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Synthesis, structural characterization, and reactivity of a bis (phosphine)(silyl) platinum(II) complex

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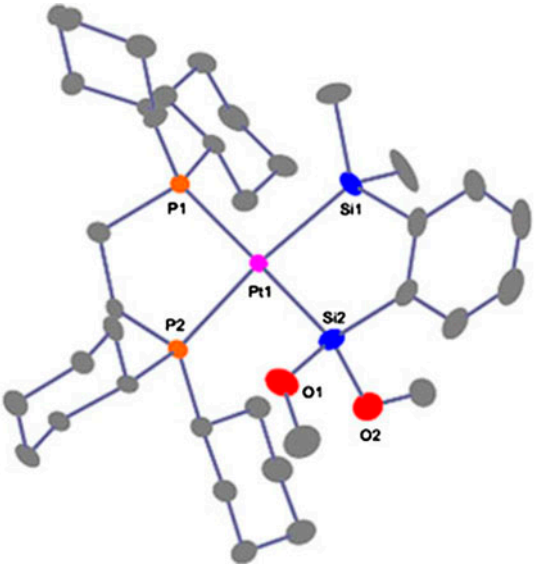

Treatment of 1,2-$C_6H_4(SiMe_2H)(SiH_3)$ (**1**) with $Pt(dcpe)(PEt_3)_2$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) in dry toluene at room temperature in the ratio of 1 : 1 leads to $\{1,2\text{-}C_6H_4(SiMe_2)(SiH_2)\}Pt^{II}(dcpe)$ (**2**), which can react with sterically unhindered alcohol to form a dimethoxy substituted silyl platinum(II) compound (**3**). There are only five examples of bis(silyl) platinum(II) complexes prepared from this silyl ligand with such structural features registered in the Cambridge Structural Database. The structures of **2** and **3** were unambiguously determined by single-crystal X-ray analysis and multinuclear NMR spectroscopic studies.

Keywords: Chelating; Silyl; Platinum

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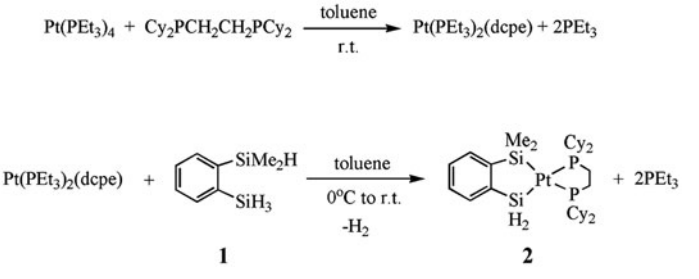
1. Introduction

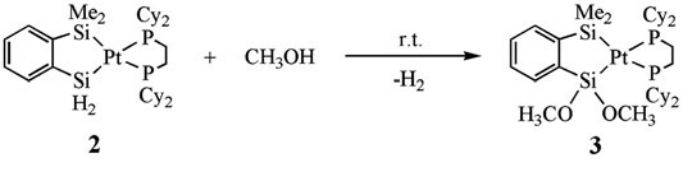
The chemistry of transition metal complexes with metal–silicon bonds has rapidly grown and research continues to prosper in this area since the first complex containing Si–M bond was synthesized by Wilkinson and co-workers in 1956 [1]. The most widely employed approach to formation of complexes that contain a silicon–transition metal bond involves the activation of the Si–H bond by low-valent transition metal complexes [2]. Hydrosilanes are used as versatile coreactants in synthetic organosilicon chemistry. Since organohydrosilanes (including $RSiH_3$, R_2SiH_2, and R_3SiH) may contain one, two, or three SiH bonds as primary, secondary, and tertiary silanes, respectively, there are many product variations upon their reaction with transition metal complexes including mononuclear, dinuclear, or trinuclear frameworks and different valency [3].

Our present research focuses on the preparation of transition metal complexes containing metal–silicon bonds with novel structure motifs using sterically less-demanding chelating silyl ligands, study of the unique structural properties, and thermal stability for the silyl–metal complexes formed by Si–H activation. We have been studying the stoichiometric reactions of 1,2-disilylbenzenes with group 10 transition metal complexes and disclosed the formation of unique complexes with silicon–metal bonds depending on the metals, the structures of 1,2-disilylbenzenes, and the ligands [4].

