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Reactions of $HOSiMe_2Ar$ with Pt–PPh_3 complexes leading to Si–C bond activation or formation of a siloxoplatinum complex

Neli Mintcheva, Yasushi Nishihara, Atsunori Mori, Kohtaro Osakada *

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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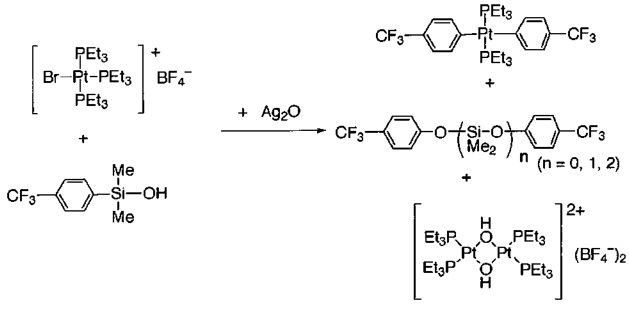
Abstract

$PtI_2(PPh_3)_2$ reacts with $HOSiMe_2(C_6H_4CF_3\text{-}4)$ at 60°C in the presence of $AgBF_4$ to give a mixture of *trans*-$PtI(C_6H_4CF_3\text{-}4)(PPh_3)_2$ (**1**) and $[Pt_2(\mu\text{-}I)_2(PPh_3)_4](BF_4)_2$ (**2**). Each of the complexes is isolated and characterized by X-ray crystallography and/or NMR spectroscopy. The $^{31}P\{^1H\}$-NMR study of the reaction of $AgBF_4$ with $PtI_2(PPh_3)_2$ in acetone-d_6 revealed the formation of *trans*-$[PtI(PPh_3)_2(\text{acetone})]BF_4$ (**3**) although isolation of the cationic complex was not feasible due to its facile conversion to **2**. Addition of $HOSiMe_2(C_6H_4CF_3\text{-}4)$ and Ag_2O to a toluene solution of *trans*-$PtI(Ph)(PPh_3)_2$ causes replacement of the iodo ligand with the siloxo group to afford *trans*-$[Pt(Ph)\{OSiMe_2(C_6H_4CF_3\text{-}4)\}(PPh_3)_2]$ (**4**). Crystallographic results of **4** show the coordination of the phenyl, siloxo, and PPh_3 ligands to the square-planar Pt center with a large Pt–O–Si angle. Complex **4** does not decompose below 60°C in a toluene solution, but reacts with CH_2Cl_2 and $CHCl_3$ at room temperature to form *trans*-$PtCl(Ph)(PPh_3)_2$ (**5**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Transmetalation; Cationic complex; Silanol; Siloxo complex

1. Introduction

Recently, we reported that the reaction of an excess amount of $HOSiMe_2(C_6H_4CF_3\text{-}4)$ with a cationic platinum(II) complex, $[PtBr(PEt_3)_3]BF_4$, in the presence of Ag_2O gave a diarylplatinum complex accompanied by formation of oligosiloxanes as shown in Scheme 1 [1]. The formation of the diarylplatinum complex and oligosiloxanes indicates occurrence of Si–C bond activation of the silanol, which is of significant interest, relevant not only to transition metal complex promoted Si–C bond cleavage [2] but also to the mechanism of Pd complex catalyzed synthetic organic reactions that involve transmetalation of an aryl ligand of silanol to Pd [3].



Scheme 1.

In this paper we report Si–C bond cleavage of silanol promoted by cationic platinum complexes with PPh_3 ligands and synthesis of a new aryl(siloxo)platinum complex by the reaction of silanol with an iodoplatinum complex.

2. Results and discussion

Heating a mixture of $PtI_2(PPh_3)_2$, $AgBF_4$ and followed by addition of $HOSiMe_2(C_6H_4CF_3\text{-}4)$ at 60°C in acetone leads to the formation of a mixture of two Pt complexes, *trans*-$PtI(C_6H_4CF_3\text{-}4)(PPh_3)_2$ (**1**) (17%) and $[Pt_2(\mu\text{-}I)_2(PPh_3)_4](BF_4)_2$ (**2**) (54%), as shown in Eq. (1). The reaction causes separation of complex **2**, which is sparingly soluble in common organic solvents, while complex **1** is obtained from the acetone soluble fraction

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* Corresponding author. Tel./fax: + 81-45-9245224.

