454 *Organometallics* **2002,** *21,* 454−456

Synthesis and X-ray Structure of a Platinum η^2-Disilene Complex

Hisako Hashimoto, Yohei Sekiguchi, Takeaki Iwamoto, Chizuko Kabuto, and Mitsuo Kira*

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

Received October 18, 2001

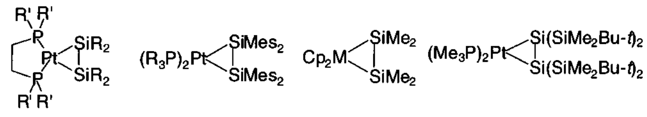
Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on January 8, 2002 on http://pubs.acs.org | doi: 10.1021/om010914+

*Summary: The platinum silyl-substituted η^2-disilene complex $(Me_3P)_2Pt[Si(SiMe_2(t\text{-}Bu))_2]_2$ (**4**) was synthesized by the reaction of cis-$(Me_3P)_2PtCl_2$ (**5**) with 1,2-dilithiotetrakis(tert-butyldimethylsilyl)disilane (**6**) in THF at −50 °C for 3 h. The X-ray structural analysis revealed that **4** can be regarded as a metalladisilacyclopropane with very weak π-complex character.*

Although a variety of isolable silicon−silicon doubly bonded compounds (disilenes) have been extensively studied,[1] there have been very few reports on the synthesis and properties of transition-metal complexes with η^2-disilene ligands.[2−4] Among the isolated mononuclear η^2-disilene complexes **1**,[2b−d], **2**,[3] and **3**[3c] (Chart 1), only the structure of **2** has been determined by X-ray crystallography.[3a]

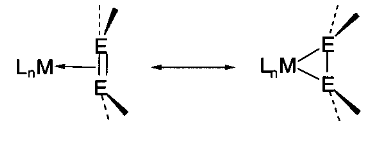
According to the Dewar−Chatt−Duncanson model,[5] the bonding nature of an olefin transition-metal complex is described by the synergistic σ-bonding and π-back-bonding interactions using olefinic π-type and metal d orbitals. In a resonance formulation, the structure is depicted as a combination of two resonance hybrids: a π-complex and a metallacyclopropane (Scheme 1), while the relative importance of the two structures depends on the electronic nature of the metal and the olefin.[6] In this context, it is an interesting issue to elucidate the bonding of a variety of η^2-disilene metal complexes. We report here the synthesis of the novel platinum η^2-disilene complex **4** and its structure as determined by X-ray crystallography. The structural parameters around the disilene moiety in **4** compared with those of the corresponding disilene have shown that **4** is better described as a metalladisilacyclopropane rather than as a π-complex. This is in good accord with the theoretical prediction.[7,8]

Chart 1

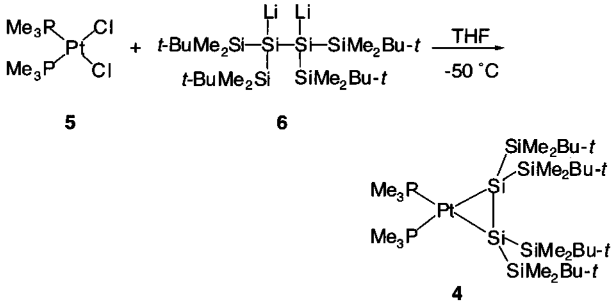


1a, R' = Ph, R = *i*-Pr
1b, R' = Ph, R = Me
1c, R' = Cy, R = Ph
1d, R = Et
1e, R = Ph
2, M = W
3, M = Mo
4

Scheme 1



The platinum η^2-disilene complex **4** was synthesized by the reaction of *cis*-$(Me_3P)_2PtCl_2$ (**5**; 0.20 g, 0.42 mmol) with 1,2-dilithiotetrakis(*tert*-butyldimethylsilyl)disilane (**6**;[9] 0.46 g, 0.87 mmol) in THF at −50 °C for 3 h, as shown in eq 1. Disilane **6** was prepared as a white powder by the reduction of the corresponding disilene with lithium metal. The solvent was replaced by toluene, and the resulting precipitate (LiCl) was filtered. Removing the solvent and then washing the solid residue with



5 **6** **4** (1)

---

* To whom correspondence should be addressed. E-mail: mkira@si.chem.tohoku.ac.jp.

(1) For reviews, see: (a) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, p 1015. (e) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (f) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (g) Grev, R. S.; *Adv. Organomet. Chem.* **1991**, *33*, 125. (h) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (i) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *611*, 236. (j) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 2001; Vol. 3, p 391.

