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Synthesis, Structural Characterization and Reactivity of a Bis(phosphine)(silyl) Platinum(II) Complex

Yonghua Li,*[,a] Wenjin Zeng,[a] Wenyong Lai,[a] Shigeru Shimada,[b] Shi Wang,[a]
Lianhui Wang,[a] and Wei Huang*[,a]

[a] *Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, Nanjing, Jiangsu 210023, 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*

Treatment of 1,2-$C_6H_4(SiH_3)(SiH_3)$ (**1**) with Pt(dmpe)$(PEt_3)_2$ (dmpe=$Me_2PCH_2CH_2PMe_2$) in the ratio of 1∶1 leads to the complex {1,2-$C_6H_4(SiH_2)(SiH_2)$}Pt^{II} (dmpe) (**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**). 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 6 examples of silyl metal complexes prepared from this ligand with such structural features registered in the Cambridge Structural Database, among them, only one silyl platinum(II) compound is presented. The structures of complexes **2** and **3** were unambiguously determined by multinuclear NMR spectroscopic studies and single crystal X-ray analysis.

Keywords silyl, chelating, platinum, multinuclear NMR

Introduction

The chemistry of transition-metal complexes with metal-silicon bonds has rapidly grown during the last decades 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 the 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 three, two, or one 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 structures 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 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 (**1**) with Pt(dmpe)$(PEt_3)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) 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 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.

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* E-mail: iamyhli@njupt.edu.cn; Tel.: 0086-025-85866533; Fax: 0086-025-85866533
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Experimental

Materials and equipment

^{1}H NMR, ^{29}Si NMR 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 ^{1}H 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 or in a glove box. 1,2-Bis(dimethylphosphino)ethane (Aldrich) was purchased and used as received, disilyl hydrosilane 1,2-C_6H_4 (SiH_3)(SiH_3) and Pt(PEt_3)$_4$ were prepared according to the relevant literature method.[4b,6]

Synthesis

Preparation of 1,2-disilylbenzene (1)[4]

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 *t*-BuLi (1.7 mol/L, 84 mL, 0.114 mol) over 30 min at 0 ℃ under nitrogen. After stirring at r.t. for 3 h, the solution was added by using polyethylene tube to a solution of SiC14 (61 g, 0.36 mol) in hexane (50 mL) at −75 ℃ over 1 h. After addition was completed, the mixture was allowed to warm to r.t. and stirred for 3 h. The solvents and excess of SiC14 were removed under reduced pressure at r.t. After the addition of hexane (50 mL) to the residue, *i*-PrOH (90 mL) was added dropwise at 0 ℃. The mixture was stirred at r.t. 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. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.20 (d, J=6 Hz, 36H), 4.34 (septet, J=6 Hz, 6H), 7.37 (dd, J=3.5, 5.5 Hz, 2H), 7.95 (dd, J=3.5, 5.5 Hz, 2H); ^{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; IR (neat) v: 3048, 2974, 1466, 1381, 1371, 1174, 1125, 1038, 886, 750, 704, 538, 505. Anal. calcd for $C_{24}H_{46}O_6Si_2$ (%): C 59.22, H 9.52; found C 59.07, H 9.57.

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 ℃ 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%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.30 (s, 6H), 7.41 (dd, J=3.5, 5.5 Hz, 2H), 7.68 (dd, J=3.5, 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 129.47, 136.52, 137.21; ^{29}Si NMR ($CDCl_3$, 300 MHz) δ: −61.05; IR (neat) v: 3053, 2163, 1126, 933, 903, 755, 734, 651 cm^{-1}.

Preparation of {1,2-C_6H_4(SiH_2)(SiH_2)}Pt^{II}(dmpe) complex (2)

A mixture of Pt(PEt_3)$_4$ (216 mg, 0.32 mmol) and dmpe (48 mg, 0.32 mmol) in toluene (4 mL) was stirred at room temperature for 40 min to give Pt(PEt_3)$_2$(dmpe). 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 ℃, and the mixture was stirred at 0 ℃ 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, 120 mg (78%). ^{31}P{^{1}H} NMR (THF-d_8, 202.0 MHz) δ: for **2**, 66.35 (s, $^1J_{Pt-P}$=1625 Hz); ^{1}H NMR (THF-d_8, 499.1 MHz) δ: for **2**, 0.51—1.15 (m, 16H, $Me_2PCH_2CH_2PMe_2$), 5.58—5.67 (m, 4H, SiH_2), 7.47 (dd, J=3, 5 Hz, 2H, aromatic-H), 7.69—7.74 (m, 2H, aromatic-H); ^{29}Si{^{1}H} NMR (THF-d_8, 99.1 MHz) δ: for **2**, −14.35 (dd, $^2J_{P-Si}$=149 Hz, $^2J_{P-Si}$=13 Hz, $^1J_{Pt-Si}$=1103 Hz, SiH_2). Anal. calcd for $C_{12}H_{24}P_2PtSi_2$: C 29.93, H 5.02; found C 30.38, H 5.43.

