Syntheses of mono- and dinuclear silylplatinum complexes bearing a diphosphino ligand *via* stepwise bond activation of unsymmetric disilanes[†]

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Zero-valence platinum complex [Pt(dppe)(η^2 -C₂H₄)] (1, dppe = 1,2-bis(diphenylphosphino)ethane) treated with disilanes HR¹R²SiSiMe₃ (**a**, R¹ = R² = Me; **b**, R¹ = R² = Ph; **c**, R¹ = H, R² = Ph) afforded the corresponding disilanylplatinum hydrides [Pt(dppe)(H)(SiR¹R²SiMe₃)] (2**a**-**c**) by oxidative addition of the Si–H bond to the platinum center. The 1,2-silyl migration in 2**a**,**b** led to the formation of bis(silyl)platinum complexes [Pt(dppe)(SiHR¹R²)(SiMe₃)] (3**a**,**b**) with a first-order rate constant of 7.2(2) × 10⁻⁴ s⁻¹ at 25 °C for 2**a** and 3.86(4) × 10⁻⁴ s⁻¹ at 40 °C for 2**b**, whereas 2**c** with R¹ = H followed by the transient generation of 3**c** dimerized rapidly to give the bis(μ -silylene)diplatinum complex [Pt(dppe)(μ -SiHPh)]₂ (4**c**) in a mixture of *cis/trans* isomers. Heating of the toluene solution of 3**b** at 100 °C resulted in a similar dimerization to 4**b**. In addition, a trinuclear platinum complex [Pt₃(dppe)₃(μ_3 -SiPh)₂] (5) with a trigonal bipyramidal Pt₃Si₂ core arose from the reaction of 4**c** with 1 at 60 °C in toluene. Unsymmetric disilanes therefore accomplished the syntheses of various monomeric and dimeric platinum complexes *via* 1,2-hydrogen and silyl migration to the platinum center.

Introduction

Activation of Si–H and Si–Si bonds is one of the important steps in the development of novel organosilicon compounds. Lowvalence transition metal complexes can activate these bonds, and among them platinum reagents are well known to be effective catalysts in hydrosilylation or double-silylation with unsaturated hydrocarbons.^{1,2} The structure and reactivity of complexes with Pt–Si bonds are interesting because of an active intermediate in the catalytic cycle.³ Zero-valence platinum complexes bearing phosphine ligands are often utilized in a variety of reactions. Many researchers have synthesized and characterized various types of Pt–Si complexes such as silylplatinum hydrides,⁴ and bis(silyl)platinum⁵ and multinuclear platinum complexes bridged by silyl or silylene ligands.^{6,7} And, N-donor ligands allow a formation of a silylplatinum(IV) hydride by oxidative addition of the Si–H bond to the Pt(II) center.⁸

A silane trihydride requires the formation of a structurally attractive platinum complex *via* a multistep Si–H bond activation. Heyn and Tilley reported that heating [Pt(dmpe)(SiH₂Ar)₂]₂(μ -dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane; Ar = Ph, *p*-Tol) at 60 °C converts it a diplatinum complex [Pt(dmpe)(H)]₂(μ -SiHAr)₂(μ - η ¹, η ¹-HArSiSiArH), indicating that four Si–H bonds are activated and a Si–Si bond is formed.⁹ Shimada *et al.* synthesized a mixed valence Pt(II)Pt(IV) complex derived from 1,2-bis(silyl)benzene which has two trihydrosilyl groups attached to a

^bDepartment of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Koyama-cho-Minami, Tottori, 680-8552, Japan † Electronic supplementary information (ESI) available: Selected ¹H and benzene ring.¹⁰ Moreover, using a group 10 transition metal Pd, the same group as Pt, generates a trinuclear complex containing a high-valence Pd(vI) center through dehydrocoupling.¹¹ These findings suggest that a silane compound with multi Si–H bonds induces the oligomerization of complexes and the formation of a multiple M–Si bond, such as silylene or silylyne ligands.

