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Novel Activation of Two Si–Si σ-Bonds in a Molecule by *tert*-Alkyl Isocyanide–Palladium Complexes

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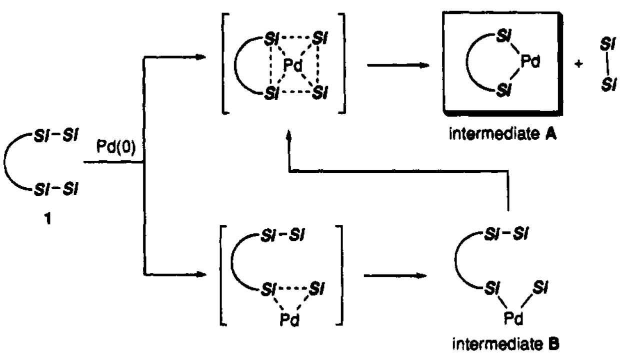
Summary: Novel activation of two Si–Si σ-bonds of bis(disilanyl)methane derivatives **1** *by palladium/tert-alkyl isocyanide complexes gave cyclic bis(silyl)palladium bis(tert-alkyl isocyanide) complexes, one of which was isolated and characterized by the single-crystal X-ray method. The activation led to new catalytic bis-silylations of phenylacetylene and electron-deficient olefins with* **1** *to give cyclic organic silicon compounds in high yields.*

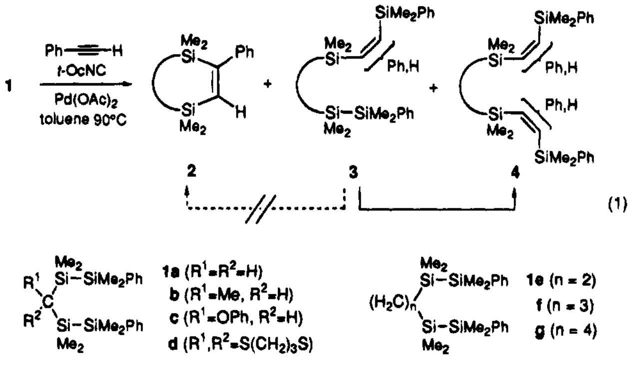
The Si–Si σ-bond possesses some interesting physical and chemical properties due to its high-lying HOMO and low-lying LUMO, which are compared with those of the carbon–carbon π-bond.[1] Interaction of the Si–Si σ-bond with transition metal complexes has made possible the bis-silylation reaction of unsaturated carbon compounds.[2] The activation of the Si–Si σ-bond has been demonstrated by isolation of bis(silyl)transition metal complexes.[3,4] Recently, we have found a new palladium/*tert*-alkyl isocyanide complex, which efficiently promotes the bis-silylation of alkenes.[2l,n] Thus, stereoselective synthesis of polyols has been achieved by an intramolecular bis-silylation of olefins catalyzed by the palladium/*tert*-alkyl isocyanide.

In the present communication, we wish to describe that palladium(0) bis(*tert*-alkyl isocyanide) induces a novel activation of two Si–Si bonds in a molecule of bis(disilanyl)alkane **1**, leading to the formation of cyclic bis(silyl)palladium(II) bis(*tert*-alkyl isocyanide) complexes (Scheme 1: intermediate A).[5] We also developed a new, catalytic bis-silylation of alkenes based on the activation of bis(disilanyl)dithiane (**1d**).

Scheme 1



Bis(disilanyl)alkanes **1** were subjected to the reaction with phenylacetylene in the presence of a catalytic amount of $Pd(OAc)_2$ and 1,1,3,3-tetramethylbutyl isocyanide (eq 1, Table 1).[6,7] The reaction with bis(disilanyl)methane (**1a**) afforded five-membered cyclic product **2a** only in low yield together with acyclic products **3a** and **4a** (76% in total, entry 1), which were



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[2] (a) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1991; Chapter 9. For recent advances in bis-silylation, see: (b) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353–2355. (c) Finckh, W.; Tang, B.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904–2911. (d) Ishikawa, M.; Sakamoto, H.; Okazaki, S.; Naka, A. *J. Organomet. Chem.* **1992**, *439*, 19–21. (e) Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483–484. (f) Kusukawa, T.; Kabe, Y.; Ando, W. *Chem. Lett.* **1993**, *985*–988. (g) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241–244. (h) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280–281. (i) Yamashita, H.; Tanaka, M. *Chem. Lett.* **1992**, 1547–1550. (j) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899–8908. (k) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948–1951. (l) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987–3988. (m) Murakami, M.; Oike, H.; Sugawara, M.; Suginome, M.; Ito, Y. *Tetrahedron* **1993**, *49*, 3933–3946. (n) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487–6498. (o) Murakami, M.; Suginome, M.; Fujimoto, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1473–1475.