E-mail address: kosakada@res.titech.ac.jp (K. Osakada).

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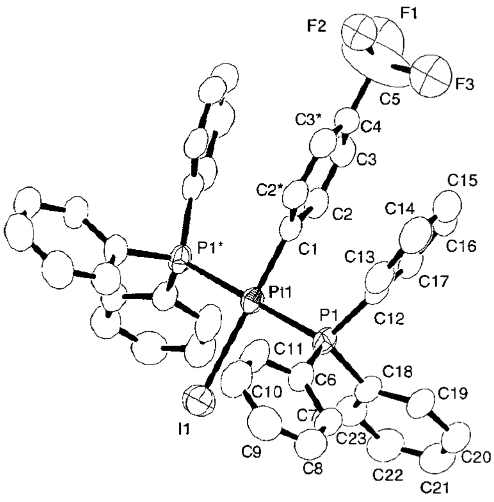


Fig. 1. ORTEP drawings of **1** at 50% ellipsoidal levels. The molecule contains a crystallographic $C2$ symmetry around the C1–Pt–I axis. The atoms with asterisks at the numbers are crystallographically equivalent to those having the same number without the asterisk. Selected bond distances (Å) and angles (°): Pt–I, 2.7011(9); Pt–P1, 2.316(1); Pt–C1, 1.963(9); I–Pt–P1, 90.43(5); I–Pt–C1, 180.00; P1–Pt–P1*, 179.14(9); P1–Pt–C1, 89.57(5).

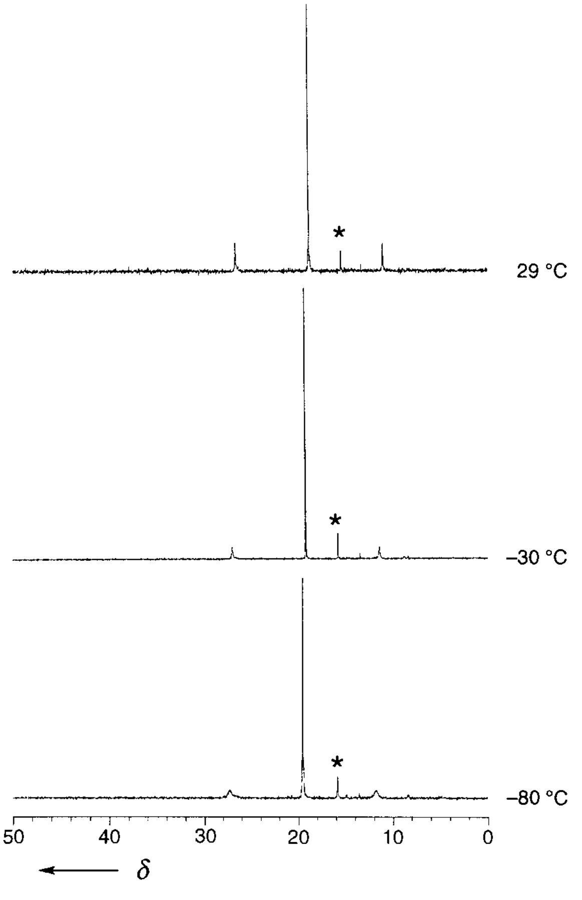
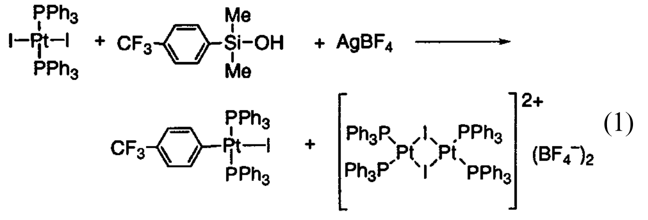


