

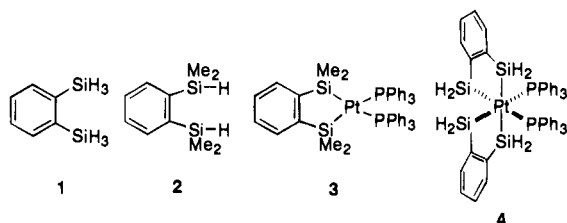
# Unusual Reactivity of 1,2-Disilylbenzene toward Pt(0) Complexes. Isolation of the First Pt<sup>IV</sup>Si<sub>4</sub>P<sub>2</sub> and Dinuclear, Mixed-Valence Pt<sup>II</sup>Pt<sup>IV</sup>Si<sub>4</sub>P<sub>4</sub> Complexes

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Transition-metal-catalyzed reaction of hydrosilanes or disilanes is one of the most useful methods to prepare monomeric and polymeric organosilicon compounds that are experiencing vigorous growth.<sup>1</sup> Platinum complexes in particular provide excellent catalysts for the transformation of hydrosilanes and disilanes. Mono- and bis(silyl)platinum(II) complexes are usually believed to play important roles in hydrosilylation,<sup>1e</sup> dehydrocoupling, and double silylation reactions with hydrosilanes and disilanes.<sup>2–4</sup> However, as several groups have demonstrated, mechanistic details appear much more complicated, depending on the structures of these compounds.<sup>5</sup> Here we report two unusual complexes being formed in the reaction of 1,2-disilylbenzene (**1**)<sup>6</sup> and platinum(0) complexes; one is a tetrakis(silyl)platinum(IV) complex, the first example of a tetrakis(silyl) transition-metal species, and the other is a dinuclear, mixed-valence complex containing a Pt<sup>II</sup>Pt<sup>IV</sup>Si<sub>2</sub> ring system.



In the course of our mechanistic study on the platinum-complex-catalyzed reaction of 1,2-bis(dimethylsilyl)benzene

(1) (a) *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988. (b) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989. (c) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. (d) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press Inc.: Greenwich, CT, 1991; Vol. 1, p 327. (e) *Comprehensive Handbook on Hydrosilylation*; Marciniak, B., Ed.; Pergamon Press: Oxford, U.K., 1992.

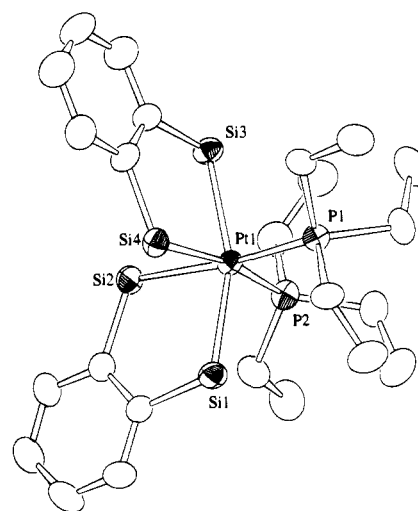
(2) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37.

(3) (a) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (b) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (c) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.

(4) (a) Tanaka, M.; Uchamaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (b) Tanaka, M.; Uchamaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1. (c) Reddy, N. P.; Uchamaru, Y.; Lautenschlager, H.-J.; Tanaka, M. *Chem. Lett.* **1992**, 45. (d) Tanaka, M.; Uchamaru, Y. *Bull. Soc. Chim. Fr.* **1992**, *129*, 667. (e) Uchamaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639. (f) Uchamaru, Y.; El Sayed, A. M. M.; Tanaka, M. *Organometallics* **1993**, *12*, 2065. (g) Uchamaru, Y.; Brandl, P.; Tanaka, M.; Goto, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744.

(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. (c) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917. (d) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955. (e) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227.

(6) 1,2-Disilylbenzene (**1**) was prepared by using the ortho lithiation method of silyl-substituted benzenes developed by Tamao's group. (a) Tamao, K.; Yao, H.; Tsutsumi, Y.; Abe, H.; Hayashi, T.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 2925. (b) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099. Recently the synthesis of **1** by an alternative method was reported: Schröck, R.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch. B* **1994**, *49*, 1036.



**Figure 1.** Molecular structure of **5** (50% probability). Important bond distances (Å) and angles (deg): Pt1–P1, 2.398(1); Pt1–P2, 2.418(2); Pt1–Si1, 2.428(2); Pt1–Si2, 2.383(1); Pt1–Si3, 2.430(2); Pt1–Si4, 2.376(2); P1–Pt1–P2, 104.71(5); Si1–Pt1–Si2, 83.12(5); Si2–Pt1–Si4, 80.02(6); Si3–Pt1–Si4, 83.29(7).