Silyl platinum complexes have been the most extensively studied. This is not only because platinum compounds generally have higher stability than the corresponding palladium and nickel complexes but also because platinum complexes are the most widely used catalysts for transformations of organosilicon compounds since the discovery of Speier's catalyst [5]. Herein, we report the reaction of 1-(dimethylsilyl)-2-silylbenzene (**1**) with Pt(dcpe)$(PEt_3)_2$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) to afford a mononuclear bis(silyl)platinum(II)



Scheme 1. The reaction of the parent chelating silane, 1,2-$C_6H_4(SiMe_2H)(SiH_3)$ (**1**) with Pt(dcpe)$(PEt_3)_2$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) in the ratio of 1 : 1, leading to a mononuclear complex {1, 2-$C_6H_4(SiMe_2)(SiH_2)$} Pt^{II}(dcpe) (**2**).



Scheme 2. The reaction of **2** with methanol affords a dimethoxy substituted silyl platinum(II) compound **3**.

complex, **2**, exclusively, and no further reaction of **2** with a second molecule of **1** takes place (scheme 1). Moreover, **2** has high reactivity toward sterically unhindered alcohol to form a di-alkoxy substituted silyl platinum(II) compound (**3**) (scheme 2). The structures of **2** and **3** were unambiguously determined by single-crystal X-ray analysis and multinuclear NMR spectroscopic studies.

2. Experimental

2.1. *Materials and equipment*

^{1}H, ^{29}Si, and ^{31}P NMR spectra were recorded on a Jeol LA500 (for solution NMR). Chemical shifts are given in ppm using external references (for solution NMR spectra, tetramethylsilane (0 ppm) for ^{1}H and ^{29}Si and 85% H_3PO_4 (0 ppm) for ^{31}P); 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 distilled from Na/benzophenone ketyl. The solvents were stored over molecular sieves (4 Å). All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk tube techniques or in a glove box. 1,2-Bis(dicyclohexylphosphino)ethane (Aldrich) was used as received. $Pt(PEt_3)_4$ and hydrosilane 1,2-$C_6H_4(SiMe_2H)(SiH_3)$ were prepared according to the relevant literature method [4(b), 6].

2.2. *Synthesis*

2.2.1. Preparation of 1-(dimethylsilyl)-2-silylbenzene (1). To a solution of phenyltris(N, N,N′-trimethylethylenediamino)-silane (48 g) in hexane (250 mL) was added a pentane solution of ^{t}BuLi (1.53 M, 217 mL) over 40 min at 0 °C 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 °C over 40 min. After the addition was completed, the mixture was allowed to warm to room temperature and then heated at 50 °C for 4 h. 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}PrOH (300 mL) was added dropwise at 0 °C. 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 mm Hg). ^{1}H 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 the

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-(dimethylsilyl)-2-silyl-benzene, 134 °C/50 Torr, as colorless liquid. ^{1}H 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, and 138.24.

