catalytic cycle and that the insertion step (**D-TS2-E**) was the rate-determining step (Figure 2).[123]

The theoretical study also indicated that the oxidative addition step (**A-TS1-B**) was exothermic, giving (silyl)(stannyl)bis(phosphine)palladium intermediate **B** as a resting state in the catalytic cycle. Nevertheless, the (silyl)(stannyl)metal complexes had been neither isolated nor characterized until recently. The first isolation of this type of complex was achieved by use of a silylstannane **202** having two 2-(diphenylphosphino)ethyl groups on both silicon and tin atoms (eq 105).[124] The reaction of the silylstannane



(105)

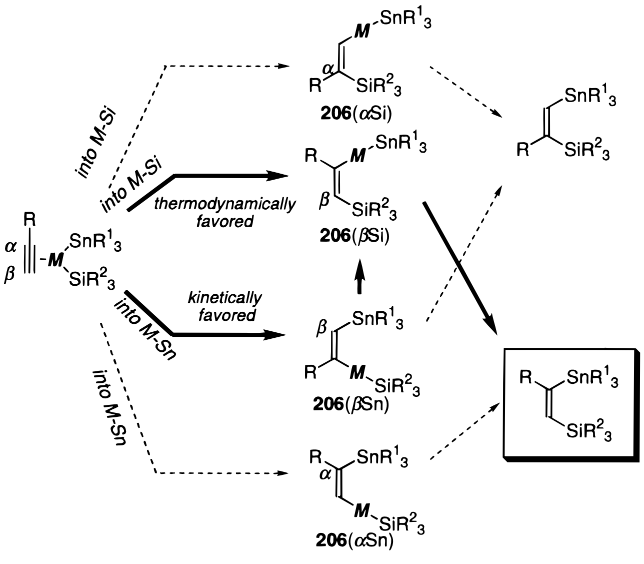
202 with $Pd_2(dba)_3{\cdot}CHCl_3$ proceeded rapidly at room temperature to give *cis*-(silyl)(stannyl)palladium complex **203** in a quantitative yield. In contrast, a silylstannane **204** having only one phosphinoethyl group afforded the corresponding bis(silyl)palladium complex **205**, presumably formed via σ-bond metathesis of the Si−Sn bond (eq 106).



(106)

A mechanistic controversy of the silastannation is the origin of the observed high regioselectivity. The four isomers **206** can be formed by insertion of alkynes into either of the Si−M or Sn−M bond (Scheme 15). The theoretical calculation of the rate-determining insertion step with propyne suggested that insertion into the Pd−Sn bond with the Sn−C bond formation at the terminal alkynyl carbon (β) proceeded with the lowest activation energy among the four possible pathways to give the **E**(βSn) intermediate (Figure 3).[123] However, the pathway in which the alkyne inserted into the Pd−Si bond with the Si−C bond formation at the β position (giving **E**(βSi)) had a higher activation energy only by 2 kcal/mol than that for the **E**(βSn) pathway and produced the intermediate **E**(βSi) which was ca. 11 kcal/mol more stable than the **E**(βSn) intermediate. Since the insertion step is endothermic and potentially reversible, the formation of the thermodynamically stable intermediate **E**(βSi) may be favored, leading to the formation of the 1-silyl-2-stannylalkyne.

Scheme 15. Possible Mechanism for the Regioselective Silastannation of Terminal Alkynes, Indicated from the Theoretical Calculations as Well as the Stoichiometric Reactions[a]



[a] *M*: L*n*Pd or L*n*Pt.

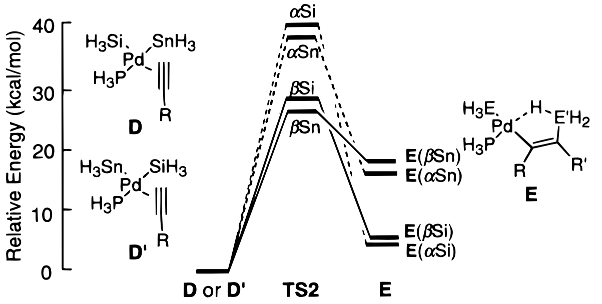
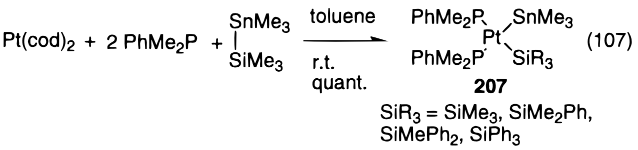


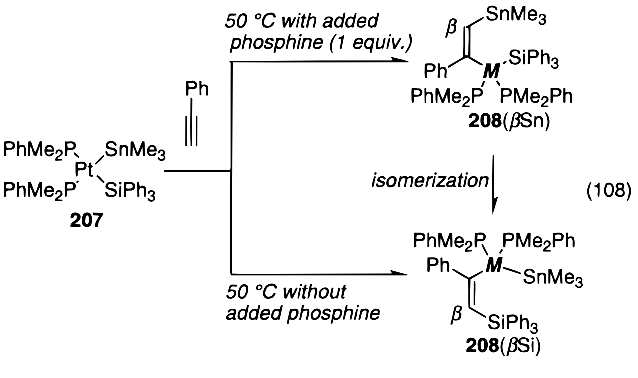
Figure 3. Energy diagram for the four possible pathways for the insertion step (**D-TS2-E**) of the silastannation of propyne (R = Me). For the designation (αSi, βSi, αSn, βSn), see Scheme 15.

Very recently, acyclic (silyl)(stannyl)bis(phosphine)platinum complexes **207** with various substituents on the silicon have successfully been prepared by oxidative addition of the corresponding silylstannanes to $Pt(cod)_2$ with 2 equiv of $PhMe_2P$ (eq 107).[125]



(107)

With the platinum complexes **207**, the regiochemical preference for the insertion of alkynes was investigated, since the alkenylplatinum complexes **208** produced by the insertion reaction were resistant to reductive elimination (eq 108). The reaction of Ph_3Si derivative at 50 °C in the presence of added $PhMe_2P$ (1 equiv) afforded **208**(βSn) and **208**(βSi) in a 93:7 ratio, each of which corresponded to **206**(βSn) and



(108)

206(βSi), respectively, in Scheme 15. In contrast, the corresponding reaction in the absence of the added phosphine gave only **208**(βSi) under the same reaction conditions. Eventually, isomerization of **208**(βSn) to **208**(βSi) took place at low concentration of the added phosphine. Furthermore, even in the presence of the added phosphine (0.1 equiv), the ratios of **208**(βSn) to **208**(βSi) as well as the reaction rates significantly varied with the substituents of the silyl groups. The Me_3Si derivative was the most reactive (rapid reaction at −70 °C) but gave only the βSi isomer, while $PhMe_2Si$ and Ph_2MeSi derivatives showed moderate reactivity as well as low selectivity (34/66 and 59/41, respectively).

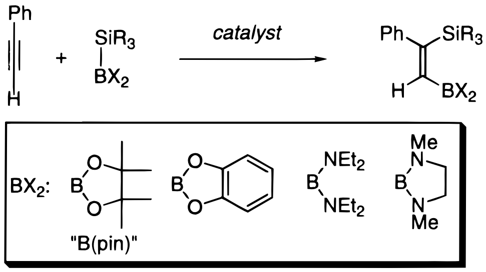
These results indicate that the insertion of the alkyne into the M−Sn bond to form **206**(βSn) is kinetically favorable, while the formation of the **206**(βSi) intermediate is thermodynamically favored (Scheme 15). This finding is in good agreement with the theoretical results, in which the formation of thermodynamically favorable **E**(βSi) is suggested, although the transition metals employed are different.

IV. Silicon–Boron Bonds

Although Cu- and Co-catalyzed reversible addition of lithium organosilyltriethylborate to alkynes was reported in 1986,[126] transition-metal-catalyzed reactions of "newtral" silylboranes[127] has not been achieved prior to the report of a series of silaboration reactions of unsaturated organic molecules catalyzed by group 10 metal complexes.

