Reactions of a Spiro Trisilane with Palladium Complexes: Synthesis and Structure of Tris(organosilyl)CpPd^{IV} and Bis(organosilyl)(μ-organosilylene)Pd$^{II}_2$ Complexes

Michinori Suginome, Yukitoshi Kato, Nobuhiko Takeda, Hideaki Oike, and Yoshihiko Ito*

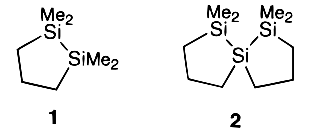
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

Received December 9, 1997

Summary: 1,1,6,6-Tetramethyl-1,5,6-trisilaspiro[4.4]-nonane was reacted with bis(tert-alkyl isocyanide)-palladium(0) and (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) through oxidative addition of the Si−Si bonds to afford a dinuclear palladium(II) complex and a stable palladium(IV) complex, respectively. The latter palladium(IV)-complex-catalyzed ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane gives organosilicon polymers with high molecular weight.

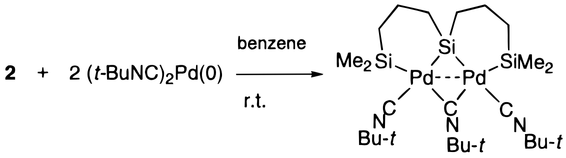
Activation of the silicon−silicon bonds of disilanes by palladium complexes has made the development of various useful synthetic methods of organosilicon compounds possible.[1] Not only stereoselective carbon−silicon bond-forming reactions but also novel silicon−silicon bond-forming reactions through σ-bond metathesis have been developed, leading to ring-enlargement oligomerization and ring-opening polymerization of cyclic disilanes.[2,3] Of particular interest is that five-membered cyclic disilane **1**, Chart 1, which is modestly strained but virtually stable,[4] exhibited notable reactivity in the activation by the palladium complexes, affording organosilicon macrocycles and polymers selectively by use of bis(*tert*-alkyl isocyanide)palladium(0) and (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) catalysts, respectively.[2] The discovery of the new synthetic reactions prompted us to investigate palladium-catalyzed reactions of 1,1,6,6-tetramethyl-1,5,6-trisilaspiro[4.4]nonane (**2**), in which the each five-membered ring contains a Si−Si bond. Herein, we describe the formation of two novel (organosilyl)palladium complexes, i.e., a four-coordinated tris(organosilyl)palladium(IV) complex and a dinuclear palladium(II) complex, in the reactions of **2** with (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) and bis(*tert*-alkyl isocyanide)palladium(0), respectively. On the basis of the new (organosilyl)palladium complex, ring-opening polymerization of **1** is also discussed.

Chart 1



1 **2**

Initially, reaction of spirocyclic **2**[5] with 2 mol equiv of bis(*tert*-butyl isocyanide)palladium(0),[6] which is able to undergo oxidative addition of the silicon−silicon bond of **1** easily,[2,7] was carried out in benzene at room temperature (eq 1). The reaction proceeded rapidly to give air-sensitive orange crystals in high yield, whose NMR and elemental analysis indicated that the molecule contains two palladium atoms and three isocyanide groups. A single-crystal X-ray analysis revealed dinuclear palladium(II) complex **3**,[8] in which a μ-silylene and μ-isonitrile are coordinated to the two palladium atoms (Figure 1). It should be noted that the two



3 (91%) (1)

---

[1] (a) Horn, K. A. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 1317−1350. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 1351−1374.

[2] (a) Suginome, M.; Oike, H.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1665−1666. (b) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *Organometallics* **1996**, *15*, 2170−2178.

[3] For cyclodimerization, see: (a) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19−21. (b) Kusukawa, T.; Kabe, Y.; Ando, W. *Chem. Lett.* **1993**, 985−988. (c) Kusukawa, T.; Kabe, Y.; Nestler, B.; Ando, W. *Organometallics* **1995**, *14*, 2556−2564. For polymerization, see: (d) Suzuki, M.; Obayashi, T.; Amii, H.; Saegusa, T. *Polym. Prepr. Jpn.* **1991**, *40*, 355. (e) Uchimaru, Y.; Tanaka, Y.; Tanaka, M. *Chem. Lett.* **1995**, 164.

[4] The high reactivity of **1** was pointed out in palladium-catalyzed bis-silylation reactions, see: (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931−932. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* **1975**, 887−890.

