

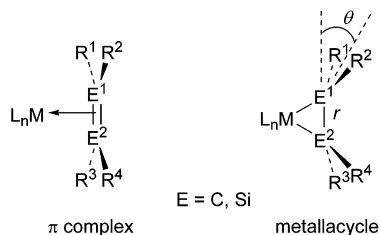
14-Electron Disilene Palladium Complex Having Strong π -Complex Character

Mitsuo Kira,* Yumiko Sekiguchi, Takeaki Iwamoto, and Chizuko Kabuto

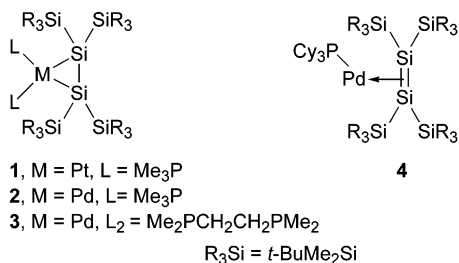
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Received June 21, 2004; E-mail: mkira@si.chem.tohoku.ac.jp

Much attention has been focused on the structure of transition metal complexes with η^2 -silicon–silicon doubly bonded species as ligands (disilene complexes). In related alkene complexes,¹ the bonding of an alkene to a transition metal center is usually understood in terms of alkene-to-metal σ -donation and metal-to-alkene π -back-donation, according to the Dewar–Chatt–Duncanson model.² The structure of an alkene complex is significantly influenced by the relative importance between the σ -donation and the π -back-donation; hence, they are classified into a π -complex having a major contribution of σ -donation and a metallacycle having dominant π -back-donation. The geometry around the alkene ligand in the π -complex is not very much different from that of the free alkene, while that in the metallacycle is significantly distorted and characterized by an elongated C¹–C² bond length (r) and a large bent-back angle (θ) defined by the angle between the R¹–C¹–R² (or R³–C²–R⁴) plane and the C¹–C² bond.

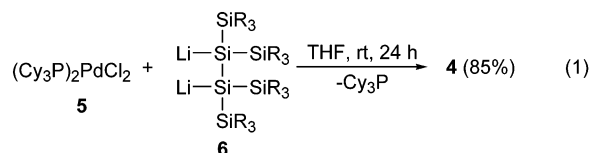


In contrast to alkene complexes, very few studies have been reported on the synthesis and properties of disilene complexes.^{3–6} All the disilene complexes whose X-ray structures are known, Cp₂W(Si₂Me₄) reported by Berry et al.⁴ and 16-electron disilene platinum and palladium complexes **1**–**3** reported by us,⁶ are characterized as the metallacycle on the basis of the above criteria. We report herein the successful synthesis of the first 14-electron disilene palladium complex **4** having strong π -complex character.⁷ Complex **4** is promising as a synthetic reagent for novel organosilicon compounds, in view of the high reactivity of three-coordinate 14-electron complexes having a vacant coordination site.⁸



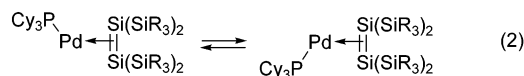
Disilene complex **4** was obtained as air-sensitive dark-red crystals in 85% yield by the reaction of (Cy₃P)₂PdCl₂ **5** with 1,2-dilithiodisilane **6**⁹ in THF at room temperature (eq 1).¹⁰ The molecular structure of **4** was determined by ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectroscopies and X-ray crystallography.¹¹ The initial reaction would be the reduction of **5** by **6** giving zerovalent

(Cy₃P)₂Pd (**7**) and free tetrakis(*tert*-butyldimethylsilyl)disilene (**8**).¹² Because both **7** and **8** were actually observed during the reaction by NMR spectroscopy, the coupling between **7** and **8** accompanied by the elimination of Cy₃P would give the final 14-electron complex **4**. During the reaction of (Cy₃P)₂PtCl₂ with **6**, (Cy₃P)₂Pt and **8** formed, but no further reaction proceeded even at reflux in THF.



