



Communication

Reaction of 1-(dimethylsilyl)-2-silylbenzene with platinum(0) phosphine complex: Isolation and characterization of the Si₃–Pt^{IV}–H complexYong-Hua Li^{a,*}, Yuan Zhang^a, Shigeru Shimada^b^a College of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, People's Republic of China^b Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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ABSTRACT

Reaction of two equivalents of 1,2-C₆H₄(SiMe₂H)(SiH₃) with Pt(depe)(PEt₃)₂ (depe = Et₂PCH₂CH₂PEt₂) in toluene at room temperature afforded two novel isomeric {1,2-C₆H₄-(SiMe₂H)(SiH₂)}{1,2-C₆H₄(SiMe₂)(SiH₂)}(H)Pt^{IV}(depe) complexes **1** and **2** in 5:1 ratio among eight possible isomers. Complex **1** is one of the few examples of tris(silyl)(hydrido)platinum(IV) complexes structurally characterized by single crystal X-ray analysis. The structure of complex **1** was unambiguously determined by multinuclear NMR and single crystal X-ray analysis.

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1. Introduction

Since the first complex containing Si–M bond was synthesized by Wilkinson and co-workers in 1956, the chemistry of transition metal complexes with metal–silicon bonds has rapidly grown during the last two decades and the pace of progress is still increasing, associated mainly with catalysis involving silicon compounds toward organic synthesis and silicon-based materials [1]. As compared with C–H bonds, Si–H bonds have higher reactivity toward transition metals, one of the most effective methods for the preparation of these complexes is by the reactions of transition metal complexes with hydrosilanes via Si–H activation [1,2]. Furthermore, activation of Si–H bonds is also very important in industrial processes such as hydrosilylation, dehydrogenative silylation, and polysilane production [1,3]. It is widely considered that oxidative addition of the Si–H bond to a metal centre is one of the crucial steps in these processes [1–4].

The reaction chemistry of transition metal complexes with primary and secondary hydrosilanes (RSiH₃ and R₂SiH₂) has been rapidly growing recently. It is often different from that with tertiary hydrosilanes (R₃SiH) because primary and secondary hydrosilanes have more than one reactive Si–H bond and/or are sterically less hindered than tertiary hydrosilanes [2]. The reaction of Pt(0) complexes with tertiary hydrosilanes usually produces (silyl)

(hydrido)platinum(II) or bis(silyl)–platinum(II) complexes [2], while that with primary and secondary hydrosilanes affords various types of platinum complexes with mononuclear [2], dinuclear [2,5], or trinuclear frameworks [6].

Our present research focus on the preparation of silicon–transition metal complexes with various numbers of Si–M bonds, especially those with high oxidation states [7]. During our attempt to synthesize poly(silyl) group 10 transition metal compounds, we have found that sterically less-demanding chelating silyl ligands are very useful to stabilize silyl transition metal compounds with high formal oxidation states and reported the first examples of multinuclear palladium compound containing palladium centers ligated by five silicon atoms [8].

Here we report the reaction of a bidentate chelating hydrosilane with platinum(0) complex, resulting in the isolation of mononuclear tris(silyl)(hydrido)platinum(IV) complex **1**. To our knowledge, there are only more than 5 examples of tris(silyl)(hydrido)platinum(IV) complexes structurally characterized by single crystal X-ray analysis [9].

2. Experimental

2.1. Materials and equipment

¹H, ²⁹Si, and ³¹P NMR spectra were recorded on JEOL LA500 (for solution NMR). Chemical shifts are given in ppm using external

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references (for solution NMR spectra, tetramethylsilane (0 ppm) for ^1H and ^{29}Si and 85% H_3PO_4 (0 ppm) for ^{31}P), and coupling constants are reported in hertz. C, H and N analyses were taken on a Perkin–Elmer 240C elemental analyzer. All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried and purified. The solvents were stored over molecular sieves (4 Å).

