Activation of silicon–silicon σ bonds by transition-metal complexes: synthesis and catalysis of new organosilyl transition-metal complexes

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Stoichiometric and catalytic reactions of organosilicon compounds having Si–Si bonds with palladium and platinum complexes are described. Bis(organosilyl)-palladium(II) and -platinum(II) complexes were synthesized by reactions of disilanes with palladium(0)– and platinum(0)–isocyanide complexes. Reactions of bis(disilanes) such as bis(disilanyl)dithianes with the palladium(0) and platinum(0) complexes afforded cyclic bis(organosilyl)-palladium(II) complexes and a tetrakis(organosilyl)platinum(IV) complex, respectively, *via* simultaneous activation of the two Si–Si bonds of the bis(disilanes). On the basis of the stoichiometric investigations, catalytic intramolecular bis-silylation of carbon–carbon multiple bonds and ring-enlargement oligomerization of cyclic disilanes were achieved by use of palladium(0)–isocyanide catalysts, demonstrating synthetic utility of the Si–Si bond activation. On the other hand, activation of the Si–Si bonds by palladium(II) complexes, which is crucially involved in ring-opening polymerization of cyclic disilanes, enabled synthesis of cyclopentadienyltris(organosilyl)palladium(IV) complexes by reaction of a spiro-trisilane with cyclopentadienyl(allyl)-palladium(II) complexes.

1 Introduction

Much interest has been focused on formation of organosilyl complexes of transition metals, which are generated by transition-metal mediated reactions with organosilicon compounds.[1–7] A variety of organosilyl transition-metal complexes have been conveniently generated from hydrosilanes through oxidative addition of the silicon–hydrogen bonds onto transition-metal complexes, leading to the development of not only hydrosilylation[8] and hydrosilative C–C bond forming reactions,[9] but also dehydrogenative Si–Si bond forming reactions.[10]

The silicon–silicon σ bond, which is characterized by its high energy σ orbital and low energy σ* orbital, has also attracted considerable attention from the viewpoint of synthesis of organosilicon compounds as well as application to new organosilicon materials. An activation of the Si–Si bonds by transition-metal complexes was first realized by a nickel-catalyzed reaction of hydrodisilanes with dienes reported by Kumada and co-workers.[11] Although the Si–Si bond activation involved a preceding silicon–hydrogen bond cleavage on the nickel complex, the discovery has promoted the rapid development of Si–Si activation chemistry using palladium catalysts.[7] However, the catalytic activation of the Si–Si bonds has not been fully exploited to a synthetically useful level, presumably due to the lack of efficient transition-metal complex catalysts for the activation.

In this paper, we describe our recent study on the chemistry of Si–Si bond activation by palladium and platinum complexes. Use of ligands of choice, mostly isocyanide, on the transition-metal complexes has been crucially important to achieve effective Si–Si activation. We begin with the synthesis and characterization of novel transition-metal complexes having multiple organosilyl ligands through to the activation, and then describe catalytic reactions using disilanes.
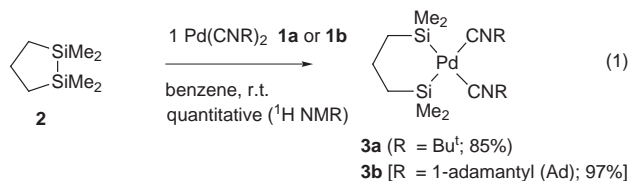
2 Stoichiometric Activation of Si–Si Bonds

Background

Soon after the nickel-catalyzed reaction of the disilane was reported,[11] more efficient activation of Si–Si bonds was found by means of palladium–phosphine complexes.[12,13] Presumably, bis(organosilyl)palladium(II) complexes were generated through oxidative addition of the Si–Si bonds, which might be pertinent to the formation of a bis(organosilyl)nickel(II) complex in the reaction of a highly activated disilane with Ni(CO)$_4$.[14] Since then, some bis(organosilyl)palladium(II) complexes have been synthesized by the oxidative addition of Si–Si bonds onto low-valent palladium complexes.[15,16] Fink's group first succeeded in a single-crystal X-ray analysis of a bis(organosilyl)palladium(II) complex prepared from a hydrodisilane and hydridopalladium complex.[17] Nevertheless, these investigations on the stoichiometric activation of the Si–Si bonds have not led to a remarkable development of catalytic reactions with disilanes.

In 1991, we reported that a catalyst prepared from Pd(OAc)$_2$ and excess *tert*-alkyl isocyanide effectively promoted an addition of the Si–Si bond of hexamethyldisilane, which had been known to be unreactive in the palladium-catalyzed reactions due to the lack of electron-withdrawing substituents on the silicon atoms, across carbon–carbon triple bonds.[18] The new palladium complex has been applied to intramolecular bis-silylation of carbon–carbon double as well as triple bonds, leading to regio- and stereo-selective syntheses of organosilicon compounds which are useful for organic synthesis. Active palladium species in the catalytic reactions were investigated on the basis of stoichiometric reactions with disilanes. It is presumed that a bis(*tert*-alkyl isocyanide)palladium(0) complex, which might be generated from Pd(OAc)$_2$ and excess *tert*-alkyl isocyanide, is a key intermediate in the catalytic reactions. Indeed, bis(*tert*-alkyl isocyanide)palladium(0), which is independently prepared by the reaction of the (cyclopentadienyl)(allyl)-palladium(II) complex [Pd^{II}Cp(CH$_2$CH=CH$_2$)] with *tert*-alkyl isocyanide,[19] showed a remarkable activation of the Si–Si bonds of disilanes.

Oxidative addition of the Si–Si bond onto Pd^0 and Pt^0

Our first attempt at the reaction of hexamethyldisilane with bis(*tert*-butyl isocyanide)palladium(0) **1** resulted in no reaction even at elevated temperature. Probably, the oxidative addition and reductive elimination of the Si–Si bond on the palladium center are in rapid equilibrium, disfavoring the formation of the bis(organosilyl)palladium(II). In order to make the formation of bis(organosilyl)palladium(II) favorable, the reaction with a strained cyclic disilane and **1** was examined. 1,1,2,2-Tetramethyl-1,2-disilacyclopentane **2**, known as a virtually stable but reactive disilane, was reacted with **1** at room temperature in benzene. As expected, oxidative addition of the silicon–silicon bond occurred instantaneously to give a six-membered cyclic bis(organosilyl)bis(*tert*-butyl isocyanide)palladium(II) complex **3a**, which was isolated by crystallization from benzene on addition of propan-2-ol in high yield [equation (1)].[20] An X-ray

Fig. 1 The crystal structure of complex **3b**

isocyanide is a desirable ligand to stabilize bis(organosilyl)palladium(II) complexes.

The formation of bis(organosilyl)palladium(II) complexes was also observed for four-membered cyclic as well as bicyclic disilanes **4** and **5**, giving the corresponding oxidative addition products **6** and **7** which could be isolated by crystallization [equations (2) and (3)].[22] Though six-membered 1,1,2,2-tetra-methyl-1,2-disilacyclohexane did not react with **1**, 1,1-dimethoxy-2,2-dimethyl-1,2-disilacyclohexane **8** afforded the seven-membered cyclic complex **9** quantitatively [equation (4)].