(2) (a) Zybill, C.; West, R. *J. Chem. Soc., Chem. Commun.* **1986**, 857. (b) Pham, E.; West, K. R. *J. Am. Chem. Soc.* **1989**, *111*, 7667. (c) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (d) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1996**, *118*, 7871.

(3) (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.

(4) (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.

(5) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(6) Young, G. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Puddephatt, R. J., Eds.; Pergamon: New York, 1995; p 533.

(7) Sakaki, S.; Ieki, M. *Inorg. Chem.* **1991**, *30*, 4218.

(8) Cundari, T. R.; Gordon, M. S. *J. Mol. Struct. (THEOCHEM)* **1994**, *313*, 47.

(9) Kira, M.; Iwamoto, T.; Yin, Z.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **2001**, 910.

10.1021/om010914+ CCC: $22.00 © 2002 American Chemical Society
Publication on Web 01/08/2002

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on January 8, 2002 on http://pubs.acs.org | doi: 10.1021/om010914+

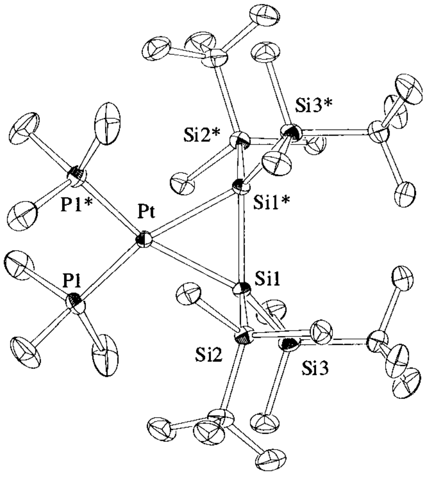


Figure 1. ORTEP drawing of the η^2-disilene platinum complex **4**, showing 50% thermal ellipsoids**.** Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−Si1, 2.4317(8); Si1−Si1*, 2.321(2); Pt−P, 2.2924(9); Si1−Si2, 2.403(1); Si1−Si3, 2.378(1); Si1−Pt−Si1*, 57.01(4); Pt−Si1−Si1*, 61.49(2); P1−Pt−P1*, 99.17(5).

hexane gave **4** as a yellow solid in 46% yield.[10] An analogous strategy was used by Castel et al. to synthesize the platinum digermene complex $(Et_3P)_2Pt(Ph_2GeGePh_2)$.[11] Complex **4** was very stable to air and moisture in the solid state as well as in solution at room temperature.

Recrystallization of **4** from a 1:1 mixture of toluene and hexane at −15 °C afforded yellow prisms suitable for a single-crystal X-ray diffraction study. The molecular structure of **4** is shown in Figure 1 with selected bond lengths and angles.[12] The molecule has a crystallographic 2-fold axis through the platinum atom that bisects the Si1−Si1* bond and adopts a highly distorted square-planar geometry around the platinum atom with a dihedral angle of 33.6° between the Pt−Si1−Si1* and Pt−P−P* planes, probably because of steric repulsion between the bulky trialkylsilyl substituents and the phosphine ligands.[13] The Pt−Si bond length of 2.4317(8) Å is within the reported single-bond distances (2.255−2.444 Å), but at the longer end,[14] while the Pt−P bond distance of 2.2924(9) Å is rather shorter than those in related platinum bis(silyl) complexes, implying a slightly weaker trans influence of the $[Si(SiMe_2(t\text{-}Bu))_2]_2$ ligand in **4** than that of other silyl groups; the Pt−P bond lengths are 2.3701(9) Å for *cis*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$[15] and 2.362(3) and 2.374(3) Å for *cis*-$(Et_3P)_2Pt(SiPh_2H)_2$.[16]

The Si1−Si1* bond length in **4** is 2.321(2) Å, which is between the known values for Si−Si single bonds (2.335−2.697 Å)[17a] and Si−Si double bonds (2.14−2.229 Å)[1j,17b] but rather close to the shortest limit of the single bond. The Si1−Si1* distance in **4** is lengthened by 0.119 Å from that of the corresponding free disilene $(t\text{-}BuMe_2Si)_2Si{=}Si(SiMe_2(t\text{-}Bu))_2$ (**7**; 2.202(1) Å).[18] The lengthening of the Si−Si distance ($\Delta l/l$)[19] in **4** is 5.4%, which is similar to that for the tungsten complex **2**[3a] (5.8%), if the Si−Si distance in $Me_2Si{=}SiMe_2$ is taken to be 2.129 Å as calculated at the HF/6-31G* level.[23]