[5] Procedure for the synthesis of **2**. To a Na−K alloy (prepared from 22 mmol of Na and 110 mmol of K) in benzene (10 mL) was added 2,6,6,10-tetrachloro-2,10-dimethyl-2,6,10-trisilaundecane (9.6 g, 26 mmol) in benzene (20 mL), which was prepared from diallyldiphenylsilane by H_2PtCl_4-catalyzed hydrosilation with chlorodimethylsilane followed by $AlCl_3$-catalyzed dephenylchlorination with hydrogen chloride, dropwise over 2 h under reflux. The mixture was stirred for 15 h under reflux and cooled to room temperature. To the mixture were added acetic acid−ethanol (1/1, 16 mL), ethanol (32 mL), 50% ethanol (16 mL), and finally water (50 mL). It should be noted that *the addition of the acetic acid−ethanol solution must be carried out slowly with great care.* Extractive workup with ether followed by distillation under reduced pressure (115−124 °C/20 mmHg) gave **2** (2.7 g, 47%): ^{1}H NMR (C_6D_6) δ 0.21 (s, 6H), 0.24 (s, 6H), 0.70−1.04 (m, 8H), 1.74−1.90 (m, 4H); ^{13}C NMR (C_6D_6) δ −3.2, −2.2, 14.4, 19.2, 24.8; ^{29}Si NMR (C_6D_6) δ −39.6, −6.1. Anal. Calcd for $C_{10}H_{24}Si_3$: C, 52.55; H, 10.58. Found: C, 52.54; H, 10.74.

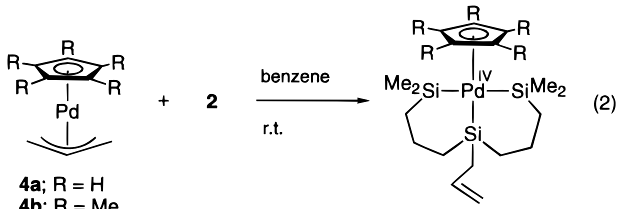
[6] For palladium−isonitrile-catalyzed bis-silylations of alkenes and alkynes, see: (a) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3061−3062. (b) Suginome, M.; Iwanami, T.; Matsumoto, A.; Ito, Y. *Tetrahedron: Asymmetry* **1997**, *8*, 859−862 and references therein.

[7] Suginome, M.; Oike, H.; Park, S.-S.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 289−299.

S0276-7333(97)01077-7 CCC: $15.00
Publication on Web 01/24/1998

palladium atoms are separated by 2.751(3) Å, which is same as the shortest metal−metal contact in metallic palladium.[9]

On the other hand, reaction of **2** with 1 mol equiv of (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) **4a** at room temperature in benzene led to the isolation of an air-stable colorless solid in 85% yield by column chromatography on silica gel (eq 2).[10] Its ^{1}H and ^{13}C NMR



(2)

4a; R = H
4b; R = Me

5a: R = H (85%)
5b: R = CH$_3$ (61%)

spectra exhibited the signals characteristic of an η^5-coordinating cyclopentadienyl group and an η^1-allyl group, suggesting the formation of palladium(IV) complex **5a**.[11] Similarly, Cp*(allyl)Pd **4b** afforded the corresponding palladium(IV) complex **5b**,[12] although the reaction with **4b** was slower than that with **4a**. An X-ray crystal structure of **5b** is shown in Figure 2 with some selected bond distances and angles. Interestingly, the palladium atom bonding to the three silyl and Cp groups is found to be tetrahedral with slight deviation, all three Si−Pd−Si angles (84−93°) are smaller than the ideal value (109°). The average bonding distance between palladium and silicon is 2.35 Å, which is almost identical with those for the bis-[2b,7,13] and tetrakis(organosilyl)palladium[11a] complexes so far characterized.

