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Synthesis and Structure of a Trinuclear Platinum Complex with μ_3-Silylyne Ligands Derived from a Disilane

Hidekazu Arii,[†] Makiko Takahashi,[†] Masato Nanjo,[†,‡] and Kunio Mochida*,[†]

[†]*Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan, and* [‡]*Present address: Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Koyama-cho-Minami, Tottori 680-8552, Japan*

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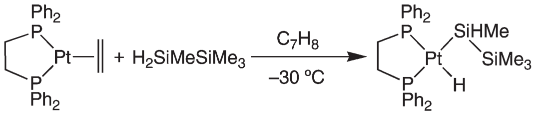
Summary: The platinum complex [Pt(dppe)(η^2-C_2H_4)] (***1***) *reacted with the disilane $H_2SiMeSiMe_3$, affording the bis-(μ-silylyne)triplatinum complex [Pt_3(dppe)$_3$(μ_3-SiMe)$_2$]* (***4***) *by a stepwise Si−H and Si−Si bond activation.*

Organosilanes bound to transition-metal centers have recently attracted the interest of researchers with regard to their structure and reactivity with various substrates. Both metal−silylene and metal−silylyne complexes have been studied in detail, but there are limited reports on the preparation of complexes with metal−silylyne character.[1] The silicon atom in a metal−silylyne complex can bind to a metal center(s) in a terminal triple-bond fashion[2] or a bridging one.[3] Bridging silylyne complexes contain three or more metal atoms, such as in the triiron complex [$Cp_3Fe_3(CO)_4SiN(SiMe_3)_2$] (Cp = cyclopentadienyl)[3c] and the tetracobalt complex [$Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}$].[3a] Group 10 transition-metal palladium and platinum complexes are well-known as catalysts for hydrosilylation and double silylation of unsaturated hydrocarbons. The mono-, di-, and trinuclear palladium or platinum complexes with silylene ligands have been characterized by structural analysis and DFT calculations,[4−6] but no silylyne complexes have yet been reported.

We have investigated the reaction of the zerovalent platinum complex [$Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)$] with symmetric disilanes $HSiR_2SiR_2H$ (R = Ph, Me) by NMR spectroscopy and X-ray diffraction analysis to characterize the several platinum complexes formed by Si−H activation, 1,2-migration, and liberation of silylene.[7] Multiactivation of Si−Si and/or Si−H bonds in disilane or oligosilane compounds makes it possible to obtain a multinuclear complex. We report herein that treatment of [Pt(dppe)(η^2-C_2H_4)] (**1**) bearing the bidentate phosphine ligand dppe (=1,2-bis(diphenylphosphino)ethane) with the disilane $H_2SiMeSiMe_3$ produces a triplatinum complex with two μ_3-silylyne ligands.

Complex **1** reacted with $H_2SiMeSiMe_3$ in toluene at −30 °C at a molar ratio of 1:1, affording the disilanylplatinum hydride [Pt(dppe)(H)($SiHMeSiMe_3$)] (**2**) by the oxidative addition of an Si−H bond to the platinum center (eq 1). The Pt−H and Si−H signals in the ^{1}H NMR spectrum of **2** were observed as a doublet of doublets with ^{195}Pt satellites at 0.73 ppm ($^1J_{PtH}$ = 1121 Hz, $^2J_{PH}$(trans) = 169 Hz, $^2J_{PH}$(cis) = 14 Hz) and a multiplet at 4.62 ppm, respectively. The Pt−H peaks shifted to a lower magnetic field compared to that of the silylplatinum hydrides reported previously (−5 to −1 ppm).[7,8] Two phosphine resonances observed at 55.9 (s, $^1J_{PtP}$ = 2001 Hz) and 62.2 ppm (s, $^1J_{PtP}$ = 1534 Hz) in **2** indicate nonequivalent phosphine atoms (Figure 1, bottom).



1 **2** (1)

Complex **2** was gradually converted into two new products, accompanied by the evolution of Me_3SiH gas at 0 °C, on the basis of ^{1}H NMR spectroscopy (eq 2). After the complete disappearance of **2**, the ^{1}H and $^{31}P\{^1H\}$ NMR spectra showed the formation of both a

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*To whom correspondence should be addressed. Tel: +81-3-3986-0221. Fax: +81-3-5992-1029. E-mail: kunio.mochida@gakushuin.ac.jp.

