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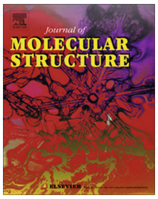

Synthesis, structural characterization and reactivity of a bis(phosphine)(silyl) platinum(**II**) complex

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HIGHLIGHTS

- A novel tetra-methoxy substituted bis(silyl) platinum(**II**) compound.
- Successive oxidative addition and reductive elimination reaction of a kind of poly(silyl) chelating hydrosilane.
- Reactivity toward proton organic reagent bearing hydroxy group.

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ABSTRACT

Treatment of 1,2-$C_6H_4(SiH_3)(SiH_3)$ **(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 the complex {1,2-$C_6H_4(SiH_2)(SiH_2)$}Pt^{II}(dcpe) **(2)**, which can react with proton organic reagent bearing hydroxy group with low steric hindrance to form a tetra-alkoxy substituted silyl platinum(**II**) compound (**3**). The structures of complexes **(2)** and **(3)** were unambiguously determined by multinuclear NMR spectroscopic studies and single crystal X-ray analysis.

Introduction

The chemistry of transition-metal complexes with metal–silicon bonds has grown immensely during the last decades since the first complex containing Si–metal bond was synthesized by Wilkinson and co-workers in 1956 [1]. Among varies kinds of methods for the formation of complexes that contain a silicon-transition metal bond, the most effective approach involves the activation of the Si–H bond by low-valent transition-metal complexes [2]. Hydrosilanes are useful synthetic precursors for the preparation of a number of silyl metal complexes in synthetic organosilicon chemistry. Since organohydrosilanes (including $RSiH_3$, R_2SiH_2, and R_3SiH) may contain one, two, or three Si–H 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 focus on the preparation of transition-metal complexes containing metal–silicon bonds with novel structures motifs using sterically less-demanding chelating silyl ligands which are very useful to stabilize silyl transition-metal compounds. We have been studying the stoichiometric reactions of 1,2-disilylbenzenes with group 10 transition-metal complexes and disclosed the formation of a number 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 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 the Speier's catalyst [5]. Herein we report the reaction of **1**, 2-disilylbenzene with Pt(dcpe)$(PEt_3)_2$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) to afford a mononuclear bis(silyl) platinum(**II**) complex **2** exclusively, and no further reaction of **2** with a second molecule of **1** takes place (Scheme 1). Moreover, complex **2** has high reactivity towards proton organic reagent

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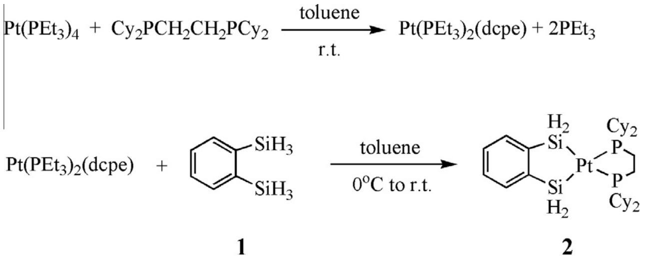


Scheme 1. The reaction of the parent chelating silane, 1,2-$C_6H_4(SiH_3)(SiH_3)$ **(1)** with Pt(dcpe)$(PEt_3)_2$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) in the ratio of 1:1, leading to a mononuclear complex {1,2-$C_6H_4(SiH_2)(SiH_2)$}Pt^{II}(dcpe) **(2)**.

bearing hydroxy group with low steric hindrance to form a tetra-alkoxy substituted silyl platinum(**II**) compound **(3)** (Scheme 2). The structures of complexes **(2)** and **(3)** were unambiguously determined by multinuclear NMR spectroscopic studies and single crystal X-ray analysis.

Experimental

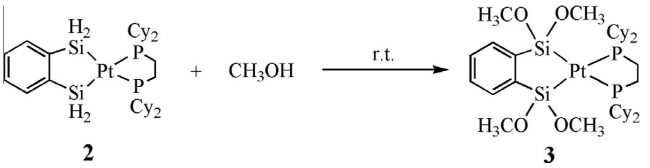
Materials and equipment

^1H, ^{29}Si and ^{31}P NMR spectra were recorded on Jeol LA500 (for solution NMR). Chemical shifts are given in ppm using external 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 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. 1,2-bis(dicyclohexylphosphino) ethane (Aldrich) were purchased and used as received, $Pt(PEt_3)_4$ and hydrosilane 1,2-$C_6H_4(SiH_3)(SiH_3)$ were prepared according to the relevant literature method [4b,6].