A. Addition to Alkynes

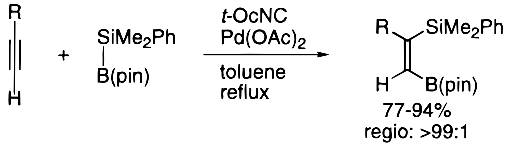
The addition of Si−B bonds across carbon−carbon triple bonds was first realized by the palladium−*tert*-alkyl isonitrile catalyst (eq 109).[128,129] Remarkably, the stereospecific *cis*-addition to terminal alkynes took place with excellent regioselectivity, where the boryl group was attached at the terminal carbon atom. A catalyst survey revealed that other palladium catalysts with ligands such as *c*-HexNC, P(OEt)$_3$, and PPh_3 also presented high catalytic activities comparable to the palladium−*tert*-alkyl isonitrile catalyst. Moreover, platinum complexes such as Pt(PPh_3)$_4$ served as fairly active catalysts in the reactions, although slightly lower regioselectivity was provided. Wilkinson's catalyst was inactive for the reaction.



(109)

A silylborane with a pinacol ligand at the boron atom was most conveniently prepared[130] and utilized for the silaboration reactions. In addition, silylboranes with diethylamine-,[128] catechol-,[129] and *N*,*N*′-dimethylethylenediamine[131] ligands on the boron atom underwent the insertion reaction of alkynes.

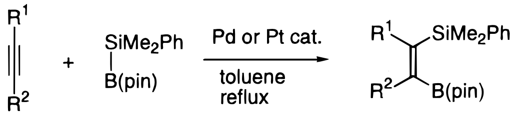
Employing the pinacol derivative of the silylborane, silaboration of a variety of alkynes was examined (eq 110). Alkynes with remote functional groups such as chloro, cyano, THPO, MEMO, and hydroxy groups underwent the silaboration reaction in good yields with complete regio- and stereoselectivity. Moreover, carbon−carbon triple bonds conjugated with carbon−carbon double bond, ester group, and keto group similarly underwent the regioselective silaboration, where the boryl group was attached to the terminal carbon. Only in the cases of trimethylsilylacetylene and gaseous ethyne were the corresponding *E* isomers formed, albeit in low yields (4% and 10%, respectively).



(110)

R = $Cl(CH_2)_3$, $NC(CH_2)_3$, $TBSOCH_2$, $THPO(CH_2)_2$, $MEMO(CH_2)_3$, $HO(CH_2)_2$, Ph, cyclohexen-1-yl, $-O_2Et$, CH_3CO, Me_3Si, H

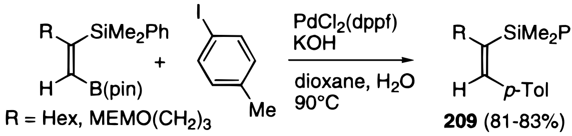
Internal alkynes also underwent the silaboration in the presence of the palladium−isonitrile catalyst (eq 111). Diphenylacetylene afforded the *Z*-silaboration product in 74% yield under reflux in toluene. Regioselective addition of the Si−B bond was observed for 1-phenylpropyne; the silyl group was preferentially attached α to the phenyl group in a ratio of 93:7. The corresponding reaction with Pt(PPh_3)$_4$ afforded a 82:18 mixture of regioisomers. For the silaboration of 5-decyne, Pt(PPh_3)$_4$ provided a better result than Pd(OAc)$_2$/*t*-OcNC to give (*Z*)-5-silyl-6-boryl-5-decene in good yield.



(111)

$R^1 = R^2 = Ph$	tOcNC/Pd(OAc)$_2$	74%
$R^1 = Ph, R^2 = Me$	tOcNC/Pd(OAc)$_2$	85% (93:7)
$R^1 = R^2 = Bu$	Pt(PPh_3)$_4$	72%

The regio- and stereochemically pure silaboration products are useful precursors for the synthesis of alkenylsilanes. Cross-coupling with aryl iodide under the Suzuki−Miyaura condition[132] afforded the corresponding β-silylstyrene derivatives **209** in good yield (eq 112). Furthermore, reaction of the silaboration products with methyl vinyl ketone in the presence of a rhodium catalyst[133] provided stereodefined δ-silyl-γ,δ-unsaturated ketones **210** in good yields (eq 113).

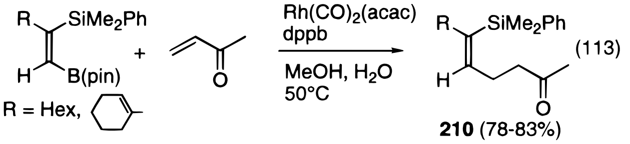


R = Hex, $MEMO(CH_2)_3$

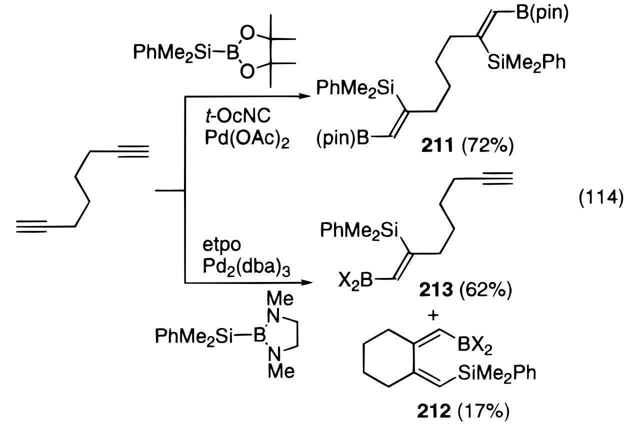
209 (81-83%)

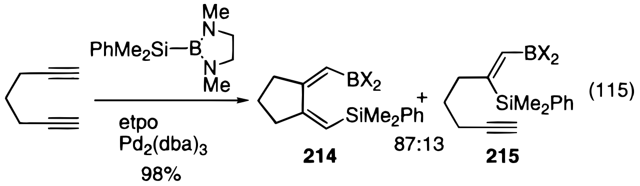
(112)

Reaction of 1,7-octadiyne with silylboranes took two courses which depend on the structure of the

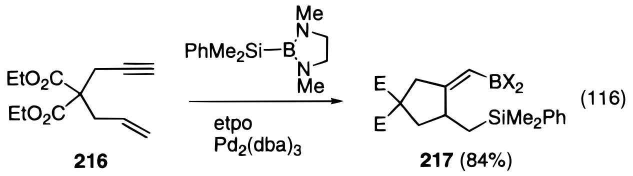


silylborane used and the ligands on the palladium catalyst. The silylborane having a pinacol ligand added to each triple bond of the diyne in a regioselective manner to provide 1,8-diboryl-2,7-disilylocta-1,7-diene **211** in good yield (eq 114).[129] In contrast, use of the ethylenediamine-derived silylborane gave a cyclization product **212** in 17% yield along with an acyclic 1:1 silaboration adduct **213** in 62% yield in the presence of the etpo−palladium catalyst.[131] The intramolecular silaborative cyclization of 1,6-heptadiyne was more selective, forming the cyclized product **214** and the acyclic 1:1 adduct **215** in a ratio of 87:13 in a high total yield (eq 115).

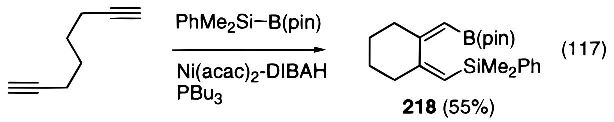




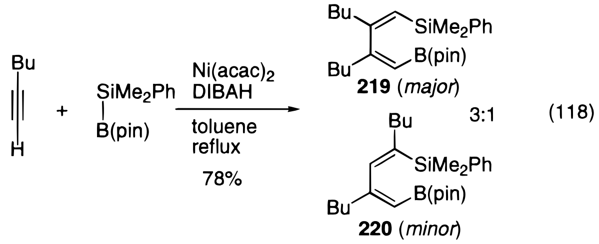
The silaborative cyclization has been successfully applied to enyne **216** to afford the five-membered cyclic product **217** with high regio- and stereoselectivity (eq 116).