(1) (a) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712–719. (b) Balázs, G.; Gregoriades, L. J.; Scheer, M. *Organometallics* **2007**, *26*, 3058–3075.

(2) (a) Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518–1520. (b) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357–360.

(3) (a) Anema, S. G.; Lee, S. K.; Mackay, K. M.; Nicholson, B. K. *J. Organomet. Chem.* **1993**, *444*, 211–218. (b) Kawano, Y.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1994**, *116*, 8575–8581. (c) Hirotsu, M.; Nishida, T.; Sasaki, H.; Muraoka, T.; Yoshimura, T.; Ueno, K. *Organometallics* **2007**, *26*, 2495–2498.

(4) (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351–1374. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175–292.

(5) (a) Chen, W.; Shimada, S.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **2001**, 1096–1097. (b) McGuinness, D. S.; Yates, B. F.; Cavell, K. J. *Organometallics* **2002**, *21*, 5408–5414. (c) Avent, A.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2003**, *686*, 321–331. (d) Watanabe, C.; Iwamoto, T.; Kabuto, C.; Kira, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5386–5389. (e) Tanabe, M.; Mawatani, A.; Osakada, K. *Organometallics* **2007**, *26*, 2937–2940.

(6) (a) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917–1919. (b) Feldman, J. D.; Mitchll, G. P.; Nolte, J.-O.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184–11185. (c) Sanow, L. M.; Chai, M.; McConnville, D. B.; Galat, K. J.; Simons, R. S.; Rinaldi, P. L.; Youngs, W. J.; Tessier, C. A. *Organometallics* **2000**, *19*, 192–205. (d) Osakada, K.; Tanabe, M.; Tanase, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4053–4055. (e) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2001**, *20*, 474–480. (f) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Dill, K. M.; French, L. M.; Rath, N. P. *Organometallics* **2004**, *23*, 4576–4584. (g) Sasaki, S.; Yamaguchi, S.; Musashi, Y.; Sugimoto, M. *J. Organomet. Chem.* **2001**, *635*, 173–186.

(7) Arii, H.; Takahashi, M.; Noda, A.; Nanjo, M.; Mochida, K. *Organometallics* **2008**, *27*, 1929–1935.

(8) (a) Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1997**, *16*, 6014–6016. (b) Chan, D.; Duckett, S. B.; Heath, S. L.; Khazal, I. G.; Perutz, R. N.; Sabo-Etienne, S.; Timmins, P. L. *Organometallics* **2004**, *23*, 5744–5756. (c) Braddock-Wilking, J.; Corey, J. Y.; Trankler, K. A.; Xu, H.; French, L. M.; Praingam, N.; White, C.; Rath, N. P. *Organometallics* **2006**, *25*, 2859–2871.

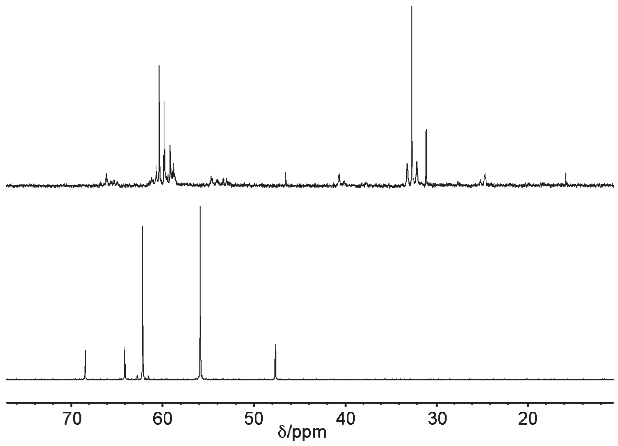
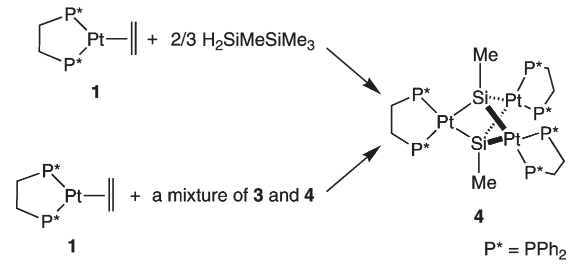


Figure 1. $^{31}P\{^1H\}$ NMR spectra of **2** in toluene-d_8 at −30 °C (bottom) and after 2 days of standing at 0 °C (top).