Fig. 2. Temperature dependent $^{31}P\{^1H\}$-NMR spectra of **3** in acetone-d_6. The signal at δ 18–19, flanked by the satellite signals, is due to **3**, while a smaller signal with an asterisk is assigned to **2**.

of the products. A similar reaction with added PPh_3 does not cause the transmetalation but forms $[PtI(PPh_3)_3]BF_4$ which is insoluble in the solvent and does not react further with the silanol. Fig. 1 shows the structure of **1** determined by X-ray crystallography. The molecule contains a crystallographically imposed $C2$ symmetry around the axis, including C5, C4, C1, Pt, and I atoms. Fluorine atoms are positioned consequently at two disordered positions.



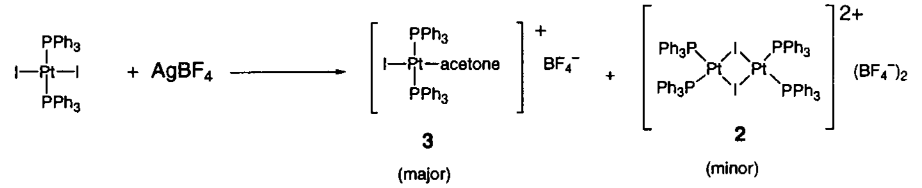
(1)

1 **2**

The $^{31}P\{^1H\}$-NMR spectrum of **1** consists of a single resonance at δ 21.89 flanked with two satellite peaks with ^{195}Pt nucleus. The coupling constant ($^1J(Pt–P) = 2999$ Hz) is in the range of already known *trans*-$PtX(Ar)(PPh_3)_2$ (X = halogeno or pseudo halogeno ligands) complexes (2830–3180 Hz) [4]. The ^1H-NMR spectrum of **1** exhibits signals of *ortho* and *meta* hydrogens of 4-(trifluoromethyl)phenyl group bonded to the Pt center. The signal at δ 6.81 is flanked by ^{195}Pt satellite signals ($^3J(Pt–H) = 54$ Hz) and assigned to the *ortho* hydrogens, while the *meta* hydrogen signal appears as a simple doublet at δ 6.41. The $^{13}C\{^1H\}$-NMR signals of the 4-(trifluoromethyl)phenyl ligand indicate the *trans* configuration of **1** clearly. The C_{ipso} signal is observed at the lowest magnetic field position (δ 154.64) as a triplet ($^2J(P–C) = 8$ Hz) accompanied by ^{195}Pt satellites ($^1J(Pt–C) = 370$ Hz).

Complex **2** gives satisfactory elemental analyses for the proposed formula, but the broad ^1H-NMR signals of the complex do not provide further information of the structure. The $^{31}P\{^1H\}$-NMR spectrum in $CDCl_3$ shows a single signal at δ 14.59. The large coupling constant with ^{195}Pt ($^1J(Pt–P) = 3530$ Hz) indicates that the ligand is positioned *trans* to the iodo ligand with a smaller degree of *trans* influence than PPh_3. These results indicate the proposed dinuclear structure with two bridging iodo ligands unambiguously.

