Dinuclear Palladium Complex with a Bridging Dialkylsilylene Ligand

Chieko Watanabe,[1] Takeaki Iwamoto,*[2] Chizuko Kabuto,[2] and Mitsuo Kira*[1]
[1]*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578*
[2]*Research and Analytical Center for Giant Molecules, Graduate School of Science,*
Tohoku University, Aoba-ku, Sendai 980-8578

(Received November 24, 2006; CL-061390; E-mail: iwamoto@mail.tains.tohoku.ac.jp, mkira@mail.tains.tohoku.ac.jp)

A novel dinuclear palladium complex with one bridging dialkylsilylene ligand **6** was synthesized by the reaction of isolable dialkylsilylene **7** (R_2Si:) with two equiv of bis(tricyclohexyl)phosphinepalladium (**8**). Complex **6** as a prototypical dipalladasilacyclopropane reacts with molecular hydrogen to give dihydrosilane **10** (R_2SiH_2) together with **8** and metallic palladium.

Multinuclear transition-metal complexes with bridging silyl and/or silylene groups have received much attention because they show unique structural and bonding properties and would be key intermediates of transformation of silane mediated by transition-metal complexes.[1] Although various multinuclear group-10 metal complexes with bridging silyl and/or silylene units have been extensively studied, there have been few reports on the corresponding dipalladium complexes. Osakada et al. have synthesized $[L_nPd(\mu\text{-SiH(R)Ph})]_2$ (**1**) as the first silyl-bridged dimeric palladium complexes with three-center-two-electron Si–H–Pd bond.[2] Fürstner et al. and Herrmann et al. have reported dipalladium complexes with two bridging *N*-heterocyclic silylenes (**2**–**4**) that were prepared by the reactions of stable *N*-heterocyclic silylenes with palladium(0) complexes.[3,4] Suginome, Ito, et al. have synthesized dipalladium complex **5**, in which μ-silylene and μ-isocyanide ligands coordinate to the two palladium atoms.[5] In the present paper, we report the synthesis, structure, and an interesting reaction of novel dinuclear palladium complex having one bridging silylene unit (**6**) using isolable dialkylsilylene **7**, which we have recently synthesized as a silylene stabilized kinetically by a bulky 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl ligand.[6] To the best of our knowledge, complex **6** is the first mono(μ-silylene) dipalladium complex without Pd–H–Si bonding or other bridging ligands and, hence, will be useful as a prototypical dipalladasilacyclopropane to investigate the electronic structure and reactions of the ring system (Chart 1).

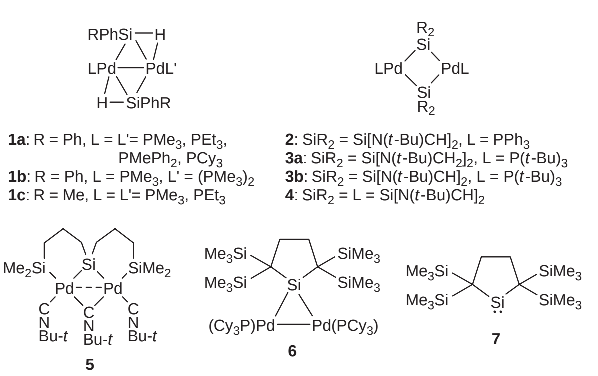


Chart 1.

Complex **6** was synthesized by the treatment of dialkylsilylene **7** with bis(tricyclohexylphosphine)palladium (**8**, 2.1 equiv) in toluene at room temperature (eq 1).[7] Recrystallization from toluene gave analytically pure **6** in 24% yield as air- and moisture-sensitive dark blue-purple crystals with the decomposition temperature of 203 °C. The structure of **6** was determined by NMR spectroscopy, elemental analysis, and X-ray crystallography.[8,9]

$$\mathbf{7} \xrightarrow[\text{toluene, rt}]{\text{2.1 equiv }(\mathrm{Cy_3P})_2\mathrm{Pd}\ (\mathbf{8})} \underset{(24\%\ \text{yield})}{\mathbf{6}} \qquad (1)$$