X-ray structural analysis revealed interesting structural characteristics of complex **4** (Figure 1). In the solid state, the central palladium atom was tricoordinated with the coordination of one tricyclohexylphosphine and an η^2 -disilene; Pd–Si1 and Pd–Si2 distances are 2.3610(9) and 2.4168(8) Å. The geometry around the palladium atom was almost planar with the sum of bond angles of 357.60(3)°. Interestingly, tricyclohexylphosphine ligand coordinates unsymmetrically to the cyclopalladadisilane ring; the angles of P–Pd–Si1 and P–Pd–Si2 were 128.94(3)° and 171.83(3)°, respectively. The central Si1–Si2 bond length was 2.274(1) Å, which is longer by 0.072 Å than that of the corresponding free disilene **8** (2.202(1) Å)¹² but considerably shorter than the reported Si–Si single bond (2.335–2.697 Å).

In ¹H, ¹³C, and ²⁹Si NMR spectra of **4** in benzene-*d*₆ at room temperature, four *t*-BuMe₂Si groups were equivalent, and the ²⁹Si resonance of disilene silicon nuclei was observed as a doublet at 65.3 ppm [$J(^{29}\text{Si}-^{31}\text{P}) = 19$ Hz]. The doublet signal was unchanged even at –80 °C. Facile flipping of the Cy₃P group shown in eq 2 would be responsible for the highly symmetric NMR patterns of **4** (vide infra).



The ²⁹Si NMR resonance at +65.3 ppm is considerably downfield-shifted compared to the corresponding resonances of complexes **2** (–46.5 ppm), **3** (–51.9 ppm), and hexakis(*tert*-butyldimethylsilyl)cyclotrisilane (–156.5 ppm)¹³ but still upfield from that of free disilene **8** (+142.1 ppm).¹² The tendency may be related to the difference in the π -complex character among these disilametallacycles.

The bent-back angle θ and bond elongation $\Delta r/r_0$ ($\Delta r = r - r_0$, where r_0 is the Si1–Si2 bond length in the corresponding free disilene) for Cp₂W(Si₂Me₄),¹⁴ **1**, **2**, and **3** are estimated to be 30.2° and 3.7%, 29.3° and 5.4%, 27.5° and 4.6%, and 26.0° and 5.3%, respectively. Theoretical calculations for (H₃P)₂Pt(Si₂H₄) and (H₃P)₂-Pd(Si₂H₄) showed the metallacycle character of these complexes, whose θ and $\Delta r/r_0$ are 25° and 5.6% for the platinum complex and 24° and 5.3% for the palladium complex.¹⁵ The bent-back angle θ around the central Si atoms of **4** were 4.41° for Si1 and 9.65° for

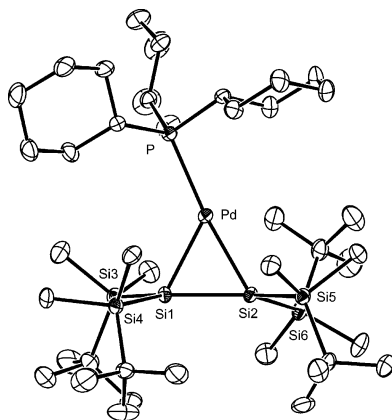
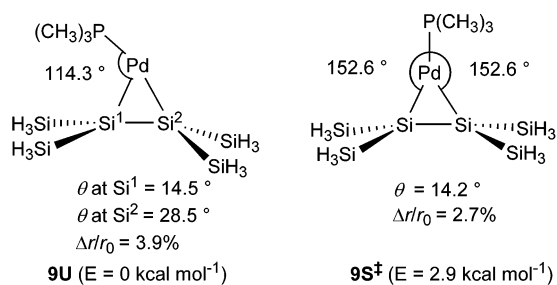


Figure 1. Molecular structure of complex **4**. In the single crystal of **4**, toluene molecules were included with the **4**:toluene ratio of 1:1. Hydrogen atoms and the toluene molecule were omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–Si1 2.3610(9), Pd–Si2 2.4168(8), Pd–P 2.3919(8), Si1–Si2 2.2740(11), Pd–Si1–Si2 62.82(3), Pd–Si2–Si1 60.35(3), Si1–Pd–Si2 56.83(3), P–Pd–Si1 128.94(3), P–Pd–Si2 171.83(3).