We investigated the reaction of a zero-valence platinum complex [Pt(PPh₃)₂(η^2 -C₂H₄)] with symmetric disilanes HR₂SiSiR₂H (R = Ph, Me) to identify several thermally unstable platinum complexes.¹² Recently, [Pt(dppe)(η^2 -C₂H₄)] (1, dppe = 1,2bis(diphenylphosphino)ethane) treated with H₂MeSiSiMe₃ afforded the unique bis(silylyne)triplatinum complex [Pt₃(dppe)₃(μ_3 -SiMe)₂], indicating the activation of all Si–H and Si–Si bonds in H₂MeSiSiMe₃.¹³ In the present paper, we focused on the reactive behavior of unsymmetric disilanes HR¹R²SiSiMe₃ (**a**, R¹ = R² = Me; **b**, R¹ = R² = Ph; **c**, R¹ = H, R² = Ph) by varying the alkyl groups on one of the two silane centers, and studied the spectroscopic and structural characterization for the platinum complexes formed by Si–H and Si–Si activation.

Experimental

General considerations

All experiments were carried out using a standard vacuum line and Schlenk techniques or in an M. Braun inert atmosphere dry box. All the reagents were of the highest grade available and were used without further purification. All solvents used for the syntheses were distilled according to the general procedure. Benzene- d_6 and toluene- d_8 were distilled from potassium metal under Ar atmosphere. Complex 1¹⁴ and disilanes **a**-**c**¹⁵ were synthesized according to previously reported methods. The ¹H NMR spectral measurements were performed on a JEOL AL-300 NMR spectrometer at 300 MHz for ¹H, 122 MHz for ³¹P and 60 MHz for ²⁹Si. The chemical shifts of the protons are

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⁴ Electronic supplementary information (ESI) available: Selected ⁴H and ${}^{31}P{}^{1}H$ NMR data and kinetics data. CCDC reference numbers 761290–761295. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000545b

reported relative to the residual protonated solvents benzene- d_6 (7.15 ppm) and toluene- d_8 (2.09 ppm). The chemical shifts of phosphorous and silicon are corrected relative to external H₃PO₄ (0 ppm) and SiMe₄ (0 ppm). Elemental analysis was performed on a CE Instruments EA1110 corrected by acetoanilide.

Syntheses of platinum complexes

Synthesis of [Pt(dppe)(H)(SiMe₂SiMe₃)] (2a)

To a toluene solution (0.5 mL) of HMe₂SiSiMe₃ (10.6 mg, 0.080 mmol) was added solid 1 (49.8 mg, 0.080 mmol) at $-30 \degree C$, and the resulting solution was stored in a chilled box at $-30 \degree C$ overnight. Pentane (4 mL) was added to the resulting solution. The solution was allowed to stand for 1 day in the chilled box to afford colorless crystals. Yield: 38.2 mg (66%); ¹H NMR (toluene- d_8 , $-30 \degree C$): δ 7.74 (m, 4H, PPh), 7.65 (m, 4H, PPh), 7.05–7.00 (m, 12H, PPh), 2.0–1.8 (br, 2H, CH₂P), 1.8–1.6 (br, 2H, CH₂P), 0.76 (d, 6H, ³J_{PtH} = 37.1 Hz, ⁴J_{PH} = 3.9 Hz (*trans*), SiMe₂SiMe₃), 0.66 (dd, 1H, ¹J_{PtH} = 1144 Hz, ²J_{PH} = 169 Hz (*trans*), ²J_{PH} = 14 Hz (*cis*), PtH), 0.53 (s, 9H, SiMe₂SiMe₃) ppm; ³¹P{¹H} NMR (toluene- d_8 , $-30 \degree C$): δ 61.6 (s, ¹J_{PtP} = 1375 Hz), 57.2 (s, ¹J_{PtP} = 2086 Hz) ppm. Found C, 51.29; H, 5.76%. Calcd for **2a** (C₃₁H₄₀P₂PtSi₂), C, 51.30; H, 5.55%.

Synthesis of [Pt(dppe)(H)(SiPh₂SiMe₃)] (2b)

Complex **2b** was synthesized by the same method as that used for **2a**, except HPh₂SiSiMe₃ was used to obtain colorless crystals. Yield: 54.7 mg (88%); ¹H NMR (toluene- d_8 , -30 °C): δ 7.80 (brs, 8H, PPh), 7.2–6.8 (22H, ArH), 1.9–1.5 (m, 4H, CH₂P), 0.52 (s, 9H, SiMe₃), 0.25 (dd, 1H, ¹J_{PH} = 1073 Hz, ²J_{PH} = 166 Hz (*trans*), ²J_{PH} = 12 Hz (*cis*), PtH) ppm; ³¹P{¹H} NMR (toluene- d_8 , -30 °C): δ 61.2 (s, ¹J_{PH} = 1524 Hz), 55.7 (s, ¹J_{PH} = 2111 Hz) ppm. Found C, 60.83; H, 5.51%. Calcd for **2b**-toluene (C₄₈H₅₂P₂PtSi₂): C, 61.19; H, 5.56%.