The total of the three Si−Si1−Si bond angles is 351.5°, which is comparable to 348.3° observed in tungsten complex **2**.[3a] The bend angle (α) defined by the angle between the Si2−Si1−Si3 plane and the plane through the Si1−Si1* bond and perpendicular to the Pt−Si1−Si1* plane in **4** is 29.3°, which is comparable to that in **2** ($\alpha = 30.2°$).[3a] These structural parameters are in good accord with those obtained by ab initio MO calculations for the model platinum η^2-disilene complex $(H_3P)_2Pt(Si_2H_4)$,[7,8,24] and hence, complex **4** is characterized to be a metalladisilacyclopropane.[25]

The NMR spectral features of **4** in benzene-d_6 are in good accord with the structure in the solid state. The $^{29}Si\{^1H\}$ signals for Si1 and Si1* appear at −79.7 ppm with a doublet of doublets pattern due to the coupling with two ^{31}P nuclei, accompanied by satellites due to a ^{195}Pt nucleus. The ^{29}Si chemical shift is markedly upfield from that of the free disilene **7** (142.1 ppm),[18] in accordance with the previous observation for the η^2-disilene complex **1e**.[2b] The $^1J_{Pt,Si}$ value in **4** (494 Hz) is significantly smaller compared to those of platinum *cis*-bis(silyl) complexes such as $(dppe)Pt(SiH_2SiMe_3)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (997 Hz) and *cis*-$(Me_3P)_2Pt[SiH(SiMe_2(t\text{-}Bu))_2]_2$ (737 Hz).[26] However, the small $^1J_{Pt,Si}$

---

[10] **4**: yellow crystals; ^1H NMR (300.1 MHz, C_6D_6, 298 K) δ 0.39 (s, 12 H; $SiMe_3$), 0.49 (s, 12 H; $SiMe_3$), 1.22 (s, 36 H; *t*-Bu), 1.29 (dd, $^2J_{P,H} = 8$ Hz, $^3J_{Pt,H} = 26$ Hz, 18 H; PMe_3); ^{13}C NMR (75.5 MHz, C_6D_6, 298 K) δ 2.6 (d, $^3J_{Pt,C} = 6$ Hz, $Si(CH_3)_2(t\text{-}Bu)$ or $SiMe_2(CMe_3)$), 2.7 (d, $^3J_{Pt,C} = 6$ Hz, $Si(CH_3)_2(t\text{-}Bu)$ or $SiMe_2(CMe_3)$), 23.0 (ddd, $^1J_{P,C} = 24$ Hz, $^3J_{P,C} = 5$ Hz, $^2J_{Pt,C} = 40$ Hz, $P(CH_3)_3$), 28.5 (s, $SiMe_2(C(CH_3)_3)$, 30.0 (s, $SiMe_2(C(CH_3)_3)$; ^{29}Si NMR (59.6 MHz, C_6D_6, 298 K) δ 2.8 (dd, $^3J_{P,Si} = 4$ Hz, $^2J_{Pt,Si} = 23$ Hz, $SiMe_2t\text{-}Bu$), −79.7 (ddd, $^2J_{cis-P,Si} = 17$ Hz, $^2J_{trans-P,Si} = 86$ Hz, $^1J_{Pt,Si} = 494$ Hz, Pt−Si); ^{31}P NMR (121.4 MHz, C_6D_6, 298 K) δ −19.9 (d, $^1J_{Pt,P} = 2476$ Hz, PMe_3).

[11] Castel, A.; Riviére, P.; Satgé, J.; Desor, D.; Ahbala, M.; Abdenadher, C. *Inorg. Chim. Acta* **1993**, *212*, 51.

[12] X-ray analysis of **4**: $C_{30}H_{78}P_2PtSi_6$; fw 864.50; yellow prism; orthorhombic; space group *Pbcn* (No. 60); $a = 16.6483(4)$ Å, $b = 12.3809(5)$ Å, $c = 21.2205(4)$ Å, $V = 4374.0(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.31$ g cm^{-3}. A total of 25 301 reflections were measured, and of these, 2978 reflections with $I > 3.5\sigma(I)$ were used in refinement: $R = 0.022$, $R_w = 0.034$. GOF = 1.14. The reflection intensities were collected on a Rigaku/MSC CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at 150 K.