Figure 1 shows the molecular structure of **6** determined by X-ray analysis. The Pd_2 unit is disordered over two positions with almost the same site occupancy factors [0.486(3) for Pd1(Pd2) and 0.514(3) for Pd1′(Pd2′)]. The geometry around the Si1–Pd1–Pd2 ring and Si1–Pd1′–Pd2′ ring are similar to each other. The dialkylsilylene unit bridges over the two palladium atoms and the silacyclopentane ring is nearly perpendicular to the $SiPd_2$ three-membered ring; the dihedral angle between C1–Si1–C4 and Pd1–Si1–Pd2 (Pd1′–Si1–Pd2′) planes is 91.62° (92.28°). Each palladium atom is coordinated by one phosphine ligand. The geometry around Pd1 and Pd2 atoms are slightly different from each other. The Si1–Pd1–P1 angle is 147.66(8), while Si1–Pd2–P2 angle is 171.15(6). The P1 and P2 atoms are slightly deviated from the central three-membered ring plane with the dihedral angles Si1–Pd2–Pd1–P1 and

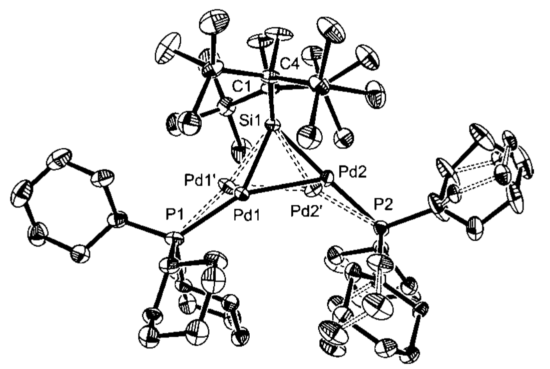
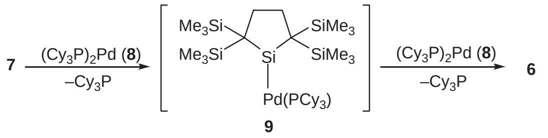


Figure 1. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Two Pd atoms and one cyclohexyl rings are disordered. The site occupancy factor of Pd1 and Pd1′ (and Pd2 and Pd2′) are 0.486(3) and 0.514(3), respectively. Selected bond lengths (Å) and angles (deg): Si1–Pd1 2.2952(15), Si1–Pd2 2.3019(13), Si1–Pd2′ 2.3073(12), Si1–Pd1′ 2.3089(14), Pd1–Pd2 2.6029(13), Pd1′–Pd2′ 2.5833(13), C1–Si1–C4 96.56(12), Pd1–Si1–Pd2 68.97(3), Pd2′–Si1–Pd1′ 68.06(3), plane(C1–Si1–C4)–plane(Pd1–Si1–Pd2) 91.62, plane(C1–Si1–C4)–plane(Pd1′–Si1–Pd2′) 92.28.

Si1–Pd1–Pd2–P2 of −172.59(18) and −169.50(7)°. The sum of the bond angles around the Pd1 and Pd2 atoms are 359.70(7) and 353.60(7)°, respectively. The Si–Pd distances of **6** (2.2952(15)–2.3089(14) Å) are significantly shorter than those of known silyl- and silylene-bridged dipalladium complexes **1**–**5** (2.318(2)–2.4543(5) Å for Si–Pd distance, 2.332(2)–2.411(2) Å for distances of Si–Pd bonds with a 3c-2e Pd–H–Si bond).[2–5] The Pd–Pd distance of **6** (2.5833(13)–2.6029(13) Å) is remarkably shorter than those of **1**–**5** (2.6501(2)–2.751(3) Å) and within the range of known Pd(I)–Pd(I) single bond lengths (2.500–3.311 Å).[10] The Pd–Si–Pd bond angles of **6** are 68.06(3)–68.97(3)°, which are close to those of **1**–**5** (Pd–Si–Pd bond angles: 66.784(10)–71.7(2)°).[2–5]