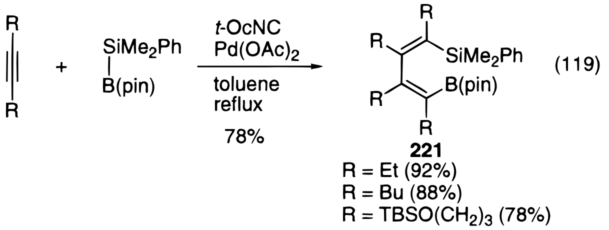
A nickel catalyst promoted the silaborative cyclization of alkynes more selectively (eq 117).[134] 1,7-Octadiyne gave the cyclization product **218** in the presence of a Ni(0) catalyst bearing PBu$_3$ without formation of any trace of acyclic products.



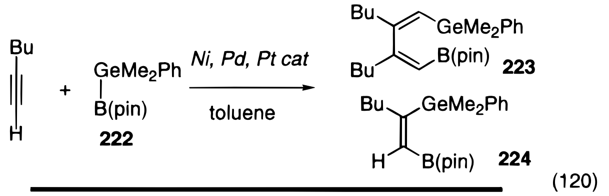
It is remarkable that the nickel catalysts enabled *inter*molecular silaborative dimerization of alkynes (eq 118). Heating a mixture of 1-hexyne (2.5−6.0 equiv) with the silylborane in the presence of a catalyst prepared from Ni(acac)$_2$ with DIBAH provided silaborative dimerization products in 50−78% yield along with a small amount of 1:1 alkyne silaboration product. Note that only two of the four possible regioisomers were formed by the dimerization in a ratio of ca. 3:1. The major isomer **219** was identified to a head-to-head dimerization product and the minor one (**220**) to a head-to-tail isomer. In both isomers, the boron was attached to the terminal carbon atom of the alkyne.



The silaborative dimerization reaction has been successfully applied to internal alkynes to afford the corresponding dienes **221** in better yields than that for the terminal alkynes (eq 119).

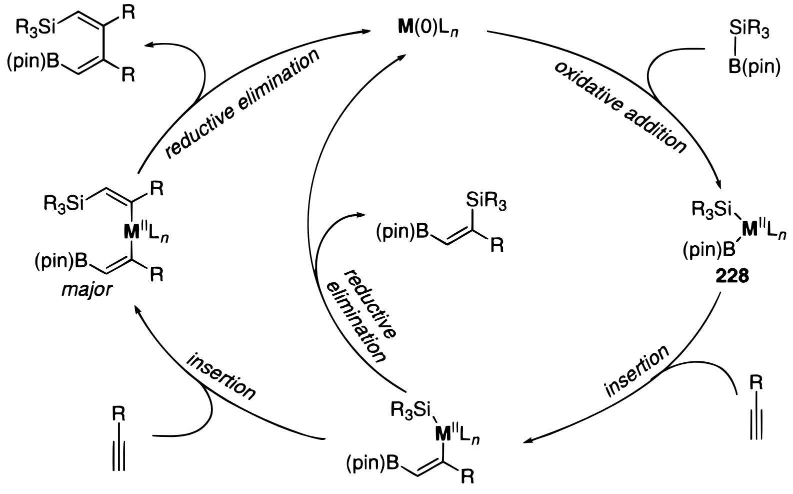


The corresponding 1:1 germaboration and germaborative dimerization of hexyne with germylborane **222** were also catalyzed by group 10 metal compounds. The ratio and regioselectivity of the two products **223** and **224** depended upon the metal complex employed (eq 120). A nickel(0) catalyst provided a germaborative dimerization product **223** as a 3:1 regioisomeric mixture, while a platinum(0) complex gave exclusively a 1:1 alkyne germaboration adduct **224** with high regioselectivity (91:9). Of interest is that the palladium(0)−isonitrile-catalyzed reactions of hexyne afforded a mixture of **223** and **224** in a ratio of 39:46.

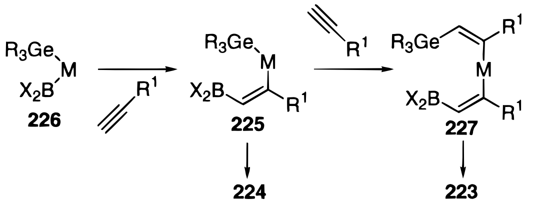


catalyst	223	224
Ni(acac)$_2$/DIBAH	74% (74:26)	trace
Pd(acac)$_2$/*t*OcNC	39% (96:4)	46% (>99:1)
Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$	0%	87% (91:9)

Scheme 16. General Mechanism of the Reactions of the Silylboranes with Alkynes in the Presence of Ni, Pd, and Pt Catalysts



A possible mechanism for germaboration may involve an (organogermyl)(1-butyl-2-borylvinyl)metal(II) intermediate **225** which is formed via regioselective insertion of 1-hexyne into the B−metal bond of the (silyl)(boryl)metal(II) complex **226** initially generated (eq 121). The (organogermyl)(1-butyl-2-borylvinyl)nickel(II) intermediate **225** (M = Ni) may preferentially undergo hexyne insertion into the Ni−Ge bond followed by reductive elimination, providing the corresponding germaborative dimerization adduct **223**. On the other hand, the (organogermyl)(1-butyl-2-borylvinyl)platinum(II) intermediate **225** (M = Pt) may undergo reductive elimination directly, leading to the formation of the corresponding 1:1 germaboration adduct **224**.

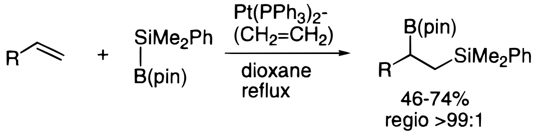


(121)

By analogy with the mechanism for the germaboration, the mechanism of the silaboration and the silaborative dimerization of alkynes may involve the regioselective insertion of the alkynes into the B−M bond (M = Ni, Pd, Pt) of **228** as depicted in Scheme 16.

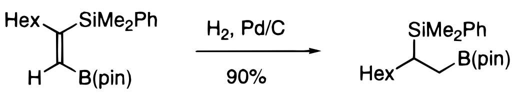
B. Addition to Alkenes

The silicon−boron bond of the silylborane added to simple terminal alkenes in the presence of a platinum catalyst (eq 122).[135] Among the platinum catalysts so far examined, Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$ displayed the highest activity. Note that the silaboration of alkenes proceeded with high regioselectivity, where the Si−C bond formation occurred at the terminal carbon of the alkene. This regiochemical preference was interestingly compared with that for the palladium- and platinum-catalyzed silaboration of terminal alkynes, which proceeds with the Si−C bond formation at the internal carbon. The regioselectivity is unambiguously confirmed by the independent synthesis of the regioisomer by the silaboration of the corresponding alkyne followed by hydrogenation (eq 123). This is the only example for the transition-metal-catalyzed addition of the σ-bonds between different elements (except for hydrides) across unsymmetrical simple alkenes, revealing the regioselectivity opposite to the corresponding reaction of alkynes.



(122)

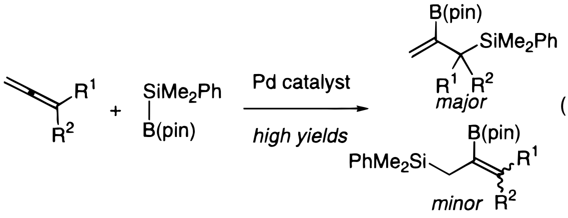
R = Hex, AcOCH$_2$CH$_2$, CH$_3$C(=O)CH$_2$CH$_2$, Ph, 4-MeOC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$, H



(123)

C. Addition to Allenes

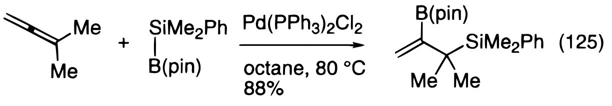
Allenes underwent the addition of the silicon−boron bond of the silylborane with a pinacol ligand (eq 124). A palladium catalyst bearing 2,6-xylyl isocyanide ligand catalyzed effectively the silaboration of nonsubstituted, monosubstituted, geminally disubstituted, and 1,3-disubstituted allenes.[136] Although *tert*-alkyl isocyanides also served as effective ligands for the silaboration reactions of allenes, the bulky aryl isocyanides generally gave slightly better yields as well as selectivity. In addition to the palladium−isonitrile catalyst, palladium−etpo was also active for the silaboration of allenes.[137]