2.2.2. Preparation of {1, 2-C6H4(SiMe2)(SiH2)}PtII(dcpe) (2). A mixture of $Pt(PEt_3)_4$ (216 mg, 0.32 mmol) and dcpe (135 mg, 0.32 mmol) in toluene (4 mL) was stirred at room temperature for 40 min to give $Pt(PEt_3)_2$(dcpe). After the removal of volatiles under vacuum, the residue was dissolved in toluene (4 mL). To this solution was added hydrosilane (**1**, 53 mg, 0.32 mmol) at 0 °C, and the mixture was stirred at 0 °C for 12 h and then 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 **2** as a colorless solid, 190 mg (76%). ^{31}P{^{1}H} NMR (THF-d_8, 202.0 MHz): for **2**, δ 73.92 (d, $^{2}J_{P-P}$ = 16 Hz, $^{1}J_{Pt-P}$ = 1364 Hz), 76.59 (d, $^{2}J_{P-P}$ = 16 Hz, $^{1}J_{Pt-P}$ = 1710 Hz). ^{1}H NMR (THF-d_8, 499.1 MHz): for **2**, δ 0.51 (dd, 6H, Si–CH_3), 1.15–1.92 (m, 48H, $Cy_2PCH_2CH_2PCy_2$), 5.54–5.62 (m, 2H, SiH_2), 7.03–7.10 (m, 2H, aromatic-H), 7.47 (d, 1H, aromatic-H), 7.59 (d, 1H, aromatic-H). ^{29}Si{^{1}H} NMR (THF-d_8, 99.1 MHz, DEPT): for **2**, δ −13.67 (dd, $^{2}J_{P-Si}$ = 146 Hz, $^{2}J_{P-Si}$ = 14 Hz, $^{1}J_{Pt-Si}$ = 1098 Hz, SiH_2). ^{29}Si{^{1}H} NMR (THF-d_8, 99.1 MHz, INEPT): for **2**, δ 25.51 (dd, $^{2}J_{P-Si}$ = 145 Hz, $^{2}J_{P-Si}$ = 10 Hz, $^{1}J_{Pt-Si}$ = 1012 Hz, $SiMe_2$). Anal. Calcd for $C_{34}H_{60}P_2PtSi_2$ (%): C, 52.22; H, 7.73. Found: C, 52.61; H, 8.09.

2.2.3. Preparation of {1,2-C6H4(SiMe2)Si(OCH3)2}PtII(dcpe) (3). In a Schlenk tube equipped with a magnetic stir bar, {1,2-$C_6H_4(SiMe_2)(SiH_2)$}Pt^{II}(dcpe) (391 mg, 0.5 mmol) and dry methanol (6 mL) were placed. The mixture was stirred at room temperature for 3 h under nitrogen and then stirred at 60 °C for 10 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 **3** as a colorless solid, 286 mg (68%). ^{31}P{^{1}H} NMR (C_6D_6, 202.0 MHz): for **3**, δ 72.92 (d, $^{2}J_{P-P}$ = 14 Hz, $^{1}J_{Pt-P}$ = 1441 Hz), 74.92 (d, $^{2}J_{P-P}$ = 14 Hz, $^{1}J_{Pt-P}$ = 1411 Hz). ^{1}H NMR (C_6D_6, 499.1 MHz): for **3**, δ 0.93 (dd, 6H, Si–CH_3), 1.12–1.69 (m, 48H, $Cy_2PCH_2CH_2PCy_2$), 3.69 (s, 6H, Si–OCH_3), 7.41 (t, 1H, aromatic-H), 7.48 (t, 1H, aromatic-H), 8.03 (d, 1H, aromatic-H), 8.11 (d, 1H, aromatic-H). ^{29}Si{^{1}H} NMR (C_6D_6, 99.1 MHz): for **3**, δ 27.58 (dd, $^{2}J_{P-Si}$ = 139 Hz, $^{2}J_{P-Si}$ = 10 Hz, $^{1}J_{Pt-Si}$ = 1148 Hz, $SiMe_2$), 48.30 (dd, $^{2}J_{P-Si}$ = 189 Hz, $^{2}J_{P-Si}$ = 11 Hz, $^{1}J_{Pt-Si}$ = 1523 Hz, $Si(OMe)_2$). Anal. Calcd for $C_{36}H_{64}O_2P_2PtSi_2$ (%): C, 51.35; H, 7.66. Found: C, 51.76; H, 7.97.

2.3. *X-ray crystallography*

The diffraction data were collected at 293 K on a Bruker Smart APEX CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å), and data reduction was performed using Bruker SAINT. An absorption correction was applied using the method of multi-scans. The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All hydrogens were placed in calculated positions with fixed isotropic thermal parameters and included in

Table 1. Crystallographic data for **2** and **3**.