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

In a Schlenk tube equipped with a magnetic stirrer bar, {1,2-C_6H_4(SiH_2) (SiH_2)}Pt^{II}(dmpe) (241 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, 210 mg (70%). ^{31}P{^{1}H} NMR (C_6D_6, 202.0 MHz) δ: for **3**, 43.45 (s, $^1J_{Pt-P}$=1345 Hz); ^{1}H NMR (C_6D_6, 499.1 MHz) δ: for **3**, 1.58—1.65 (m, 12H, —Me_2P—), 1.71—1.79 (m, 4H, —PCH_2CH_2P—), 3.34 (s, 12H, Si(OCH_3)$_2$), 7.22 (dd, J=3, 6 Hz, 2H, aromatic-H), 7.72 (dd, J=3, 6 Hz, 2H, aromatic-H); ^{29}Si{^{1}H} NMR (C_6D_6, 99.1 MHz) δ: for **3**, 28.43 (dd, $^2J_{P-Si}$=139 Hz, $^2J_{P-Si}$=10 Hz, Si(OMe)$_2$). Anal. calcd for $C_{16}H_{32}O_4P_2PtSi_2$: C 31.94, H 5.36; found C 32.43, H 5.72.

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.

Table 1 Crystallographic data for **3**

Compound	**3**
Formula	$C_{16}H_{32}O_4P_2PtSi_2$
Formula weight	601.63
Crystal color	colorless
Crystal system	monoclinic
Space group	*Cc*
a/Å	9.2860(19)
b/Å	17.296(4)
c/Å	14.360(3)
α/(°)	90
β/(°)	102.06(3)
γ/(°)	90
Volume/Å^3	2255.5(8)
Z	4
T/K	293(2)
D_x/(Mg•m^{-3})	1.772
F(000)	1184
μ/mm^{-1}	6.486
θ range for data collection/(°)	2.36—27.51
Index ranges	$-12\leqslant h\leqslant 12$, $-22\leqslant k\leqslant 22$, $-18\leqslant l\leqslant 18$
Measured reflections	11105
Independent reflections	5067
Data/restraints/parameters	5067/2/234
R_{int}	0.101
Reflections with $I>2\sigma(I)$	4749
R_1 [$I>2\sigma(I)$]	0.052
wR_2 (all data)	0.128

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

Pt1—Si1	2.328(3)	Pt1—Si2	2.343(3)
Pt1—P1	2.327(3)	Pt1—P2	2.323(3)
Si1—O1	1.669(7)	Si1—O2	1.667(11)
Si2—O3	1.672(9)	Si2—O4	1.666(7)
Si1—Pt1—Si2	84.01(9)	P1—Pt1—P2	85.13(9)
P1—Pt1—Si2	176.49(10)	P2—Pt1—Si2	96.86(9)
P2—Pt1—Si1	177.61(10)	Si1—Pt1—P1	94.12(9)
Pt1—P1—C11	116.7(4)	Pt1—P2—C15	116.8(4)
O1—Si1—O2	102.1(5)	O3—Si2—O4	96.9(4)
O1—Si1—Pt1	117.6(3)	O3—Si2—Pt1	117.8(4)