[3] (a) Seyferth, D.; Goldman, E. W.; Escudié, J. *J. Organomet. Chem.* **1984**, *271*, 337–352. (b) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447–1450. (c) Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495–3497. (d) Murakami, M.; Yoshida, T.; Ito, Y. *Organometallics* **1994**, *13*, 2900–2902. (e) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237–3243. (f) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419–421 and references therein.

[4] Ab initio calculation for interaction of the Si–Si bond with transition metal complexes: (a) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373–2381. (b) Sakaki, S.; Ieki, M. *Inorg. Chem.* **1994**, *33*, 1660–1665.

[5] Similar activation of two Si–Si bonds may be involved in palladium-catalyzed disproportionation of disilanes. (a) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19–22. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1977**, *131*, 147–152. See also ref 2f.

[6] The experimental procedure for the reaction of **1a** with phenylacetylene is representative: To a mixture of palladium(II) acetate (0.9 mg, 4 μmol) and 1,1,3,3-tetramethylbutyl isocyanide (8.4 mg, 0.06 mmol) in toluene (0.3 mL) were added **1a** (80 mg, 0.20 mmol) and phenylacetylene (61 mg, 0.60 mmol) under an argon atmosphere. The mixture was stirred at 90 °C for 7 h, cooled to room temperature and then subjected to preparative TLC (hexane) to furnish **2a** (2 mg, 4%), **3a** (48 mg, 48%), and **4a** (34 mg, 28%).

[7] The expression "Ph,H" in eq 1 means that there are two positional isomers.

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Table 1. Palladium-Catalyzed Reaction of 1 with Phenylacetylene at 90 °C[a]

entry	substrate	**2** (% yield)[b]	**3**	**4** (% yield)[b]
1	**1a**	4 (**2a**)	48 (**3a**)	28 (**4a**)
2[c]	**1b**	67 (**2b**)	18 (**3b**)	<3
3	**1c**	91 (**2c**)	0	0
4	**1d**	91 (**2d**)	0	0
5	**1e**	39 (**2e**)	15 (**3e**)	30 (**4e**)
6	**1f**	0	50 (**3f**)	33 (**4f**)
7	**1g**	0	38 (**3g**)	49 (**4g**)

[a] All reactions used $Pd(OAc)_2$ (0.02 equiv), 1,1,3,3-tetramethylbutyl isocyanide (0.3 equiv), and phenylacetylene (3 equiv) unless otherwise noted. [b] Isolated yield. [c] $Pd(OAc_2)$ (0.1 equiv) and 1,1,3,3-tetramethylbutyl isocyanide (1.5 equiv) were used.

derived from insertion of phenylacetylene into intermediate **B** formed via three-centered activation. The formation of **2a** may suggest that two Si−Si bonds of **1a** were activated in a five-centered manner by the palladium catalyst to generate a cyclic bis(silyl)palladium(II) intermediate **A** (Scheme 1), which was subsequently reacted with phenylacetylene. The five-centered activation may be explained by simultaneous activation of the two Si−Si bonds of **1a** or stepwise activation of the Si−Si bonds via intermediate **B**.

Of note is that substitution at the methylene tether of **1a** may favor the reaction through intermediate **A**. Thus, methyl-substituted **1b** gave **2b** in 67% yield along with **3b** (entry 2). Moreover, phenoxy-substituted **1c** and trimethylenedithio-substituted **1d** exclusively provided the corresponding five-membered cyclic products **2c** and **2d** in high yields (entries 3 and 4).[8]

On the other hand, bis(disilanyl)alkanes **1e**−**g** tethered by the C_2, C_3, and C_4 chain preferred the insertion with phenylacetylene via intermediate **B** (entries 5−7), although 1,2-bis(disilanyl)ethane (**1e**) competitively underwent the reaction via intermediate **A**, leading to the six-membered 1-phenyl-3,6-disila-1-cyclohexene (**2e**) (39%). As expected, the partial insertion product **3e** once formed was reacted with phenylacetylene under the same reaction conditions to afford selectively acyclic diene **4e** without formation of **2e**.