Si2, respectively. The $\Delta r/r_0$ value for **4** was 3.2%. On the basis of the considerably smaller θ and $\Delta r/r_0$ values for **4** than those for **1–3**, **4** is regarded as the complex having the strongest π -complex character among the known disilene complexes, due to the intrinsic electron-deficient nature of the central metal of 14-electron complex.

DFT calculations¹⁶ for a model 14-electron complex [**9**, $(\text{Me}_3\text{P})_2\text{Pd}\{(\text{H}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiH}_3)_2\}$] revealed that as shown in the following chart, the unsymmetrical (T-type)¹⁷ structure observed for **4** was well reproduced by the optimized structure (**9U**), while the P–Pd–Si¹ angle for **9U** was much smaller than that observed for **4** (128.9°) probably due to the steric effects of bulky trialkylsilyl substituents in **4**. Unsymmetrical complex **9U** was 2.9 kcal/mol more stable than symmetrical (Y-type)¹⁷ complex **9S[‡]**, which was found to be a transition state for the inversion process shown in eq 2. The calculated very low barrier for the inversion is compatible with the symmetric NMR spectra of **4** at even low temperatures.¹⁸



The planarity around the Si=Si bond increased in the order $[(\text{Me}_3\text{P})_2\text{Pd}\{(\text{H}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiH}_3)_2\}]$ (**10**) < **9U** < **9S[‡]**; the θ and $\Delta r/r_0$ values were 28.2° and 4.3%, 21.5° (av) and 3.9%, and 14.2° and 2.7%, for **10**, **9U**, and **9S[‡]**, respectively. The order would be understood by the effective π -back-donation, depending on the overlap between the lone-pair orbital of a phosphine ligand and a d orbital responsible for the π -back-donation.¹⁹ Since the π -back-donation in a three-coordinate 14-electron complex is expected to decrease with increasing P–Pd–Si¹ angle, the higher planarity around the Si=Si bond in **4** than that in **9U** may be attributed in part to the larger P–Pd–Si1 angle in **4**.

Further works on the unique reactions of complex **4** are in progress.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan

(Grant-in-Aid for Scientific Research on Priority Areas (No. 14078203, “Reaction Control of Dynamic Complexes”).