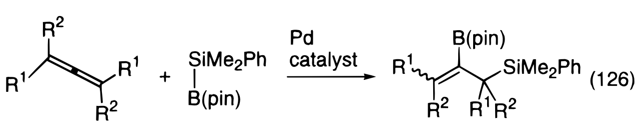


(124)

(R^1,R^2, ratio): (Me, H, 100/0), (PhCH$_2$CH$_2$, H, >99/1), (c-Hex, H, >99/1), (t-Bu, H, 94/6), (Ph, H, 86/14), (MeO, H, >99/1), (H, H, -)

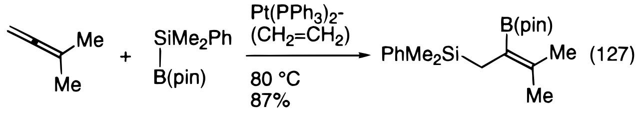
In general, the addition of the silylborane proceeded with high selectivity for B−C bond formation at the central carbon of the allene. Moreover, the addition of the silylborane selectively occurred at the internal C=C bond of the monosubstituted allenes, as reported for bis-silylation of the allenes. Even an allene with a bulky *tert*-butyl group underwent the selective silaboration in high yield, although addition to the terminal C=C bond was observed as the minor side reaction. The silaboration of 1,1-disubstituted allenes was best catalyzed by $Pd(PPh_3)_2Cl_2$ or $Pd(dba)_2$−PPh_3 to give the internal addition product in high yield (eq 125). 1,3-Disubstituted and tetrasubstituted allene provided the corresponding addition products in good yield, although the former gave a 62/38 mixture of *E* and *Z* isomers (eq 126).

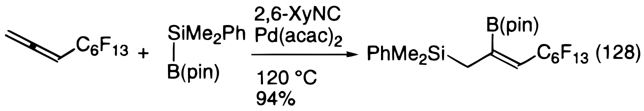




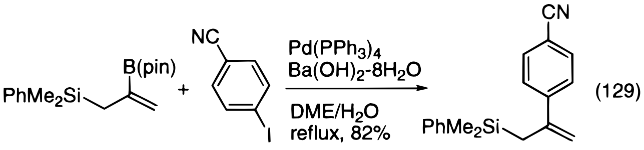
R^1 = Pr, R^2 = H (88%, E/Z = 62/38 with XyNC/$Pd(acac)_2$)
R^1 = R^2 = Me (90% with etpo/$Pd(dba)_2$)

An interesting reversal of the regiochemistry of the silaboration of olefins has also been found. Platinum-catalyzed addition of the silylborane to a 1,1-disubstituted allene resulted in the exclusive formation of the terminal adduct in high yield (eq 127).[137] On the other hand, an allene with a perfluoroalkyl group provided the terminal adduct as a single isomer of undetermined geometry (eq 128).[136]





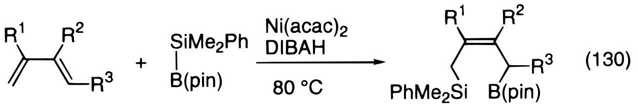
The synthetic utility of the silaboration adduct has been demonstrated by palladium-catalyzed cross-coupling of the silaboration product of allene with an aryl iodide to give the allylsilane derivative **229** in good yield (eq 129).[136]



229

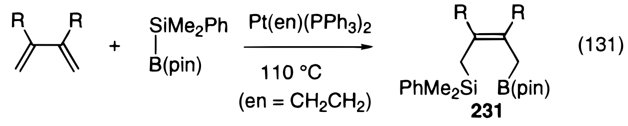
D. Addition to 1,3-Dienes

1,4-Addition of silylborane to 1,3-dienes was catalyzed by a mixture of $Ni(acac)_2$ and DIBAH (eq 130).[138] The reactions of symmetrical dienes such as 1,3-butadiene and 2,3-dimethyl-1,3-butadiene with the silylborane provided the corresponding *Z*-alkene **230** bearing silyl and boryl groups at the 1- and 4-positions in a regio- and stereoselective manner. The nickel complex catalyzed the silaboration of unsymmetrical dienes such as isoprene and 2-methyl-1,3-pentadiene in high yields but with low regioselectivity.



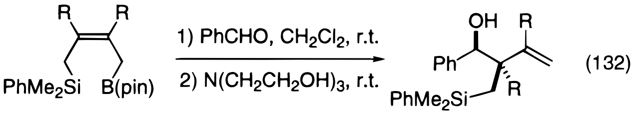
230 (100% *Z*)
R^1 = R^2 = Me, R^3 = H: 90%
R^1 = R^2 = R^3 = H: 90%
R^1 = Me, R^2 = R^3 = H: 92% (72/28)
R^1 = R^3 = Me, R^2 = H: 84% (67/33)

Although the Pd−isonitrile complexes, e.g. $Pd(OAc)_2$/*t*-OcNC, completely failed to catalyze the reaction of the dimethylbutadiene at 110 °C, a Pt−phosphine complex catalyzes the silaboration of 1,3-dienes in good yield but with poor *Z*−*E* selectivity (95% yield, 48:52) (eq 131). The platinum-catalyzed silaboration of 1,2-dimethylenecyclohexane afforded the 1,4-addition product **231b** in high yield.



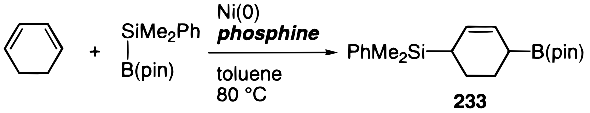
231
a: R = Me: 95% (*E*/*Z* = 1/1)
b: 2R = -$(CH_2)_4$-: 97% (*Z* only)

Reaction of the 1,4-silaboration products **231** with benzaldehyde afforded the corresponding homoallyl alcohol **232** stereoselectively as expected for an allylic borane (eq 132).



232
R = H (87%)
R = Me (85%)

Of synthetic interest is that 1,4-silaboration of cyclic dienes was catalyzed by a phosphine−nickel complex (eq 133). No product was produced by the reaction of 1,3-cyclohexadiene with the silylborane in the absence of phosphine ligands. In contrast, addition of dialkylarylphosphines or alkyldiarylphoshine facilitated the reaction to give a 1,4-addition product **233** in high yields. In particular, cyclohexyldiphenylphosphine was the ligand of choice, cata-



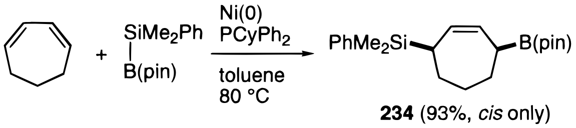
233

(133)

phosphine	%yield	*cis*/*trans*
none	0	-
PBu_3	39	94/6
PMe_2Ph	92	60/40
$PMePh_2$	97	93/7
$PCyPh_2$	99	>99/1
PPh_3	0	-

lyzing the highly stereoselective 1,4-addition. Similarly, a platinum complex catalyzed the silaboration of cyclohexadiene at 110 °C albeit in low yield (21%).

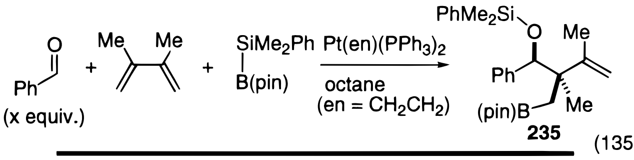
In the presence of the nickel–cyclohexyldiphenylphosphine catalyst, 1,3-cycloheptadiene selectively afforded the 1,4-silaboration product **234** in high yield (eq 134).



(134)

E. Coupling of 1,3-Dienes to Aldehydes

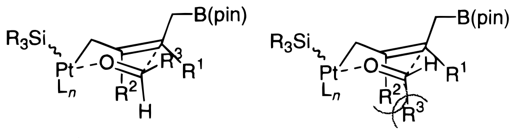
A new catalytic C–C bond forming reaction was achieved by the platinum-catalyzed reaction of the silylborane with 1,3-dienes *in the presence of aldehydes.*[139] Heating of a mixture of the silylborane, 2,3-dimethyl-1,3-butadiene, and benzaldehyde in refluxing octane in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ afforded a silaborative coupling product **235** in 74% yield, in which the B–C, C–C, and O–Si bond formation took place at once (eq 135). The product **235**, i.e., a silyl-protected homoallylic alcohol bearing a boryl group, was unexpectedly different from **232** derived from the stepwise silaboration–allylboration sequence exemplified above (eq 132). The silaborative coupling of 1,3-diene to aldehyde proceeded with high stereoselectivity. Although a syn/anti ratio of 81:19 was attained at 120 °C, the ratio was remarkably improved by lowering the reaction temperature (95:5 at 80 °C, 98:2 at 50 °C).