Results and Discussion

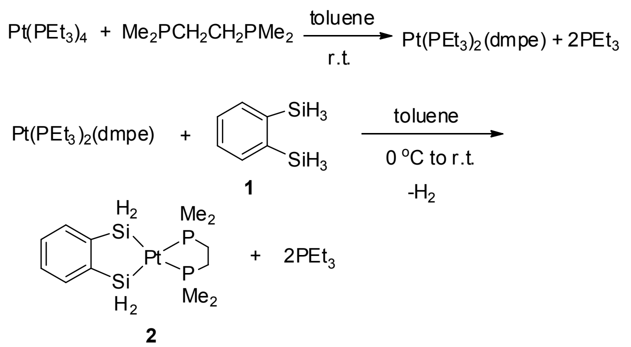
We have studied the reaction of a chelating hydrosilane, 1,2-bis(silyl)benzene, which has two trihydrosilyl groups, with group 10 transition-metal complexes. Silane **1**, 1,2-disilylbenzene which has relatively high reactivity toward transition metals can react with $Pt(dmpe)(PEt_3)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) in dry toluene at room temperature in the ratio of 1∶1 to afford the bis(silyl)platinum(II) complex **2** bearing a chelating dmpe ligand exclusively (Scheme 1). The whole reaction process underwent the successive oxidative addition of the Si—H bond to the Pt(0) center and dissociation of PEt_3 molecules. Most of the similar mononuclear bis(silyl) platinum(II) complexes bearing organophosphorus ligands with low steric hindrance reported previously are thermally unstable and can be partially converted to the corresponding dinuclear platinum complexes with the bridging silylene. For this silyl coordination compound **2**, it was also unstable and NMR spectra in THF-d_8 showed that complex **2** seemed to be in equilibrium with a certain mixed valent polynuclear platinum complex in solution. Although monomer **2** could not be obtained as a crystal, **2** can be trapped by proton organic reagent. 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). In addition, no further reaction of **2** with a second molecule of **1** takes place even at elevated temperature, which can be mainly attributed to the high coordination ability of the aliphatic alkylphosphine ligand dmpe with chelating structure to the platinum center and the steric effect caused by methyl groups on phosphorus atoms.

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 6 examples of silyl metal complexes prepared from this ligand with such structural features registered in the Cambridge Structural Database, among them, only one silyl platinum(II) compound is presented.[8]

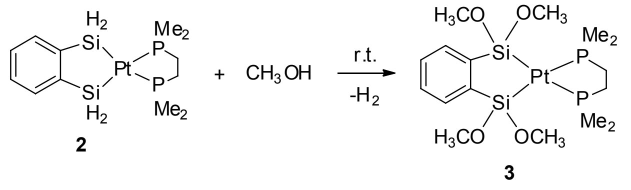
Crystals of **3** suitable for single-crystal X-ray analysis were grown by cooling a dimethoxyethane solution to 0 ℃, and the molecular structure determined at 293 K was unambiguously confirmed by single-crystal X-ray structure analysis (Figure 1). Tetra-methoxy substituted silyl complex **3** crystallizes in the monoclinic space group *Cc* (Table 1). The central Pt atom in compound **3** adopts a distorted square-planar $P_2Si_2Pt(II)$ coordination geometry and is surrounded by two chelating P atoms, two chelating Si atoms from one hydrosilane ligand. The bond angles of P2—Pt1—Si1 (177.61(10)°) and Si1—Pt1—Si2 (84.01(9)°) are slightly greater than those of the reported similar complex. The average bond lengths of Pt—Si (2.336(3) Å) and Pt—P (2.325(3) Å) are slightly shorter than those of the analogous silyl platinum(II) compound.[8a] There exists some deviation from the P_2PtSi_2 plane at the Pt atom which can be attributed to the steric repulsion between the substituent groups on the silyl and phosphorus ligands (Table 2).

The structures of complexes **2** and **3** were also well identified by multinuclear NMR spectroscopic studies. In the $^{31}P\{^1H\}$ 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.[9] The signals for P—P coupling with very small $^2J_{P-P}$ values in the spectrum suggest that both P atoms are in *cis*-position. Signals for SiH_2 groups in the proton-decoupled ^{29}Si NMR spectrum are also consistent with the structure. The SiH_2 signals (a doublet of 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.

Scheme 1 The reaction of the parent chelating silane, 1,2-$C_6H_4(SiH_3)(SiH_3)$ (**1**) with $Pt(dmpe)(PEt_3)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) in the ratio of 1∶1, leading to a mononuclear complex {1,2-$C_6H_4(SiH_2)(SiH_2)$}-Pt^{II}(dmpe) (**2**)



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



Conclusions

In this contribution, a bis(silyl) platinum(II) complex **2** bearing a chelating dmpe 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 applications of these silyl transition-metal complexes to organic synthesis are currently in progress.

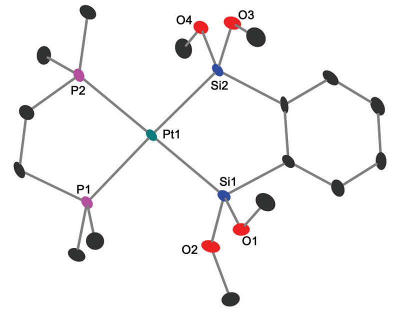


Figure 1 The structure of **3**, showing the coordination environment of Pt atom and the hydrogen atoms bound to carbon atoms are omitted for clarity.

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