Synthesis

*Preparation of 1,2-disilylbenzene complex **(1)***

To a solution of phenyltris(N,N,N′-Trimethyl ethylenediamino)silane (20.4 g, 0.05 mol) in hexane (100 mL) was added a pentane solution of ^tBuLi (1.7 M, 84 mL, 0.114 mol) over 30 min at 0 °C under nitrogen. After stirring at rt for 3 h, the solution was added by using polyethylene tube to a solution of $SiC1_4$ (61 g, 0.36 mol) in hexane (50 mL) at −75 °C over 1 h. After addition was completed, the mixture was allowed to warm to rt and stirred for 3 h. The solvents and excess of $SiC1_4$ were removed under reduced pressure at rt. After the addition of hexane (50 mL) to the residue, ^iPrOH (90 mL) was added dropwise at 0 °C. The mixture was stirred at rt for 12 h. Volatiles were removed under vacuum, hexane (140 mL) was added, and the mixture was filtered through Celite. The filtrate was further filtered through a short pad of SiO_2 to remove a remaining salt. After evaporation, the residue was subjected to bulb-to-bulb distillation to give 14.5 g (60 %) of 1,2-bis(triisopropoxysilyl) benzene. The product obtained by bulb-to-bulb distillation was used for the next step without further purification. IR (neat) 3048, 2974, 1466, 1381, 1371, 1174, 1125, 1038, 886, 750, 704, 538, 505; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (36H, d, *J* = 6), 4.34 (6H, septet, *J* = 6), 7.37 (2H, dd, *J* = 3.5, 5.5), 7.95 (2H, dd, *J* = 3.5, 5.5); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 25.53, 65.39, 128.30, 136.75, 139.99; ^{29}Si NMR ($CDCl_3$, 300 MHz) δ-62.94. Calcd. (%) Elemental analysis for $C_{24}H_{46}O_6Si_2$: C, 59.22; H, 9.52. Found: C, 59.07; H, 9.57.



Scheme 2. The reaction of complex **2** with methanol affords a novel tetra-methoxy substituted silyl platinum(**II**) compound **3**.

To an ether suspension (30 mL) of $LiAlH_4$ (0.97 g, 26 mmol) was added dropwise a solution of 1,2-bis(triisopropoxysilyl)benzene (4.6 g, 9.5 mmol) in ether (20 mL) at 0 °C over 40 min. The mixture was stirred for 5 h at room temperature. GC–MS analysis of the mixture at this stage showed the presence of partially reduced products. Then, $LiAlH_4$ (0.3 g) was added and the mixture was stirred for another 3 h at room temperature. After removal of ether under reduced pressure, the remaining mixture was extracted with pentane (20 mL ∗ 3), and then filtered through Celite. After evaporation, the residue was distilled to gave 1,2-disilylbenzene **1** (0.76 g, 59%). IR (neat) 3053, 2163, 1126, 933, 903, 755, 734, 651; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.30 (6H, s), 7.41 (2H, dd, *J* = 3.5, 5.5), 7.68 (2H, dd, *J* = 3.5, 5.5); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 129.47, 136.52, 137.21; ^{29}Si NMR ($CDCl_3$, 300 MHz) δ-61.05.

*Preparation of {1,2-$C_6H_4(SiH_2)(SiH_2)$}Pt^{II}(dcpe) complex **(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 removal of volatiles under vacuum, the residual was dissolved in toluene (4 mL). To this solution was added hydrosilane (**1**, 44 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 the product **2** as a colorless solid, 181 mg (75%). $^{31}P\{^1H\}$ NMR (THF-d_8, 202.0 MHz): for **2**, δ 78.13 (s, $^1J_{\text{Pt-P}}$ = 1653 Hz). ^1H NMR (THF-d_8, 499.1 MHz): for **2**, δ 0.51 (dd, 6H, Si–CH_3), 1.16–1.91 (m, 44H, –Cy_2P–), 2.26–2.36 (m, 4H, –PCH_2CH_2P–), 5.69 (dd, 4H, SiH_2), 7.04 (dd, 2H, aromatic-H), 7.64 (dd, 2H, aromatic-H). $^{29}Si\{^1H\}$ NMR (THF-d_8, 99.1 MHz, DEPT): for **2**, δ-14.09 (dd, $^2J_{\text{P-Si}}$ = 149 Hz, $^2J_{\text{P-Si}}$ = 13 Hz, $^1J_{\text{Pt-Si}}$ = 1097 Hz, SiH_2). Calcd. (%) Elemental analysis for $C_{32}H_{56}P_2PtSi_2$: C, 50.97; H, 7.49. Found: C, 51.36; H, 7.78.