2.2. Syntheses

2.2.1. Preparation of 1-(dimethyl)-2-silylbenzene

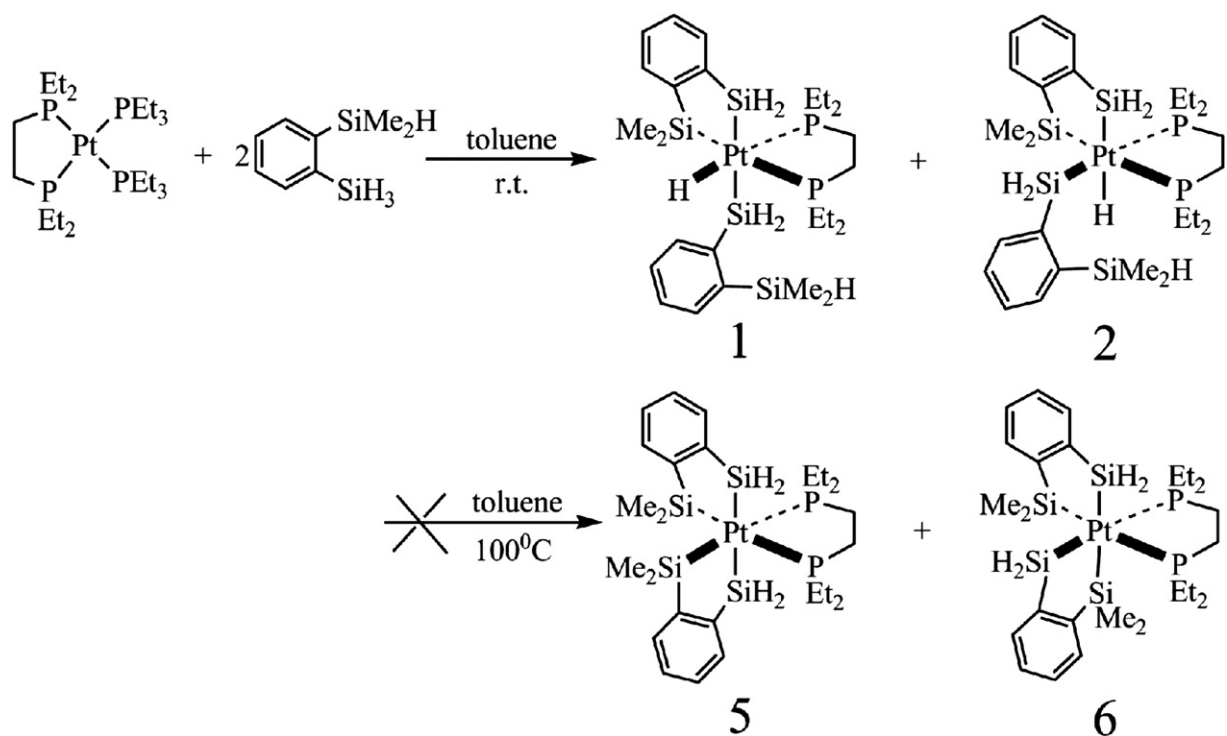
To a solution of phenyltris($\text{N,N,N}'$ -trimethylethylenediamino)-silane (48 g) in hexane (250 mL) was added a pentane solution of $^t\text{BuLi}$ (1.53 M, 217 mL) over 40 min at 0 degree under nitrogen. After stirring at room temperature for 3 h, the solution was added by using a polyethylene tube to a solution of Me_2SiCl_2 (195 g) in hexane (120 mL) at 0 degree over 40 min. After the addition was completed, the mixture was allowed to warm to room temperature and then heated at 50 degree for about 4 h. Most of the solvents and excess of Me_2SiCl_2 were removed under reduced pressure at room temperature. After the addition of Me_2SiCl_2 (20 mL) to the residue, $^i\text{PrOH}$ (300 mL) was added dropwise at 0 degree. The mixture was stirred at room temperature for 12 h. Volatiles were removed under vacuum, hexane (600 mL) was added, and the mixture was filtered through Celite. The filtrate was further filtered through a short pad of SiO_2 (50 g) to remove the remaining salt. After evaporation, the residue was subjected to bulb-to-bulb distillation to give 34 g (75%) of 1-dimethyl(isopropoxy)silyl-2-(triisopropoxysilyl)benzene (oven temperature 150 °C/1 mmHg). ^1H NMR (CDCl_3 , 300 MHz) δ 0.51 (6H, s), 1.23 (18H, d), 1.26 (6H, d), 4.11 (1H, septet), 4.26 (3H, septet), 7.35–7.45 (2H, m), 7.82–7.85 (1H, m), 7.97–8.05 (1H, m).