Synthesis of [Pt(dppe)(H)(SiHPhSiMe₃)] (2c)

Complex **2c** was synthesized by the same method as that used for **2a**, except that H₂PhSiSiMe₃ was used to obtain colorless crystals. Yield: 53.1 mg (80%); ¹H NMR (toluene- d_8 , -30 °C): δ 8.32 (d, 2H, ${}^{3}J_{\rm HH} = 6.9$ Hz, SiPh), 7.85–7.6 (m, 4H, PPh), 7.44 (apparent triplet, 2H, PPh), 7.31 (t, 2H, ${}^{3}J_{\rm HH} = 7.2$ Hz, SiPh), 7.18 (t, 1H, ${}^{3}J_{\rm HH} = 7.2$ Hz, SiPh), 7.1–6.8 (m, 12H, PPh), 4.71 (dd, 1H, ${}^{3}J_{\rm PH} = 20$ Hz (*trans*), ${}^{3}J_{\rm PH} = 7.5$ Hz (*cis*), SiH), 2.0–1.7 (br, 4H, CH₂P), 0.87 (dd, 1H, ${}^{1}J_{\rm PtH} = 1097$ Hz, ${}^{2}J_{\rm PH} = 168$ Hz (*trans*), ${}^{2}J_{\rm PH} = 14$ Hz (*cis*), PtH), 0.39 (s, 9H, SiMe₃) ppm; ${}^{31}P{}^{1}H{}$ NMR (toluene- d_8 , -30 °C): δ 62.0 (s, ${}^{1}J_{\rm PtP} = 1629$ Hz), 55.8 (d, ${}^{1}J_{\rm PtP} = 1976$ Hz, ${}^{2}J_{\rm PP} = 10$ Hz) ppm. Found C, 54.66; H, 5.24%. Calcd for **2c** (C₃₅H₄₀P₂PtSi₂), C, 54.32; H, 5.21%.

Synthesis of [Pt(dppe)(SiHMe₂)(SiMe₃)] (3a)

To a toluene solution (2 mL) of HMe₂SiSiMe₃ (11.5 mg, 0.087 mmol) was added a toluene solution (2 mL) of 1 (50.0 mg, 0.80 mmol) at room temperature, and the resulting solution was stored overnight. Pentane (2 mL) was added to the resulting solution. The solution was allowed to stand for 1 day to afford colorless crystals. Yield: 35.3 mg (61%); ¹H NMR (toluene- d_8 ,

RT): δ 7.71 (m, 4H, PPh), 7.59 (m, 4H, PPh), 7.15–7.0 (m, 12H, PPh), 4.85 (dsept, 1H, ${}^{2}J_{PH} = 96$ Hz, ${}^{3}J_{HH} = 42$ Hz, ${}^{3}J_{PH} = 18$ Hz, SiH), 1.9–1.6 (m, 4H, CH₂P), 0.56 (d, 9H, ${}^{3}J_{PH} = 27$ Hz, ${}^{4}J_{PH} = 2.7$ Hz (*trans*), SiMe₃), 0.49 (dd, 6H, ${}^{3}J_{PH} = 30$ Hz, ${}^{3}J_{HH} = 3.9$ Hz, ${}^{4}J_{PH} = 3.3$ Hz (*trans*), SiHMe₂) ppm; ${}^{31}P{}^{1}H$ NMR (toluene- d_{8} , RT): δ 58.5 (d, ${}^{1}J_{PH} = 1217$ Hz, ${}^{2}J_{PP} = 7$ Hz), 58.2 (d, ${}^{1}J_{PH} = 1405$ Hz, ${}^{2}J_{PP} = 8$ Hz) ppm. Found C, 51.08; H, 5.54%. Calcd for **3a** (C₃₁H₄₀P₂PtSi₂), C, 51.30; H, 5.55%.