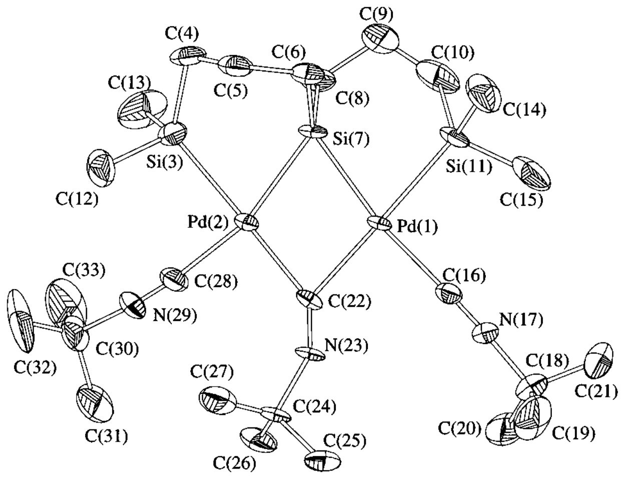


Figure 1. ORTEP drawing of **3** (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)−Pd(2) = 2.751(3), Pd(1)−Si(7) = 2.350(6), Pd(1)−Si(11) = 2.399(6), Pd(1)−C(22) = 2.15(2), Pd(1)−C(28) = 2.03(3), Pd(2)−Si(3) = 2.401(7), Pd(2)−Si(7) = 2.348(5), Pd(2)−C(16) = 2.04(3), Pd(2)−C(22) = 2.13(2), C(16)−N(17) = 1.14(3), C(22)−N(23) = 1.19(3), C(28)−N(29) = 1.14(3); Si(7)−Pd(1)−Si(11) = 76.3(2), C(22)−Pd(1)−C(28) = 85.8(9), Si(3)−Pd(2)−Si(7) = 75.4(3), C(16)−Pd(2)−C(22) = 94.0(9), Pd(1)−Si(7)−Pd(2) = 71.7(2), Pd(1)−C(22)−Pd(2) = 80.0(7).

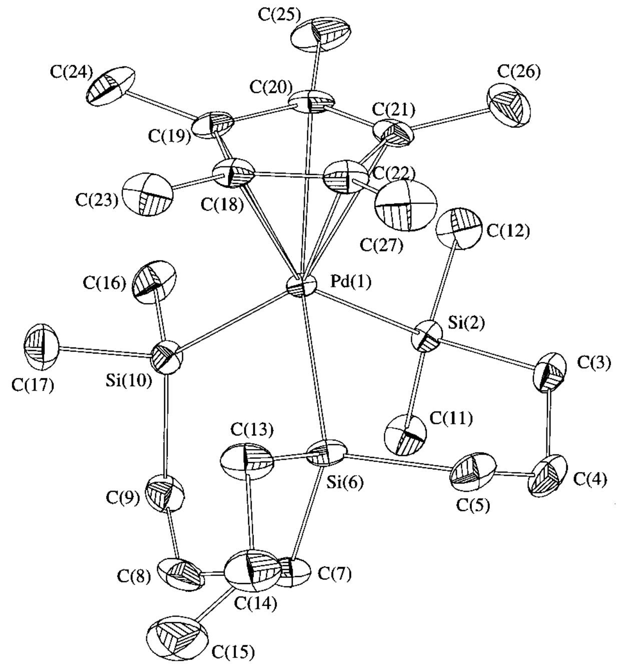


Figure 2. ORTEP drawing of **5b** (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)−Si(2) = 2.364(3), Pd(1)−Si(6) = 2.346(3), Pd(1)−Si(10) = 2.349(3); Si(2)−Pd(1)−Si(6) = 84.0(1), Si(2)−Pd(1)−Si(10) = 93.3(1), Si(6)−Pd(1)−Si(10) = 85.7(1).

Although the 18-electron palladium(IV) complex **5a** hardly reacted with various unsaturated organic mol-