To an ether suspension (100 mL) of LiAlH_4 (10 g) was added dropwise a solution of 1-dimethyl(isopropoxy)silyl-2-(triisopropoxysilyl)benzene (34 g) in ether 80 mL at 0 °C over 40 min. The mixture was stirred for 5 h at room temperature and 7 h at reflux.

GC-MS analysis of the mixture at this stage showed the presence of partially reduced products. Then, LiAlH_4 (1.5 g) was added and the mixture was refluxed for another 13 h. After removal of ether under reduced pressure, the remaining mixture was extracted with hexane (250 mL*3), and then filtered through Celite. Hexane was removed under reduced pressure, the product was transferred to a cold flask under high vacuum. Purification by distillation gave 9.6 g of 1-(dimethyl)-2-silylbenzene, 134 °C/50 Torr, as colorless liquid. ^1H NMR (CDCl_3 , 300 MHz) δ 0.39 (6H, d), 4.32 (3H, s), 4.66 (1H, septet), 7.35–7.45 (1H, m), 7.32–7.45 (1H, m), 7.59 (1H, dd), 7.68 (1H, dd); ^{13}C NMR (CDCl_3 , 300 MHz) δ -3.27, 128.57, 129.29, 134.22, 135.40, 137.51, 138.24.

2.2.2. Preparation of $\{1,2\text{-C}_6\text{H}_4\text{-(SiMe}_2\text{H)(SiH}_2\text{)}\}\{1,2\text{-C}_6\text{H}_4\text{(SiMe}_2\text{)}\text{(SiH}_2\text{)}\}\text{(H)Pt}^{\text{IV}}$ (depe) complexes (**1** and **2**)

A mixture of $\text{Pt}(\text{PET}_3)_4$ (216 mg, 0.32 mmol) and depe (66 mg, 0.32 mmol) in toluene (4 mL) was stirred at room temperature for 40 min to give $\text{Pt}(\text{PET}_3)_2(\text{depe})$. After removal of volatiles under vacuum, the residual was dissolved in toluene (4 mL). To this solution was added hydrosilane (117 mg, 0.70 mmol) at 0 °C, and the mixture was stirred at room temperature for 24 h. Removal of volatiles under vacuum afforded a light yellow residue, which was washed with hexane (2 mL*3) and dried under vacuum to give a mixture of **1** and **2** (5:1 judged by ^1H NMR integration) as a colorless solid, 155 mg (76%). $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6 , 202.0 MHz): for **1**, δ 5.89 (d, $^2J_{\text{P-P}}=8$, $^1J_{\text{Pt-P}}=974$), 0.67 (d, $^2J_{\text{P-P}}=8$, $^1J_{\text{Pt-P}}=1436$); for **2**, δ 16.25 (d, $^2J_{\text{P-P}}=17$, $^1J_{\text{Pt-P}}=1035$), 15.97 (d, $^2J_{\text{P-P}}=17$, $^1J_{\text{Pt-P}}=1115$). ^1H NMR (benzene- d_6 , 499.1 MHz): δ -10.24 (br d, $^2J_{\text{P-H}}=180$, $^1J_{\text{Pt-H}}=862$, Pt-H for **1**), -8.50 (t, $^2J_{\text{P-H}}=19$, $^1J_{\text{Pt-H}}=796$, Pt-H for **2**), 0.41 (dd, $J=4, 16$, $\text{CH}_3 \times 2$ for **2**), 0.59 (dd, $J=4, 17$, $\text{CH}_3 \times 2$ for **1**), 0.78–1.27 (m, $\text{CH}_3 \times 2$, (PCH_2CH_3) $\times 4$ and $\text{PCH}_2\text{CH}_2\text{P}$ for **1** and **2**), 4.34–5.35 (m, $\text{SiH}_2 \times 2$ for **1** and **2**), 7.17–7.24 (m, aromatic-H $\times 3$ for **1** and **2**), 7.32 (t, $J=8$, aromatic-H $\times 1$ for **1**), 7.42 (t, $J=7$, aromatic-H $\times 1$ for **2**), 7.61–7.70 (m, aromatic-H $\times 2$ for **1** and **2**), 8.08 (d, $J=7$, aromatic-H $\times 1$ for **2**),



Scheme 1. The reaction of two equivalents of 1,2- $\text{C}_6\text{H}_4(\text{SiMe}_2\text{H})(\text{SiH}_3)$ with $\text{Pt}(\text{depe})(\text{PET}_3)_2$ (depe = $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PET}_2$).