Synthesis of [Pt(dppe)(SiHPh₂)(SiMe₃)] (3b)

Complex **3b** was synthesized by the same method as that used for **3a**, except that HPh₂SiSiMe₃ was used to obtain colorless crystals. Yield: 115.5 mg (84%); ¹H NMR (toluene- d_8 , RT): δ 7.8–7.6 (m, 8H, ArH), 7.33 (m, 4H, PPh), 7.15–7.05 (m, 12H, PPh), 6.95–6.85 (m, 6H, SiPh), 5.81 (dd, 1H, ²J_{PtH} = 80 Hz, ³J_{PH} = 19 Hz (*trans*), ³J_{PH} = 9.3 Hz (*cis*), SiH), 1.85–1.60 (m, 4H, CH₂P), 0.44 (d, 9H, ²J_{PtH} = 25 Hz, ⁴J_{PH} = 2.7 Hz (*trans*), SiMe₃) ppm; ³¹P{¹H} NMR (toluene- d_8 , RT): δ 58.0 (d, ¹J_{PtP} = 1588 Hz, ²J_{PP} = 8 Hz), 57.3 (d, ¹J_{PtP} = 1187 Hz, ²J_{PP} = 8 Hz) ppm. Found C, 60.96; H, 5.39%. Calcd for **3b**-toluene (C₄₈H₅₂P₂PtSi₂), C, 61.19; H, 5.56%.

Synthesis of [Pt(dppe)(µ-SiPh₂)]₂ (4b)

Heating a toluene solution of **3b** at 100 °C for 11 days gave a yellow powder of **4b**. Identification was carried out by ¹H and ³¹P{¹H} NMR spectroscopy according to the previous report.^{6d}

Synthesis of [Pt(dppe)(µ-SiHPh)]₂ (4c)

To a toluene solution (2 mL) of H₂PhSiSiMe₃ (29.6 mg, 0.164 mmol) was added a toluene solution (2 mL) of **1** (100 mg, 0.161 mmol) at room temperature, and the resulting solution was stored overnight. Pentane (2 mL) was added to the solution. The solution was allowed to stand for 1 day to afford light yellow crystals. Yield: 61.0 mg (54%); ¹H NMR (toluene- d_8 , RT): δ 7.8–7.6 (m, 8H, PPh), 7.50 (m, 4H, SiPh), 7.30 (m, 8H, PPh), 7.1–6.6 (30H, ArH), 6.59 (apparent septet, 2H, ² J_{PtH} = 32 Hz, ³ J_{PH} = 8.0 Hz, SiH for *trans*-**4c**), 6.21 (apparent septet, 2H, ² J_{PtH} = 43 Hz, ³ J_{PH} = 11 Hz, SiH for *cis*-**4c**), 2.0–1.6 (br, 8H, CH₂P) ppm; ³¹P{¹H} NMR (toluene- d_8 , RT): δ 59.3 (s, ¹ J_{PtP} = 1458 Hz, ³ J_{PtP} = 214 Hz, ⁴ J_{PP} = 25 Hz for *trans*-**4c**) ppm; ¹H–²⁹Si HMQC NMR (toluene- d_8 , RT): δ -100, -107 ppm. Found C, 55.34; H, 4.62%. Calcd for **4c** (C₆₄H₆₀P₄Pt₂Si₂), C, 54.93; H, 4.32%.

Kinetics

The conversion of disilanylplatinum hydride into the corresponding bis(silyl)platinum complex was confirmed by decreasing the peak intensity at 0.66 of **2a** and 7.25 ppm of **2b**, respectively, in ¹H NMR spectra. A residual protonated solvent at 2.09 ppm in toluene- d_8 was used as an internal standard, and the conversion rate of **2a** was estimated from the area ratio of the each peak to that at 2.09 ppm. The data collection was performed at 5 or 10 min intervals at verified temperature over three times that of the halflife. The data were analyzed with Igor (WaveMatrics, Inc.) on a Macintosh computer and fitted to an exponential function by a non-linear least-squares method.