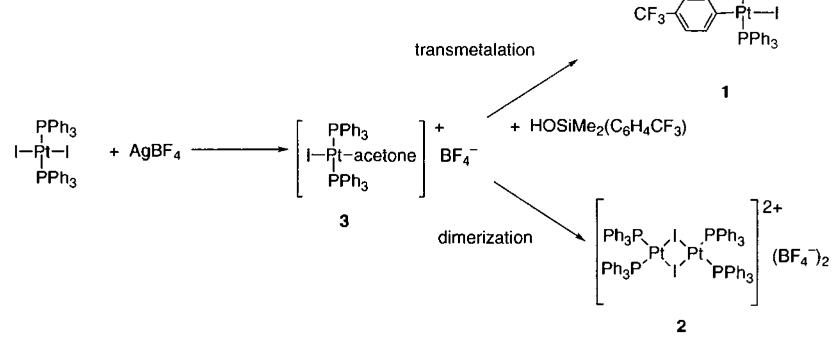
Fig. 2 shows results of an NMR study of an equimolar reaction of $AgBF_4$ with $PtI_2(PPh_3)_2$. An acetone-d_6 solution of a mixture of the two compounds exhibits the $^{31}P\{^1H\}$-NMR signal at δ 18.93 ($^1J(Pt–P) = 2530$ Hz) and a smaller signal of **2** at δ 15.69, while the signal of $PtI_2(PPh_3)_2$ (δ 13.39) is not observed at all. The presence of BF_4 counterion in the solution is demonstrated by the precipitation of AgI during the reaction and by the ^{19}F-NMR spectrum consisting of a singlet at δ −150.8, which is the position of the uncoordinated BF_4 anion. Variable-temperature measurement of the $^{31}P\{^1H\}$-NMR spectrum does not show a significant change of its peak positions and coupling constant, suggesting no occurrence of structural change of the molecule on the NMR time scale. The major complex in the solution is assigned to *trans*-$[PtI(PPh_3)_2(acetone)]BF_4$ (**3**) rather than its *cis* isomer or $[Pt(PPh_3)_2(acetone)_2](BF_4)_2$ based on the above results. The coupling constant (^1J(Pt–P) = 2530 Hz) is smaller than those of common neutral Pt(II) complexes with two *trans* PPh_3 ligands. Similar difference of ^1J(Pt–P) values between cationic platinum complexes with two *trans* PPh_3 ligands and those of the corresponding neutral complexes is observed commonly; the coupling constants of *trans*-$[PtPh(CO)(PPh_3)_2]^+$ (2651 Hz) and *trans*-$[PtCl(C_5H_4NMeCl)(PPh_3)_2]^+$ (2637 Hz) are smaller than *trans*-$PtCl(Ph)(PPh_3)_2$ (3152 Hz) and *trans*-$[PtCl(C_5H_4NMeCl)(PPh_3)_2]$ (3151 Hz) [4]. Thus, the reaction of $AgBF_4$ with $PtI_2(PPh_3)_2$ gives a mixture of complexes **2** and **3**, the latter of which exists as the major species in the solution as shown in Eq. (2). Since addition of Et_2O to the solution causes precipitation of a solid containing **2** and $PtI_2(PPh_3)_2$, due to much higher solubility of **3** than these dinuclear complexes, isolation of mononuclear cationic complex **3** was not successful.



(2)

The reaction pathways giving **1** and **2** in reaction (1) are summarized in Scheme 2. The initially formed mononuclear cationic complex **3** dimerizes to give **2**, which tends to precipitate from the solution, or reacts with silanol to cause transmetalation of the aryl group of silanol to give complex **1**. The reactions of the silanol with $PtI_2(PPh_3)_2$ in the presence of $AgPF_6$, $AgNO_3$, and $AgB(C_6H_3(CF_3)_2)_4)$ do not give **1** via the Si–C bond activation but cause formation of a mixture of fluoroplatinum complexes, $[Pt_2(\mu\text{-}I)_2(PPh_3)_4](NO_3)_2$, and a mixture of uncharacterized products, respectively.