(135)

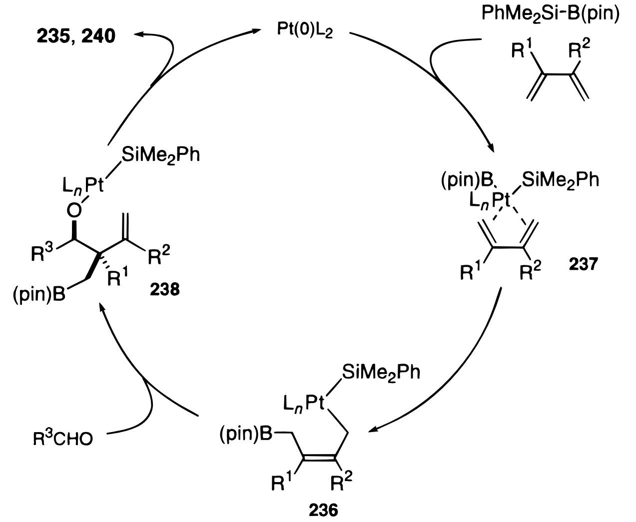
temp/°C	x/equiv.	yield/%	syn/anti
120	1.5	74	81/19
80	1.5	78	95/5
50	1.5	61	98/2
80	1.0	63	93/7
80	3.0	85	96/4

The reaction mechanism for the formation of **235** was presumed to involve the formation of an allylic (silyl)platinum intermediate **236**, which was formed through insertion of the 1,3-diene into the B–Pt bond of the (silyl)(boryl)platinum intermediate **237** in a 1,4-fashion (Scheme 17). The σ-allylplatinum species **236** may nucleophilically react with aldehyde at the position γ to the platinum to give the homoallyloxyplatinum intermediate, which undergoes reductive elimination with the O–Si bond formation to give **235**. A chairlike cyclic transition state (**239**) for the nucleophilic allylation may explain the observed high stereoselectivity.

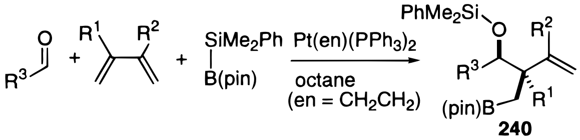


239

Scheme 17. Possible Mechanism for the Silaborative Coupling of Dienes to Aldehydes



The silaborative coupling reaction was successfully extended to other dienes (eq 136, Table 8). The reactions of 1,3-butadiene and 1,2-dimethylenecyclohexane with benzaldehyde afforded the corresponding coupling products **240** in good yields with high stereoselectivities (entries 7 and 8). Furthermore, unsymmetrical 2-phenyl-1,3-butadiene underwent the silaborative coupling to various aldehydes including aliphatic ones (entries 1–6). Note that in all cases the reactions proceeded with the regioselective B–C and C–C bond formation at the less substituted C=C bond as well as remarkably high stereoselectivity for the syn products.



(136)

F. Miscellaneous

Although isonitriles served as highly effective ligands for the palladium-catalyzed silaboration, they underwent an insertion into the Si–B bond even in the absence of the transition-metal catalysts.[140] This finding was in sharp contrast to the insertion of isonitriles with Si–Si and Si–Sn bonds, which required the palladium catalyst to undergo insertion of isonitriles.

A theoretical study (MP2-MP4(SDQ) and CCSD(T) methods) on an oxidative addition of the Si–B bond onto Pd and Pt complexes disclosed that the oxidative addition of the Si–B bond was made favorable by a charge-transfer interaction of the empty p_π orbital of the boron with the d orbital of the transition metal at the transition state.[141]

V. Other Silicon-Containing Bonds

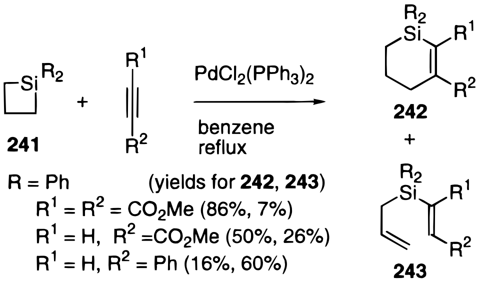
A. Si–C Bonds

Catalytic activation of the Si–C bond still remains relatively unexplored. Only the Si–C bonds in highly

Table 8. Platinum-Catalyzed Stereoselective Silaborative Coupling of 1,3-Dienes to Aldehydes

entry	dienes (R^1,R^2)	aldehydes (R^3)	temp/°C	yield of **240**/%	*syn*/*anti*
1	H, Ph	Ph	120	79	99/1
2	H, Ph	*p*-$MeOC_6H_4$	120	77	99/1
3	H, Ph	*o*-$MeOC_6H_4$	120	83	99/1
4	H, Ph	*p*-NCC_6H_4	120	80	99/1
5	H, Ph	*n*-Hex	120	71	93/7
6	H, Ph	*c*-Hex	120	60	96/4
7	H, H	Ph	50	63	95/5
8	$-(CH_2)_4-$	Ph	80	60	99/1

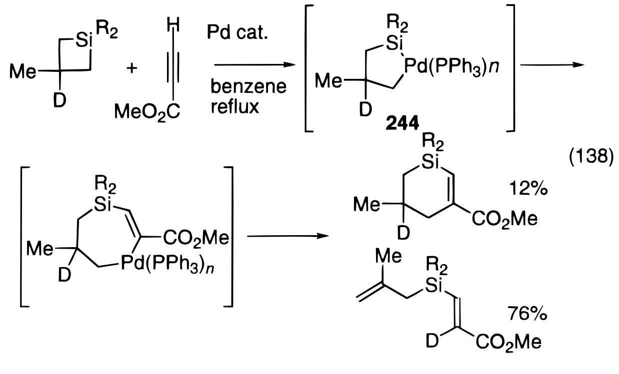
strained rings or the Si−CN bond of silylcyanides are known to undergo addition to unsaturated organic molecules. Catalytic addition of the Si−C bond was first realized by the palladium-catalyzed addition of silacyclobutane with alkynes (eq 137).[142] The reaction of 1,1-dimethyl-1-silacyclobutane **241** with dimethyl acetylenecarboxylate in the presence of $PdCl_2(PPh_3)_2$ afforded a 1-silacyclohex-2-ene derivative **242** in high yield. Use of terminal alkynes such as methyl propiolate and phenylacetylene afforded the corresponding product in much lower yield but with high regioselectivity for Si−C bond formation at the terminal carbon of the alkynes. Unsymmetrical 2-methylsilacyclobutane underwent insertion of the acetylenedicarboxylate with moderate regioselectivity.



R = Ph (yields for **242**, **243**)
$R^1 = R^2 = CO_2Me$ (86%, 7%)
$R^1 = H$, $R^2 = CO_2Me$ (50%, 26%)
$R^1 = H$, $R^2 = Ph$ (16%, 60%)

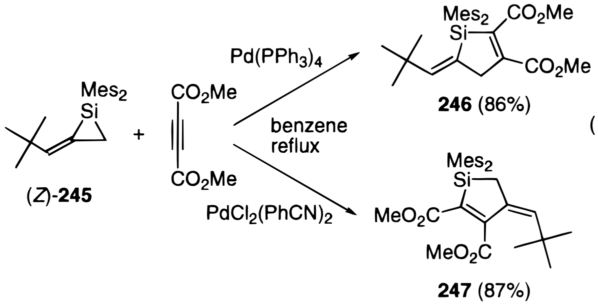
(137)

The reaction of **241** was carefully reexamined to reveal that the allylvinylsilane derivatives **243** were also formed under the reaction conditions.[143] Deuterium-labeling experiments indicated that insertion of the alkyne into the Si−Pd bond of a 1-pallada-2-silacyclopentane intermediate **244** was involved in both the reactions, i.e., the silacyclohexene (**242**) and allylvinylsilane (**243**) formations (eq 138).