Noteworthy is that the spirocyclic trisilane **10**, in which both the five-membered rings contain a Si–Si bond, reacted with **1** to give the dinuclear palladium(II) complex **11** having μ-silylene and μ-isocyanide ligands co-ordinated to the two palladium atoms [equation (5)].[23] Interestingly, an X-ray analysis showed

that the two palladium atoms are separated by 2.75 Å, which is the same as the shortest metal–metal contact in metallic palladium (Fig. 2).

analysis of the air-sensitive crystal of the bis(1-adamantyl iso-cyanide)palladacycle complex **3b** revealed a square planar structure with two co-ordinated isocyanide ligands on the palladium atom (Fig. 1).[21] It should be noted that addition of phosphine ligands to a solution of **3** induced reductive elimination of the Si–Si bond to give **2**, suggesting that *tert*-alkyl
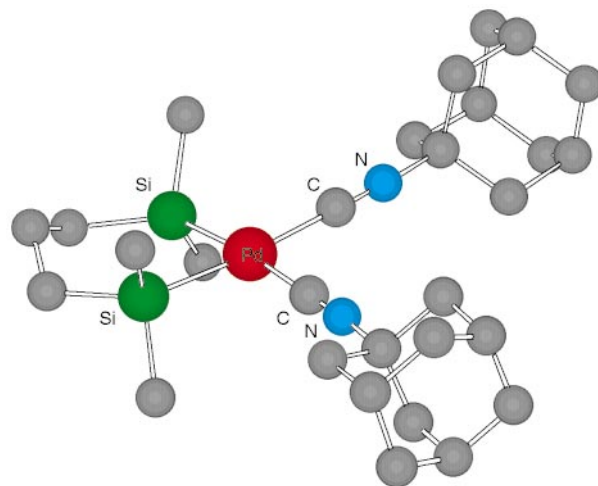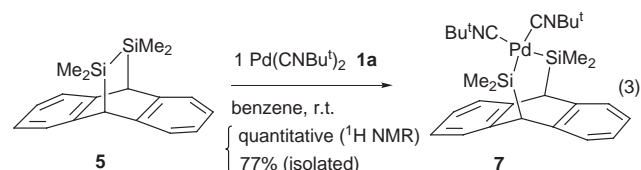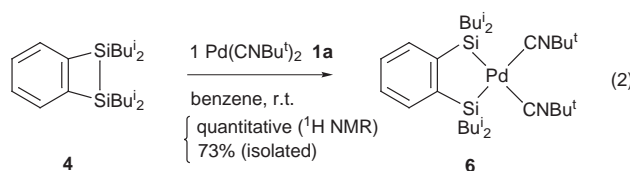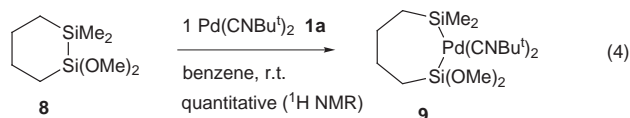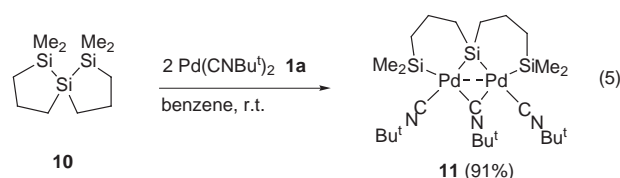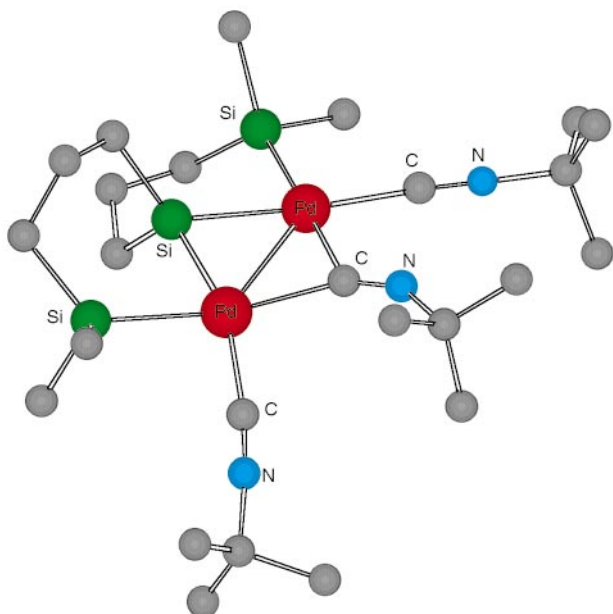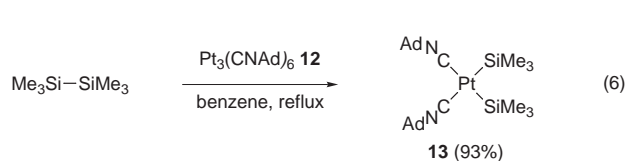
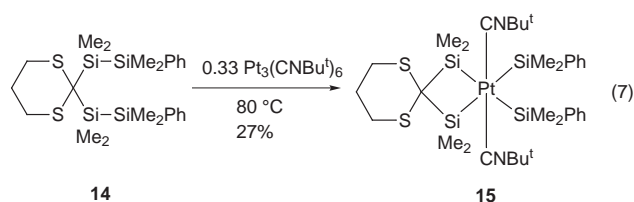**Fig. 2** The crystal structure of complex **11**

The oxidative addition of the Si–Si bonds onto the palladium(0)–isocyanide complex described thus far provided the corresponding bis(organosilyl)palladium complexes in high yields in the cases of disilanes having ring strain or heteroatom substituents on the silicon atom. In contrast, the platinum(0)–isocyanide complex **12** underwent the oxidative addition reaction with hexamethyldisilane to give bis(trimethylsilyl)bis(*tert*-butyl isocyanide)platinum(II) complex **13** in high yield in the presence of a large excess of the disilane [equation (6)].[24]

$$Me_3Si-SiMe_3 \xrightarrow[\text{benzene, reflux}]{Pt_3(CNAd)_6 \ \mathbf{12}} \quad \begin{matrix} Ad_N \overset{C}{\diagdown}_{Pt} \diagup^{SiMe_3} \\ Ad^{N} \diagup^{C} \diagdown_{SiMe_3} \end{matrix} \qquad (6)$$

13 (93%)

Though the assignment of the geometry of **13**, *cis* or *trans*, is still tentative, to our best knowledge, this may be the first example of a bis(trimethylsilyl)transition-metal complex produced by oxidative addition of hexamethyldisilane.

Double oxidative addition of Si–Si bonds onto Pt[0]

The success of the oxidative addition of the Si–Si bond onto the platinum(0)–isocyanide complex **12** prompted us to examine the reaction with bis(disilanes), expecting double oxidative addition of the two Si–Si bonds at the platinum center. Bis(disilanyl)dithiane **14** was synthesized and reacted with complex **12** in benzene at 80 °C for 24 h. Column chromatography on silica gel afforded the tetrakis(organosilyl)bis(isocyanide)platinum(IV) complex **15** in 27% yield [equation (7)].[24] The formation of **15**

$$\text{equation (7)}$$

14   **15**

arises from double oxidative addition of the two Si–Si bonds of **14** to the platinum(0) complex. No complex corresponding to **15** was formed when **14** was treated with the complex Pt-(PPh$_3$)$_2$(H$_2$C=CH$_2$) at 50 to 80 °C. A crystal structure of the stable platinum(IV) complex revealed that the two isocyanide
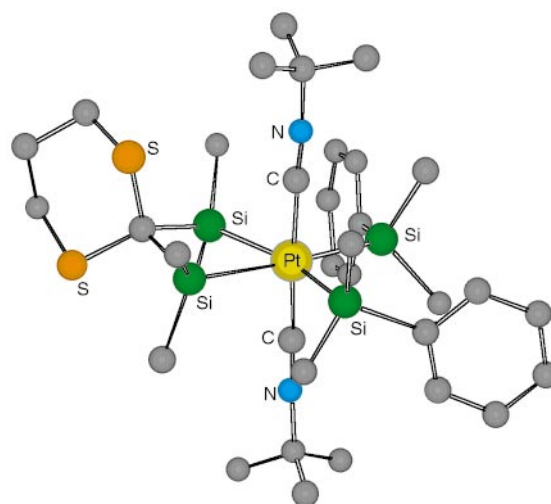

Fig. 3 The crystal structure of complex **15**

ligands occupy the apical positions and the four silyl ligands lie at the vertices of a distorted square with the platinum atom at the center in the octahedral complex (Fig. 3).