(**2**),<sup>4</sup> we came across the reaction of a large excess of **2** with Pt(CH<sub>2</sub>=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> giving cyclic Pt<sup>II</sup>Si<sub>2</sub>P<sub>2</sub> complex **3** quantitatively, which Eaborn and co-workers had already reported.<sup>7</sup> Pt<sup>II</sup>Si<sub>2</sub>P<sub>2</sub> complexes are normal products of the reaction of hydrosilanes with Pt(0) or Pt(II) complexes.<sup>7,8</sup> However, treatment of 2.2 equiv of **1** with Pt(CH<sub>2</sub>=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> in toluene-*d*<sub>8</sub> at room temperature gave Pt(IV) complex **4** nearly quantitatively, rather than a Pt<sup>II</sup>Si<sub>2</sub>P<sub>2</sub> complex similar to **3**. NMR analysis, in particular, the small <sup>1</sup>J<sub>P–Pt</sub> value (1188 Hz)<sup>5c,9</sup> and unusually high field shift of the <sup>195</sup>Pt NMR signal (–6568 ppm), clearly indicated a Pt(IV) structure.<sup>10</sup> Furthermore, the X-ray structure analysis of PEt<sub>3</sub> derivative **5** (vide infra) confirmed the Pt<sup>IV</sup>Si<sub>4</sub>P<sub>2</sub> structure (Figure 1).

Treatment of **1** (2.5 equiv) with Pt(PEt<sub>3</sub>)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> at 80 °C also formed a similar Pt<sup>IV</sup>Si<sub>4</sub>P<sub>2</sub> complex, **5**, a PEt<sub>3</sub> derivative of **4**. However, when the reaction was effected at 0 °C (in toluene), totally different products, **6a** and **6b** (3:1 mixture), resulted,<sup>11</sup> and heating the mixture at 80 °C converted **6a** and **6b** to **5** quantitatively.

On the other hand, treatment of only 1 equiv of **1** with Pt(PEt<sub>3</sub>)<sub>3</sub> in toluene at 0 °C gave Pt<sup>II</sup>Si<sub>2</sub>P<sub>2</sub> complex **7** as a white powder. The structure could be assigned by low-temperature NMR. <sup>31</sup>P NMR gave a typical signal for *cis*-Pt<sup>II</sup>Si<sub>2</sub>P<sub>2</sub> species (δ = 14.01, <sup>1</sup>J<sub>P–P</sub> = 1776).<sup>3a,12</sup> Complex **7** was relatively air and thermally stable as a solid, but unstable (reactive) in solution even at room temperature. In line with the instability of **7**, the reaction of 1 equiv of **1** with Pt(PEt<sub>3</sub>)<sub>3</sub> at 60 °C in C<sub>6</sub>D<sub>6</sub>, when monitored by multinuclear NMR, revealed quantitative forma-

(7) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.

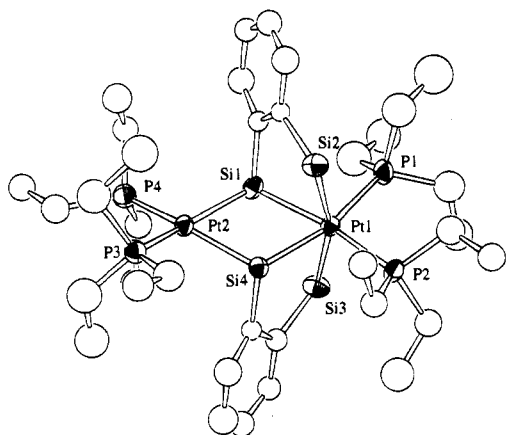
(8) (a) Yamamoto, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1971**, *28*, C37. (b) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1975**, 2212.

(9) (a) Grundy, S. L.; Holmes-Smith, R. D.; Stobart, S. R.; Williams, M. A. *Inorg. Chem.* **1991**, *30*, 3333. (b) <sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Phosphine Complex; Pregosin, P. S., Kunz, R. W., Eds.; NMR, basic principles and progress, 16; Springer-Verlag: Berlin and Heidelberg, 1979.

(10) We found that <sup>195</sup>Pt NMR is informative for the assignment of polysilylated Pt(IV) species; <sup>195</sup>Pt NMR chemical shifts of **4**, **5**, **6a**, **6b**, and the Pt(IV) nucleus of **8** appeared at extremely high field positions (–6568, –6844, –6566, –6704, and –6176 ppm, respectively) as compared with those of Pt<sup>II</sup>Si<sub>2</sub>P<sub>2</sub> complexes (to our knowledge, <sup>195</sup>Pt NMR chemical shifts of Pt<sup>II</sup>Si<sub>2</sub>P<sub>2</sub> complexes appear between –3800 and –5240 ppm).

(11) Heyn and Tilley reported a complex similar to **6b**, *fac*-(dmpe)Pt(H)(SiH<sub>2</sub>Ph)<sub>3</sub> (dmpe = 1,2-bis(dimethylphosphino)ethane); see ref 5c.

(12) Holmes-Smith, R. D.; Stobart, S. R.; Cameron, T. S.; Jochem, K. *J. Chem. Soc., Chem. Commun.* **1981**, 937.