*Preparation of {1,2-$C_6H_4[Si(OCH_3)_2Si(OCH_3)_2]$}$Pt^{II}$(dcpe) complex **(3)***

In a Schlenk tube equipped with a magnetic stirrer bar, {1,2-$C_6H_4(SiH_2)$ (SiH_2)}Pt^{II}(dcpe) (377 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° for about 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 the product **3** as a colorless solid, 284 mg (65%). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.0 MHz): for **3**, δ 75.54 (s, $^1J_{\text{Pt-P}}$ = 1411 Hz). ^1H NMR (C_6D_6, 499.1 MHz): for **3**, δ 0.51 (dd, 6H, Si–CH_3), 1.18–1.81 (m, 44H, –Cy_2P–), 2.31–2.41 (m, 4H, –PCH_2CH_2P–), 3.66 (s, 12H, OCH_3), 7.47 (dd, 2H, aromatic-H), 8.18 (dd, 2H, aromatic-H). $^{29}Si\{^1H\}$ NMR (C_6D_6, 99.1 MHz, INEPT): for **3**, δ 27.58 (dd, $^2J_{\text{P-Si}}$ = 139 Hz, $^2J_{\text{P-Si}}$ = 10 Hz, $SiMe_2$). Calcd. (%) Elemental analysis for $C_{36}H_{64}O_2P_2PtSi_2$: C, 51.35; H, 7.66. Found: C, 51.76; H, 7.97.

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 the 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 nonhydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL programs [7]. The crystallographic data are summarized in Table 1 and selected geometric parameters are listed in Table 2.

Results and discussion

We have studied the reaction of a chelating hydrosilane, 1,2-bis(silyl)benzene, which has two trihydrosilyl groups, with group 10 transition-metal complexes. Silane **1**, 1,2-disilylbenzene 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 ligand exclusively (Scheme 1). The whole reaction process underwent the successive oxidative addition of the Si–H bond in a hydrosilane to the Pt(0) center and reductive elimination of PEt_3 molecules. Heating compound **2** even after 7 days at 100 °C in toluene could not result in slow intermolecular dehydrogenative dimerization reaction, probably due to the high coordination ability of the aliphatic alkylphosphine ligand dcpe with chelating structure to the platinum center. In addition, no further reaction of **2** with a second molecule of **1** takes place which can be mainly attributed to the steric effect caused by cyclohexyl groups on phosphorus atoms. However, complex **2** has high reactivity towards proton organic reagent bearing hydroxy group with low steric hindrance. Treatment of complex **2** with methanol gives a novel tetra-methoxy substituted silyl platinum(**II**) compound **3** (Scheme 2).

Crystals of **3** suitable for single-crystal X-ray analysis were grown by cooling a THF solution to 0 °C, and the molecular structures determined at 293 K were unambiguously confirmed by single-crystal X-ray structure analysis (Fig. 1). Tetra-methoxy substituted silyl complex **3** crystallizes in the monoclinic space group P 21/n (Table 1). The coordination geometry of the Pt atom is completed by two chelating P atoms, two chelating Si atoms from one free hydrosilane ligand. The central Pt atom in compound **3** forms P_2Si_2Pt(**II**) which attained a distorted-square-planar geometry with P1–Pt1–P2 = 86.31(4)°, P2–Pt1–Si1 = 175.81(4)°, P1–Pt1–Si2 = 174.76(4)°, and P2–Pt1–Si2 = 94.06(4)° bond angles respectively. The average bond lengths of Pt–Si and Pt–P are in good agreement with the reported similar complexes [4]. There exists some deviation from the P_2PtSi_2 plane at the Pt atom which can be attributed to the steric repulsion between the silyl and phosphorus ligands. All the cyclohexyl groups adopt the typical chair configuration (Table 2).

Table 1
Crystallographic data for **3**.