8.12–8.14 (*m*, aromatic-H \times 1 for **1**), 8.36 (*d*, $J = 8$, aromatic-H \times 1 for **1**), 8.81 (*d*, $J = 7$, aromatic-H \times 1 for **2**). $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 99.1 MHz): for **1**, δ –49.8 (dd, $^2J_{\text{P-Si}} = 12, 17$, $^1J_{\text{Pt-Si}} = 693$, SiH_2), –33.6 (*t*, $^2J_{\text{P-Si}} = 13$, $^1J_{\text{Pt-Si}} = 599$, SiH_2), 7.2 (dd, $^2J_{\text{P-Si}} = 7$, 138, $^1J_{\text{Pt-Si}} = 645$, SiMe_2Pt) = –19.2 (*s*, $^4J_{\text{Pt-Si}} = 6$, SiMe_2H); for **2**, δ –35.6 (dd, $^2J_{\text{P-Si}} = 16, 152$, $^1J_{\text{Pt-Si}} = 753$, SiH_2), –26.6 (*t*, $^2J_{\text{P-Si}} = 10$, $^1J_{\text{Pt-Si}} = 666$, SiH_2), 5.7 (dd, $^2J_{\text{P-Si}} = 10, 147$, $^1J_{\text{Pt-Si}} = 674$, SiMe_2Pt), –19.0 (*s*, $^4J_{\text{Pt-Si}} = 7$, SiMe_2H).

3. Results and discussion

The reaction of 1,2- $\text{C}_6\text{H}_4(\text{SiMe}_2\text{H})(\text{SiH}_3)$ and $\text{Pt}(\text{depe})(\text{PEt}_3)_2$ ($\text{depe} = \text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$) in 2:1 ratio in toluene at room temperature afforded tris(silyl)(hydrido)bis-(phosphine)platinum(IV) complexes as a mixture of two isomers **1** and **2** in 5:1 ratio (Scheme 1). Crystallization of the mixture from toluene afforded X-ray quality single crystals only for the major isomer **1**, and its structure was unambiguously confirmed by single crystal X-ray structure analysis (Fig. 1) [10,11]. Complex **1** crystallizes in the monoclinic group $\text{P}2_1/n$ (Table 1). The coordination geometry of the Pt atom is completed by two chelate P atoms, two chelate Si atoms and one Si atom from one free hydrosilane ligand. The central Pt atom forms $(\text{Si})_3(\text{H})\text{Pt}^{\text{IV}}$ which attained a distorted square-bipyramidal geometry with a $\text{Si}1\text{--Pt--Si}3$ angle of 168.1 degree. The average bond lengths Pt--Si (2.39 Å) and Pt--P (2.35 Å) are in good agreement with the reported similar complexes [7,9]. The hydrido ligand occupies the equatorial coordination site. The apical Pt--Si bond distance is almost the same as that of equatorial Pt--Si bond (Table 2).

The structure of complex **1** was also well identified by elemental analysis and multinuclear NMR [12]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in C_6D_6 showed a pair of doublets with relatively small $^1J_{\text{Pt--P}}$ values typical for silylplatinum(IV) species [13]; $^1J_{\text{Pt--P}} = 974$ and 1436 Hz for the major isomer and $^1J_{\text{Pt--P}} = 1035$ and 1115 Hz for the minor isomer. P–H signals in the ^1H NMR spectrum are a broad doublet ($^2J_{\text{P--H}} = 180$ Hz) for the major isomer and a triplet ($^2J_{\text{P--H}} = 19$ Hz) for the minor isomer. This suggests that one P atom is trans and the other P atom is cis to the hydrido ligand in the major isomer and both P atoms are cis to the hydrido ligand in the minor isomer. The Me_2SiPt signal in each isomer appeared as a doublet of doublets with a large and a small $^2J_{\text{P--Si}}$ value, indicating the Me_2Si groups have one cis and one trans P atom in both isomers. $^{29}\text{Si}\{^1\text{H}\}$ and ^{29}Si NMR spectra clearly showed the presence of an unreacted SiMe_2H