A similar reaction of **12** with bis(silylgermyl)dithiane **16** provided the bis(organogermyl)bis(organosilyl)bis(isocyanide)-platinum(IV) complex **17** in 30% yield along with the un-expected formation of the tetrakis(organogermyl)platinum(IV) complex **18** in 11% yield, whose structure was determined by an X-ray analysis, revealing the apical co-ordination of the two isocyanide ligands to the platinum atom [equation (8)].

$$\text{equation (8)}$$

16   **17** (30%)

18 (11%)
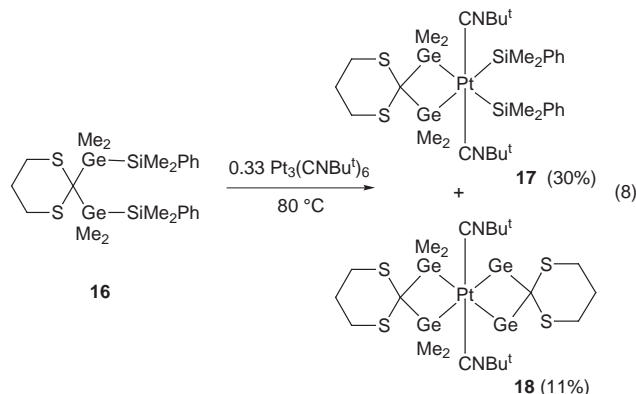
The double oxidative addition reaction of Si–Si bonds onto the platinum atom may suggest the possibility of the simultaneous activation of the two Si–Si bonds with palladium complexes. Next, we examined reactions of bis(disilanes) with bis(isocyanide)palladium(0) complexes.

Intramolecular Si–Si bond metathesis on Pd[0]

Reaction of bis(disilanyl)dithiane **14** with an equimolar amount of **1** in benzene was examined at room temperature. The reaction was completed within 5 min, affording 1,1,2,2-tetramethyl-1,2-diphenyldisilane and a four-membered cyclic bis(organosilyl) complex **19** in 85% yield after isolation by crystallization with pentane [equation (9)].[25] A crystal structure of

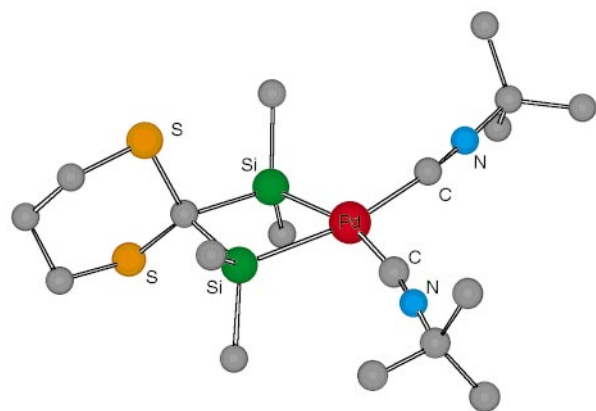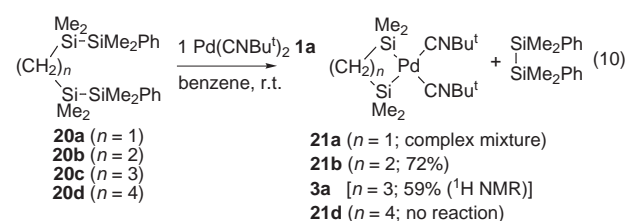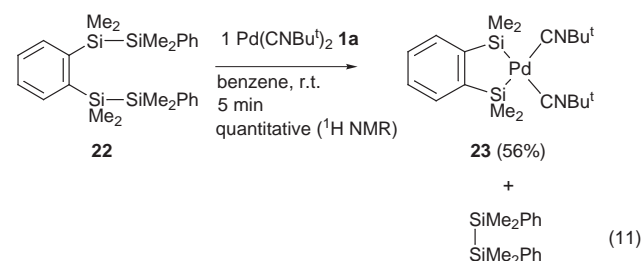$$\text{equation (9)}$$

19 (85%)
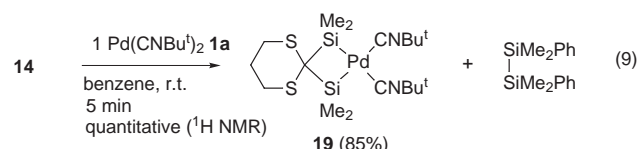
Fig. 4 The crystal structure of complex **19**

19 exhibited a distorted square planar structure, in which the two silicon atoms in the ring are separated only by 2.61 Å (Fig. 4). Presumably, the formation of **19** may have arisen from the simultaneous activation of the two Si–Si bonds on palladium, which led to intramolecular metathesis (disproportionation).

The intramolecular metathesis of the Si–Si bonds giving bis(organosilyl)palladium(II) complexes took place in the reactions of various bis(disilanyl)alkanes with **1**.[22] However, the success of the intramolecular metathesis depended upon the tethers connecting the two disilanyl groups [equation (10)].

20a (*n* = 1)
20b (*n* = 2)
20c (*n* = 3)
20d (*n* = 4)

21a (*n* = 1; complex mixture)
21b (*n* = 2; 72%)
3a [*n* = 3; 59% (^{1}H NMR)]
21d (*n* = 4; no reaction)

Bis(disilanyl)methane **20a** conceivably underwent the intramolecular metathesis to produce tetramethyldiphenyldisilane, although the expected four-membered cyclic complex **21a** could not be detected by ^{1}H NMR spectroscopy presumably due to rapid decomposition of unstable **21a**. The corresponding ethane and propane derivatives **20b** and **20c** gave the cyclic bis(organosilyl)palladium complexes **21b** and **3a**, respectively, the reaction of the latter being much slower. No reaction took place with 1,4-bis(disilanyl)butane **20d**, which has a longer tether. *o*-Bis(disilanyl)benzene **22** also underwent the intramolecular metathesis very rapidly to give **23** in high yield [equation (11)].


The ethylene glycol-derived bis(disilanyl ether) **24a** underwent the intramolecular metathesis to give the seven-membered complex **25a** in good yield [equation (12)]. This may be interestingly compared with the attempted metathesis of **20d**, suggesting that the oxygen substituents and phenyl groups on the silicon atoms favor the intramolecular metathesis. Accordingly, reaction of tartrate-derived **24b** proceeded smoothly to give **25b** in high yield. Similarly, bis(disilanyl ethers) with longer tethers (**24c** and **24d**) gave the corresponding cyclic bis(organosilyl)palladium complexes and tetramethyldiphenyldisilane, although

24a R = H
24b R = CO$_2$Et

25a R = H (73%)
**25b** R = CO$_2$Et (95%)

24c   **24d**
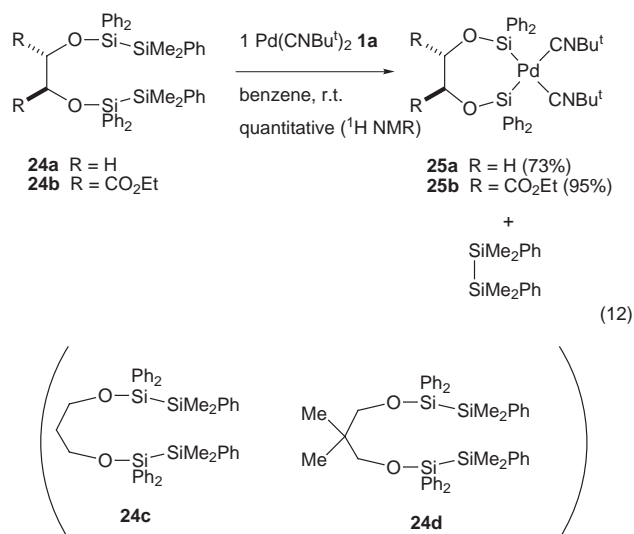
the reactions were too sluggish to obtain the palladium complexes in reasonable yields.