Compound	3
Formula	$C_{36}H_{64}O_4P_2PtSi_2$
Formula weight	827.09
Crystal color	Colorless
Crystal system	Monoclinic
Space group	P 21/n
a (Å)	12.158(2)
b (Å)	18.979(4)
c (Å)	17.597(4)
β (°)	105.26(3)
Volume (Å^3)	3917.3(13)
Z	4
T (K)	273(2)
D_x (Mg m^{-3})	1.482
F(000)	1792
μ (mm^{-1})	3.760
θ range for data collection (°)	1.61–27.59
Index ranges	$-14 \leqslant h \leqslant 15$, $-24 \leqslant k \leqslant 24$, $-18 \leqslant l \leqslant 22$
Measured reflections	28532
Independent reflections	9022
Data/restraints/parameters	9022/0/410
R_{int}	0.059
Reflections with $I > 2\sigma(I)$	5778
R_1 [$I > 2\sigma(I)$]	0.031
wR_2 (all data)	0.054

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

Pt1–Si1	2.3459(13)	Pt1–Si2	2.3310(14)
Pt1–P1	2.3372(12)	Pt1–P2	2.3342(12)
Si1–O1	1.656(3)	Si1–O2	1.645(3)
Si2–O3	1.665(3)	Si2–O4	1.646(3)
Si1–Pt1–Si2	82.83(5)	P1–Pt1–P2	86.31(4)
P1–Pt1–Si2	174.76(4)	P2–Pt1–Si2	94.06(4)
P2–Pt1–Si1	175.81(4)	Si1–Pt1–P1	96.53(4)
Pt1–P1–C11	106.77(14)	Pt1–P2–C12	107.58(14)
O1–Si1–O2	100.84(16)	O3–Si2–O4	101.52(19)
O1–Si1–Pt1	117.18(11)	O3–Si2–Pt1	118.74(12)

The structures of complexes **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 equivalent phosphorus atoms give rise to a singlet with relatively moderate $^1J_{Pt-P}$ values which are within the typical range of those observed in *cis*-bis(silyl)bis(phosphine) platinum(**II**) complexes [8]. P–H signals of SiH_2 group in compound **2** appear as a doublet of doublets in the ^{1}H NMR spectrum which suggests that one P atom is trans and the other P atom is cis to the SiH_2 unit. Signals for SiH_2 groups in compound **2** in the proton-decoupled ^{29}Si NMR spectrum are also consistent with the structure. The SiH_2 signals (a doublet of

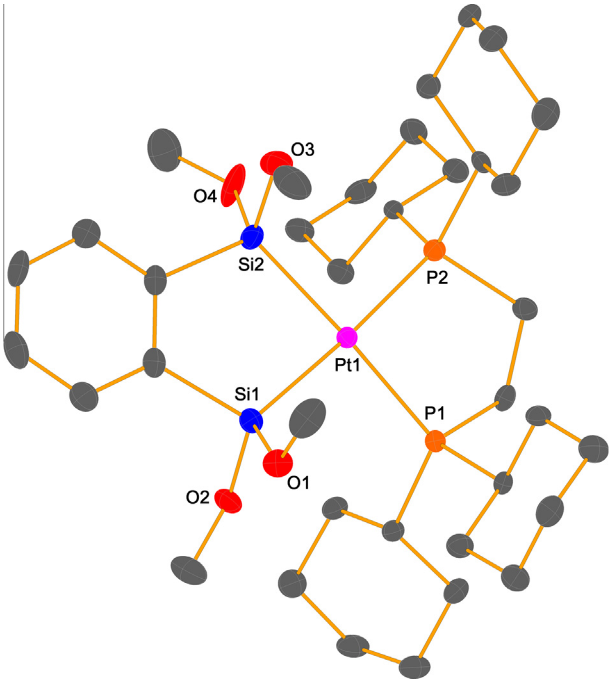


Fig. 1. The structure of **3**, showing the coordination environment of Pt atom and the hydrogen atoms bound to carbon atoms are omitted for clarity.

doublets) with a large (149 Hz) and a small (13 Hz) $^2J_{P-Si}$ value, indicate that the SiH_2 group is in cis-position relative to one P atom and trans to the other P atom.

Conclusion

In this contribution, a bis(silyl) platinum(**II**) complex **2** bearing a chelating dcpe ligand by successive oxidative addition and reductive elimination reaction of a kind of poly(silyl) chelating hydrosilane has been established. We report the synthesis, preliminary coordination chemistry studies, thermodynamic behavior and reactivity toward proton organic reagent bearing hydroxy group of this new complex. Further application 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 Centre, CCDC – 1043314 for the complex 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).

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