Table 1 Crystallographic data for the platinum compl	exes
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	2a·THF	$\pmb{2b}{\cdot}C_7H_8$	2c	3a	3b	$4c \cdot C_7 H_8$
Formula	$C_{35}H_{48}O_1P_2PtSi_2$	$C_{48}H_{52}P_2PtSi_2$	$C_{35}H_{40}P_2PtSi_2$	$C_{31}H_{40}P_2PtSi_2$	$C_{41}H_{44}P_2PtSi_2$	$C_{71}H_{68}P_4Pt_2Si_2$
Fw	797.94	942.11	773.88	725.84	849.97	1491.49
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	P1 (#2)	C2/c (#15)	$P2_12_12_1$ (#19)
a/Å	13.049(3)	9.2600(4)	9.133(4)	9.4840(4)	40.488(1)	12.6750(3)
b/Å	10.517(2)	41.553(2)	31.933(12)	11.5970(8)	10.2430(6)	16.3880(6)
c/Å	26.795(6)	11.4170(6)	11.720(4)	16.377(1)	20.520(1)	29.958(1)
$\alpha / ^{\circ}$	90	90	90	107.605(3)	90	90
$\beta/^{\circ}$	103.762(3)	101.692(3)	104.992(5)	98.424(4)	115.089(3)	90
$\gamma /^{\circ}$	90	90	90	107.803(4)	90	90
$V/Å^3$	3571.8(14)	4301.9(4)	3302(2)	1576.97(17)	7707.1(7)	6222.8(3)
Ζ	4	4	4	2	8	4
$\rho_{\rm c}/{\rm g~cm^{-3}}$	1.484	1.455	1.557	1.529	1.465	1.592
μ (Mo-K α)/mm ⁻¹	4.111	3.424	4.442	4.645	3.814	4.674
Total no. of data	36 745	34 573	16071	15156	34 652	54920
No. of unique data (R_{int})	8162 (0.0665)	9176 (0.090)	6084 (0.1189)	6961 (0.042)	8848 (0.061)	8147 (0.089)
No. of params	379	481	371	361	418	719
R_1^a	0.0874	0.0568	0.0530	0.0495	0.0405	0.0526
WR_2 (all data) ^b	0.2112	0.1496	0.1082	0.1235	0.1028	0.1396

X-Ray crystallography†

Single crystals of **2a**, **2b**, **2c**, **3a**, **3b**, and **4c** suitable for X-ray diffraction analyses were obtained by allowing their corresponding solutions to stand for a few days. Each crystal was mounted on a loop or a glass fiber, and the data were collected on a Bruker-AXS $M06X^{CE}$ Imaging Plate for **2b**, **3a**, **3b** and **4c** or APEX II CCD detector for **2a** and **2c** using graphite monochromated Mo-K α radiation. The crystal data and experimental details are listed in Table 1.

All the structures were solved by the combination of the direct method and Fourier techniques, and all the non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. The atomic scattering factors and anomalous dispersion terms were obtained from the International Tables for X-ray Crystallography IV.¹⁶ The location of the hydrogen atoms of Si–H and Pt–H were determined from difference Fourier maps and refined. All the calculations were carried out on a Silicon Graphic work station by the maXus program.

Results and discussion

Reaction of complex 1 with disilanes a-c at -30 °C

Treatment of **1** with **a**–**c** in toluene at -30 °C produced a corresponding disilarlyplatinum hydride (**2a–c**) by oxidative addition of the Si–H bond to the platinum center (Scheme 1). In the ¹H NMR spectra, the Pt–H signals were observed as a doublet of a doublet with ¹⁹⁵Pt satellites centered at 0.66 ppm for **2a**, 0.25 ppm for **2b**, and 0.87 ppm for **2c** accompanied by the disappearance of the Si–H signal of free **a–c**. The hydride resonances of **2a–c** with a bidentate ligand, dppe, shifted to a lower magnetic field than that of a monodentate ligand system in the range of –5–0 ppm.^{4,17} The Si–H signal in **2c** appeared as a doublet of a doublet with ¹⁹⁵Pt satellites at 4.71 ppm. The ³¹P{¹H} NMR spectra of **2a–c** had two singlets with ¹⁹⁵Pt satellites of which one is flanked with the small



Scheme 1 Reaction of 1 with unsymmetric disilanes a-c.

 ${}^{1}J_{PtP}$ because of strong *trans* influence of Si, which is consistent with the existence of two unequivalent phosphorus atoms.

In the crystal structures of $2\mathbf{a}-\mathbf{c}$ (Fig. 1, Table 2), the platinum atoms have a planar structure with a P2SiH donor set. A strong *trans* influence of Si causes the Pt(1)–P(1) bond lengths to elongate compared with the Pt(1)–P(2) ones. The Pt–Si bond lengths were similar to those of silylplatinum complexes reported previously,^{4,5,12} and the Pt–Si bond length of $2\mathbf{a}$ was shorter by *ca*. 0.02 Å than that of $2\mathbf{b}$ and $2\mathbf{c}$ because the phenyl groups on the Si atom avoid steric repulsion to the phenyl groups of dppe. The Pt–H bond lengths were 1.51(8) Å for $2\mathbf{a}$, 1.49(9) Å for $2\mathbf{b}$, and 1.56(8) Å for $2\mathbf{c}$, within the range of the characteristic Pt–H bond length. Coordination of the disilanes to the platinum center does not affect the Si–Si bond lengths of 2.34 to 2.36 Å diagnostic of the Si–Si single bond in disilanes.¹⁸ The Si–Si alignment is perpendicular to the P2Si plane because the phenyl groups of dppe prevent accessibility to the sterically bulky SiMe₃ group.