Reactions of bis(organosilyl)palladium(II) complexes

With a variety of bis(silyl)palladium(II) complexes on hand, their reactions with cyclic disilanes were examined next [equation (13)].[22] Reaction of **7** with the five-membered cyclic
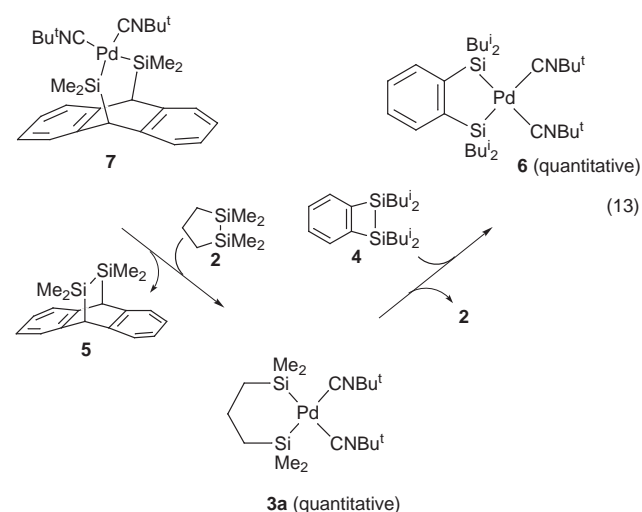
disilane **2** gave the six-membered cyclic bis(organosilyl)palladium complex **3a** and the bicyclic disilane **5** by 'bis(silyl)-exchange'. Similarly, the five-membered cyclic palladium complex **6** and disilane **2** were obtained in the reaction of complex **3** with the four-membered cyclic disilane **4**. Furthermore, the four-membered cyclic complex **19** was formed in the reaction of the palladium complex **3a** with bis(disilanyl)dithiane **14′**, although the reaction was much more sluggish than the reaction of **14′** with bis(isocyanide)palladium(0) **1** [equation (14)].
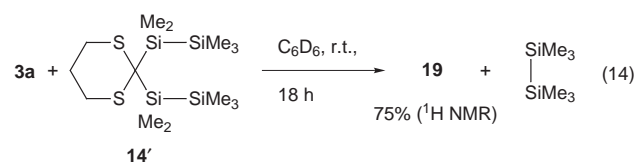
The bis(silyl)-exchange reactions evidenced the reversibility of the Si–Si bond activation through an oxidative addition–reductive elimination process.

The isocyanide ligands in the four-membered complex **19** were replaced by phosphine ligands. Thus, addition of an equimolar amount of triphenylphosphine gave the correspond-

ing mono(isocyanide)mono(phosphine)palladium(II) complex **26** in high yield [equation (15)]. A less bulky phosphine,

$$\textbf{26 (84\%)} \quad \xleftarrow{\text{1 PPh}_3} \quad \textbf{19} \quad \xrightarrow{\text{2 PMe}_2\text{Ph}} \quad \textbf{27 (84\%)} \tag{15}$$
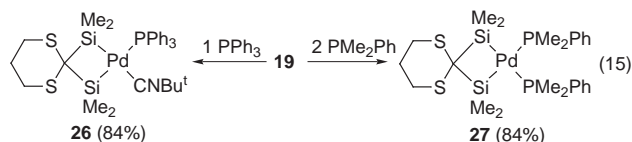
dimethylphenylphosphine, could replace both isocyanide ligands to afford the bis(phosphine)palladium(II) complex **27**. Use of the bidentate ligand, bis(diphenylphosphino)ethane (dppe) and the five-membered palladium complex **6** gave the corresponding dppe complex **28**, whose structure was determined by a single-crystal X-ray analysis [equation (16)]. As already

$$\textbf{6} \quad \xrightarrow[\text{benzene, r.t.}]{\text{Ph}_2\text{P}\frown\text{PPh}_2} \quad \textbf{28 (91\%)} \tag{16}$$
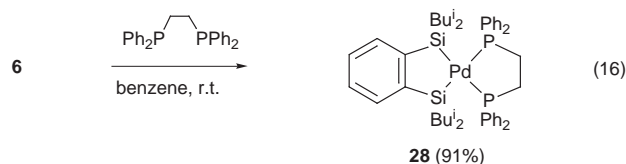
mentioned, addition of dppe to the six-membered ring complex **3** resulted in reductive elimination to give disilane **2** along with an unidentified palladium complex having dppe ligands.

A stoichiometric reaction of the bis(organosilyl)palladium(II) complex **19** with terminal alkynes or bis(methoxycarbonyl)acetylene took place smoothly at room temperature, giving the corresponding spiro-disilacyclopentene derivatives in high yields (Table 1, entries 1–3). Reaction of **19** with diphenylacetylene proceeded at 90 °C in high yield (entry 4), although attempts at the reaction with dialkylacetylenes as well as unactivated alkenes have all failed even under forced conditions.

A ^{1}H NMR spectroscopic study of the stoichiometric bissilylation of phenylacetylene with **19** revealed a rapid formation of bis(*tert*-butyl isocyanide)(spiro-disilacyclopentene)palladium(0) **29a·Pd**, which is spectroscopically identified by comparison with the palladium complex formed in the reaction of **29a** with **1** (Scheme 1). It is noteworthy that the oxidative metathesis of **14′** onto **29a·Pd** proceeded much more slowly than the insertion step, regenerating **19** with production of **29a**.

### Activation of the Si–Si bond by Pd^{II} complexes

In the course of our study on palladium-catalyzed polymerization of cyclic disilanes (see below), we were interested in the possibility of activation of the Si–Si bond by the complex Pd^{II}-Cp(CH$_2$CH=CH$_2$). In fact, a stoichiometric reaction of **2** with Pd^{II}Cp(CH$_2$CH=CH$_2$) gave the ring-opened product **30**, which could be formed through initial oxidative addition of the Si–Si bond onto palladium(II) (giving **31**) followed by a stepwise reductive elimination of the Si–allyl and Si–Cp bonds probably *via* the cyclopentadienyl(organosilyl)palladium complex **32** [equation (17)].[21] Similar treatment of the spirocyclic trisilane

$$\tag{17}$$

$$\tag{17}$$
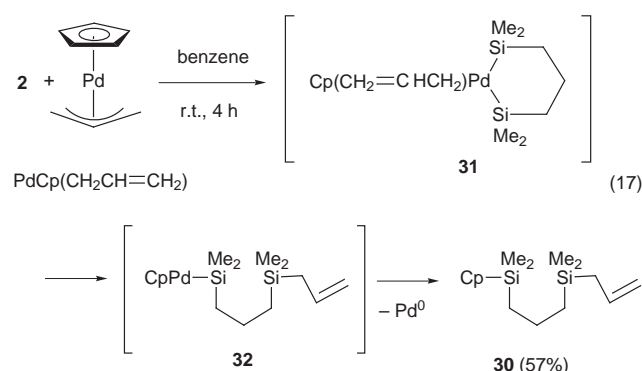
Table 1 Stoichiometric reaction of compound **19** with alkynes

Entry	Alkyne	Conditions*	Products (yield/%)
1	Ph — H	Benzene, r.t., 5 min	**29a** (98)
2	Me$_3$Si — H	Toluene, r.t., 3.5 h	**29b** (90)
3	MeO$_2$C — CO$_2$Me	Benzene, r.t., 5 min	**29c** (99)
4	Ph — Ph	Toluene, 90 °C, 12 h	**29d** (96)

