Journal of Molecular Structure 1097 (2015) 181–184

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

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

Yong-Hua Li *, Cheng-Long Yang, Wen-Yong Lai, Zheng-Feng Huang, Shi Wang, Lian-Hui Wang, Wei Huang

Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China

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.

ARTICLE INFO

Article history:
Received 24 January 2015
Received in revised form 29 April 2015
Accepted 5 May 2015
Available online 21 May 2015

Keywords:
Silyl
Chelating
Platinum
Multinuclear NMR

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].

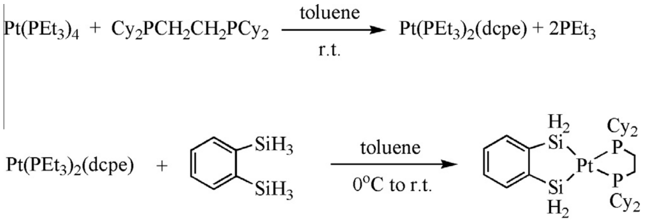
Our present research focus on the preparation of transition-metal complexes containing metal–silicon bonds with novel structures motifs using sterically less-demanding chelating silyl ligands which are very useful to stabilize silyl transition-metal compounds. We have been studying the stoichiometric 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

---

* Corresponding author. Tel./fax: +86 25 85866396.
E-mail address: iamyhli@njupt.edu.cn (Y.-H. Li).

http://dx.doi.org/10.1016/j.molstruc.2015.05.005



1

2

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

^{1}H, ^{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 ^{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. 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 ^{t}BuLi (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, ^{i}PrOH (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; ^{1}H 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.

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; ^{1}H 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)***

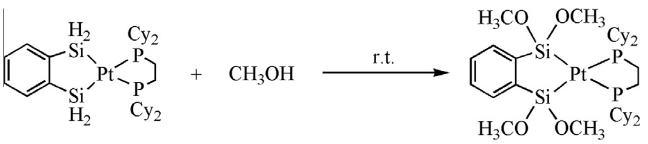
A mixture of $Pt(PEt_3)_4$ (216 mg, 0.32 mmol) and dcpe (135 mg, 0.32 mmol) in toluene (4 mL) was stirred at room temperature for 40 min to give $Pt(PEt_3)_2$(dcpe). After removal of volatiles under vacuum, the residual was dissolved in toluene (4 mL). To this solution was added hydrosilane (**1**, 44 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%). $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.0 MHz): for **2**, δ 78.13 (s, $^{1}J_{Pt\text{-}P} = 1653$ Hz). ^{1}H 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). $^{29}Si\{^{1}H\}$ NMR (THF-d_8, 99.1 MHz, DEPT): for **2**, δ-14.09 (dd, $^{2}J_{P\text{-}Si} = 149$ Hz, $^{2}J_{P\text{-}Si} = 13$ Hz, $^{1}J_{Pt\text{-}Si} = 1097$ 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%). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.0 MHz): for **3**, δ 75.54 (s, $^{1}J_{Pt\text{-}P} = 1411$ Hz). ^{1}H 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). $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99.1 MHz, INEPT): for **3**, δ 27.58 (dd, $^{2}J_{P\text{-}Si} = 139$ Hz, $^{2}J_{P\text{-}Si} = 10$ 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),



2

3

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