

Synthesis, structural characterization and reactivity towards methanol of a bis(silyl)platinum(II) complex bearing a chelating depe ligand



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ABSTRACT

Treatment of 1,2-C₆H₄(SiH₃)(SiH₂) (**1**) with [Pt(depe)(PEt₃)₂] (depe = Et₂PCH₂CH₂PEt₂) in the ratio of 1:1 yields the complex [Pt^{II}{1,2-C₆H₄(SiH₂)(SiH₂)}(depe)] (**2**), which has unique reactivity towards sterically unhindered alcohol to form an unusual tetra-alkoxy substituted silyl platinum(II) compound (**3**). Only 2 examples of bis(silyl)platinum(II) complexes prepared from this chelating hydrosilane ligand have been registered in the Cambridge Structural Database. The structure of complex (**3**) was unambiguously determined by multinuclear NMR spectroscopic studies and single crystal X-ray analysis.

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1. Introduction

The chemistry of transition metal–silyl complexes has rapidly grown during the last decades, and a number of novel structures have been elucidated since the first complex containing metal–silicon bond was synthesized by Wilkinson and co-workers [1]. One of the most important methods for preparing silyl transition–metal complexes involves the reaction of hydrosilanes with low-valent transition metal complexes via Si–H bond activation [2]. Since organohydrosilanes (including RSiH₃, R₂SiH₂, and R₃SiH) may contain three, two, or one 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 mainly focuses on the preparation of sterically unhindered chelating silyl ligands, investigation of their reactive behavior toward transition metal complexes, study of the unique bonding structures and reactivity toward hydrosilane ligands for the silyl–metal complexes formed by Si–H activation. We have reported a number of unusual silyl group 10 transition metal complexes with various disilylbenzene 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 in particular provide excellent catalysts for the transformation of hydrosilanes and disilanes. Mono- and bis(silyl)platinum(II) complexes are usually believed to play important roles in hydrosilylation, dehydrocoupling, and double silylation reactions with hydrosilanes and disilanes [5]. Herein we report the reaction of 1,2-disilylbenzene (**1**) with [Pt(depe)(PEt₃)₂] (depe = Et₂PCH₂CH₂PEt₂) to afford a mononuclear bis(silyl)platinum(II) complex **2**. This silyl metal compound reacts readily with MeOH to form an unusual tetra-alkoxy substituted silyl platinum(II) compound **3** which was unambiguously determined by multinuclear NMR spectroscopic studies and single crystal X-ray analysis.

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 references (tetramethylsilane (0 ppm) for ¹H and ²⁹Si and 85% H₃PO₄ (0 ppm) for ³¹P), 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 obtained from commercial suppliers. All solvents were dried and stored over molecular sieves

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(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(diethylphosphino)ethane (Aldrich) was purchased and used as received, 1,2-C₆H₄(SiH₃)(SiH₃) and Pt(PEt₃)₄ were prepared according to the relevant literature method [4b,6].

2.2. Syntheses

2.2.1. Preparation of 1,2-disilylbenzene

To a solution of phenyltris(*N,N,N'*-trimethylethylenediamino)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 SiCl₄ (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 SiCl₄ 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 SiO₂ 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. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 300 MHz) δ 25.53, 65.39, 128.30, 136.75, 139.99; ²⁹Si NMR (CDCl₃, 300 MHz) δ -62.94. *Anal.* Calc. for C₂₄H₄₆O₆Si₂: C, 59.22; H, 9.52. Found: C, 59.07; H, 9.57%.

To an ether suspension (30 mL) of LiAlH₄ (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, LiAlH₄ (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 give 1,2-disilylbenzene **1** (0.76 g, 59%). ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 300 MHz) δ 129.47, 136.52, 137.21; ²⁹Si NMR (CDCl₃, 300 MHz) δ -61.05.