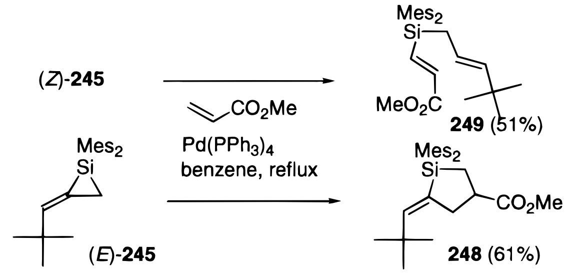


(138)

Highly strained silacyclopropane **245** also underwent the palladium-catalyzed reaction with unsaturated organic molecules.[144] The reaction of the *Z* isomer of 1,1-dimesityl-2-neopetylidenesilirane ((*Z*)-**245**) with dimethyl acetylenedicarboxylate afforded two regioisomeric insertion products selectively, depending on the palladium catalyst used (eq 139). Use of $Pd(PPh_3)_4$ gave **246**, which arises from insertion to the sterically less hindered Si−C bond, whereas use of $PdCl_2(PhCN)_2$ resulted in the formation of **247**, arising from the insertion into another Si−C bond. In contrast to these results with acetylenedicarboxylate, acetylene as well as *tert*-butylallenes inserted into the more hindered Si−C bond even in the presence of $Pd(PPh_3)_4$. Another interesting result was given in the reaction of methyl acrylate with *E* and *Z* isomers of the silirane **245** (eq 140). The *E* isomer ((*E*)-**245**) selectively formed the expected five-membered ring product **248** in the presence of $Pd(PPh_3)_4$, whereas acyclic allylvinylsilane derivative **249** was obtained in the reaction of (*Z*)-**245** with methyl acrylate.

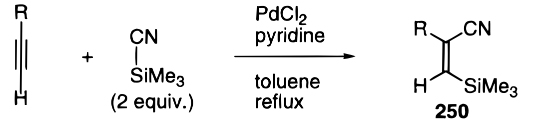


(139)



(140)

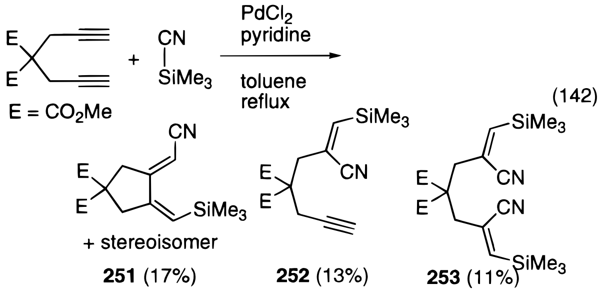
Silylcyanides exist as equilibrium mixtures with silyl isocyanides. Palladium complexes catalyzed cyanosilylation of alkynes, i.e., *cis*-addition of the silyl and cyano group across the carbon−carbon triple bond (eq 141).[145] Among the palladium complexes



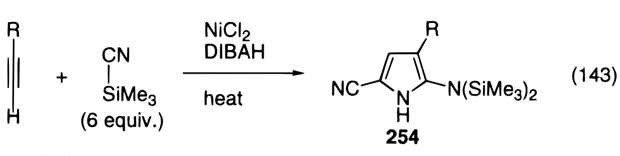
(141)

R (yields, *E*/*Z*) = Ph (93%, 95/5), *p*-$MeOC_6H_4$ (88%, 95/5), 3,4-methylenedioxy C_6H_3 (56%, 92/8), *p*-FC_6H_4 (52%, >95:5)), *o*-$MeOC_6H_4$ (78%, 83/17), *p*-ClC_6H_4 (50%, 94/6), 2-Nap (77%, 93/7), 1-Nap (80%, 71/29), $AcO(CH_2)_2$ (26%, 80/20), $NC(CH_2)_3$ (63%, 84/16), Me_3SiOCH_2 (34%, 88/12) examined, a catalytic amount of $PdCl_2$ with pyridine as an additive (2 equiv to Pd) was most effective. A variety of arylacetylenes having functionalities on the benzene including methylenedioxy, methoxy, fluoro, and chloro groups underwent the cyanosilylation in fair-to-good yields in the presence of $PdCl_2$. The reactions proceeded with high regio- and stereoselectivity with Si−C bond formation at the terminal position of the alkynes, giving *Z*-*β*-silyl-α-arylacrylonitriles **250** selectively. The stereoselectivity for the *cis*-products was influenced by the position of the substituent on the aromatic ring: the selectivity decreased in the order of *para*-, *meta*-, and *ortho*-substitution. The *E* isomers were selectively produced by photoisomerization of the corresponding *Z* isomers prepared by the cyanosilylation. Under the same reaction conditions, terminal aliphatic acetylenes gave the cyanosilylation products with moderate stereoselectivities.

Cyanosilylative carbocyclization proceeded with diethyl dipropargylmalonate to give five-membered ring products **251** in low yield along with acyclic cyanosilylation products **252** and **253** (eq 142).[146] No cyclization, however, was observed in the reaction of diethyl allylpropargylmalonate under the same reaction conditions.

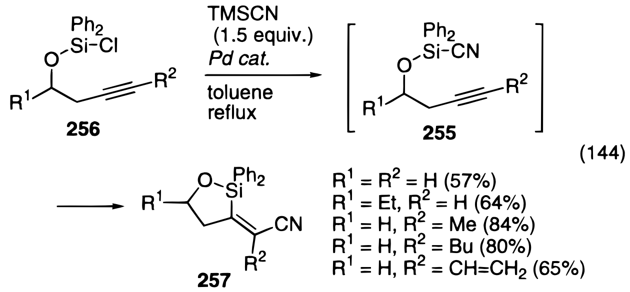


A nickel catalyst generated from $NiCl_2$ and DIBAH also catalyzed the cyanosilylation reaction in lower yield and in lower stereoselectivity than the palladium catalyst. A pyrrole derivative **254** was formed as a byproduct (10%) in the reaction. The pyrrole derivative **254** was obtained as a major product when the reaction was carried out in the presence of a large excess of TMSCN without solvent (eq 143).

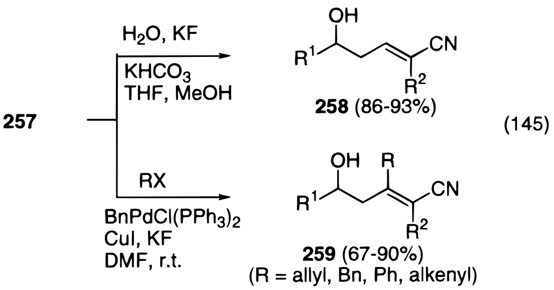


R (yields) = Ph (58%), *p*-$MeOC_6H_4$ (66%), *p*-ClC_6H_4 (52%), *o*-$MeOC_6H_4$ (54%)

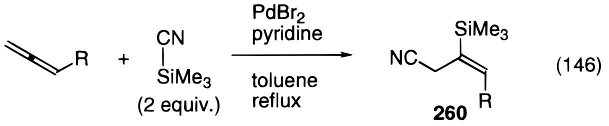
Cyanodiphenylsilyl ethers of homoallylic alcohols **255**, generated in situ from the corresponding chlorodiphenylsilyl ethers **256** with TMSCN, underwent intramolecular cyanosilylation in the presence of palladium catalysts (eq 144).[147] The cyanosilylation proceeded regioselectively with 5-exo ring closure and *cis*-addition. Consequently, selective formation of the Si−C bond at the internal alkynyl carbon was observed in the reactions of terminal alkynes, in contrast to the intermolecular cyanosilylation. Internal alkynes also gave the corresponding cyanosilylation products **257** in high yields. For these reactions, $Pd(acac)_2$ and $Pd_2(dba)_3CHCl_3$ served as the most effective palladium catalysts while $PdCl_2$/pyridine showed low catalytic activity. The palladium−isonitrile catalyst was found to be the most effective for intramolecular cyanosilylation of the conjugated enyne in terms of cis−trans selectivity (13:1), which decreased to 4:1 in the presence of the ligand-free palladium catalysts.