* r.t. = Room temperature.
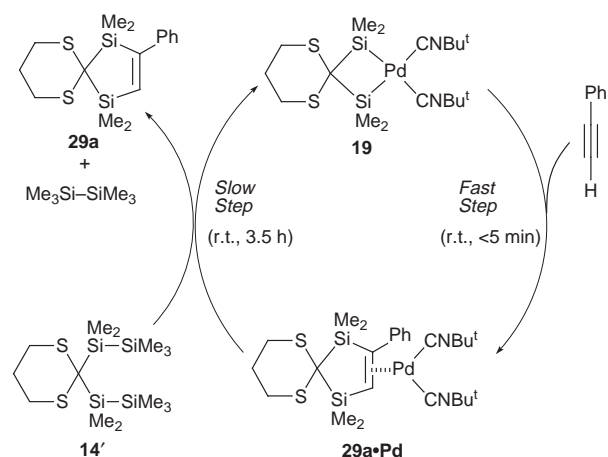
Scheme 1

10 with Pd^{II}Cp(CH$_2$CH=CH$_2$), however, afforded a novel Pd^{IV} complex **33** having three silyl groups and an η^5-Cp or η^5-Cp* group at the palladium center [equation (18)].[23] A single-crystal

$$\textbf{10} \quad + \quad \xrightarrow[\text{r.t.}]{\text{benzene,}} \quad \tag{18}$$

R = H
R = Me

33a R = H (85%)
33b R = Me (61%)
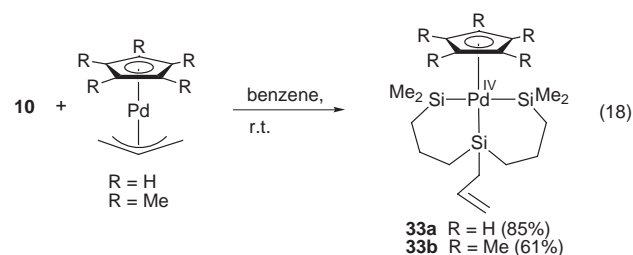
X-ray analysis of the corresponding Cp* derivative **33b** revealed a tetrahedral structure, in which the average bonding distance between palladium and silicon is identical with those for the bis- and tetrakis-(organosilyl)palladium complexes so far characterized (Fig. 5). It is interesting to note that the Pd^{IV} complexes were stable in air as well as moisture to allow us to isolate them by column chromatography on silica gel. The catalytic activity of the Pd^{IV} complexes in polymerization reactions will be discussed below.

3 The Catalytic Activation of Si–Si Bonds for New Synthesis of Organosilanes

Bis-silylation of unsaturated organic compounds

The catalytic addition of the Si–Si bond to unsaturated organic compounds such as alkynes, alkenes, dienes, α,β-unsaturated

ketones and isocyanides has been developed to provide new methodologies for the efficient synthesis of organic silicon compounds.[7] Palladium(0)–isocyanide complexes have been found to serve as highly effective catalysts to promote the bis-silylation reactions of alkynes and alkenes. For the catalytic use of the bis(isocyanide)palladium(0) complexes, the presence of a slight excess of isocyanide is essential to complete the bis-silylation reaction. In practice, the catalyst can be conveniently prepared by mixing the Pd[II] precursors such as Pd(OAc)$_2$ and Pd(acac)$_2$ with 4 to 15 molar equivalents of *tert*-alkyl isocyanide under an inert atmosphere. The palladium–isocyanide complex generated *in situ* is capable of activation of Si–Si bonds of disilanes, leading to the formation of bis(organo-silyl)palladium(II) intermediates. It should be pointed out that the *tert*-alkyl isocyanide on palladium is essential for the following insertion reaction with alkenes and alkynes.
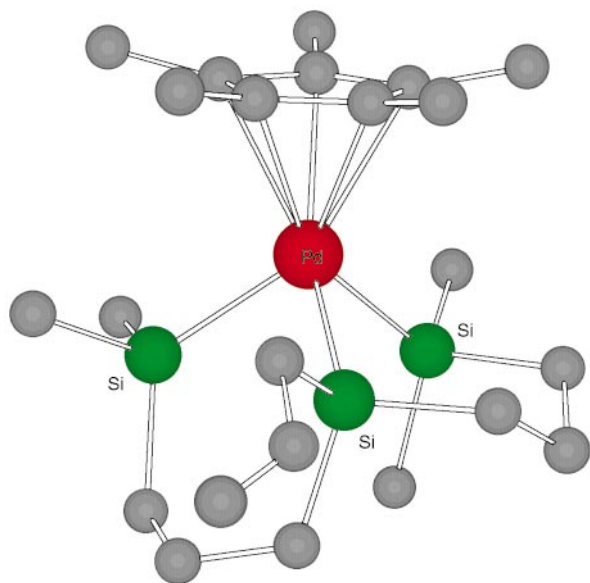

Fig. 5 The crystal structure of complex **33b**

An intramolecular bis-silylation of carbon–carbon multiple bonds has intrigued us from the viewpoint of synthetic useful-ness as follows: (1) starting substrates are readily available from chloropenta(organyl)disilanes with unsaturated alcohols, amines and organometallic reagents; (2) the intramolecular bis-silylation is facilitated under moderate reaction conditions, being compared with the corresponding intermolecular one; and (3) the reactions proceed with high regio- and stereo-selectivities through well ordered cyclic intermediates.[26] Scheme 2 summarizes some representative synthetic appli-cations which have been accomplished by the intramolecular bis-silylation of alkynes and alkenes. We describe briefly the individual synthetic applications, focusing on reactivity, regioselectivity and stereoselectivity of the intramolecular bis-silylation reactions.

Intramolecular bis-silylation of alkynes. Internal alkynes have been reluctant to undergo intermolecular bis-silylation reactions even with activated disilanes. The palladium(0)–isocyanide catalyst also failed to promote the intermolecular bis-silylation of internal alkynes. However, disilanyl ethers **34** of homopropargylic alcohols having internal carbon–carbon triple bonds underwent intramolecular bis-silylation with 5-*exo* ring-closure to give cyclic oxasilolanes **35** in good yields in the presence of the palladium–isocyanide catalyst [equation (19)].[18]
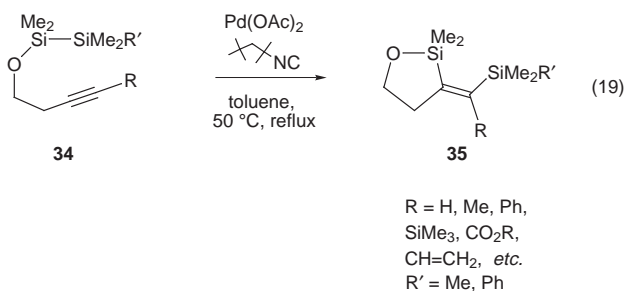

Carbon–carbon triple bonds bearing a variety of substituents such as alkyl, aryl, vinyl, ester and silyl groups under-went intramolecularly *cis*-addition of the Si–Si bonds.[27] A
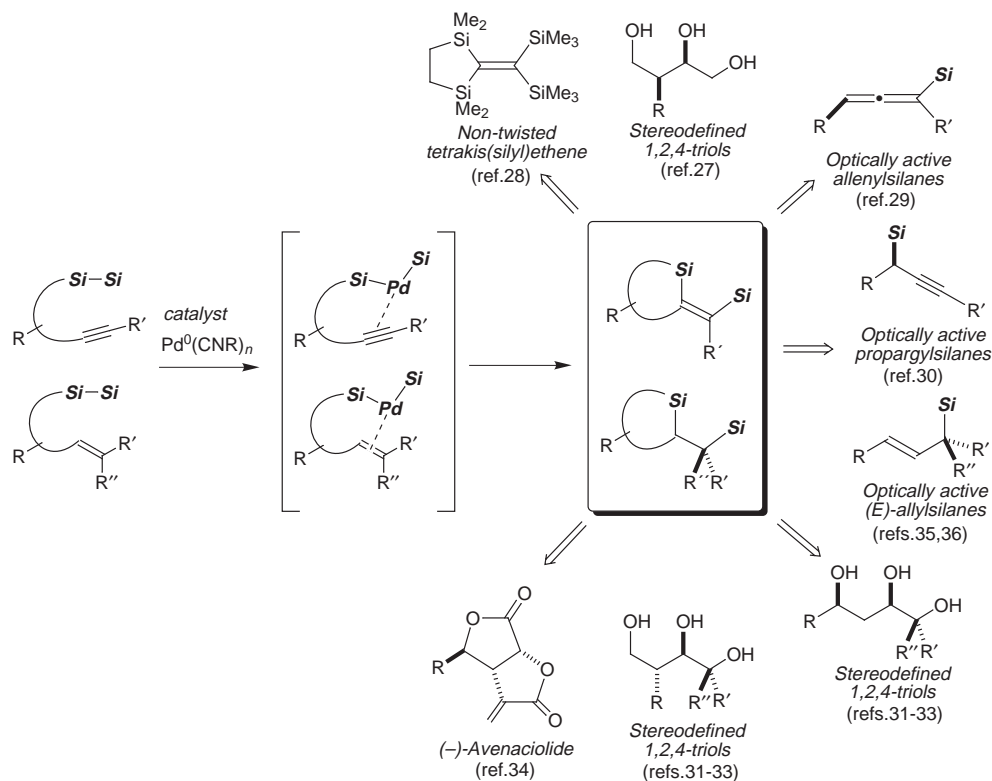