 Table 2
 Selected bond lengths (Å) and angles (°) for 2a–c

	2a	2b	2c
Pt(1)–P(1)	2.311(3)	2.3000(17)	2.286(3)
Pt(1) - P(2)	2.279(3)	2.2877(16)	2.264(3)
Pt(1)-Si(1)	2.345(3)	2.3694(18)	2.352(3)
Pt(1)-H	1.51(8)	1.49(9)	1.56(8)
Si(1)-Si(2)	2.351(5)	2.362(2)	2.337(4)
P(1) - Pt(1) - P(2)	85.13(11)	85.92(6)	86.60(10)
P(1) - Pt(1) - Si(1)	173.57(12)	172.85(6)	174.87(10)
P(2)-Pt(1)-Si(1)	99.60(12)	101.19(6)	97.49(10)



Fig. 1 Crystal structure of 2a (A), 2b (B) and 2c (C) showing 50% probability thermal ellipsoids. The hydrogen atoms except for one on Pt and Si are omitted for clarity.



Fig. 2 ${}^{31}P{}^{1}H$ NMR spectra of **2a** at $-30 \degree C$ in toluene- d_8 (bottom) and after standing for 2 days at RT (top).

Conversion of complexes 2a-c at room temperature

In the ¹H NMR spectra of **2a** and **2b** in toluene- d_8 at room temperature, the Pt-H signal disappeared and a new peak appeared as a doublet of a septet at 4.85 ppm and a doublet of a doublet at 5.81 ppm, respectively, in the typical Si-H region. The ${}^{31}P{}^{1}H$ NMR spectra had two unequivalent phosphine signals approaching each other, which indicates the similar chemical environment of two phosphorus atoms (Fig. 2). The ${}^{1}J_{PP}$ value around 1200 Hz was attributed to a strong trans influence of the peralkylated silicon found in cis-[Pt(PR₃)₂(H)(SiR'₂R'')]^{4d} and cis-[Pt(PEt₃)₂(SiMe₃)₂].^{5e} These new species could be assigned to the bis(silyl)platinum complexes [Pt(dppe)(SiHMe₂)(SiMe₃)] (3a) and [Pt(dppe)(SiHPh₂)(SiMe₃)] (3b) because the reaction of the zero-valence platinum complex with symmetrical disilanes, $H_n R_{3-n} SiSiR_{3-n} H_n$, generates a bis(silyl)platinum complex by 1,2silyl migration in a disilanylplatinum hydride (Scheme 2). The conversion rate of 2a and 2b obeyed first-order kinetics in the range of 25–55 °C, and the activation parameters $\Delta H^{\ddagger}_{\ddagger}$ and $\Delta S^{\ddagger}_{\ddagger}$ estimated from Eyring plots were $\Delta H^{\ddagger}_{\ddagger} = 62(4) \text{ kJ mol}^{-1}, \Delta S^{\ddagger}_{\ddagger} =$ -97(12) J K⁻¹ mol⁻¹ for 2a and $\Delta H^{\ddagger}_{\ddagger} = 83(3)$ kJ mol⁻¹, $\Delta S^{\ddagger}_{\ddagger} =$ -44(9) J K⁻¹ mol⁻¹ for **2b**, respectively (Fig. 3). We reported that in the $[Pt(PPh_3)_2(\eta^2-C_2H_4)]/HPh_2SiSiPh_2H$ system, the first-order



Fig. 3 Eyring plots for the conversion of 2a (circle) and 2b (triangle).