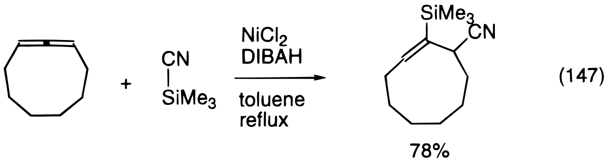
The five-membered ring products were transformed into stereodefined α,*β*-unsaturated nitriles **258** and **259** through protodesilylation with KF as well as C−C bond formation by palladium-catalyzed cross-coupling with organic halides (eq 145).



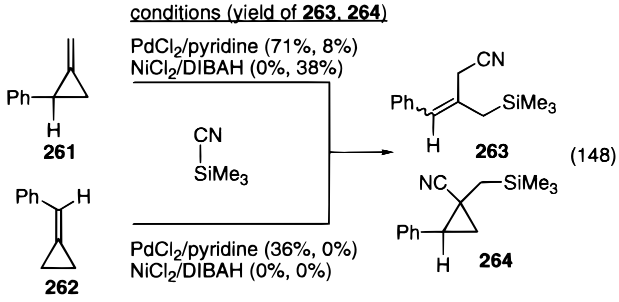
Palladium-catalyzed cyanosilylation of terminal allenes took place regioselectively with the C−CN bond formation at the terminal carbon in the presence of $PdBr_2$/pyridine catalyst, which was a little more reactive than $PdCl_2$ (eq 146).[148] The *E* isomers **260** were predominantly produced, whose stereoselectivities depended upon the starting allene substrates. 1,2-Cyclononadiene underwent the cyanosilylation in good yield in the presence of a ligand-free nickel(0) catalyst (eq 147).



R (yields, E/Z): Hex (87%, 89/11), Ph (75%, 89/11)



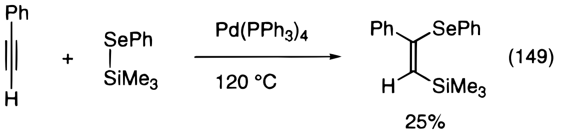
Reaction of TMSCN with methylenecyclopropanes gave two isomeric products, i.e., the allylsilane **263**, derived from C−C bond cleavage of the cyclopropane ring, and cyanocyclopropane **264**, derived from an addition of Si−CN bond to the C=C bond (eq 148).[149]

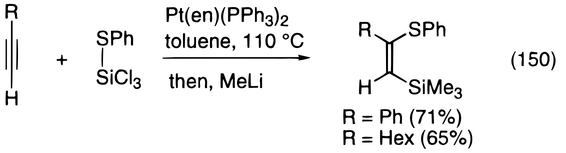


In general, the $PdCl_2$/pyridine system afforded **263** selectively as mixture of *E*−*Z* mixtures, while the Ni(0) catalyst gave the C=C addition products **264** in low yield. The yields for the reactions depended much on the substituents on the methylenecyclopropane. The reaction of benzylidenecyclopropane gave the same product as that for the reaction of methylenephenylcyclopropane.

B. Si–S and Si–Se Bonds

Additions of Si−S[150] and Si−Se[98] bonds across terminal alkynes have been achieved by using platinum and palladium catalysts, respectively (eqs 149 and 150). Both addition reactions proceeded with the regioselective terminal Si−C bond formation and complete *cis*-addition.





VI. Concluding Remarks

A variety of the silicon−element σ-bonds add to the unsaturated organic molecules by the aid of the transition-metal catalysts, mostly group 10 metal complexes. These catalytic addition reactions provide promising methods for the introduction of silicon and other elements into organic molecules in regio- and stereoselective manners. Extensive exploitation of transition-metal catalysts which enable more effective and more selective additions of those σ-bonds may lead to further development of new fields of organic synthesis and materials science.

Although not mentioned in this review, a variety of other element−element σ-bonds such as Sn−Sn[151] and B−B[152] bonds are known to react with the unsaturated organic molecules in the presence of transition-metal catalysts. They may involve common mechanistic features to the addition of the silicon-containing σ-bonds dealt in this review.

VII. Acknowledgments

We are grateful to Mr. Takanori Matsuda for his assistance in the literature search.

VIII. References

(1) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 26.
(2) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, p 763.
(3) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419.
(4) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.
(5) Suginome, M.; Ito, Y. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer: Berlin, 1999; Vol. 3, p 131.
(6) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317.
(7) Recatto, C. A. *Aldrichimica Acta* **1995**, *28*, 85.
(8) Murakami, M.; Suginome, M.; Ito, Y. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 509 (Japanese).
(9) Ishikawa, M.; Naka, A. *Synlett* **1995**, 794.
(10) Suginome, M.; Ito, Y. *J. Synth. Org. Chem. Jpn.* **1997**, *55*, 1040 (English).
(11) Suginome, M.; Ito, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 1925.
(12) Suginome, M.; Ito, Y. In *Transition-Metal Catalyzed Reactions*; Murahashi, S.-i., Davies, S. G., Eds.; Blackwell: London, 1999; p 419.
(13) Han, L.-B.; Tanaka, M. *Chem. Commun.* **1999**, 395.
(14) Ito, Y. *J. Organomet. Chem.* **1999**, *576*, 300.
(15) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435.
(16) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27.
(17) Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867.
(18) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19.
(19) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51.
(20) Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43.
(21) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149.
(22) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 932.
(23) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948.
(24) Suginome, M.; Oike, H.; Park, S.-S.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 289.
(25) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241.
(26) Kusumoto, T.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 1807.
(27) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237.
(28) Seyferth, D.; Goldman, E. W.; Escudié, J. *J. Organomet. Chem.* **1984**, *271*, 337.
(29) Kusukawa, T.; Kabe, Y.; Ando, W. *Chem. Lett.* **1993**, 985.
(30) Kusukawa, T.; Kabe, Y.; Nestler, B.; Ando, W. *Organometallics* **1995**, *14*, 2556.
(31) Finckh, W.; Tang, B.-Z.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904.
(32) Naka, A.; Hayashi, M.; Okazaki, S.; Ishikawa, M. *Organometallics* **1994**, *13*, 4994.
(33) Suginome, M.; Oike, H.; Ito, Y. *Organometallics* **1994**, *13*, 4148.
(34) Murakami, M.; Oike, H.; Sugawara, M.; Suginome, M.; Ito, Y. *Tetrahedron* **1993**, *49*, 3933.
(35) Tamao, K. In *Advances in Silicon Chemistry*; JAI Press: London, 1996; Vol. 3, p 1.
(36) Murakami, M.; Suginome, M.; Fujimoto, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1473.
(37) Sekiguchi, A.; Ichinohe, M.; Kabuto, C.; Sakurai, H. *Organometallics* **1995**, *14*, 1092.
(38) Sekiguchi, A.; Ichinohe, M.; Kabuto, C.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2981.
(39) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 4884.
(40) Suginome, M.; Takama, A.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1930.
(41) For the silicon-tethered reactions, see: Bols, M.; Skrydstrup, T. *Chem. Rev.* **1995**, *95*, 1253. Fensterbank, L.; Malacria, M.; Sieburth, S. McN. *Synthesis* **1997**, 813.
(42) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780.
(43) For the discussion of the mechanism of the Peterson elimination, see: Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 7598. Naganuma, K.; Kawashima, T.; Okazaki, R. *Chem. Lett.* **1999**, 1139.
(44) Suginome, M.; Takama, A.; Matsumoto, A.; Ito, Y. Manuscript in preparation.
(45) Tamao, K.; Okazaki, S.; Kumada. M. *J. Organomet. Chem.* **1978**, *146*, 87.
(46) Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185.
(47) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* **1975**, 887.