Scheme 1



bis(μ-silylene)diplatinum complex (**3**) and a bis(μ_3-silylyne)triplatinum complex (**4**) (Figure 1, top). In previous work, the reaction of $[Pt(PEt_3)_3]$ with $H_2SiMeSiMe_3$ evolves Me_3SiH gas, although no platinum complexes with a Pt−Si bond such as a disilanylplatinum hydride were detected in NMR spectroscopy.[9] Two phosphine resonances at 60.1 and 60.6 ppm in **3** have two sets of ^{195}Pt satellites and correlate with the two Si−H signals at 6.25 and 6.52 ppm, respectively, in the $^1H-^{31}P$ HMBC spectrum. These peaks are attributed to the presence of cis/trans isomers of **3** with respect to the orientation of the methyl group on the Si atom, and the cis/trans isomer ratio was roughly 1:3, estimated from the integral value of the Si−H signals. The silicon resonances of *cis*- and *trans*-**3** in a $^1H-^{29}Si$ HMQC experiment were observed as a single peak at −94 ppm, due to overlap with each other, and the chemical shift of this peak was diagnostic of a diplatinum complex with bridging silylenes SiHR, as reported previously.[6c,6e,10] Considering the formation process of **3** according to the literature,[11,12] at first a 1,2-silyl migration in **2** could produce a transient (silyl)(silylene)platinum hydride, $[Pt(dppe)(H)({=}SiHMe)(SiMe_3)]$, in which one end of phosphine dissociates from the platinum atom, and a 1,2-hydrogen migration from Pt to Si followed by a phosphine recoordination affords the bis(silyl)platinum complex $[Pt(dppe)(SiH_2Me)(SiMe_3)]$. An oxidative addition of the Si−H bond in the bis(silyl)platinum complex occurs at a platinum atom of another molecule of $[Pt(dppe)(SiH_2Me)(SiMe_3)]$, and finally a reductive elimination of $SiHMe_3$ from the diplatinum complex generates **3**. Unfortunately, a pure sample of **3** could not be obtained due to contamination with unreacted **2** or simultaneous formation of **4**.

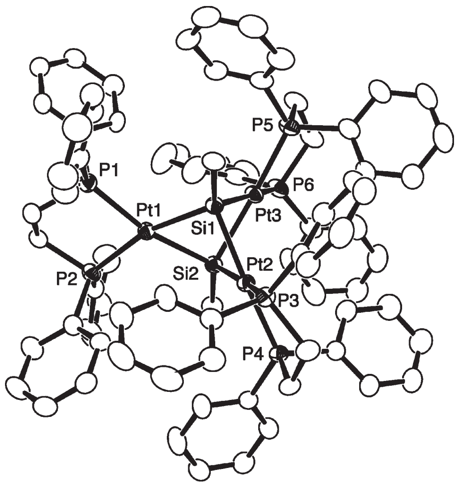
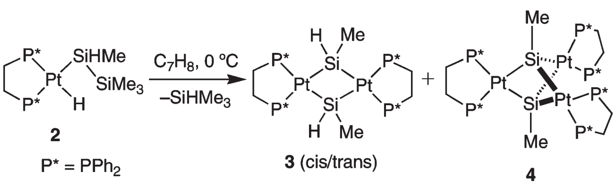


Figure 2. Crystal structure of **4**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−Si(1) = 2.3679(14), Pt(1)−Si(2) = 2.3726(16), Pt(2)−Si(1) = 2.3749(14), Pt(2)−Si(2) = 2.3740(15), Pt(3)−Si(1) = 2.3838(15), Pt(3)−Si(2) = 2.3831(14), Si(1)−Si(2) = 2.642(2); Pt(1)−Si(1)−Pt(2) = 93.03(5), Pt(1)−Si(1)−Pt(3) = 93.38(5), Pt(2)−Si(1)−Pt(3) = 89.87(5), Pt(1)−Si(2)−Pt(2) = 92.93(5), Pt(1)−Si(2)−Pt(3) = 93.28(5), Pt(2)−Si(2)−Pt(3) = 89.91(5).