Scheme 2 Conversion of 2 into 3.

rate constant of a disilarylplatinum hydride to a bis(silyl)platinum complex was $5.5(2) \times 10^{-4} \text{ s}^{-1}$ at $-40 \,^{\circ}\text{C}^{.12}$ The rate constants at $-40 \,^{\circ}\text{C}$ of **2a** and **2b**, calculated by an extrapolation from the activation parameters, were $5.1 \times 10^{-7} \text{ s}^{-1}$ and $4.7 \times 10^{-9} \text{ s}^{-1}$, respectively, and were approximately 10^{3-5} times slower than that of the PPh₃ ligand. For 1,2-silyl migration, a coordinative saturated platinum complex acquires a vacant site by liberating one of two phosphine atoms to afford a bis(silyl)platinum complex *via* an intermediate (silyl)(silylene)platinum hydride.¹⁹ The high coordination ability of the bidentate ligand dppe to the platinum center increases the thermal stability of **2a** and **2b**. Moreover, the ΔH^{+}_{+} is likely to correlate with the ${}^{1}J_{\text{PP}}$ with respect to the Pt–P bond cleavage, which implies that strong *trans* influence of a

Table 3Selected bond lengths (Å) and angles (°) for 3a and 3b

	3a ^a	3b
Pt(1) - P(1)	2.3183(12)	2.3375(11)
Pt(1) - P(2)	2.3237(13)	2.3170(12)
Pt(1)-Si(1)	2.3855(15)	2.3602(12)
Pt(1)-Si(2)	2.398(3)	2.3973(12)
P(1) - Pt(1) - P(2)	84.13(5)	84.48(4)
P(1) - Pt(1) - Si(1)	94.83(5)	97.44(4)
P(2)-Pt(1)-Si(2)	99.73(10)	96.41(4)
Si(1) - Pt(1) - Si(2)	81.36(10)	83.33(4)

^{*a*} The bond lengths and angles associated with Si(2A) are listed as one of the disordered components.

silicon atom with an aliphatic alkyl group supports the liberation of a phosphine ligand.

The platinum centers in **3a** and **3b** have a four-coordinate planar geometry with a P2Si2 donor set (Fig. 4, Table 3). All Pt–P bond lengths elongate more than 2.31 Å due to the *trans* influence of Si atom, and the bite angle of dppe in **3b** becomes slightly smaller than that of **2b**. The small bite angle results in the large Si–Pt–Si angle of **3a** and **3b** compared with the *cis*-[Pt(PR₃)₂(SiR¹R²₂)₂] complexes (79–81°) with a monodentate phosphine ligand.^{5,12} The location of Si–H in **3a** could not be determined because the two silyl groups are disordered.





Fig. 4 Crystal structure of **3a** (A) and **3b** (B) showing 50% probability thermal ellipsoids. One of the two disordered positions of the silyl groups in **3a** is shown. The hydrogen atoms except for one on Si in **3b** are omitted for clarity.

Although 2c converted into bis(silyl)platinum complex, [Pt(dppe)(SiH₂Ph)(SiMe₃)] (3c), a small amount of 3c maintained despite the reduction of 2c to proceed a subsequent reaction to a dinuclear complex 4c, as described in the next section.

Dimerization of platinum-silylene species derived by the elimination of $SiHMe_{3}$

The ¹H NMR spectrum of **3b** in toluene- d_8 at 100 °C changed to a bis(μ -silylene)diplatinum complex [Pt(dppe)(μ -SiPh₂)]₂ (**4b**) after 11 days accompanied by the exsertion of SiHMe₃ gas (a doublet at 0.02 ppm and a dectet at 4.16 ppm) while **3a** decomposed gradually to complete a homoleptic zero-valence complex [Pt(dppe)₂] under the same conditions (Scheme 3).²⁰ The ³¹P{¹H} NMR spectrum exhibited part of an AA'A''A'''XX' spin system pattern diagnostic for dinuclear platinum complexes.²¹ Complex **4b** was synthesized by Osakada and coworkers by ligand exchange of the diplatinum complex [Pt(PCy₃)(μ -SiHPh₂)]₂ with two equivalents of dppe.



Scheme 3 Dimerization of 3 to 4.

On the other hand, thermolysis of **2c** also involved the reductive elimination of SiHMe₃ and the generation of **4c** in which two phosphine resonances were observed at 58.9 and 59.3 ppm flanked by two sets of satellites. Complex **3c** observed transiently on ¹H and ³¹P NMR spectra may rapidly convert to **4c** (Fig. 5(C)). The ¹H NMR spectrum of **4c** had two apparent septets of Si–H at 6.21 and 6.59 ppm that correlated with two silicon resonances at upfield –107 and –100 ppm, respectively, characteristic of the bis(μ silylene)diplatinum complexes in the ¹H–²⁹Si HMQC experiment.²⁰ The two peaks were attributed to a mixture of *cis/trans* isomers due to the orientation of the phenyl group on the Si atom, and the ratio of *cis* to *trans* isomers independent of ambient temperature was roughly 1:4, as estimated from the integral value of Si–H signals. The structure of *trans*-**4c** was confirmed by XRD analysis



Fig. 5 ³¹P{¹H} NMR spectra of **2c** in benzene- d_6 (A), standing for 4 h (B) and for 3 days at RT (C). The peaks marked with an asterisk are assigned to the bis(silyl)platinum complex **3c**.