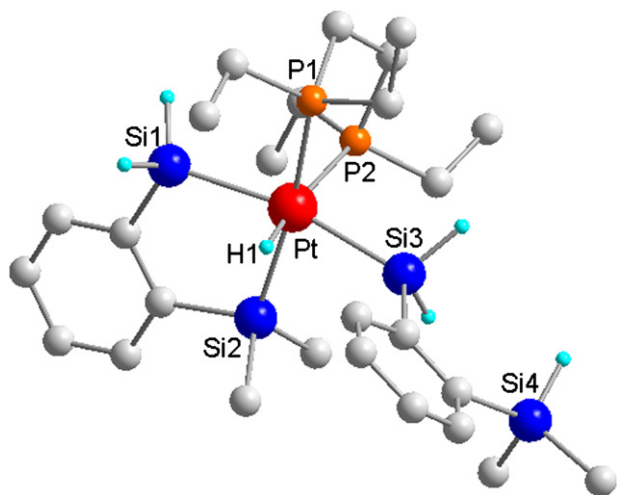


Fig. 1. The structure of **1**, showing the coordination environment of Pt atom and the hydrogen atoms bound to carbon atoms are omitted for clarity.

Table 1
Crystal data of compound **1**.

Structure parameters	1
Empirical formula	$\text{C}_{26}\text{H}_{50}\text{P}_2\text{PtSi}_4$
fw	732.04
Cryst syst	Monoclinic
Space group	$\text{P}2_1/n$
Cryst size (mm)	$0.10 \times 0.12 \times 0.13$
<i>a</i> (Å)	18.035 (4)
<i>b</i> (Å)	9.921 (2)
<i>c</i> (Å)	18.529 (4)
β (°)	103.51 (3)
<i>V</i> (Å ³)	3223.6 (13)
<i>Z</i>	4
<i>T</i> (K)	293 (2)
<i>F</i> (000)	1480
ρ_{calc} (g cm^{-3})	1.508
μ (mm^{-1})	4.615
θ range (deg)	1.8–26.00
Total no. of data collected	20762
No. of unique data	6334
<i>R</i> indexes [$I > 2\sigma(I)$]	$R_1 = 0.0273$ $wR_2 = 0.0409$
<i>R</i> (all data)	$R_1 = 0.0403$ $wR_2 = 0.0418$
Largest diff map hole and peak (e Å^{-3})	1.02 and –1.07
$R_1 = \sum F_o - F_c / \sum F_o $; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.	

group in both isomers; a signal for the silicon atom with one directly connected hydrogen (a broad doublet in the ^{29}Si NMR spectrum, $^1J_{\text{H--Si}} = \text{ca. } 190$ Hz) was, respectively, observed at –19.2 ppm ($J_{\text{Pt--Si}} = 6$ Hz) for the major isomer and at –19.0 ppm ($J_{\text{Pt--Si}} = 7$ Hz) for the minor isomer in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum. The small $J_{\text{Pt--Si}}$ values suggest no direct interaction between these Si atoms and Pt atoms. From these NMR data, the structures of the major isomer **1** and the minor isomer **2** can be assigned as shown in Scheme 1. Signals for SiH_2 groups in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum are also consistent with these assignment; the major isomer showed two SiH_2 signals (a triplet and a doublet of doublets) with small $^2J_{\text{P--Si}}$ values (12–17 Hz), suggesting that both of the SiH_2 groups are in cis-position relative to both of the P atoms. On the other hand, the minor isomer also showed a triplet and a doublet of doublets signals for SiH_2 groups, one of which had a large (152 Hz) and a small (16 Hz) $^2J_{\text{P--Si}}$ value and the other had small $^2J_{\text{P--Si}}$ values (10 Hz), suggesting that one of the SiH_2 groups is in cis-position relative to one P atom and in trans-position relative to the other P atom, while the other SiH_2 group is in cis-position relative to both of the P atoms. Judging from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture, which showed some unidentified signals with very weak intensity, the amount of other six isomers (e.g., see **3** and **4** in Fig. 2) is very low even if they are present. Selective formation of the two isomers **1** and **2** can be mainly attributed to the steric repulsion caused by methyl groups on silicon and ethyl groups on

Table 2
Selected bond lengths and angles for **1**.