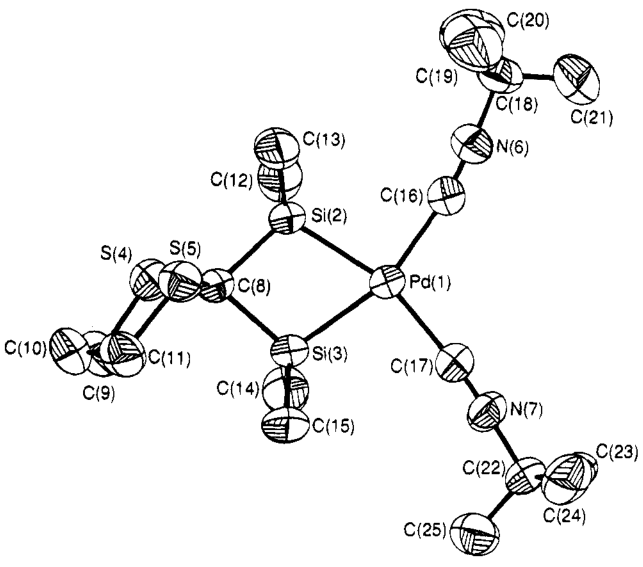
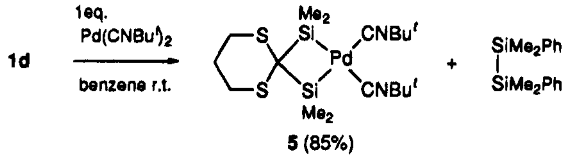


Figure 1. Crystal structure of **5**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)−Si(2) = 2.336(1), Pd(1)−Si(3) = 2.356(1), Pd(1)−C(16) = 2.053(5), Pd(1)−C(17) = 2.053(4), Si(2)−Si(3) = 2.613(2), N(6)−C(16) = 1.151(6), N(7)−C(17) = 1.146(6); Si(2)−Pd(1)−Si(3) = 67.68(4), Si(2)−Pd(1)−C(16) = 92.0(1), C(16)−Pd(1)−C(17) = 105.9(2), Si(3)−Pd(1)−C(17) = 94.4(1), Pd(1)−Si(2)−C(8) = 103.0(1), Pd(1)−Si(3)−C(8) = 102.3(1), Si(2)−C(8)−Si(3) = 85.1(1), Pd(1)−C(16)−N(6) = 171.3(4), Pd(1)−C(17)−N(7) = 173.8(4), C(16)−N(6)−C(18) = 175.8(4), C(17)−N(7)−C(22) = 177.5(4).

Isolation and characterization of a four-membered cyclic bis(silyl)palladium(II) bis(*tert*-butyl isocyanide) **5**, which may be formed through the five-centered activation, are remarked. Stirring a solution of Pd(CNBu-*t*)$_2$ and **1d** in benzene at room temperature for 10 min,[9] followed by addition of pentane to the solution, afforded an 85% yield of colorless crystals which were assigned to be four-membered bis(silyl)palladium(II) **5** having two molecules of *tert*-butyl isocyanide as ligands on palladium (eq 2).[10] Monitoring this reaction by ^1H NMR spectroscopy revealed a clean formation of complex **5** and *sym*-diphenyltetramethyldisilane. In this reaction, *tert*-butyl isocyanide ligands are essential for the five-centered activation of the two Si−Si bonds. Thus, tetrakis(triphenylphosphine)palladium(0) did not give any complexes corresponding to **5** in the reaction with **1d** even at high temperature. The structure of bis(silyl)palladium complex **5** was established by a single-crystal X-ray diffraction study.[11] The crystal structure is shown in Figure 1, together with selected bond distances and angles. The two silicon, two isocyano carbon, and palladium atoms are nearly on the same plane. The two isocyanide ligands coordinate to palladium with a relatively large angle (C−Pd−C = 105.9(2)°). The unusual short cross-ring Si−Si distance (2.613(2) Å) may suggest a possibility of covalently bonded Si−Si in the four-membered ring.[12,13]



5 (85%)

(2)

Bis(silyl)palladium(II) complex **5** thus isolated was immediately reacted with phenylacetylene to give **2d** in almost quantitative yield (eq 3).

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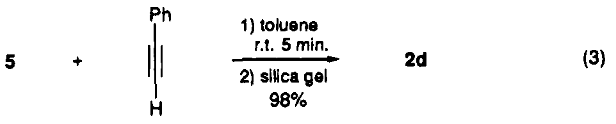
(8) $PhMe_2SiSiMe_2Ph$ formed via the five-centered activation and an acetylene insertion product coming from the disilane were also isolated in high total yields.

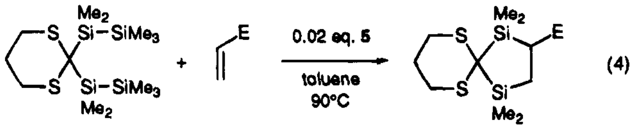
(9) Bis(*tert*-butyl isocyanide)palladium(0) was prepared by the procedure in the literature. Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994−6999.