2.2.2. Preparation of {1,2-C₆H₄(SiH₂)(SiH₂)}Pt^{II}(depe) complex (**2**)

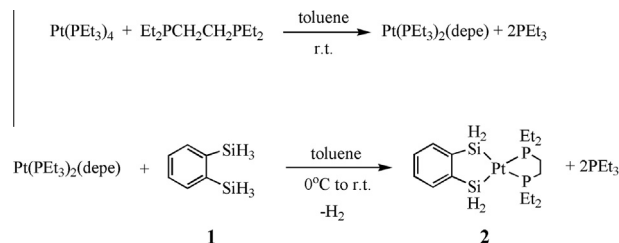
A mixture of Pt(PEt₃)₄ (216 mg, 0.32 mmol) and depe (66 mg, 0.32 mmol) in toluene (4 mL) was stirred at room temperature for 40 min to give Pt(PEt₃)₂(depe). After removal of volatiles under vacuum, the residual was dissolved in toluene (4 mL). To this solution was added hydrosilane (**1**, 44 mg, 0.32 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 a colorless solid, 131 mg (76%). NMR analysis of this solid in THF-*d*₈ at room temperature showed the formation of bis(silyl)platinum(II) complex **2** as a major product together with a certain amount of **4**. ³¹P{¹H} NMR (THF-*d*₈, 202.0 MHz): for **2**, δ 66.52 (s + d, ¹*J*_{Pt-P} = 1628 Hz); for **4**, δ 12.99 (¹*J*_{Pt-P} = 897 Hz, ³*J*_{Pt-P} = 181 Hz), 17.72 (¹*J*_{Pt-P} = 1034 Hz, ³*J*_{Pt-P} = 209 Hz). ¹H NMR (THF-*d*₈, 499.1 MHz): for **2**, δ 0.49–1.45 (m, 24H, Et₂PCH₂CH₂PEt₂), 5.58–5.67 (m, 4H, SiH₂), 7.47 (dd, 2H, aromatic-H), 7.60–7.64 (m, 2H, aromatic-H). ²⁹Si{¹H} NMR (THF-*d*₈, 99.1 MHz): for **2**, δ -14.11 (dd, ²*J*_{P-Si} = 149 Hz, ²*J*_{P-Si} = 13 Hz, ¹*J*_{Pt-Si} = 1100 Hz, SiH₂).

2.2.3. Preparation of {1,2-C₆H₄[Si(OCH₃)₂Si(OCH₃)₂]}Pt^{II}(depe) complex (**3**)

In a Schlenk tube equipped with a magnetic stirrer bar, {1,2-C₆H₄(SiH₂)(SiH₂)}Pt^{II}(depe) (269 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 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, 240 mg (73%). ³¹P{¹H} NMR (THF-*d*₈, 202.0 MHz): for **3**, δ 67.95 (s + d, ¹*J*_{Pt-P} = 1392 Hz). ¹H NMR (THF-*d*₈, 499.1 MHz): for **3**, δ 1.07–2.21 (m, 24H, Et₂PCH₂CH₂PEt₂), 3.34 (s, 12H, 2 * Si(OCH₃)₂), 7.24 (dd, 2H, aromatic-H), 7.70–7.75 (m, 2H, aromatic-H). ²⁹Si{¹H} NMR (THF-*d*₈, 99.1 MHz): for **3**, δ 48.42 (dd, ²*J*_{P-Si} = 190 Hz, ²*J*_{P-Si} = 11 Hz, ¹*J*_{Pt-Si} = 1552 Hz, Si(OMe)). *Anal.* Calc. for C₂₀H₄₀O₄P₂PtSi₂: C, 36.52; H, 6.13. Found: C, 37.02; H, 6.54%.

3. 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 complex. Silane **1**, 1,2-disilylbenzene has high reactivity toward platinum complex [Pt(depe)(PEt₃)₂] (depe = Et₂PCH₂CH₂PEt₂) in the ratio of 1:1 to afford a bis(silyl)platinum (II) complex **2** bearing a chelating depe ligand in high yield (Scheme 1). The reaction is proposed to proceed through the successive oxidative addition of the Si–H bond to the Pt(0) center and dissociation of PEt₃ molecules accompanied by the reductive elimination of dihydrogen. Most of the similar mononuclear bis(silyl)platinum(II) complexes bearing organophosphine ligands with low steric hindrance can be partially converted to the corresponding polynuclear platinum complexes with the bridging silylene by intermolecular dimerization [4f]. For this silyl metal compound **2**, it was also unstable (reactive) in solution even at room temperature. The NMR spectra in THF-*d*₈ at room temperature showed the formation of a mononuclear bis(silyl)platinum (II) complex **2** as a major product together with a certain amount of **4** which maybe in equilibrium in solution. Judging from the characteristic coupling signals with satellite peaks in the ³¹P NMR spectrum, we inferred that complex **4** may be dinuclear platinum species with the bridging silylene by intermolecular dimerization of **2**. Although silyl compound **2** could not be obtained as a crystal, **2** can be trapped by four MeOH molecules in view of its high reactivity towards sterically unhindered alcohol. The Si–H bonds in the SiH₂ moiety of the similar silyl palladium and nickel complexes prepared from this disilyl ligand do not have such a unique reactivity [4h,i]. Treatment of a mixture of **2/4** with methanol gives a novel tetra-methoxy substituted silyl platinum(II) compound **3** (Scheme 2). Although the mechanism for the formation of complex **3** is not clear, the formation of complex **3** may be explained by a sequence of oxidative addition of the O–H and Si–H bonds to the Pt center, followed by Si–O coupling accompanied by the reductive elimination of dihydrogen. As previously



Scheme 1. Synthesis of the mononuclear complex {1,2-C₆H₄(SiH₂)(SiH₂)}Pt^{II}(depe) (**2**).

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