(2)

The addition of **1** to a mixture of **3** and **4** resulted only in the formation of **4**, with complete consumption of **3** (Scheme 1). The isolation of **4** was carried out by a reaction of **1** with $H_2SiMeSiMe_3$ at a 3:2 molar ratio in toluene/pentane at room temperature. The structure of **4** (Figure 2)[13] is a trinuclear platinum complex with a pseudo-3-fold axis on the Si−Si alignment in which the three Pt(dppe) units are bridged by two SiMe silylynes. The three platinum centers have a four-coordinate planar geometry and form an equilateral triangle. All Pt−Pt distances are 3.36−3.46 Å, indicating that there is no interaction between the platinum atoms. The Si−Si distance (2.644(2) Å) is close to those of the bis(μ-silylene)diplatinum complexes.[6c,6e,10,14] A tetranuclear platinum complex with a triply bridging silylene containing one Pt···H···Si bond in a nonclassical 3c-2e interaction has been synthesized by the reaction of $[Pt(PEt_3)_3]$ with (n-hexyl)SiH_3, where Si−H bond activation

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(9) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227–3232.

(10) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Inorg. Chim. Acta* **2002**, *330*, 82–88.

(11) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524–2526.

(12) Shimada, S.; Rao, M. L. N.; Li, Y.-H.; Tanaka, M. *Organometallics* **2005**, *24*, 6029–6036.

(13) Crystal data for **4**: $C_{80}H_{78}P_6Pt_3Si_2$, $M_r = 1866.69$, orthorhombic, space group *Pcab*, $a = 17.3690(2)$ Å, $b = 19.5120(3)$ Å, $c = 42.7330(6)$ Å, $V = 14482.4(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.712$ g cm^{-3}, μ(Mo Kα) = 5.991 mm^{-1}, 117 859 collected reflections, 16 926 crystallographically independent reflections ($R_{int} = 0.064$), 14 426 reflections with $I > 2\sigma(I)$, R1 = 0.0442 ($I > 2\sigma(I)$), wR2 = 0.1162 (all data).

(14) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068–4070.

of the μ-silylene Si(H)(*n*-Hexyl) does not occur.[6c] Complex **4** is a rare example of a platinum complex with a bridging silylyne. The simple ^{1}H NMR spectrum of **4** is consistent with a structure with a pseudo-3-fold axis, and the absence of Pt−H and Si−H signals in the ^{1}H NMR and IR spectra indicates that there are no hydrides present in **4**. The broadness of the Si−Me peak at 0.58 ppm is independent of a temperature change from −70 to 50 °C and is related to the coupling to phosphine and platinum nuclei. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at 33.0 ppm with two or more sets of satellites associated with a multinuclear platinum complex. A silicon resonance of **4** at 42.2 ppm in a ^{1}H−^{29}Si HMBC experiment showed a remarkable downfield shift as compared to that of the bis(μ-silylene)diplatinum complexes, which implies that the Pt−Si bonds of **4** have a character similar to that of a Pt−Si single bond. It was unclear how **4** could be generated in a toluene solution of **3** in the absence of a zerovalent platinum species. However, some zerovalent platinum species are likely to be produced, since the formation of [Pt(dppe)$_2$] was confirmed by the observation of the characteristic peak at 30.9 ppm ($^1J_{PtP}$ = 3727 Hz)[15] in the ^{31}P NMR spectrum during the conversion of **3** to **4**.

In summary, a stepwise Si−H and Si−Si bond activation affords a unique triplatinum complex with two bridging silylyne ligands in moderate yield through the use of $H_2SiMeSiMe_3$.

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Supporting Information Available: Text and figures giving details of the syntheses and selected NMR data of **2**−**4** and a CIF file giving crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Clark, H. C.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107–115.