The reaction of the silanol with an arylplatinum complex in the presence of a silver salt was then conducted with the expectation of transmetalation of an organic group from Si to Pt. *trans*-$[PtPh(PPh_3)_2$-(solvent)]BF_4, prepared in situ from *trans*-$PtI(Ph)$-$(PPh_3)_2$ and $AgBF_4$, reacts with the silanol to give a mixture of several uncharacterized Pt complexes with poor solubility in organic solvents. On the other hand, addition of Ag_2O to a toluene or THF solution of a mixture of the silanol and *trans*-$PtI(Ph)(PPh_3)_2$ unexpectedly leads to the formation of a new phenyl-(siloxo)platinum(II) complex, *trans*-$PtPh\{OSiMe_2$-$(C_6H_4CF_3\text{-}4)\}(PPh_3)_2$ (**4**) in 65% yield, as shown in Eq. (3). The siloxoplatinum complexes were prepared first by Fukuoka and Komiya who determined the molecular structure of $OSiMe_3$ coordinated Pt(II) complexes and suggested their potential utility as a precursor of inorganic materials [5]. The structure of **4** determined by X-ray crystallography is displayed in Fig. 3. The molecule has a typical square-planar geometry around the Pt(II) with Pt–O bond distance (2.091(4) Å) which is longer than those of previously reported platinum complexes such as *trans*-$PtR(OR')(PR''_3)_2$ (1.99–2.07 Å) [6,7] and *trans*-$PtR(OSiR'_3)(PR''_3)_2$ (1.99–2.00 Å) [5]. The Pt–O–Si angle (170.8(5)°) is much larger than the Pt–O–C angles observed in the alkoxo platinum complexes (< 125°) and the Pt–O–Si angles of the siloxo complexes (139.5–144.2°). The small Pt–O–C bond angles of late transition metal alkoxides have been accounted for by repulsive interactions between filled dπ



Scheme 2.

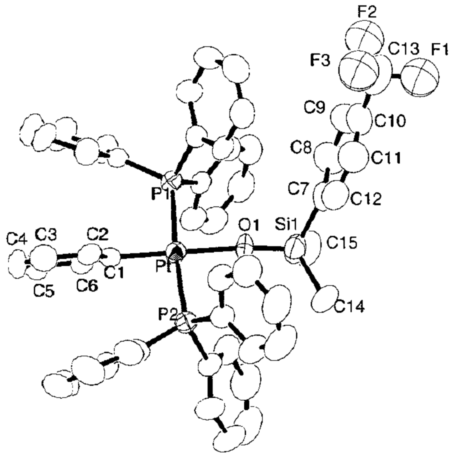
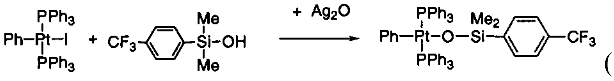


Fig. 3. ORTEP drawing of **4** at 50% ellipsoidal levels. One of the two disordered positions of fluorine atoms is shown. Solvated toluene molecule is omitted for simplicity. Selected bond distances (Å) and angles (°): Pt–P1, 2.292(2); Pt–P2, 2.294(2); Pt–C1, 1.987(6); Pt–O1, 2.091(4); Si–O1, 1.564(4); P1–Pt–P2, 175.15(6); C1–Pt–O1, 179.4(2); Pt–O1–Si, 170.8(5); P1–Pt–C1, 92.7(2); P2–Pt–C1, 92.1(2); P1–Pt–O1, 87.8(1); P2–Pt–O1, 87.4(1).

orbital of the metal center and p orbitals of the coordinated oxygen atom [8]. A severe steric repulsion between PPh_3 and the bulky siloxo ligand seems to render the Pt–O–Si angle large in spite of such an interaction between Pt and O atoms.

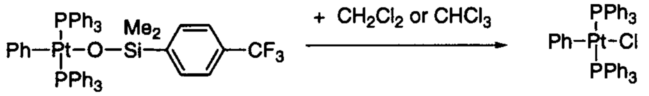


(3)

4

The ^1H-NMR spectrum of **4** in benzene-d_6 shows signals of the hydrogens of the phenyl ligand at δ 6.80, 6.32, and 6.15. They are assigned to *ortho*, *para*, and *meta* hydrogens, respectively, based on the peak positions and intensities as well as the coupling patterns. The signals of a 4-(trifluoromethyl)phenyl group are observed as two sets of doublets at δ 7.35 and 7.21. The upfield resonance at δ -0.33 is attributed to methyl protons bonded to Si. The single ^{31}P-NMR signal is observed at δ 25.01 with ^1J(Pt–P) of 3277 Hz which falls in the largest coupling constants of already reported Pt(II) complexes with two *trans* PPh_3 ligands.

