

A Stable 1,2-Disilacyclohexene and Its 14-Electron Palladium(0) Complex

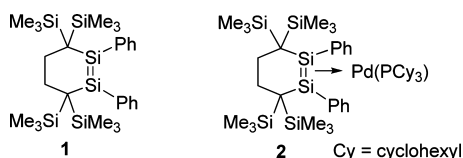
Takashi Abe, Takeaki Iwamoto,* and Mitsuo Kira*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Received February 25, 2010; E-mail: iwamoto@m.tains.tohoku.ac.jp; mkira@mail.tains.tohoku.ac.jp

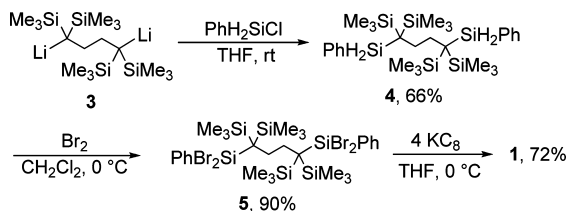
Although various types of stable disilenes have been studied extensively since the first isolation of tetramesityldisilene in 1981,¹ cyclic disilenes are still very limited.^{2,3} Herein we report the synthesis of a novel type of stable six-membered cyclic disilene, the 1,2-disilacyclohexene **1** (Chart 1), using a unique reagent for introducing sterically protecting groups. The reaction of disilene **1** with bis(tricyclohexylphosphine)palladium [(Cy₃P)₂Pd] was found to afford the stable 14-electron tricoordinate disilene-palladium complex **2** having an unprecedented Y-shaped structure.

Chart 1



The synthesis of **1** was achieved in four steps from 1,1-bis(trimethylsilyl)ethylene in a rather good yield, as shown in Scheme 1. The reaction of PhSiH₂Cl with 1,4-dilithio-1,1,4,4-tetrakis(trimethylsilyl)butane **3**,⁴ which was prepared by the reaction of 1,1-bis(trimethylsilyl)ethylene with lithium in tetrahydrofuran (THF) at room temperature, gave the corresponding 1,4-bis(phenylsilyl)butane **4** in 66% yield; **4** was converted to the corresponding tetrabromo derivative **5** in 90% yield by reaction with bromine. Cyclic disilene **1**^{5,6} was synthesized in 72% yield as yellow crystals by the reduction of **5** with potassium graphite (KC₈) in THF. Details of the synthesis are given in the Supporting Information. The structure of **1** was characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopies, mass spectrometry (MS), and X-ray diffraction (XRD). Whereas 1,4-dilithiobutane **3** has been utilized for the synthesis of an isolable dialkylsilylene,⁷ the present study indicates that **3** is also an effective reagent for kinetic stabilization of a six-membered cyclic disilene having relatively small residual substituents such as phenyl groups.

Scheme 1



The molecular structure of 1,2-disilacyclohexene **1** was determined by single crystal XRD analysis (Figure 1).⁸ The Si1–Si2 bond length is 2.1595(9) Å, which is in the range of typical Si=Si double-bond lengths (2.14–2.29 Å).² The Si1 and Si2 atoms are slightly pyramidalized, with bond-angle sums of 358.35(8) and 356.66(8)° around the unsaturated silicon atoms Si1 and Si2,

respectively. Because the geometry around the Si=Si double bond is trans-bent as expected,⁹ the six-membered ring of **1** adopts a conformation between an ideal chair and an ideal half-chair, which are known as the most stable conformations in all-carbon cyclohexane and cyclohexene, respectively.

The ²⁹Si resonance for the unsaturated silicon nuclei of **1** appeared at +100.9 ppm, which is close to those expected for tetraalkyl- and tetraaryldisilenes.² Two kinds of singlet signals due to the Me₃Si groups were observed in the ¹H, ¹³C, and ²⁹Si NMR spectra, indicating that the ring inversion accompanying the pyramidal inversion at the unsaturated silicon atoms is slow on the NMR time scales, probably because of the significant steric repulsion between the vicinal trimethylsilyl and phenyl groups during the inversion.