Compound	**2**	**3**
Formula	$C_{36}H_{65}OP_2PtSi_2$	$C_{36}H_{64}O_2P_2PtSi_2$
Formula weight	827.09	842.07
Crystal color	Colorless	Colorless
Crystal shape	Block	Block
Crystal system	Monoclinic	Orthorhombic
Space group	*C* 2/*c*	*P* 21 21 21
a (Å)	27.279(6)	11.354(2)
b (Å)	17.861(4)	17.186(3)
c (Å)	18.006(4)	19.387(4)
β (°)	119.30(3)	90.00
Volume (Å^3)	7650(3)	3783(1)
Z	8	4
T (K)	293	293
D_x (Mg m^{-3})	1.436	1.479
μ (mm^{-1})	3.840	3.887
F(000)	736	324
θ range for data collection (°)	1.71–27.49	1.58–25.00
Index ranges	$-35 \le h \le 35$, $-23 \le k \le 23$, $-23 \le l \le 23$	$-13 \le h \le 13$, $-20 \le k \le 20$, $-23 \le l \le 23$
Measured reflections	38277	31763
Independent reflections	8752	6660
Data/restraints/parameters	8752/0/390	6660/3/391
R_{int}	0.094	0.041
Reflections with $I > 2\sigma(I)$	7419	6181
R_1 [$I > 2\sigma(I)$]	0.033	0.020
wR_2 (all data)	0.081	0.047

Table 2. Selected bond lengths (Å) and angles (°) for **2** and **3**.

Selected bond lengths for **2**				Selected bond lengths for **3**			
Pt1–P1	2.319(1)	Pt1–P2	2.321(1)	Pt1–P2	2.331(1)	Pt1–P1	2.332(1)
Pt1–Si2	2.338(1)	Pt1–Si1	2.370(1)	Pt1–Si2	2.331(1)	Pt1–Si1	2.362(1)
Si1–C8	1.895(4)	Si1–C7	1.901(4)	Si1–C8	1.868(4)	Si1–C7	1.913(5)
Si1–C1	1.907(4)	Si2–C6	1.892(3)	Si2–O2	1.693(3)	Si2–C8	1.892(3)
Si1–H1	1.440(4)	C1–C6	1.401(5)	Si2–O1	1.662(3)	O1–C9	1.409(6)
P1–C9	1.841(3)	C11–H17	0.9800	P1–C19	1.844(4)	C13–C14	1.521(6)
Selected bond angles for **2**							
P2–Pt1–Si2		93.32(4)		P2–Pt1–P1		86.45(4)	
Si2–Pt1–P1		178.25(3)		P2–Pt1–Si1		176.24(3)	
Si2–Pt1–Si1		83.02(4)		C8–Si1–C7		102.01(17)	
C8–Si1–Pt1		117.69(12)		C6–Si2–Pt1		112.53(12)	
C6–Si2–H1		102.7(16)		Pt2–Si2–H1		114.9(15)	
C6–C1–C2		118.2(3)		C9–P1–C11		103.76(17)	
Selected bond angles for **3**							
P2–Pt1–Si2		94.59(4)		P2–Pt1–P1		85.93(4)	
Si2–Pt1–P1		173.86(4)		P2–Pt1–Si1		172.18(4)	
Si2–Pt1–Si1		82.57(5)		Si1–Pt1–P1		97.67(4)	
C2–C1–Si1		123.9(4)		C8–Si1–C7		104.6(2)	
C8–Si1–Pt1		121.16(16)		O2–Si2–O1		100.49(17)	
C6–C1–C2		119.6(4)		C10–O2–Si2		117.7(3)	

structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using SHELXTL [7]. The bis(silyl) platinum(II) complexes were relatively more stable than the corresponding silyl nickel and palladium compounds

during data collection at room temperature. The crystallographic data are summarized in table 1, and selected geometric parameters are listed in table 2.