Complex **4** is stable in a toluene solution at room temperature and 60°C, while it reacts readily with CH_2Cl_2 or $CHCl_3$ even at room temperature to cause its clean conversion into *trans*-$PtCl(Ph)(PPh_3)_2$ (**5**) (Eq. (4)). The product exhibits reasonable NMR (^1H, $^{31}P\{^1H\}$) signals for the formula and crystallizes in the same crystal lattices as those previously reported [9]. The above-mentioned high reactivity of the siloxoplatinum complex is not observed in alkoxoplatinum complexes that are usually stable in CH_2Cl_2 solutions. Since heating **4** in hydrocarbon solvent does not cause Si–C bond cleavage of the siloxo ligand, the siloxoplatinum complex does not participate as an intermediate in the transmetalation from silanol to Pt in reaction (1) and in our previous study [1].



4 **5**

(4)

Thus, the reactions of $HOSiMe_2(C_6H_4CF_3\text{-}4)$ with $PtI_2(PPh_3)_2$ in the presence of $AgBF_4$ and with $PtI(Ph)(PPh_3)_2$ in the presence of Ag_2O produce the iodo(aryl)platinum complex **1** and aryl(siloxo)platinum complex **4**, respectively. These results contrast with our previous results of the reaction of the silanol with $PtBr_2(PEt_3)_3$ in the presence of $AgBF_4$ and Ag_2O giving $Pt(C_6H_4CF_{-4})_2(PEt_3)_2$. The reactions of the silanol with Pt complexes having auxiliary $PPhMe_2$ ligands were conducted in order to study the effect of the kind of phosphine ligands on the reactivity of the Pt complexes. $PtI_2(PPhMe_2)_2$, on heating at 60°C in the presence of the silanol and $AgBF_4$, is converted into $[Pt(\mu\text{-}I)(PPhMe_2)_2](BF_4)_2$ exclusively, while $PtI(Ph)(PPhMe_2)_2$ does not react with the silanol in the presence of Ag_2O at all. The low reactivity of the iodoplatinum complexes for the transmetalation can be attributed to more stable coordination and less-favorable dissociation of $PPhMe_2$ than PPh_3 ligand.

The present study provided the reaction of silanol with Pt(II)–PPh_3 complexes to cause the transmetalation of silanol giving a new Pt–C bond or the siloxo complex formation depending on the coexisting ligands attached to Pt (I or Ph) and the Ag containing additives. The siloxo ligand bonded to Pt is thermally stable and does not induce intramolecular Si–C bond cleavage but reacts readily with CH_2Cl_2 or $CHCl_3$ to give the corresponding chloroplatinum complex. Further elucidation of transmetalation of organosilicon compounds to Group 10 transition metals would serve to comprehend the reaction mechanism of synthetic organic reactions that involve these transmetalation processes.

3. Experimental

Manipulations of the complexes were carried out under N_2 or Ar using the standard Schlenk technique. The NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded on JEOL EX-400 or Varian Mercury300 spectrometers at 25°C unless otherwise stated. Elemental analyses were carried out on a Yanaco MT-5 CHN Autorecorder. $PtI_2(PPh_3)_2$ and $PtI(Ph)(PPh_3)_2$ were prepared from the reaction of PPh_3 with PtI_2(cod) and PtI(Ph)(cod), respectively [10].

3.1. Reaction of $HOSiMe_2(C_6H_4CF_3$-4) with $PtI_2(PPh_3)_2$ in the presence of $AgBF_4$

An Me_2CO solution (30 cm^3) of $PtI_2(PPh_3)_2$ (195 mg, 0.20 mmol) and $AgBF_4$ (39 mg, 0.20 mmol) was stirred for 30 min at room temperature (r.t.). After removing the precipitated AgI by filtration, $HOSiMe_2(C_6H_4CF_3$-4) (44 mg, 0.20 mmol) was added to the filtrate. The solution was heated at 60°C for 2 h, during which a yellow solid was precipitated. The solid was collected by filtration and dried in vacuo to give **2** as a yellow solid (102 mg, 54%). The remained filtrate was evaporated to dryness, and the yellow solid obtained was washed with hexane (5 cm^3) and then extracted with C_6H_6 to remove a small amount of **2**. Evaporation of the C_6H_6 extract and washing of the resulting solid product with hexane gave **1** as a pale yellow solid (33 mg, 17%). Further recrystallization from C_6H_5Me–hexane afforded crystals for X-ray analysis grade.