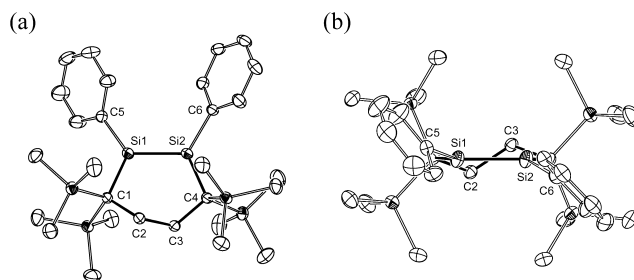


Figure 1. Molecular structure of 1,2-disilacyclohexene **1**: (a) top view; (b) side view. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2, 2.1595(9); Si1–C1, 1.889(2); Si1–C5, 1.878(2); C1–C2, 1.581(3); C2–C3, 1.548(3); C3–C4, 1.586(3); Si2–C4, 1.890(2); Si2–C6, 1.874(2); Si2–Si1–C1, 113.50(6); Si2–Si1–C5, 121.14(7); C1–Si1–C5, 123.71(9); Si1–Si2–C4, 113.05(7); Si1–Si2–C6, 119.73(7); C4–Si2–C6, 123.88(9).

The reaction of disilene **1** with (Cy₃P)₂Pd was investigated, with expectation that the geometry and electronic nature of the disilene palladium complex thus obtained may be significantly different from those of other complexes previously reported by us.^{10,11} A new disilene palladium complex, **2**, was obtained as purple crystals in 56% yield together with free PCy₃ (eq 1):¹²



The structure of **2** was determined by ¹H, ¹³C, and ²⁹Si NMR spectroscopies, MS, and XRD. The resonance of the unsaturated ²⁹Si nuclei was observed at +40.2 ppm as a doublet with *J*(²⁹Si–³¹P) = 17 Hz.

The molecular structure of **2** is shown in Figure 2 together with selected bond lengths and bond angles.¹³ The central palladium atom of **2** is tricoordinated by one phosphine P atom and the two Si atoms of disilene **1**, similarly to the 14-electron disilene complex (Cy₃P)(R₂Si=SiR₂)Pd (**6**; R = SiMe₂Bu-*t*).^{10a} The geometry around Pd in **2** is slightly pyramidalized, probably to avoid steric hindrance

between the bulky trimethylsilyl groups and tricyclohexylphosphine; the sum of the bond angles around Pd in **2** is $349.46(17)^\circ$, as opposed to $357.60(3)^\circ$ in **6**. However, the location of the phosphine is very different in **2** relative to **6**. Complex **2** is a Y-shaped tricoordinate complex with symmetric coordination of the phosphine, while **6** is a T-shaped complex with unsymmetric coordination of the phosphine;^{10a} the two P–Pd–Si angles in **2** are close to each other [$142.66(2)$ and $151.48(2)^\circ$], while those in **6** are significantly different [$128.94(3)$ and $171.83(3)^\circ$]. The Si1–Si2 bond length in **2** [$2.2009(7)$ Å] is only 0.0411 Å longer than that in free disilene **1**.

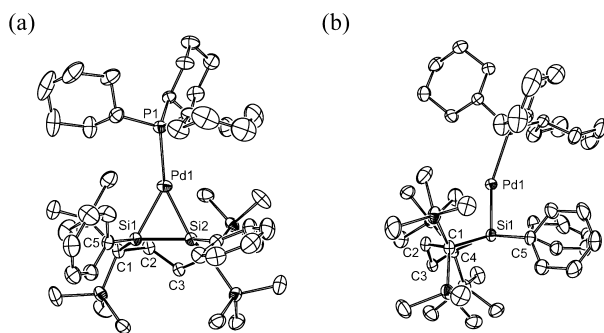


Figure 2. Molecular structure of disilene palladium complex **2**: (a) top view; (b) side view. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–Si1, $2.3916(6)$; Pd1–Si2, $2.3488(6)$; Pd1–P1, $2.4284(6)$; Si1–Si2, $2.2009(7)$; P1–Pd1–Si1, $142.66(2)$; P1–Pd1–Si2, $151.48(2)$; Si1–Pd1–Si2, $55.32(2)$.