Supporting Information Available: Details for the synthesis of **4** and the X-ray structure determination of **4**-(toluene), theoretical results for model compounds **9** and **10**. The X-ray crystallographic data are also available in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) 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, 1982; Vol. 6.
- (2) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.
- (3) (a) Zybilla, C.; West, R. *J. Chem. Soc., Chem. Commun.* **1986**, 857. (b) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667. (c) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517.
- (4) (a) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 452. (b) Hong, P.; Damrauer, N. H.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 3698. (c) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *Polyhedron* **1991**, *10*, 1189.
- (5) (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577.
- (6) (a) Hashimoto, H.; Sekiguchi, Y.; Iwamoto, T.; Kabuto, C.; Kira, M. *Organometallics* **2002**, *21*, 454. (b) Hashimoto, H.; Sekiguchi, Y.; Sekiguchi, Y.; Iwamoto, T.; Kabuto, C.; Kira, M. *Can. J. Chem.* **2003**, *81*, 1241.
- (7) A 14-electron silene platinum complex $(\text{Cy}_3\text{P})\text{Pt}(\text{silene})$ (Cy = cyclohexyl) has recently been synthesized: Bravo-Zhivotovskii, D.; Peleg-Vasserman, H.; Kosa, M.; Molev, G.; Botoshanskii, M.; Apeloig, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 745.
- (8) (a) Stambuli, J. P.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346. (b) Stambuli, J. P.; Incarvito, C. D.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184. (c) Yamashita, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5344.
- (9) Kira, M.; Iwamoto, T.; Yin, D.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **2001**, 910.
- (10) For experimental details, see the Supporting Information. **4**: air-sensitive dark-red crystals; mp 190 °C dec; ¹H NMR (C_6D_6 , δ) 0.55 (s, 12 H, Me), 0.69 (s, 12 H, Me), 1.26 (s, 36 H, *t*-Bu), 1.43–1.93 (m, 33 H, cyclohexyl); ¹³C NMR (C_6D_6 , δ) 2.3 (SiCH₃), 3.8 (SiCH₃), 20.0 (C(CH₃)₃), 26.5 (PCHCH₂CH₂CH₂), 27.9 (d, ¹J(P–C) = 11 Hz, PCH), 30.3 (C(CH₃)₃), 31.6 (d, ³J(P–C) = 6 Hz, PCHCH₂CH₂), 34.4 (d, ²J(P–C) = 7 Hz, PCHCH₂); ²⁹Si NMR (79 MHz, C_6D_6 , δ) 3.9 (SiMe₂Bu-*t*), 65.3 (d, ²J(P–Si) = 19 Hz); ³¹P NMR (161 MHz, C_6D_6 , δ) 17.5; UV–vis (hexane) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 362 (3800), 433 (2200), 472 (3000). Anal. Calcd for $\text{C}_{42}\text{H}_{93}\text{P}_2\text{Si}_6$: C, 55.80; H, 10.37. Found: C, 55.90; H, 10.20.
- (11) Crystal data for **4** (150 K): $\text{C}_{42}\text{H}_{93}\text{P}_2\text{Si}_6 \cdot (\text{C}_7\text{H}_8)$; FW: 995.23; triclinic; *P*1 (No. 2); *a* = 12.0473(2) Å; *b* = 12.7355(4) Å; *c* = 20.3952(1) Å; α = 76.653(8)°; β = 71.024(7)°; γ = 85.812(9)°; D_{calc} = 1.140 g/cm³; *Z* = 2; *R*1 = 0.0463 (*I* > 2 σ (*I*)); *wR*2 = 0.0962 (all data); GOF = 1.070.
- (12) Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489.
- (13) Kira, M.; Iwamoto, T.; Maruyama, T.; Kuzuguchi, T.; Yin, D.; Kabuto, C.; Sakurai, H. *J. Chem. Soc., Dalton Trans.* **2002**, 1539.
- (14) The *r*₀ value for Me₂Si=SiMe₂ was determined to be 2.180 Å by theoretical calculations at the MP2/6-31G(d) level.
- (15) (a) Sakaki, S.; Ieki, M. *Inorg. Chem.* **1991**, *30*, 4218. (b) Sakaki, S.; Yamaguchi, S.; Musashi, Y.; Sugimoto, M. *J. Organomet. Chem.* **2001**, *635*, 173.
- (16) All calculations were carried out at the B3LYP level using a Gaussian 98 program, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 2001. The basis sets were 6-31G* for H, C, Si, P and Lan12dz for Pd. See the Supporting Information for the details of the calculations.
- (17) See ref 8 for the terminology of T- and Y-types.
- (18) Similar T-type structures have been found for other three-coordinate 14-electron complexes.^{7,8} Because the energy difference between **9U** and **9S[‡]** is very small, the possibility that **4** having bulky trialkylsilyl substituents adopts a symmetric structure similar to that of **9S[‡]** in solution may not be ruled out. It is an interesting issue to explain why unsymmetric complex **9U** is more stable than symmetric complex **9S[‡]** in this particular case. More detailed MO analysis of these and related complexes is currently in progress.
- (19) If we take *x* and *y* axes to be parallel and perpendicular to the Si=Si bond, respectively, through the Pd metal in the three-membered ring plane, the *d*_{xy} orbital should be responsible for the π -back-donation. The electron donation from *d*_{xy} to Si=Si π^* orbital will increase with increasing the overlap between phosphine *n* and *d*_{xy} orbitals. The overlap in **10** is approximately twice of that in **9U**, and no such overlap is expected in **9S[‡]**. The natural bond orbital (NBO) analysis indicates that, while σ -donation is similar among **9U**, **9S[‡]**, and **10**, the extent of π -back-donation decreases in the order **10** > **9U** > **9S[‡]**, being in accord with the order of the planarity around the Si=Si bond.¹⁶ The θ values at Si¹ and Si² of **9U** are significantly different from each other, suggesting strong trans influence of the phosphine ligand.

JA046354Y