---

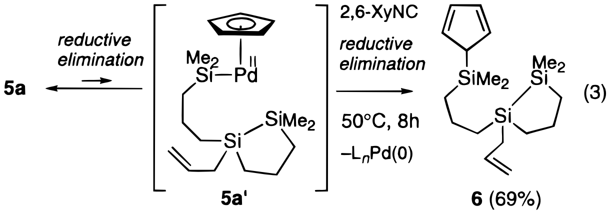
(8) Procedure for the synthesis of **3**. All manupulations were carried out under argon. To a solution of **4a** (125 mg, 0.59 mmol) in pentane (1 mL) was added *tert*-butyl isocyanide (186 mg, 2.4 mmol) at −10 °C. Immediately, the bis(*tert*-butyl isocyanide)palladium(0) complex was precipitated as an orange solid. The supernatant liquid was removed, and the resultant solid was washed with pentane. To this were added benzene (0.5 mL) and then **2** (73 mg, 0.32 mmol) at room temperature. Addition of dry 2-propanol (1.5 mL) to the orange solution resulted in precipitation of orange crystals on standing for 5 h. Removal of the supernatant liquid and washing with dry 2-propanol under argon afforded **3** (144 mg, 71%). The mother liquid also gave **3** (42 mg, 21%) by evaporation of the solvent followed by washing the resultant residue with 2-propanol. **3**: ^{1}H NMR (C_6D_6) δ 0.79 (s, 6H), 0.82 (s, 6H), 0.88−0.97 (m, 2H), 1.15 (s, 27H), 1.10−1.17 (m, 2H), 1.23−1.32 (m, 2H), 1.66−1.75 (m, 2H), 1.85−1.96 (m, 2H), 2.34−2.45 (m, 2H); ^{13}C NMR (C_6D_6) δ 4.7, 9.4, 22.2, 22.3, 30.2, 56.0; ^{29}Si NMR (C_6D_6) δ 3.1, 96.0. Anal. Calcd for $C_{25}H_{51}N_3Pd_2Si_3$: C, 43.47; H, 7.44; N, 6.08. Found: C, 43.49; H, 7.63; N, 5.98. Crystal data for **3**: in a sealed capillary; crystal size 0.90 × 0.75 × 0.50 mm; monoclinic, space group $P2_1/a$ (No. 14), $Z = 4$; $a = 21.668(9)$ Å, $b = 10.993(7)$ Å, $c = 14.539(6)$ Å; $\beta = 96.03(3)°$; $V = 3444(3)$ Å^3, $\rho_{calcd} = 1.33$ g/cm^3; $\mu = 97.805$ cm^{-1}; max $2\theta = 125°$ (Cu Kα, $\lambda = 1.541\ 78$ Å, graphite monochromator, $\omega/2\theta$ scan, $T = 293$ K); 12 335 reflections measured, 5472 independent, 4646 included in the refinement, Lorentzian polarization; direct methods, anisotropical refinement by full-matrix least-squares against $|F|^2$, 349 parameters; $R = 0.074$, $R_w = 0.097$.

(9) Maitlis, P. M.; Espinet, P.; Russel, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 6, pp 233−242.

(10) Procedure for the synthesis of **5a**. To a solution of **4a** (21 mg, 0.10 mmol) in benzene (0.6 mL) was added **2** (23 mg, 0.10 mmol) at room temperature under argon. The solution was stirred at room temperature for 1 h and passed through a short column of silica gel (hexane). Evaporation of the solvent gave **5a** (37 mg, 85%) as a white solid. **5a**: ^{1}H NMR (C_6D_6) δ 0.34 (s, 6H), 0.46 (s, 6H), 0.55−0.63 (m, 2H), 0.67−0.75 (m, 2H), 0.85−1.00 (m, 4H), 1.72−1.86 (m, 4H), 1.92 (dt, $J = 8.2$, 1.1 Hz, 2H), 4.92−4.95 (m, 2H), 5.77−5.87 (m, 1H), 5.53 (s, 5H); ^{13}C NMR (C_6D_6) δ 6.8, 10.5, 17.7, 19.4, 23.7, 31.7, 100.1, 112.7, 136.2; ^{29}Si NMR (C_6D_6) δ 19.9, 25.6. Anal. Calcd for $C_{18}H_{34}PdSi_3$: C, 49.01; H, 7.71. Found: C, 48.74; H, 7.89.

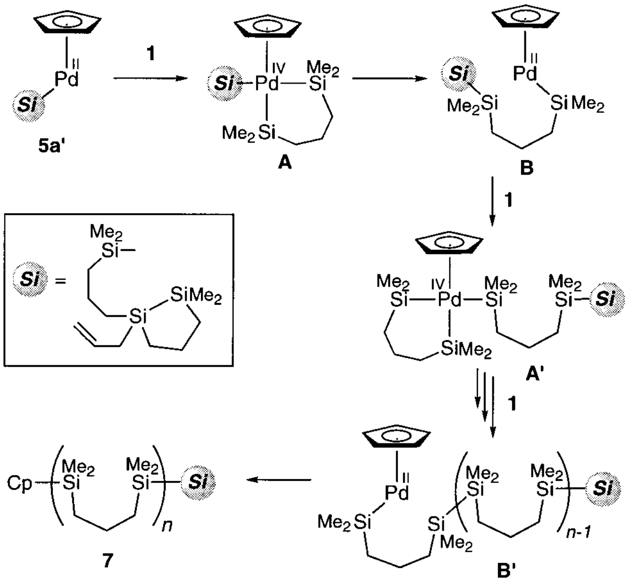
(11) (a) Recently, a six-coordinated bis(phosphine)tetrakis(organosilyl)palladium(IV) complex was reported, see: Shimada, S.; Tanaka, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1856−1858. For alkyl derivatives of palladium(IV) complexes, see: (b) Canty, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Puddephatt, R. J., Eds.; Pergamon Press: Oxford, 1995; Vol. 9, pp 225−290. (c) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; White, A. H. *Organometallics* **1996**, *15*, 5713−5722.

ecules, e.g., alkynes and alkenes, addition of 2.5 mol equiv of 2,6-xylyl isocyanide in benzene induced *double reductive elimination* to give five-membered disilane **6** (eq 3). The reaction may proceed with reductive elimination of the Si–Si bond giving **5a′**, which is followed by the second elimination of the Si–Cp bond.