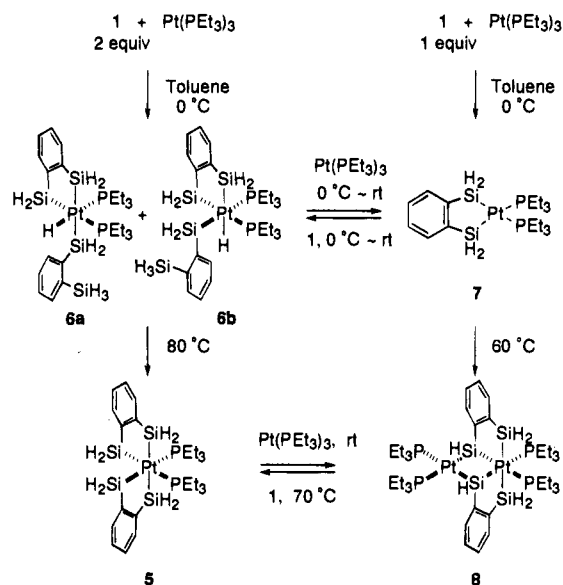
**Figure 2.** Molecular structure of **8** (30% probability). Important bond distances (Å) and angles (deg): Pt1–P1, 2.43(1); Pt1–P2, 2.392(9); Pt1–Si1, 2.415(9); Pt1–Si2, 2.44(1); Pt1–Si3, 2.40(1); Pt1–Si4, 2.41(1); Pt2–P3, 2.31(1); Pt2–P4, 2.32(1); Pt2–Si1, 2.39(1); Pt2–Si4, 2.352(9); P1–Pt1–P2, 100.1(3); Si1–Pt1–Si2, 79.0(4); Si1–Pt1–Si4, 68.6(3); P3–Pt2–P4, 103.2(4); Si1–Pt2–Si4, 70.0(3); Pt1–Si4–Pt2, 111.2(4).

tion of another entirely new dinuclear complex, **8**.  $^{31}\text{P}$  NMR ( $\delta$  –46.18 (t,  $^2J_{\text{P-P}} = 17$ ,  $^1J_{\text{Pt-P}} = 1078$ ,  $^3J_{\text{Pt-P}} = 299$ );  $\delta$  16.54 (t,  $^2J_{\text{P-P}} = 17$ ,  $^1J_{\text{Pt-P}} = 2013$ ,  $^3J_{\text{Pt-P}} = 173$ )) and  $^{195}\text{Pt}$  NMR ( $\delta$  –6176 and –4599) $^{10}$  clearly showed the existence of Pt(IV) and Pt(II) nuclei. The structure of **8** was confirmed by X-ray structure analysis (Figure 2). Complex **8** is the first example of a mixed-valence Pt<sup>II</sup>Pt<sup>IV</sup>Si<sub>2</sub> ring system, although related complexes involving Pt<sup>II</sup>Si<sub>2</sub> $^{5a-d}$  or Pt<sup>IV</sup>Si<sub>2</sub> $^{5c}$  ring systems have been reported.

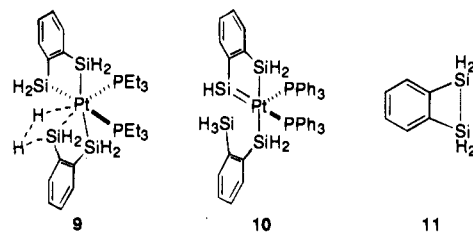
Interconversion among the foregoing complexes cleanly took place. Thus, as shown in Scheme 1, the reaction (0 °C to room temperature) of Pt(PEt<sub>3</sub>)<sub>3</sub> (1 equiv) with a mixture of complexes **6a** and **6b** (3:1) mainly gave **7**, while **7** was converted to a mixture of **6a** and **6b** (3:1) by treatment (0 °C to room temperature) with **1** (1 equiv). Complex **5** was obtained by the reaction of **8** with **1** (1 equiv) at 70 °C, while complex **5** readily reacted with Pt(PEt<sub>3</sub>)<sub>3</sub> at room temperature to give **8**.

An oxidative addition–reductive elimination mechanism can explain most of the reactions summarized in Scheme 1. However, the same mechanistic argument, if considered for the formation of **5** from **6**, requires a Pt(VI) intermediate, which appears quite unusual. $^{13}$  Accordingly, we tentatively propose the following three pathways: (1)  $\sigma$ -bond metathesis through a transition state like **9**, (2) a silylene intermediate, e.g., **10**, and (3) reaction of **7** with disilacyclobutene **11**, which will be formed

## Scheme 1



directly from **6** or reversibly through **7**. The formation of **8** from **7** may also involve similar elemental processes.



**Supporting Information Available:** Text giving experimental procedures and characterization data for **1** and **3–8**, tables of  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{195}\text{Pt}$  NMR data for **3–8**, and full details of the crystal structure analysis for **5** and **8** (25 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) Owing to the electron-donating nature of the silyl ligand (and of the phosphine ligand), the real valence state of the platinum center is envisioned to be much lower than the formal one. Accordingly we are unable to rigorously exclude the intermediacy of a Pt(VI) species. For recent theoretical and experimental studies relevant to this, see: (a) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373. (b) Jiang, Q.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 3679.