Scheme 2 Alkyl and aryl groups on the silicon atom (***Si***) and the isocyanide ligand(s) on the palladium atom (***Pd***) are omitted for clarity

highly sterically congested tetrakis(organosilyl)ethene **37** was successfully synthesized by intramolecular bis-silylation of **36** under high pressure [equation (20)].[28]


(20)
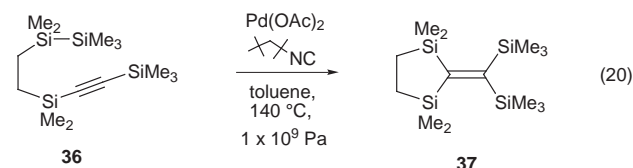
The intramolecular bis-silylation of propargylic alcohols is noteworthy, since few examples have been known for 4-*exo* cyclization reactions producing four-membered ring organosilicon compounds containing Si–O bonds.[37] Reaction of disilanyl ether **38a** prepared from a primary propargylic alcohol gave the eight-membered ring compound **39a** in good yield [equation (21)].[29]


38a R = R′ = H
38b R = Me, R′ = H
38c R = R′ = Me

40b R = Me, R′ = H
40c R = R′ = Me

(21)
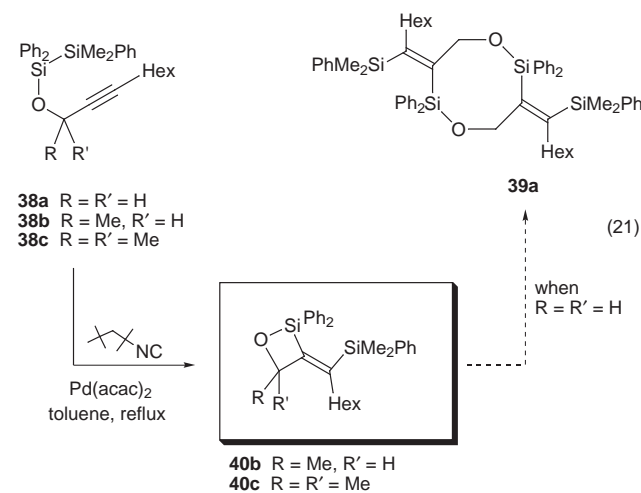
(21)].[29] The formation of **39a** may be rationalized by initial 4-*exo* cyclization followed by dimerization of the unstable oxasiletane. In fact, the four-membered cyclic compound **40b** was formed quantitatively in the reaction of **38b** prepared from a secondary alcohol, although it was difficult to isolate by column chromatography on silica gel or by distillation. Interestingly, reaction of tertiary **38c** afforded chromatographically stable oxasiletane **40c** in high yield.[30] These results suggest that steric repulsion between the 3-alkylidene groups and substituents at the 4-position may prevent cleavage of the Si–O bonds in the four-membered rings. The oxasiletane derivatives have been applied to the synthesis of allenylsilanes and propargylsilanes through subsequent Peterson-elimination[29] and acid-catalyzed [1,2] silyl migration reactions,[30] respectively.

Intramolecular bis-silylation of alkenes. Unlike alkynes, bis-silylation of alkenes has been difficult even with the use of activated disilanes or palladium-isocyanide catalysts.[38,39] However, we were pleased to find that intramolecular bis-silylation of carbon–carbon double bonds proceeded very cleanly in the presence of the palladium-isocyanide catalyst under mild conditions.[31–33] Our examination on the intramolecular bis-


41

42

(22)
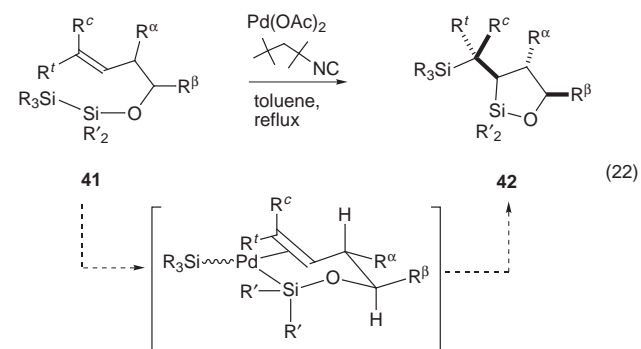
silylation of homoallylic alcohols [equation (22)] may deserve the following comments: (1) the reaction proceeds with highly regioselective 5-*exo* cyclization; (2) reactivities of the C=C bonds decreased in the order CH=CH₂ > CR=CH₂ > CH= CHR ≫ trisubstituted double bonds (unreactive); (3) phenyl groups on the silicon atoms of disilane increased the rate of bis-silylation; and (4) intramolecular bis-silylation of homo-allylic alcohols having substituents α or β to the C=C bond proceeds in high diastereoselectivities to give *trans* or *cis* five-membered ring oxasilolanes, respectively. The regioselective 5-*exo* cyclization for the intramolecular bis-silylation of homoallylic alcohols may involve bis(organosilyl)palladium(II) intermediates, which were formed by the oxidative addition of the Si–Si bond on palladium. The observed high diastereoselectivity can be rationalized by assuming the chair-like conformation of the bis(organosilyl)palladium(II) intermediate, in which the α or β substituent occupies the equatorial position.

The intermediacy of the chair-like palladium(II) complex made stereochemical control of three contiguous stereogenic centers possible. Thus, intramolecular bis-silylation of optically active (>98% e.e.) **43**, which has two diastereotopic vinyl groups, afforded one of the four possible diastereomers (**44**) selectively [equation (23)].[34] In the bis-silylation reaction, sub-

(*R*)-**43** (>98% e.e.)

(*R*,*R*,*R*)-**44**

(23)

(−)-avenaciolide
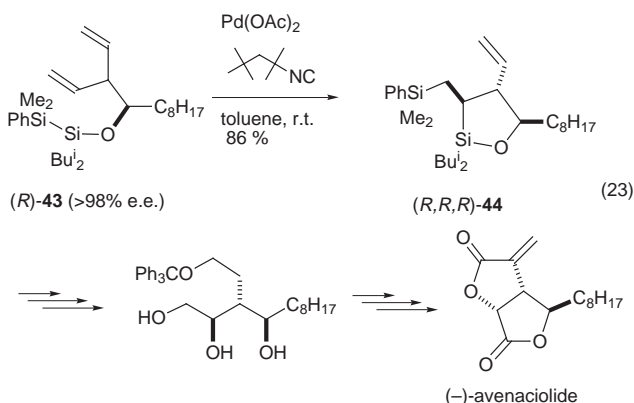
stituents on the silicon atom proximal to the ether oxygen played an important role in controlling the selectivity. The isobutyl group was found to be effective for the production of the (*R*,*R*,*R*) and (*R*,*S*,*R*) isomers in a ratio of 9:1 without formation of (*R*,*S*,*S*) and (*R*,*R*,*S*) isomers. Starting from the optically active oxasilolane derivative obtained stereoselectively the natural antifungal metabolite (−)-avenaciolide was synthesized *via* oxidation of the silicon–carbon bonds.