(Fig. 6). The Pt–Si bond lengths of 2.404(3) and 2.422(4) Å for Pt(1) were at the upper limit of the Pt–Si single bond length. The shorter Pt–Pt distance of 3.8885(5) Å relevant to the reported diplatinum complexes²¹ was associated with a puckering of the Pt2Si2 ring by 23.5(2)° to accommodate the acute Si–Pt–Si angles of 67.95(11)° for Pt(1) and 68.76(11)° for Pt(2). The Si–Si bond distance of 2.697(5) Å indicates a very weak interaction between the two silylene ligands on the base of the theoretical calculation of [Pt₂(PH₃)₄(μ -SiH₂)₂] reported hitherto.²² The analogues of **4c** were prepared using various methods, such as the dealkylation coupling of monosilane with the alkylplatinum complex and ligand exchange on the dinuclear platinum complex.



Fig. 6 Crystal structure of 4c showing 50% probability thermal ellipsoids. The hydrogen atoms except for one on Si are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)-P(1) 2.311(3), Pt(1)-P(2) 2.331(3), Pt(1)-Si(1) 2.422(4), Pt(1)-Si(2) 2.404(3), Pt(2)-P(3) 2.330(3), Pt(2)-P(4) 2.302(3), Pt(2)-Si(1) 2.394(3), Pt(2)-Si(2) 2.382(3); P(1)-Pt(1)-P(2) 84.97(10), Si(1)-Pt(1)-Si(2) 67.95(11), P(3)-Pt(2)-P(4) 84.56(10), Si(1)-Pt(2)-Si(2) 68.76(11).

We reported that a bis(silyl)platinum complex [Pt(PPh₃)₂-(SiHPh₂)₂], followed by the formation of the silvlplatinum hydride due to the elimination of silvlene SiPh₂, converts into the bis(μ -silyl)diplatinum complex [Pt(PPh₃)(μ -SiHPh₂)]₂.¹² The analogue complexes 3b and 3c induce a reductive elimination of trimethylsilane to obtain the corresponding diplatinum complexes with the bridging silylene μ -SiR₁R₂. According to the previous reports, the formation of 3b and 3c involves dimerization by the intermolecular oxidative addition of the platinum center to the Si–H bond of the SiHR₁ R_2 group, and reductive elimination of trimethylsilane subsequently occurs to generate 4b and 4c. The coordinative saturated platinum complex rules out the formation of a mononuclear platinum-silylene complex,¹⁹ whereas the group 6 and 8 transition metal-silylene complexes are often synthesized by the coupling of intramolecular 1,2-silyl migration and reductive elimination.23

Complex **4c** reacted with one equivalent of **1** at 60 °C for several hours and afforded the bis(μ_3 -silylyne)triplatinum complex [Pt₃(dppe)₃(μ_3 -SiPh)₂] (**5**) with the phosphine resonance at 33.2 ppm (${}^1J_{PtP} = 1949$ Hz, ${}^3J_{PtP} = 118$ Hz), similar to that of [Pt₃(dppe)₃(μ_3 -SiMe)₂] reported previously (Scheme 4).¹³ The formation of **5** competes with the decomposition of **4c** into [Pt(dppe)₂], which results in a low yield of **5** based on 1H NMR. The bulky phenyl group on the Si atom prevents the zero-



Scheme 4 Reaction of 4c with zero-valence complex 1.

valence platinum complex from approaching the Si–H bond of the bridging silylene.

Conclusions

The reaction of a platinum complex $[Pt(dppe)(\eta^2-C_2H_4)]$ (1) with a bidentate phosphine ligand dppe was investigated by NMR spectroscopy and XRD analysis. For unsymmetric disilane, the bis(µ-silylene)diplatinum complex forms *via* the disilanylplatinum hydride and subsequent bis(silyl)platinum complex, except for HMe₂SiSiMe₃. In particular, H₂PhSiSiMe₃ is activated the Si– H bond to effect conversion into the bis(µ₃-silylyne)triplatinum complex.

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