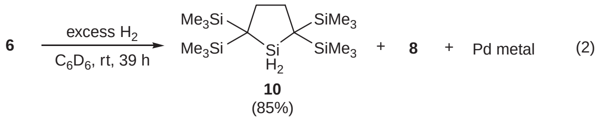
All proton nuclei of four trimethylsilyl groups of complex **6** are equivalent to show a singlet signal in the ^{1}H NMR spectrum, indicating that complex **6** has a highly symmetric or fluxional structure in solution. The ^{29}Si NMR resonance of the silylene silicon nucleus of **6** (δ 304, t, $^{2}J(\text{Si–P}) = 78.5$ Hz) is upfield-shifted from the corresponding resonance of **7** (δ 567.4) but close to that of [{Pt(μ-SiPh$_2$)(PMe$_3$)}$_3$] complex (δ 279.4).[11]

A plausible mechanism for the formation of **6** is shown in Scheme 1. The ligand-exchange reaction of dialkylsilylene **7** with Pd^{0} complex **8** will give initially (dialkylsilylene)(Cy$_3$P)Pd complex **9**, which then reacts with another molecule of **8** to form complex **6**. The intermediary formation of complex **9** was confirmed by NMR spectroscopy.[12]



Scheme 1. A stepwise formation of **6** from **7**.

Complex **6** reacts slowly with an excess amount of molecular hydrogen under atmospheric pressure in benzene-d_6 to give dialkylsilane **10**[13] in 85% yield (eq 2). Because no reaction occurs between silylene **7** with molecular hydrogen under similar conditions, the hydrogenation should occur on the palladium metals of complex **6**. A possible mechanism involves the oxidative addition of hydrogen molecule to one of the palladium atoms followed by 1,2-hydride migration from palladium to silicon.



This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (Specially Promoted Research (No. 17002005)).

References and Notes

1 T. D. Tilley, in *The Chemistry of Organic Silicon Compounds*, ed. by S. Patai, Z. Rappoport, John Wiley & Sons, New York, **1989**, Chap. 24; P. D. Lickiss, *Chem. Soc. Rev.* **1992**, 271; M. S. Eisen, in *The Chemistry of Organic Silicon Compounds*, ed. by Z. Rappoport, Y. Apeloig, John Wiley & Sons, New York, **1998**, Chap. 35; H. Tobita, H. Ogino, *Adv. Organomet. Chem.* **1998**, 42, 223; J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, *99*, 175; B. Gehrhus, M. F. Lappert, *J. Organomet. Chem.* **2001**, *617–618*, 209; H. Ogino, *Chem. Rec.* **2002**, *2*, 291; M. Okazaki, H. Tobita, H. Ogino, *Dalton Trans.* **2003**, 493; N. J. Hill, R. West, *J. Organomet. Chem.* **2004**, *689*, 4165.

2 Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, J.-C. Choi, T. Yamamoto, *Organometallics* **1998**, *17*, 4929; Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, J.-C. Choi, T. Yamamoto, *J. Chem. Soc., Dalton Trans.* **2000**, 417; M. Tanabe, T. Yamada, K. Osakada, *Organometallics* **2003**, *22*, 2190.

3 A. Fürstner, H. Krause, C. W. Lehmann, *Chem. Commun.* **2001**, 2372.

4 W. A. Herrmann, P. Härter, C. W. K. Gstöttmayr, F. Bielert, N. Seeboth, P. Sirsch, *J. Organomet. Chem.* **2002**, *649*, 141; A. Zeller, F. Bielert, P. Haerter, W. A. Herrmann, T. Strassner *J. Organomet. Chem.* **2005**, *690*, 3292.