Pt1–Si1	2.3976 (14)	Pt1–Si2	2.3896 (11)
Pt1–Si3	2.4067 (13)	Pt1–P1	2.3584 (11)
Pt1–P2	2.3344 (11)	Si1–C1	1.887 (4)
Si2–C6	1.896 (4)	Si3–C9	1.891 (4)
Si1–Pt1–Si2	83.71 (5)	Si1–Pt1–Si3	168.05 (5)
Si2–Pt1–Si3	86.75 (5)	P1–Pt1–P2	85.28 (5)
Si1–Pt1–P1	90.68 (5)	Si2–Pt1–P1	171.08 (5)
Si3–Pt1–P1	97.86 (5)	Si1–Pt1–P2	96.71 (5)
Si2–Pt1–P2	102.22 (5)	Si3–Pt1–P2	92.33 (5)
Si3–Pt1–H1	81.00	P2–Pt1–H1	173.23
Si1–Pt1–H1	89.75	P1–Pt1–H1	96.73

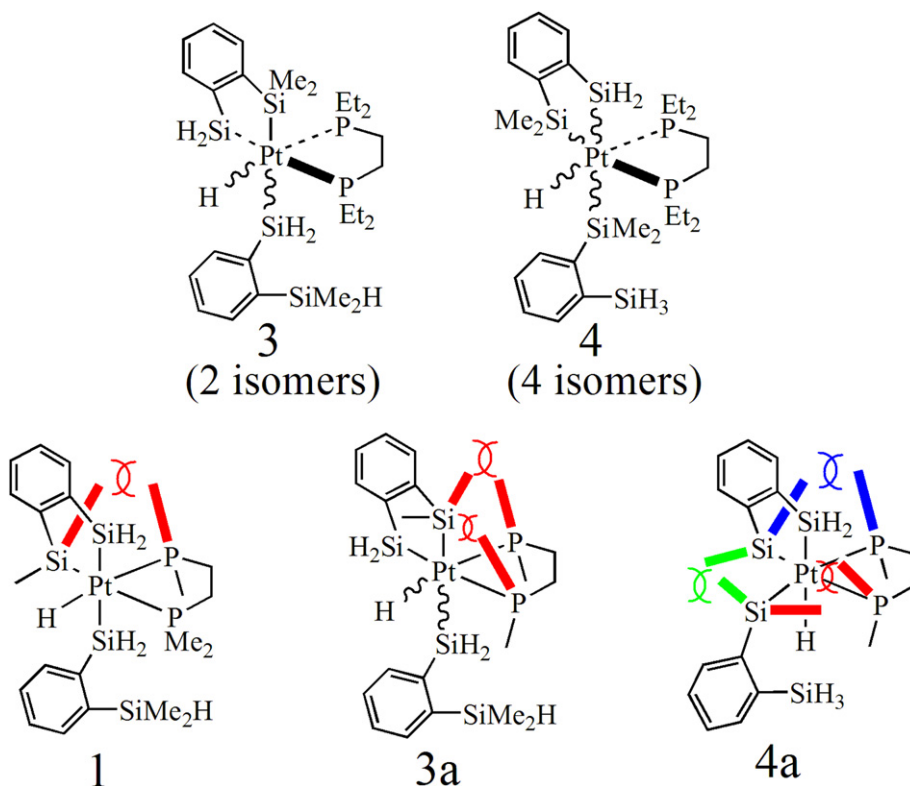


Fig. 2. Schematic drawings showing steric repulsions between methyl and ethyl groups in complexes **1**, **3a** and **4a**.

phosphorus atoms. Analysis of molecular structures of complexes **1** determined by X-ray diffraction suggests that severe steric repulsion is present between some of the methyl groups on silicon and methyl groups on phosphorus atoms in complexes **1–4**. Such steric repulsion is found between one pair of methyl and ethyl groups in complexes **1** and **2** (e.g., see **1** in Fig. 2), while between two pairs of methyl and ethyl groups in complexes **3** (e.g., see **3a** in Fig. 2) and between three or four pairs of methyl and ethyl groups in complexes **4** (e.g., see **4a** in Fig. 2). Heating the mixture of **1** and **2** even after 7 days at 100 °C in toluene could not result in slow intramolecular dehydrogenative cyclization to afford a mixture of isomeric {1,2-C₆H₄(SiMe₂)(SiH₂)₂}Pt^{IV}(depe) **5** and **6**, probably due to the steric effect caused by the ethyl groups on phosphorus atoms.