We have recently shown¹⁰ that a disilene complex has a character between a π complex and a metallacycle such as an alkene complex.¹⁴ The π -complex character is estimated using the bent back angle around the Si=Si double bond (θ), the Si=Si bond elongation ($\Delta r/r_0$), and the extent of high-field shift of the unsaturated ^{29}Si nuclei ($\Delta\delta_{\text{Si}}$);¹⁵ the smaller these values are, the stronger the π -complex character. On the basis of these criteria, the 14-electron T-shaped complex **6** with $\theta = 7.0^\circ$ (the average of 4.41 and 9.65°), $\Delta r/r_0 = 3.2\%$, and $\Delta\delta_{\text{Si}} = 76.8$ ppm is characterized as a π complex, while the related 16-electron complex ($\text{Me}_3\text{P})_2(\text{R}_2\text{Si}=\text{SiR}_2)\text{Pd} (**7**; R = SiMe₂Bu-*t*) is a typical metallacycle.^{10a} However, theoretical calculations for the model 14-electron disilene complex ($\text{Me}_3\text{P})(\text{R}_2\text{Si}=\text{SiR}_2)\text{Pd}(0) (**6'**; R = SiH₃)^{10a} showed that the π -complex character is enhanced when the complex has a symmetric Y-shaped structure, although that structure is a transition state only 2.9 kcal mol^{−1} higher in energy than the T-shaped structure. The θ , $\Delta r/r_0$, and $\Delta\delta_{\text{Si}}$ values for complex **2** are 6.9° (the average of 6.70 and 7.15°), 1.9% , and 60.7 ppm, respectively, which are even smaller than those for **6**. The results indicate that the Y-shaped complex **2** has the strongest π -complex character among known disilene palladium complexes, in accord with the theoretical prediction.$$

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan [Specially Promoted Research (17002005 to M.K. and T.I.)].