3. Results and discussion

We have studied the reaction of a chelating hydrosilane, 1,2-bis(silyl)benzene, which has a trihydrosilyl group, with group 10 transition metal complexes. Silane **1**, 1-(dimethylsilyl)-2-silylbenzene, which has relatively high reactivity toward transition metals, can react with Pt(dcpe)(PEt_3)$_2$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) in dry toluene at room temperature in the ratio of 1 : 1 to afford the bis(silyl)platinum(II) complex, **2**, bearing a chelating dcpe exclusively (scheme 1). The whole reaction process underwent successive oxidative addition of the Si–H bond to the Pt(0) center and dissociation of PEt_3 molecules accompanying the reductive elimination of dihydrogen. Most similar mononuclear bis(silyl) platinum(II) complexes bearing organophosphorus ligands with low steric hindrance reported previously are thermally unstable and can easily be converted to the corresponding dinuclear platinum complexes with the bridging silylene by intermolecular dimerization even at room temperature. The mononuclear bis(silyl) platinum(II) complexes bearing a chelating dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$) or depe (depe = $Et_2PCH_2CH_2PEt_2$) prepared from this chelating disilyl ligand are difficult to be trapped as crystals because of their unstability. However, the increased steric hinderance of the cyclohexyl groups plays an important role in the stability of **2** and **2** can be easily trapped by recrystallization in suitable solvent. Heating **2** in THF-d_8 at elevated temperature did not result in intermolecular dehydrogenative dimerization and no new peaks could be observed judging from the ^{31}P NMR spectrum, probably due to the high coordination ability of the aliphatic alkylphosphine dcpe with chelating structure to the platinum center and large steric hindrance resulted from cyclohexyl groups on phosphorus. In addition, no further reaction of **2** with a second molecule of **1** takes place which can be mainly attributed to the steric repulsion caused by methyl groups on silicon and cyclohexyl groups on phosphorus. However, **2** has high reactivity toward sterically unhindered alcohols. Treatment of **2** with methanol gives a dimethoxy substituted silyl platinum(II) compound, **3** (scheme 2). Compounds **2** and **3** are the very rare examples of silyl transition metal complexes derived from this chelating hydrosilane ligand. To the best of our knowledge, there are only six examples of bis(silyl) metal complexes prepared from this ligand with such structural features registered in the Cambridge Structural Database, and among them, only five bis(silyl) platinum(II) compounds are presented.

Crystals of **2** and **3** suitable for single-crystal X-ray analysis were grown by cooling a dimethoxyethane solution to 0 °C, and the molecular structures determined at 293 K were unambiguously confirmed by single-crystal X-ray structure analysis (figures 1 and 2). Complexes **2** and **3** crystallize in the monoclinic space group *C* 2/*c* and orthorhombic space group *P* 21 21 21, respectively (table 1). Compound **2** crystallizes with 0.5 molecule of dimethoxyethane. The coordination geometry of Pt is completed by two chelating P atoms and two Si atoms from one hydrosilane ligand. The average bond lengths of Pt–Si and Pt–P are in good agreement with reported similar complexes [4]. The central Pt in **2** forms P_2Si_2Pt(II) which attained a distorted square-planar geometry with P1–Pt1–P2 = 86.45(4)°, P2–Pt1–Si1 = 176.24(3)°, P1–Pt1–Si2 = 178.25(3)°, and P2–Pt1–Si2 = 93.32(4)° bond angles, respectively. Dimethoxy substituted silyl **3** also has similar configuration. The central Pt ion adopts a distorted square-planar P_2Si_2Pt(II) coordination geometry and is

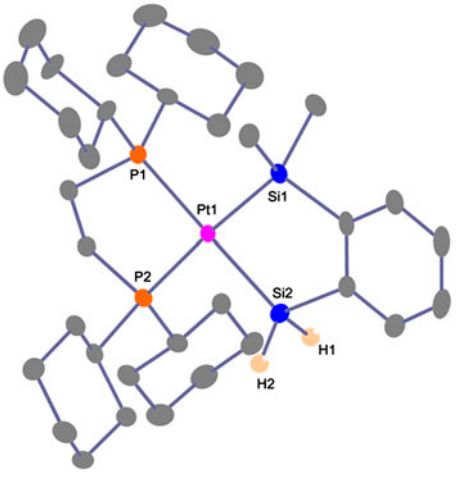


Figure 1. The structure of **2** showing the coordination environment of Pt; the hydrogens bound to carbon are omitted for clarity.