5 M. Suginome, Y. Kato, N. Takeda, H. Oike, Y. Ito, *Organometallics* **1998**, *17*, 495.

6 M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722.

7 In a Schlenk flask (200 mL) equipped with a magnetic stirrer bar, a mixture of dialkylsilylene **7** (0.943 g, 2.53 mmol) and palladium complex **8** (3.76 g, 5.63 mmol) in toluene (70 mL) was stirred at room temperature for 65.5 h under argon atmosphere. Removal of toluene in vacuo and then recrystallization at −35 °C from toluene twice gave pure **6** (709 mg, 0.618 mmol, 24% yield). **6**: air-sensitive dark blue-purple crystals; mp 203 °C (dec.); ^{1}H NMR (C_6D_6, δ) 0.71 (s, 36H, SiC$\underline{\text{H}}_3$), 1.28–2.16 (m, 66H, Cy), 2.25 (s, 4H, CH$_2$); ^{13}C NMR (C_6D_6, δ) 5.5, 26.8, 28.1, 31.7, 34.1, 35.0, 37.6; ^{29}Si NMR (C_6D_6, δ) −0.70 ($\underline{\text{Si}}$CH$_3$), 303.5 (t, $^{2}J_{\text{SiP}} = 78.5$ Hz, Si:); ^{31}P NMR (C_6D_6, δ) 28.3; UV–vis (hexane) λ_{max}/nm (ε) 254 (29000), 301 (38000), 497 (1900), 568 (1600); Anal calcd for $C_{52}H_{106}Si_5Pd_2P_2$: C, 54.47; H, 9.32%. Found: C, 54.23; H, 9.35%. Chemical shifts are expressed in ppm down field from external tetramethylsilane (^{1}H, ^{13}C, and ^{29}Si) and 85% H_3PO_4 (^{31}P).

In the above reaction, the corresponding bis(μ-dialkylsilylene)-dipalladium complex did not form probably owing to severe steric hindrance during the introduction of silylene **7** to **6**.

8 Single crystals of **6** suitable for X-ray diffraction study were obtained by recrystallization from toluene at −35 °C. Crystallographic data for compound **6** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 627230. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033). The final $R1$ and $wR2$ values were 0.0545 [$I > 2\sigma(I)$] and 0.0941 (for all data).

9 When the refinement is carried out regardless of disorder at Pd atoms, bond lengths and angles showed different values with stretched ellipsoids of Pd atoms. The final $R1$ and $wR2$ values were 0.0825 [$I > 2\sigma(I)$] and 0.1481 (for all data). Selected bond lengths (Å) and angles (deg) regardless of disorder is below: Pd1–Pd2 2.5676(9); Si1–Pd1 2.2891(12); Si1–Pd2 2.2934(12); C1–Si1–C4 96.64(19); Pd1–Si1–Pd2 68.15(4); plane (C1–Si1–C4)–plane (Pd1–Si1–Pd2) 92.01.

10 The Pd$^{\text{I}}$–Pd$^{\text{I}}$ distances are obtained from the Cambridge Crystallographic Database (http://www.ccdc.cam.ac.uk).

11 K. Osakada, M. Tanabe, T. Tanase, *Angew. Chem.* **2000**, *39*, 4053.

12 By monitoring the reaction of **7** with 2 equiv of **8** by NMR spectroscopy, we observed that (dialkylsilylene)(Cy$_3$P)Pd (**9**) was formed at the early stage of the reaction and then complex **9** slowly converted to complex **6**. Complex **9** formed as an air-sensitive purple oil in a good yield by the reaction of **7** with one equivalent of **8**, but the isolation of **9** was failed because of the difficult separation from tri(cyclohexyl)phosphine produced during the reaction. **9**: ^{1}H NMR (C_6D_6, δ) 0.52 (s, 36H, SiMe$_3$), 2.12 (s, 4H, CH$_2$); ^{29}Si NMR (C_6D_6, δ) −1.15 (SiMe$_3$), 413.5 (d, $^{2}J(\text{Si–P}) = 132.3$ Hz); ^{31}P NMR (C_6D_6, δ) 35.2. The ^{1}H NMR resonances due to cyclohexyl moiety of **9** were unseparable from the resonances of tri(cyclohexyl)-phosphine.

13 M. Kira, T. Hino, Y. Kubota, N. Matsuyama, H. Sakurai, *Tetrahedron Lett.* **1988**, *29*, 6939.

Published on the web (Advance View) January 18, 2007; doi:10.1246/cl.2007.284