(10) **5**: mp 168−170 °C dec; ^1H NMR (C_6D_6) δ 0.84 (s, 18 H), 1.00 (s, 12 H), 1.96−2.09 (m, 2 H), 2.68−2.76 (m, 4 H); ^{13}C NMR (C_6D_6) δ 3.1, 27.5, 27.8, 30.0, 30.7, 55.9, 147.5; IR (C_6H_6) 2164, 2144 cm^{-1}. Anal. Calcd for $C_{18}H_{36}N_2PdS_2Si_2$: C, 42.62; H, 7.15. Found: C, 42.34; H, 7.35.

(11) Crystal data for **5**: crystal size 0.35 × 0.15 × 0.30 mm; triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$; $a = 8.257(1)$, $b = 10.829(3)$, $c = 15.360(3)$ Å; $\alpha = 94.14(2)$, $\beta = 99.72(2)$, $\gamma = 101.92(2)°$; $V = 1316.2(4)$ Å^3, $\varrho_{calcd} = 1.28$ g/cm^3; max $2\theta = 50°$ (Mo Kα, $\lambda = 0.710\ 73$ Å, graphite monochromator, $\omega/2\theta$ scan, $T = 293$ K); 4792 reflections measured, 4389 independent, 4135 included in the refinement, Lorentzian polarization and absorption corrections by analytical function ($\mu = 8.70$ cm^{-1}); direct method, anisotropical refinement for non-hydrogen atoms by full-matrix least-squares against $|F^2|$ with the program package CrystanG (Mac Science), 337 parameters; $R = 0.048$, $R_w = 0.048$; residual electron density +0.58/−0.64 e Å^{-3}. All hydrogen atoms except for that on C(19) were located on a difference electron density map and refined with isotropic thermal parameters calculated from those of the bonded atoms.

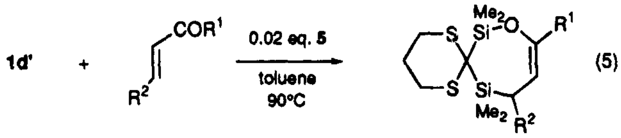
(12) The longest Si−Si bond has been reported to be 2.70 Å in hexa-*tert*-butyldisilane. Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 79−80.





1d'

6a; E = CN (86%)
b; E = CO$_2$Me (88%)



7a; R^1=Me, R^2=H (96%)
b; R^1=R^2=Me (99%)
c; R^1=Ph, R^2=H (82%)

Furthermore, electron-deficient olefins underwent the bis-silylation with bis(disilanyl)dithiane **1d'** in quantitative yield by a catalytic amount of **5** without an excess of *tert*-butyl isocyanide.[14] α,β-Unsaturated ketones provided 1,4-bis-silylation adducts **6** (eq 4),whereas the corresponding ester and nitrile gave 1,2-adducts **7** (eq 5).[15] It may be remarked that no products derived from insertion of alkenes into the Si–Si bonds of the starting **1d'** and hexamethyldisilane produced in the reaction were detectable. This indicates the five-centered activation of Si–Si σ-bonds of **1d'** by bis(*tert*-butyl isocyanide)palladium(0) was a highly favorable process, giving a reactive bis(silyl)palladium complex.

Supplementary Material Available: Detailed experimental procedures and characterization for new compounds (text), ^{1}H NMR spectra for the reaction of **1d** with Pd(CN-Bu-*t*)$_2$ giving **5**, and tables of final atomic coordinates, thermal parameters, bond distances, and bond angles for compound **5** (10 pages). Ordering information is given on any current masthead page.

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(13) Unusually short Si–Si distances in some four-membered rings were also reported. (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068–4070. (b) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517–1523. (c) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917–1919. (d) Ohtaki, T.; Ando, W. *Chem. Lett.* **1994**, 1061–1064.

(14) General procedure for the catalytic bis-silylation of alkenes: To a mixture of **1d'** (152 mg, 0.40 mmol) and **5** (4.0 mg, 8.0 μmol) in toluene (0.4 mL) was added alkenes (0.60 mmol) under an argon atmosphere. The mixture was stirred at 90 °C for 15 h, cooled to room temperature, and then subjected to preparative TLC (for **6b** and **7a–c**), or bulb-to-bulb distillation (for **6a**) to furnish the cyclized product.

(15) To our best knowledge, these are the first successful examples for 1,2-bis-silylation of acrylate and acrylonitrile. For 1,4-bis-silylation of α,β-unsaturated ketones, see: (a) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 4147–4150. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5579–5581.