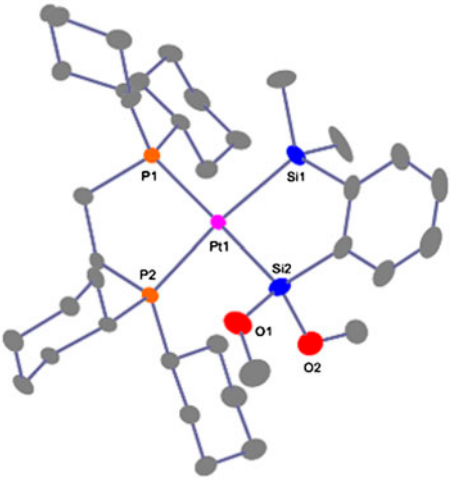


Figure 2. The structure of **3** showing the coordination environment of Pt; the hydrogens bound to carbon are omitted for clarity.

surrounded by two chelating P atoms and two chelating Si atoms from one hydrosilane ligand. The average bond lengths of Pt–Si (2.3319(12)–2.3628(12) Å) and Pt–P (2.3316 (11)–2.3326(10) Å) are in agreement with those observed in other similar complexes [4]. The bond angles of P1–Pt1–Si2 and P2–Pt1–Si1 are 173.86(4)° and 172.18(4)°, respectively, showing Pt ion slightly deviates from the P_2Si_2 plane, which can be attributed to steric repulsion between the silyl and phosphorus ligands. Furthermore, P1, C11, C12, and P2 are not on the same plane. The plane bounded by P1, C11, and C12 makes an angle of 43.57° to the plane C11–C12–P2. The two methyl carbons (C9 and C10) on the two

methoxy groups are situated in cis-positions of the plane bounded by O1–Si2–O2. All the cyclohexyl groups adopt the typical chair configuration (table 2).

The structures of **2** and **3** were also well identified by the elemental analysis and multinuclear NMR spectroscopic studies. In the $^{31}P\{^{1}H\}$ NMR spectrum, the two chemically inequivalent phosphorus atoms are a pair of doublets with relatively moderate $^{1}J_{Pt\text{-}P}$ values which are within the typical range of those observed in cis-bis(silyl)bis(phosphine)platinum (II) complexes [8]. The signals for P–P coupling with small $^{2}J_{P\text{-}P}$ values in the spectrum suggest that P atoms are cis. P–H signals for $Si(CH_3)_2$ groups of **2** and **3** in which the hydrogens on the two methyl groups are chemically equivalent appear as a doublet of doublets in the ^{1}H NMR spectrum, which suggests that one P is trans and the other P atom is cis to the $Si(CH_3)_2$ unit. Signals for SiH_2 groups in the proton-decoupled ^{29}Si NMR spectra are also consistent with the structure. The SiH_2 signals (a doublet of doublets) with a large (146 Hz) and a small (14 Hz) $^{2}J_{P\text{-}Si}$ value indicate that the SiH_2 group is cis to one P and trans to the other P. The phosphorus–platinum coupling ($^{1}J_{Pt\text{-}P}$) with a larger value (1710 Hz) was attributed to the phosphorus trans to SiH_2 unit. The silicon–platinum coupling ($^{1}J_{Pt\text{-}Si}$) value of Si connected with two methoxy groups is much larger than that of the Si from the SiH_2 unit, which may be due to the electronic effects of the methoxy group on Si.

4. Conclusion

In this contribution, a bis(silyl) platinum(II) complex, **2**, bearing a chelating dcpe ligand by successive oxidative addition and reductive elimination of a poly(silyl) chelating hydrosilane has been established. We report the synthesis, molecular structure, reactivity toward hydrosilane ligand and sterically unhindered alcohol, and the thermodynamic behavior of this new complex. Further applications of these silyl transition metal complexes to organic synthesis are currently in progress.

Supplementary material

Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Center, CCDC-1038769 for **2** and CCDC-1038773 for **3**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail for inquiry: www.ccdc.cam.ac.uk/datarequest/cif; E-mail for deposition: deposit@ccdc.cam.ac.uk).

Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental data

Supplemental data for this article can be accessed http://dx.doi.org/10.1080/00958972.2015.1099635.

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