Data for **1**. Anal. Found: C, 52.17; H, 3.85; F, 5.61; I, 10.91. Calc. for $C_{43}H_{34}F_3IP_2Pt$: C, 52.08; H, 3.46; F, 5.75; I, 12.80%. ^{1}H-NMR (300 MHz, benzene-d_6): $\delta = 7.73$–7.66 (m, 12H, C_6H_5), 6.98–6.96 (m, 18H, C_6H_5), 6.81 (d, 2H, ^3J(H–H) = 8 Hz, ^3J(Pt–H) = 54 Hz, Pt–C_6H_4-*o*), 6.41 (d, 2H, ^3J(H–H) = 8 Hz, Pt–C_6H_4-*m*). ^{31}P{^{1}H}-NMR (121.5 MHz, benzene-d_6): $\delta = 21.89$ (s, ^1J(Pt–P) = 2999 Hz). ^{13}C{^{1}H}-NMR (75.3 MHz, $CDCl_3$): $\delta = 154.64$ (t, ^1J(Pt–C) = 370 Hz, ^2J(P–C) = 8 Hz, Pt–C_{ipso}), 136.03 (t, ^3J(P–C) = 3 Hz, Pt–C_6H_4-*o*), 134.87 (vt, $J = 6$ Hz, P–C_6H_5-*o*), 130.90 (q, ^2J(F–C) = 58 Hz, Pt–C_6H_4-*p*), 130.70 (vt, $J = 28$ Hz, P–C_6H_5-*ipso*), 130.09 (s, P–C_6H_5-*p*), 127.93 (q, ^1J(F–C) = 190 Hz, CF_3), 127.70 (vt, $J = 5$ Hz, P–C_6H_5-*m*), 123.22 (q, ^3J(Pt–C) = 67 Hz, ^3J(F–C) = 4 Hz, Pt–C_6H_4-*m*). ^{19}F{^{1}H}-NMR (188.2 MHz, benzene-d_6): $\delta = -61.56$ (s). Data for **2**. Anal. Found: C, 46.62; H, 3.31; F, 6.40; I, 13.48. Calc. for $C_{72}H_{60}P_4B_2F_8I_2Pt_2$: C, 46.33; H, 3.24; F, 8.14; I, 13.60%. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.35$ (br, C_6H_5). ^{31}P{^{1}H}-NMR (121.5 MHz, $CDCl_3$): $\delta = 14.59$ (s, ^1J(Pt–P) = 3530 Hz); (161.5 MHz, acetone-d_6): $\delta = 15.69$ (s, ^1J(Pt–P) = 3525 Hz).

A similar reaction with addition of PPh_3 caused separation of insoluble $[PtI(PPh_3)_3]BF_4$ from the solution and did not give **1** at all.

3.2. Reaction of $AgBF_4$ with $PtI_2(PPh_3)_2$

To an Me_2CO solution (10 cm^3) of $PtI_2(PPh_3)_2$ (195 mg, 0.20 mmol) was added $AgBF_4$ (39 mg, 0.20 mmol), and the mixture was stirred for 30 min at r.t. The precipitated AgI was removed by filtration. The ^{31}P{^{1}H}-NMR spectrum of the solution shows the signals of **2** and **3** in a ca. 5:95 ratio. After concentration of the solution to 3 or 4 cm^3 under vacuum, Et_2O (10 cm^3) was added to cause precipitation of a yellow solid. The ^{31}P{^{1}H}-NMR spectrum of the solid product contains the signals of **2** and $PtI_2(PPh_3)_2$ in a 30:70 ratio.