Supporting Information Available: Synthetic details for **1** and **2** and their X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.
- (2) For recent comprehensive reviews of disilenes, see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds Volume 3*; Rappaport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; p 391. (c) West, R. *Polyhedron* **2002**, *21*, 467. (d) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73.
- (3) Three-membered cyclic disilenes: (a) Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 886. (b) Ichinohe, M.; Matsuno, T.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2194. (c) Lee, V. Y.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 9034. Four-membered cyclic disilenes: (d) Kira, M.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1996**, *118*, 10303. (e) Wiberg, N.; Niedermayer, W.; Noeth, H.; Warchhold, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1717. (f) Wiberg, N.; Auer, H.; Noeth, H.; Knizek, J.; Polborn, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2869. (g) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 1436. (h) Lee, V. Y.; Takamashi, K.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 4758. (i) Wiberg, N.; Vaisht, S. K.; Fischer, G.; Mayer, P. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823. Five-membered cyclic disilenes: (j) Grybat, A.; Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2010. Six-membered cyclic disilenes: (k) Wiberg, N.; Vaisht, S. K.; Fischer, G.; Mayer, P. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823. (l) Tanaka, R.; Iwamoto, T.; Kira, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6371. (m) Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumimoto, M.; Nagase, S. *J. Am. Chem. Soc.* **2007**, *129*, 7766.
- (4) Kira, M.; Hino, T.; Kubota, Y.; Matsuyama, N.; Sakurai, H. *Tetrahedron Lett.* **1988**, *29*, 6939.
- (5) Analysis data for **1**: Yellow crystals; mp $> 100^\circ\text{C}$ (decomp.). ^1H NMR (400 MHz, C_6D_6): δ 0.16 (s, 18H, SiMe₃), 0.46 (s, 18H, SiMe₃), 2.40–2.50 (m, 4H, CH₂), 6.96–7.76 (m, 10H, aryl). ^{13}C NMR (100 MHz, C_6D_6): δ 1.1 (SiMe₃), 4.0 (SiMe₃), 32.2 (CH₂), 127.5, 128.3, 129.1, 136.3. ^{29}Si NMR (79 MHz, C_6D_6): δ 2.3 (SiMe₃), 2.9 (SiMe₃), 100.9 (Si=Si). MS (EI, 70 eV) m/z (%): 540 (10, $[\text{M}^+ - 15]$), 477 (35), 73 (100). UV–vis (hexane) $\lambda_{\text{max}}/\text{nm}$ (ϵ): 427 (8400).
- (6) A 1,2-disilacyclohexene has been generated as a transient species by the photolysis of 1,4-bis[phenylbis(trimethylsilyl)silyl]butane. See: Sakurai, H.; Iimura, T.; Matsumoto, S.; Sanji, T. *Chem. Lett.* **2002**, *31*, 22.
- (7) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722. For a recent review of the chemistry of the silylene, see: Kira, M.; Iwamoto, T.; Ishida, S. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258.
- (8) Crystal data for **1** (173 K): $\text{C}_{28}\text{H}_{50}\text{Si}_6$, fw 555.22; monoclinic; space group $P2_1/a$; $a = 17.071(6)$ Å, $b = 9.127(3)$ Å, $c = 22.864(8)$ Å, $\beta = 111.7874(11)^\circ$; $V = 3307.9(19)$ Å³; $Z = 4$; D_{calc} = 1.115 Mg/m³; $R = 0.0534$ [$I > 2\sigma(I)$], $wR_2 = 0.1144$ (all data); GOF = 1.227. For details, see the Supporting Information.
- (9) The bent angles, which are defined as the angles between the C–Si1(Si2)–C planes and the Si1–Si2 axis, are 13.7 and 19.1° . The twist angle, which is defined as the angle between the two axes bisecting the C1–Si1–C5 and C4–Si2–C6 angles in a Newman projection view along the Si1–Si2 bond, is 4.76° .
- (10) (a) Kira, M.; Sekiguchi, Y.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **2004**, *126*, 12778. (b) Hashimoto, H.; Sekiguchi, Y.; Sekiguchi, Y.; Iwamoto, T.; Kabuto, C.; Kira, M. *Can. J. Chem.* **2003**, *81*, 1241. (c) Iwamoto, T.; Sekiguchi, Y.; Yoshida, N.; Kabuto, C.; Kira, M. *Dalton Trans.* **2006**, 177.
- (11) For other disilene transition-metal complexes, see: (a) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (b) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667. (c) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1996**, *118*, 7871. (d) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 452. (e) Berry, D. H.; Chey, J.; Zipin, H. S.; Carroll, P. J. *Polyhedron* **1991**, *10*, 1189. (f) Hong, P.; Damrauer, N. H.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 3698. (g) Fischer, R.; Zirngast, M.; Flock, M.; Baumgartner, J.; Marschner, C. *J. Am. Chem. Soc.* **2005**, *127*, 70. (h) Zirngast, M.; Flock, M.; Baumgartner, J.; Marschner, C. *J. Am. Chem. Soc.* **2009**, *131*, 15952. (i) Nguyen, T.-I.; Scheschkewitz, D. *J. Am. Chem. Soc.* **2005**, *127*, 10174.
- (12) Analysis data for **2**: Purple crystals; mp 175°C (decomp.). ^1H NMR (400 MHz, C_6D_6): δ 0.60 (s, 18H, SiMe₃), 0.69 (s, 18H, SiMe₃), 1.53–1.93 (m, 33H, cyclohexyl), 2.20–2.40 (m, 4H, CH₂), 6.80–8.10 (m, 10H, aryl). ^{13}C NMR (100 MHz, C_6D_6): δ 4.2 (SiMe₃), 4.8 (SiMe₃), 23.1 (C), 27.0 (CH₂), 26.5 (PCHCH₂CH₂CH₂), 27.9 (d, $^1J(\text{P}-\text{C}) = 11$ Hz, PCH), 31.7 (d, $^3J(\text{P}-\text{C}) = 6$ Hz, PCHCH₂CH₂), 33.5 (d, $^2J(\text{P}-\text{C}) = 7$ Hz, PCHCH₂), 125.7, 126.9, 129.3, 136.9. ^{29}Si NMR (79 MHz, C_6D_6): δ 2.7 (SiMe₃), 3.1 (SiMe₃), 40.2 (d, $^2J(\text{P}-\text{Si}) = 17$ Hz). ^{31}P NMR (161 MHz, C_6D_6): δ 23.0.
- (13) Crystal data for **2** (173 K): $\text{C}_{46}\text{H}_{83}\text{PPdSi}_6$, fw 942.03; monoclinic; space group $P2_1/n$; $a = 11.231(2)$ Å, $b = 20.760(4)$ Å, $c = 22.617(5)$ Å, $\beta = 99.409(2)^\circ$; $V = 5202.6(18)$ Å³; $Z = 4$; D_{calc} = 1.203 Mg/m³; $R = 0.0258$ [$I > 2\sigma(I)$], $wR_2 = 0.0701$ (all data); GOF = 1.058. For details, see the Supporting Information.
- (14) For recent reviews of olefin complexes, see: (a) Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717. (b) Hartly, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1982; Vol. 6.
- (15) For a complex with an $\text{R}_2\text{Si}=\text{SiR}_2$ ligand, θ is defined as the angle between an R_2Si plane and the Si=Si bond, $\Delta r/r_0 = (r-r_0)/r_0$, where r_0 is the Si=Si bond length in the corresponding free disilene, and $-\Delta\delta_{\text{Si}} = \delta_{\text{Si}}(\text{coordinated disilene}) - \delta_{\text{Si}}(\text{free disilene})$.

JA101654B