Noteworthy was that complex **5a** (1 mol %) catalyzed the polymerization of **1** at 50 °C to give organosilicon polymers **7** of high molecular weight (46%, $M_n = 8.5 \times 10^4$, $M_w/M_n = 1.88$) (Scheme 1). Presumably, the polymerization is initiated by reductive elimination from palladium(IV) complex **5a**, generating a palladium(II) intermediate (**5a′**), which is now susceptible to oxidative addition of **1** forming the palladium(IV) intermediate (**A**). Formation of a new Si–Si bond through reductive elimination from the palladacycle complex (**A**) constitutes the propagation step for the ring-opening polymerization of **1**. Termination of the polymerization may involve a reductive elimination with a cyclopentadienyl–silicon bond formation, as in the double reductive elimination reaction shown in eq 3. Concomitant formation of a cyclic dimer (9%) as a byproduct may result from "back biting" of the growing palladium(II) complex (**B′**) during the propagation.[14] Although the polymerization mechanism still remains to be elucidated, involvement of the palladium(IV) intermediate is strongly suggested in the palladium-catalyzed ring-opening polymerization of cyclic disilanes.

Scheme 1. Proposed Mechanism for the Polymerization of 1 in the Presence of 5[a]



[a] The assignment of the termini is tentative.

Acknowledgment. We are grateful to Mr. Haruo Fujita (Kyoto University) for his assistance in the NMR measurements. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (Grant No. 09239226, "The Chemistry of Inter-element Linkage") from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Text giving detailed experimental procedures and characterization data for the new compounds and tables of final atomic coordinates, thermal parameters, bond distances, and bond angles for the complexes **3** and **5b** (10 pages). Ordering information is given on any current masthead page.

OM9710778

---

(12) By a procedure similar to that for the synthesis of **5a** (toluene, −30 °C, 4 h), **5b** (32 mg, 61%) was synthesized from **4b** (29 mg, 0.10 mmol) and **2** (23 mg, 0.10 mmol). **5b**: ^{1}H NMR (C_6D_6) δ 0.46 (s, 6H), 0.54 (s, 6H), 0.79–1.14 (m, 8H), 1.85 (s, 15H), 1.89–1.99 (m, 4H), 2.04 (dt, $J = 8.2$, 1.1 Hz, 2H), 5.00–5.07 (m, 2H), 5.86–6.00 (m, 1H); ^{13}C NMR (C_6D_6) δ 5.2, 6.0, 11.2, 14.9, 19.5, 21.7, 26.2, 109.2, 112.6, 137.1; ^{29}Si NMR (C_6D_6) δ 14.8, 20.6. Anal. Calcd for $C_{23}H_{44}PdSi_3$: C, 54.03; H, 8.67. Found: C, 53.78; H, 8.53. Crystal data for **5b**: crystal size 0.40 × 0.50 × 0.60 mm; monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$; $a = 15.035(3)$ Å, $b = 18.175(3)$ Å, $c = 9.434(2)$ Å; $\beta = 91.15(2)°$; $V = 2577.4(8)$ Å^3, $\rho_{calcd} = 1.317$ g/cm^3; $\mu = 73.43$ cm^{-1}; max $2\theta = 125°$ (Cu Kα, $\lambda = 1.541\ 78$ Å, graphite monochromator, $\omega/2\theta$ scan, $T = 293$ K); 4715 reflections measured, 4286 independent, 4086 included in the refinement, Lorentzian polarization; direct methods, anisotropical refinement by full-matrix least-squares against $|F|^2$, 294 parameters; $R = 0.056$, $R_w = 0.088$.

(13) (a) Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495–3497. (b) Murakami, M.; Yoshida, T.; Ito, Y. *Organometallics* **1994**, *13*, 2900–2902.

(14) The mechanism of the "back biting" may involve intramolecular metathesis of the Pd–Si and Si–Si bonds as outlined in the following equation.