(48) Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229.
(49) Obora, Y.; Tsuji, Y.; Kawamura, T. *Organometallics* **1993**, *12*, 2853.
(50) Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483.
(51) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353.
(52) Obora, Y.; Tsuji, Y.; Kakehi, T.; Kobayashi, M.; Shinkai, Y.; Ebihara, M.; Kawamura, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 599.
(53) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343.
(54) Hayashi, T.; Kobayashi, T.-a.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.
(55) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987.
(56) Ito, Y.; Suginome, M. *Pure Appl. Chem.* **1996**, *68*, 505.
(57) Suginome, M.; Matsumoto, A.; Nagata, K.; Ito, Y. *J. Organomet. Chem.* **1995**, *499*, C1.
(58) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487.
(59) Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608.
(60) Suginome, M.; Matsunaga, S.; Iwanami, T.; Matsumoto, A.; Ito, Y. *Tetrahedron Lett.* **1996**, *37*, 8887.
(61) Suginome, M.; Matsunaga, S.; Ito, Y. *Synlett* **1995**, 941.
(62) Suginome, M.; Nakamura, H.; Ito, Y. *Tetrahedron Lett.* **1997**, *38*, 555.
(63) Suginome, M.; Matsumoto, A.; Ito, Y. Unpublished results.
(64) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3061.
(65) Suginome, M.; Iwanami, A.; Matsumoto, A.; Ito, Y. *Tetrahedron: Asymmetry* **1997**, *8*, 859.
(66) For the synthetic utility of chiral allylsilanes, see: Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293.
(67) Suginome, M.; Iwanami, T.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 6096.
(68) Suginome, M.; Iwanami, T.; Ito, Y. *Chem. Commun.* **1999**, 2537.
(69) Ito, Y.; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293.
(70) Weidenbruch, M.; Kroke, E.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1993**, *461*, 35.
(71) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.
(72) Murakami, M.; Suginome, M.; Matsuura, T.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8899.
(73) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 4147.
(74) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5579.
(75) Yamashita, H.; Reddy, N. P.; Tanaka, M. *Chem. Lett.* **1993**, *315*.
(76) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1977**, *131*, 147.
(77) Uchimaru, Y.; Tanaka, M. *J. Organomet. Chem.* **1996**, *521*, 335.
(78) Suginome, M.; Oike, H.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1665.
(79) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *Organometallics* **1996**, *15*, 2170.
(80) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31.
(81) Yamashita, H.; Tanaka, M. *Chem. Lett.* **1992**, 1547.
(82) Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801.
(83) Ito, Y.; Suginome, M.; Murakami, M.; Shiro, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1494.
(84) Weidenbruch, M.; Hamann, J.; Pohl, S.; Saak, W. *Chem. Ber.* **1992**, *125*, 1043.
(85) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331.
(86) Murakami, M.; Yoshida, T.; Ito, Y. *Organometallics* **1994**, *13*, 2900.
(87) Suginome, M.; Kato, Y.; Takeda, N.; Oike, H.; Ito, Y. *Organometallics* **1998**, *17*, 495.
(88) Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447.
(89) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955.
(90) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *J. Organomet. Chem.* **1996**, *521*, 405.
(91) Liu, C.-s.; Cheng, C.-w. *J. Am. Chem. Soc.* **1975**, *97*, 6746.
(92) Groshens, T. J.; Klabunde, K. J. *Organometallics* **1982**, *1*, 564.
(93) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373.
(94) Sakaki, S.; Ogawa, M.; Kinoshita, M. *J. Phys. Chem.* **1995**, *99*, 9933.
(95) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *Inorg. Chem.* **1994**, *33*, 1660.
(96) Ozawa, F.; Kamite, J. *Organometallics* **1998**, *17*, 5630.
(97) Kobayashi, T.-a.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467.
(98) Ogawa, A.; Kuniyasu, H.; Takeba, M.; Ikeda, T.; Sonoda, N.; Hirao, T. *J. Organomet. Chem.* **1998**, *564*, 1.
(99) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354.
(100) Chenard, B. L.; Laganis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3666.
(101) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561.
(102) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868.
(103) Beaudet, I.; Parrain, J.-L.; Quintard, J.-P. *Tetrahedron Lett.* **1991**, *32*, 6333.
(104) Murakami, M.; Amii, H.; Takizawa, N.; Ito, Y. *Organometallics* **1993**, *12*, 4223.
(105) Casson, S.; Kocienski, P.; Reid, G.; Smith, N.; Street, J. M.; Webster, M. *Synthesis* **1994**, 1301.
(106) Ritter, K. *Synthesis* **1989**, 218.
(107) Mori, M.; Watanabe, N.; Kaneta, N.; Shibasaki, M. *Chem. Lett.* **1991**, 1615.
(108) Overman, L. E.; Wild, H. *Tetrahedron Lett.* **1989**, *30*, 647.
(109) Farina, V.; Krishnamurthy, V.; Scott, W. J. In *Organic Reactions*; Paquett, L. A., Ed.; Wiley: New York, 1997; Vol. 50, p 1.
(110) Curran, D. P.; van Elburg, P. A. *Tetrahedron Lett.* **1989**, *30*, 2501.
(111) Ritter, K. *Tetrahedron Lett.* **1990**, *31*, 869.
(112) Norley, M. C.; Kociénski, P. J.; Faller, A. *Synlett* **1994**, 77.
(113) Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359.
(114) Murakami, M.; Morita, Y.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 428.
(115) Ikenaga, K.; Hiramatsu, K.; Nasaka, N.; Matsumoto, S. *J. Org. Chem.* **1993**, *58*, 5045.
(116) Tsuji, Y.; Obora, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9368.
(117) Mitchell, T. N.; Schneider, U. *J. Organomet. Chem.* **1991**, *407*, 319.
(118) Barrett, A. G. M.; Wan, P. W. H. *J. Org. Chem.* **1996**, *61*, 8667.
(119) Obora, Y.; Tsuji, Y.; Asayama, M.; Kawamura, T. *Organometallics* **1993**, *12*, 4697.
(120) Ito, Y.; Bando, T.; Matsuura, T.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 980.
(121) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1987**, *109*, 7888.
(122) Murakami, M.; Matsuura, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 355.
(123) Hada, M.; Tanaka, Y.; Ito, M.; Murakami, M.; Amii, H.; Ito, Y.; Nakatsuji, H. *J. Am. Chem. Soc.* **1994**, *116*, 8754.
(124) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6408.
(125) Ozawa, F.; Sakamoto, Y.; Sagawa, T.; Tanaka, R.; Katayama, H. *Chem. Lett.* **1999**, 1307.
(126) Nozaki, K.; Wakamatsu, K.; Nonaka, W.; Tückmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1986**, *27*, 2007.
(127) Buynak, J. D.; Geng, B. *Organometallics* **1995**, *14*, 3112.
(128) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777.
(129) Suginome, M.; Matsuda, T.; Nakamura, H.; Ito, Y. *Tetrahedron* **1999**, *55*, 8787.
(130) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics*, in press.
(131) Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229.
(132) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
(133) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 4229.
(134) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **1998**, *17*, 5233.
(135) Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516.
(136) Suginome, M.; Ohmori, Y.; Ito, Y. *Synlett* **1999**, 1567. The 76th Annual Meeting of the Chemical Society Japan, Yokohama, March 28−31, 1999; Abstract 1B635.
(137) Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1999**, 1863.
(138) Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1567.
(139) Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4248.
(140) Suginome, M.; Fukuda, T.; Ito, Y. *Organometallics*, in press.
(141) Sakaki, S.; Kai, S.; Sugimoto, M. *Organometallics* **1999**, *18*, 4825.
(142) Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891.
(143) Takeyama, Y.; Nozaki, K.; Matsumoto, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1461.
(144) Saso, H.; Ando, W. *Chem. Lett.* **1988**, 1567.
(145) Chatani, N.; Hanafusa, T. *J. Chem. Soc., Chem. Commun.* **1985**, 838.
(146) Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539.
(147) Suginome, M.; Kinugasa, H.; Ito, Y. *Tetrahedron Lett.* **1994**, *35*, 8635.

(148) Chatani, N.; Takeyasu, T.; Hanafusa, T. *Tetrahedron Lett.* **1986**, *27*, 1841.
(149) Chatani, N.; Takeyasu, T.; Hanafusa, T. *Tetrahedron Lett.* **1988**, *29*, 3979.
(150) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 8249.
(151) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow. D. *J. Organomet. Chem*. **1986**, *304*, 257.
(152) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018. Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R. Wright, L. J. *Chem. Rev*. **1998**, *98*, 2685. Marder, T. B.; Norman, N. C. *Topics in Catalysis* **1998**, *5*, 63 and references therein.

CR9902805