Furthermore, use of an optically active *tert*-alkyl isocyanide induced enantioselective intramolecular bis-silylation. In the presence of a chiral palladium(0)–*tert*-alkyl isocyanide complex, which was generated *in situ* from a catalytic amount of Pd(acac)₂ and chiral isocyanide **45**, olefinic disilane **46** underwent bis-silylation to give compound **47** in 78% e.e. [equation (24)].[40] To the best of our knowledge, this is the first example of

46 R = *o*-Tol

47 (59%; 78% e.e.)

(24)
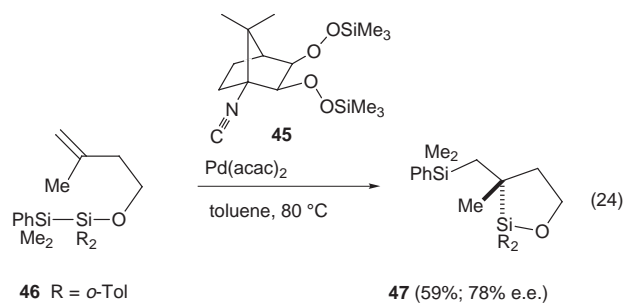
utilization of optically active isocyanides as chiral ligands on transition metals in catalytic asymmetric reactions.

Intramolecular bis-silylation of allylic alcohols also proceeded with extremely high stereoselectivity.[35,36] The reactions
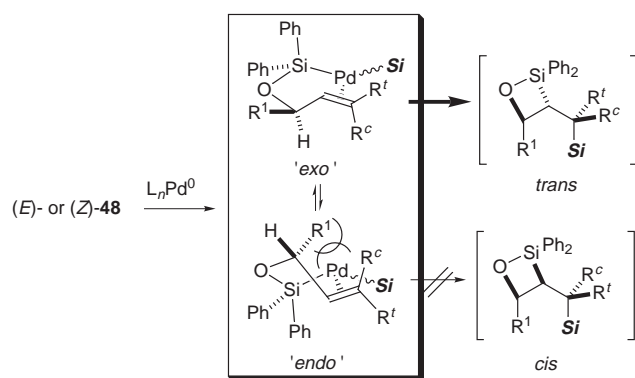
**Scheme 3** The SiMe$_2$Ph is represented by *Si* for clarity

with disilanyl ethers of optically pure (*E*)- or (*Z*)-allylic alcohol afforded eight-membered ring dimers as single enantiomers [equation (25)].[41] X-Ray analyses of the cyclic dimers **49a** and
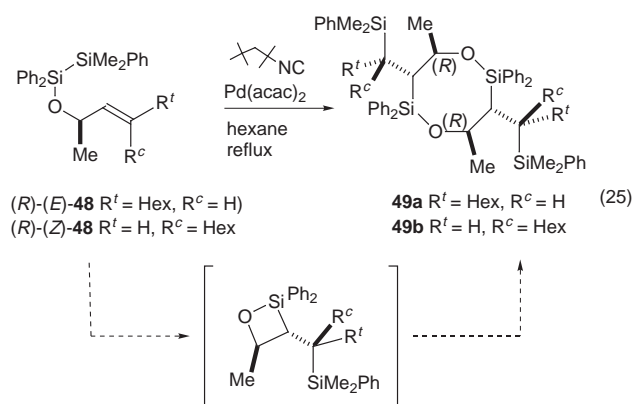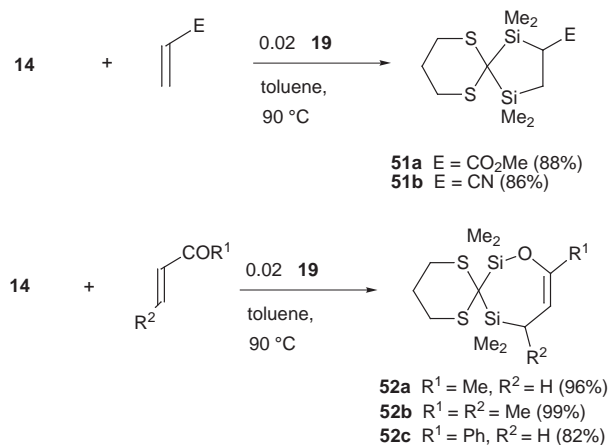

49b revealed that 4-*exo* cyclizations took place with high diastereoselectivity to provide *trans*-oxasiletanes, which dimerize to give eight-membered ring products. It is notable that the bissilylation leading to the formation of the four-membered product is highly diastereoface-selective due to the steric reason shown in Scheme 3. The bis-silylation of optically active allylic alcohols has successfully been applied to the stereoselective synthesis of optically active (*E*)-allylsilanes through subsequent Peterson-elimination reactions.[35,36]

Bis-silylation through intramolecular Si–Si metathesis

Generation of a cyclic bis(organosilyl)palladium(II) intermediate *via* facile intramolecular Si–Si metathesis has resulted in a new bis-silylation reaction. Thus, in the presence of the palladium–isocyanide catalyst **19**, reaction of **14** with phenylacetylene gave the five-membered cyclic alkene **50** in 91% yield [equation (26)].[22,25] It is remarkable that insertion of the alkyne
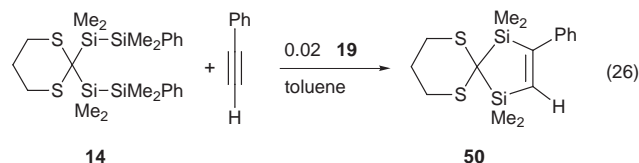

into the Si–Si bonds of **14** did not take place at all, indicating that the intramolecular Si–Si metathesis took place rapidly to give the four-membered intermediate **19**. The new bis-silylation reaction through the Si–Si metathesis has been applied to other alkynes and activated alkenes in the presence of a catalytic amount of **19** (Scheme 4). In the reactions of α,β-unsaturated ketones, 1,4-addition occurred to give the seven-membered ring silyl enol ethers **52** in high yields.[22]

51a E = CO$_2$Me (88%)
51b E = CN (86%)

52a R^1 = Me, R^2 = H (96%)
52b R^1 = R^2 = Me (99%)
52c R^1 = Ph, R^2 = H (82%)