4. Conclusion

In conclusion, reaction of two equivalents of 1,2-C₆H₄(SiMe₂H)(SiH₃) with Pt(depe)(PEt₃)₂ (depe = Et₂PCH₂CH₂PEt₂) afforded two novel isomeric tris(silyl)hydrido platinum(IV) complexes **1** and **2** which are very rare. Selective formation of the two isomers **1** and **2** can be mainly attributed to the steric repulsion caused by methyl groups on silicon and ethyl groups on phosphorus atoms. This result indicates that sterically less-demanding, multi-chelating silyl ligands are very useful to stabilize silyl transition metal compounds with high formal oxidation states and to the formation of poly(silyl) complexes.

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Appendix A. Supplementary material

CCDC-764201 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary material associated with this article can be found in the online version, at doi: 10.1016/j.jorganchem.2010.05.023.

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- [10] Crystal data for 1: $M = 732.04$, Monoclinic, $P2_1/n$, $a = 18.035(4)$ Å, $b = 9.921(2)$ Å, $c = 18.529(4)$ Å, $\alpha = 90.000^\circ$, $\beta = 103.510(3)^\circ$, $\gamma = 90.000^\circ$, $V = 3223.6(3)$ Å³, $Z = 4$, $F(000) = 1480$, $R1 = 0.0273$, $wR2 = 0.0418$ [$I > 2\sigma(I)$]. Structural data for was collected on a Bruker Smart Apex CCD with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.
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- [12] Elemental analysis and multinuclear NMR data for 1 and 2: Anal. (for the mixture of 1 and 2) Calcd. for C₂₆H₅₀P₂Si₄: C, 42.66; H, 6.88. Found: C, 42.82; H, 6.85. ³¹P{¹H} NMR (benzene-d₆, 202.0 MHz): for 1, δ 5.89 (d, ²J_{P-P} = 8, ¹J_{Pt-P} = 974), 0.67 (d, ²J_{P-P} = 8, ¹J_{Pt-P} = 1436); for 2, δ 16.25 (d, ²J_{P-P} = 17, ¹J_{Pt-P} = 1035), 15.97 (d, ²J_{P-P} = 17, ¹J_{Pt-P} = 1115). ¹H NMR (benzene-d₆, 499.1 MHz): δ -10.24 (br d, ²J_{P-H} = 180, ¹J_{Pt-H} = 862, Pt-H for 1), -8.50 (t, ²J_{P-H} = 19, ¹J_{Pt-H} = 796, Pt-H for 2), 0.41 (dd, $J = 4, 16$, CH₃ × 2 for 2), 0.59 (dd, $J = 4, 17$, CH₃ × 2 for 1), 0.78–1.27 (m, CH₃ × 2, (PCH₂CH₃) × 4 and PCH₂CH₂P for 1 and 2), 4.34–5.35 (m, SiH₂ × 2 for 1 and 2), 7.17–7.24 (m, aromatic-H × 3 for 1 and 2), 7.32 (t, $J = 8$, aromatic-H × 1 for 1), 7.42 (t, $J = 7$, aromatic-H × 1 for 2), 7.61–7.70 (m, aromatic-H × 2 for 1 and 2), 8.08 (d, $J = 7$, aromatic-H × 1 for 2), 8.12–8.14 (m, aromatic-H × 1 for 1), 8.36 (d, $J = 8$, aromatic-H × 1 for 1), 8.81 (d, $J = 7$, aromatic-H × 1 for 2). ²⁹Si{¹H} NMR (benzene-d₆, 99.1 MHz): for 1, δ -49.8 (dd, ²J_{P-Si} = 12, 17, ¹J_{Pt-Si} = 693, SiH₂), -33.6 (t, ²J_{P-Si} = 13, ¹J_{Pt-Si} = 599, SiH₂), 7.2 (dd, ²J_{P-Si} = 7, 138, ¹J_{Pt-Si} = 645, SiMe₂Pt) = -19.2 (s, ⁴J_{Pt-Si} = 6, SiMe₂H); for 2, δ -35.6 (dd, ²J_{P-Si} = 16, 152, ¹J_{Pt-Si} = 753, SiH₂), -26.6 (t, ²J_{P-Si} = 10, ¹J_{Pt-Si} = 666, SiH₂), 5.7 (dd, ²J_{P-Si} = 10, 147, ¹J_{Pt-Si} = 674, SiMe₂Pt), -19.0 (s, ⁴J_{Pt-Si} = 7, SiMe₂H).
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