[13] Our preliminary calculations for $(H_3P)_2Pt[\eta^2\text{-}(H_3Si)_2SiSi(SiH_3)_2]$ (**4′**) have shown that the optimized structure adopts a planar geometry around Pt at the B3LYP/6-31G(d) level, similarly to $(H_3P)_2Pt(\eta^2\text{-}Si_2H_4)$.[7,8] The Si−Si, Pt−Si, and Pt−P bond lengths for **4′** are 2.254, 2.439, and 2.368 Å, respectively.

[14] Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

[15] Ozawa, F.; Kamite, J. *Organometallics* **1998**, *17*, 5630.

[16] Kim, Y.; Park, J.; Lee, S.; Osakada, K.; Tanabe, M.; Choi, J.; Koizumi, T. Yamamoto, T. *Organometallics* **1999**, *18*, 1349.

[17] (a) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Part 1, Chapter 5, p 181. (b) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479.

[18] Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489.

[19] l = Si−Si bond distance in free disilene; Δl = the increase in the Si−Si bond distance in the complex from l. The corresponding C−C bond lengthenings in $(Ph_3P)_2Pt[C_2(CN)_4]$[20,21] as a model for metallacyclopropane and $K[Pt(C_2H_4)Cl_3]$[20,22] as a model of the π-complex are 11 and 1.3%, respectively.

[20] Hartley, F. R. In *Comprehensive Organometallic Chemistry I*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Part 39, p 471.

[21] (a) Panattoni, C.; Bombieri, G.; Belluco, U.; Baddley, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 798. (b) Bombieri, G.; Forsellini, E.; Panattoni, C.; Graziani, R.; Bandoli, G. *J. Chem. Soc. A* **1970**, 1313.

[22] (a) Wunderlich, J. A.; Mellor, D. P. *Acta Crystallogr.* **1954**, *7*, 130. (b) Jarvis, J. A. J.; Kilbourn, B. T.; Owston, P. G. *Acta Crystallogr.* **1971**, *B27*, 366.

[23] West, R.; Cavalieri, J. D.; Buffy, J. J.; Fry, C.; Zilm, K. W.; Duchamp, J. C.; Kira, M.; Iwamoto, T.; Muller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4872.

[24] Theoretical $\Delta l/l$ and α values are 5.6% and 24° for $(H_3P)_2Pt(Si_2H_4)$ and 5.0% and 24° for **4′**.[13]

[25] The bent angle is much larger than that of 5° in $K[Pt(C_2H_4)Cl_3]$[20,22] but close to 32.6° in $(Ph_3P)_2Pt[C_2(CN)_4]$.[20,21]

value may not be an indication of the π-complex character of **4**, because $^1J_{\mathrm{Si,H}}$ values in $(\mathrm{Me_3Si})_n\mathrm{Me}_{3-n}\mathrm{SiH}$ ($n = 1-3$) decrease linearly with increasing n;[27] as an extrapolation of the linear dependence of $^1J_{\mathrm{Pt,Si}}$ values in *cis*-$(\mathrm{R'_3P})_2\mathrm{Pt}[\mathrm{SiH}_{3-n}(\mathrm{SiR_3})_n]_2$ type compounds on n, the $^1J_{\mathrm{Pt,Si}}$ value for the *cis*-$(\mathrm{R'_3P})_2\mathrm{Pt}[\mathrm{Si(SiR_3)_3}]_2$ type complex is estimated to be ca. 500 Hz, in good accord with the observed value for **4**.

In conclusion, the η^2-disilene platinum complex **4** has been well characterized as a metalladisilacyclopropane with very weak π-complex character. The extent of the metalladisilacyclopropane character in **4** is suggested to be similar to that in the η^2-disilene tungsten complex **2**,[3a] on the basis of their $\Delta l/l$ values and the bent angles of the disilene moiety (α). Further work is 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 (B) No. 11440185 (M.K.)). We thank Prof. S. Sakaki (Kumamoto University) for his helpful discussion.

Supporting Information Available: Tables giving the details of the X-ray structure determination and bond angles and figures giving thermal ellipsoid plots for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010914+

---

(26) The synthesis and structure of these bis(silyl) platinum complexes will be published elsewhere.

(27) (a) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 8, p 511. (b) Urenovich, J. V.; West, R. *J. Organomet. Chem.* **1965**, *3*, 138. (c) Bürger, H.; Kilian, W. *J. Organomet. Chem.* **1969**, *18*, 299. (d) Chatgilialoglu, C.; Guerrini, A.; Lucarini, M. *J. Org. Chem.* **1992**, *57*, 3405.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on January 8, 2002 on http://pubs.acs.org | doi: 10.1021/om010914+