Scheme 4

**Oligomerization and polymerization of cyclic disilanes**

Ring-enlargement oligomerization. Bis(organosilyl)palladium complexes have also been regarded as key intermediates in intermolecular Si–Si bond metathesis.[42,43] Our investigation has shown that palladium(0)–isocyanide catalysts are highly effective for intramolecular Si–Si bond metathesis. The development of a new catalyst to activate the Si–Si bond prompted us to examine intermolecular Si–Si bond metathesis of five-membered **2**, whose cyclodimerization reaction was achieved by the use of a conventional palladium–phosphine catalyst.[42] Interestingly, reaction of **2** in the presence of bis(*tert*-butyl isocyanide)palladium(0) **1** at 50 °C afforded a mixture of macrocyclic oligomers **53** (up to a 40-membered octamer) each of which was isolated by preparative GPC (gel permeation chromatography) in 93% total yield [equation (27)].[20,21] A cyclic dimer,
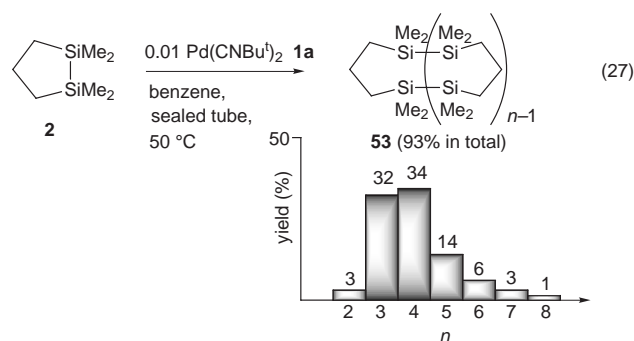
which was exclusively formed in the phosphine–palladium-catalyzed reaction, was obtained only in 3% yield. When each of the trimer and tetramer was subjected to the reaction conditions identical to the oligomerization, only (*n* − 1) and (*n* + 1) polymers were formed in low yields. This result implies that the ring-enlargement oligomerization does not proceed by σ-bond metathesis between the two macrocyclic oligomers, but between the cyclic oligomer and the five-membered disilane **2** *via* the six-membered cyclic bis(organosilyl)palladium(II) complex **3a**. The catalytic cycle may involve double oxidative addition of the Si–Si bonds onto the palladium complex, as previously demonstrated in the formation of the Pt^{IV} complex **15** by double oxidative addition of intramolecular Si–Si bonds (Scheme 5). The striking effect of the *tert*-alkyl isocyanide ligands on palladium may be remarked in that bis(isocyanide)-palladium(0) activates the Si–Si bond of **2** to give **3** effectively, which is able to undergo further oxidative addition of the Si–Si bond of the non-strained macrocyclic oligomers.
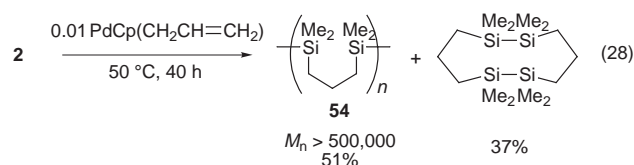
Ring-opening polymerization. The cyclic disilane **2** polymerized in the presence of a catalytic amount (1 mol%) of PdCp-
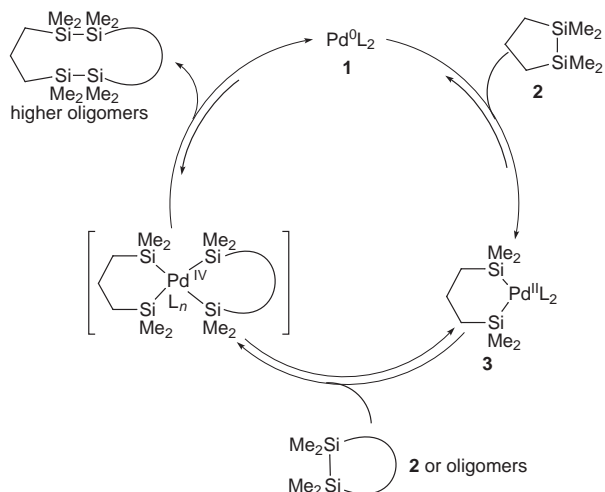
Scheme 5   L = CNR

(CH$_2$CH=CH$_2$) to give the high molecular weight polymers **54**[44,45] and a cyclic dimer without formation of any higher cyclic oligomers [equation (28)].[21] The stoichiometric reaction of **2**

$$2 \xrightarrow[\text{50 °C, 40 h}]{0.01\ \text{PdCp(CH}_2\text{CH=CH}_2)} \left(\overset{\text{Me}_2\ \text{Me}_2}{\underset{}{\text{Si}\ \text{Si}}} \right)_n + \left(\overset{\text{Me}_2\text{Me}_2}{\underset{\text{Me}_2\text{Me}_2}{\text{Si–Si}}} \atop \text{Si–Si} \right) \quad (28)$$

54

$M_n > 500{,}000$
51%   37%

with PdCp(CH$_2$CH=CH$_2$) already mentioned indicated that the polymerization proceeded through a ring-opening mechanism rather than the ring-enlargement mechanism. We can presume that the Pd^{II} complex **32** might be a possible key intermediate for the polymerization.[23] The proposed mechanism is shown in Scheme 6. Oxidative addition of the Si–Si bond of **2** onto PdCp(CH$_2$CH=CH$_2$) followed by reductive elimination gives the cyclopentadienyl(organosilyl)palladium(II) complex **32**. The intermediate **32**, which can afford **30** by reductive elimination, undergoes further oxidative addition of the Si–Si bond of **2** to give the cyclopentadienyltris(organosilyl)palladium(IV) intermediate **55**. Subsequent reductive elimination at **55** with the formation of a new Si–Si bond constitutes the propagation step for the polymerization. Termination of the polymerization may involve reductive elimination with a Cp–Si bond formation, as presented in the stoichiometric reaction of **2** with PdCp(CH$_2$CH=CH$_2$).

4 Conclusion

The isocyanide ligand on palladium and platinum complexes has enabled the highly effective generation of new organosilyl-palladium and -platinum complexes through oxidative addition of the Si–Si bonds. The catalytic activation of Si–Si bonds followed by the inter- and intra-molecular reactions with carbon–carbon multiple bonds led to the development of new methodologies for the synthesis of organosilicon compounds. Moreover, we disclosed that palladium(IV) complexes may be involved in the palladium-catalyzed oligomerization and poly-merization reactions.

Finally, it should be emphasized that the chemistry of Si–Si bond activation can be extended to those of other intermetallic bonds including silicon, germanium, tin and boron. Indeed, the palladium–isocyanide complexes and related transition-metal complexes were found to be highly effective for the activation of silicon–tin[46,47] and silicon–boron[48–50] bonds, leading to a new synthesis of organometallic compounds.
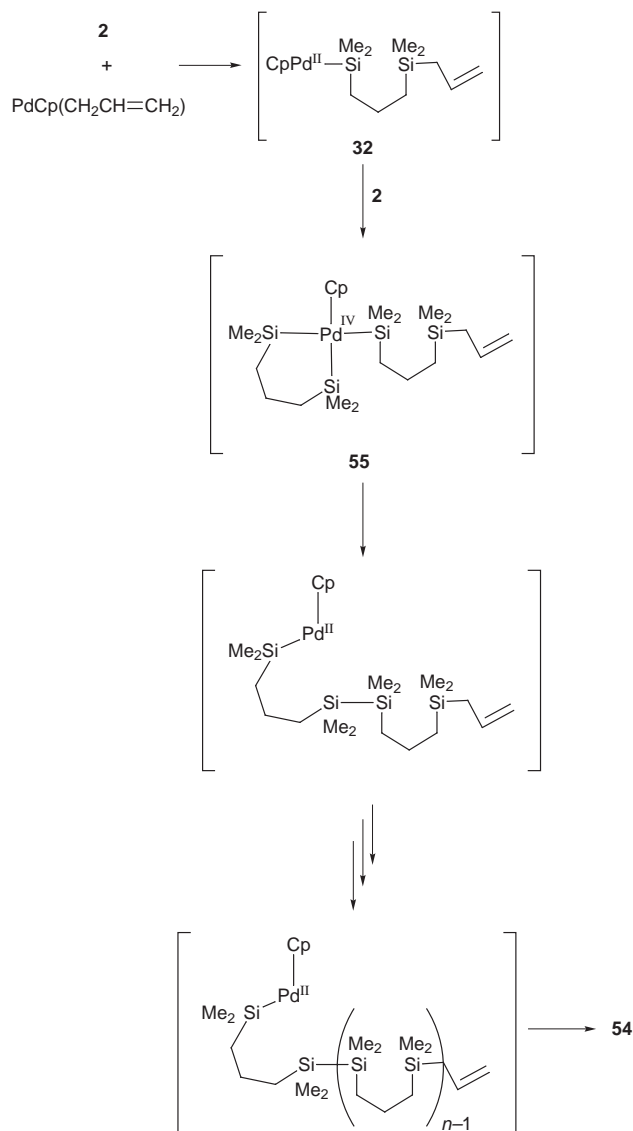
Scheme 6

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