3.3. Reaction of $HOSiMe_2(C_6H_4CF_3$-4) with $PtI(Ph)(PPh_3)_2$ in the presence of Ag_2O

To a C_6H_5Me (25 cm^3) suspension of $PtI(Ph)(PPh_3)_2$ (323 mg, 0.35 mmol) were added Ag_2O (81 mg, 0.35 mmol) and $HOSiMe_2(C_6H_4CF_3$-4) (93 mg, 0.42 mmol), in this order. The reaction mixture was stirred 24 h at r.t. The resulting gray suspension was then filtrated to remove a gray solid, and the solid was washed with C_6H_5Me (5 $cm^3 \times 2$). The combined filtrate and washings were evaporated to give a white solid, which was washed with hexane (10 $cm^3 \times 3$) and dried in vacuo to give **4** as a colorless solid (232 mg, 0.23 mmol, 65%). Recrystallization from a toluene–hexane solution afforded colorless crystals appropriate for X-ray analysis. Anal. Found: C, 60.45; H, 4.76; F, 5.44. Calc. for $C_{51}H_{45}F_3OP_2PtSi$: C, 60.29; H, 4.46; F, 5.61%. ^{1}H-NMR (300 MHz, benzene-d_6): $\delta = 7.74$–7.67 (m, 12H, $P(C_6H_5)_3$), 7.35 (d, 2H, ^3J(H–H) = 8 Hz, C_6H_4-*o*), 7.21 (d, 2H, ^3J(H–H) = 8 Hz, C_6H_4-*m*), 7.02–6.94 (m, 18H, $P(C_6H_5)_3$), 6.80 (d, 2H, ^3J(H–H) = 8 Hz, ^3J(Pt–H) = 49 Hz, Pt–C_6H_5-*o*), 6.32 (t, 1H, ^3J(H–H) = 7 Hz, Pt–C_6H_5-*p*), 6.15 (t, 2H, ^3J(H–H) = 7 Hz, C_6H_5-*m*), -0.33 (s, 6H, CH_3). ^{31}P{^{1}H}-NMR (121.5 MHz, benzene-d_6): $\delta = 25.01$ (s, ^1J(Pt–P) = 3277 Hz). ^{13}C{^{1}H}-NMR (100.4 MHz, THF-d_8): $\delta = 153.67$ (br, Pt–C_6H_5-*ipso*), 139.47 (s, Pt–C_6H_5-*o*), 139.44 (s, Si–C_6H_4-*ipso*), 135.91 (vt, $J = 6$ Hz, P–C_6H_5-*o*), 134.36 (q, $J = 9$ Hz, Si–C_6H_4-*p*), 134.24 (s, Si–C_6H_4-*o*), 131.70 (vt, $J = 26$ Hz, P–C_6H_5-*ipso*), 130.75 (s, P–C_6H_5-*p*), 128.57 (vt, $J = 6$ Hz, P–C_6H_5-*m*), 127.44 (s, Pt–C_6H_5-*m*), 125.96 (q, $J = 272$ Hz, CF_3), 123.54 (q, ^3J(F–C) = 4 Hz, Si–C_6H_4-*m*), 120.82 (s, Pt–C_6H_5-*p*), 2.84 (s, CH_3).

3.4. Reaction of $HOSiMe_2(C_6H_4CF_3$-4) with *trans*-$[PtPh(PPh_3)_2]BF_4$ in the presence and absence of Ag_2O

To a THF or C_6H_5Me (5 cm^3) solution of PtI(Ph)-$(PPh_3)_2$ (195 mg, 0.21 mmol) was added $AgBF_4$ (39 mg, 0.20 mmol), and the mixture was stirred for 30 min. The residue of AgI and insoluble Pt complexes was formed. $HOSiMe_2(C_6H_4CF_3$-4) (44 mg, 0.20 mmol) or a mixture of the silanol (44 mg, 0.20 mmol) and Ag_2O (46 mg, 0.20 mmol) was added to the above reaction mixture. Heating the mixture did not cause significant conversion of the initially formed cationic phenylplatinum species.

3.5. Reaction of $HOSiMe_2(C_6H_4CF_3\text{-}4)$ with $PtI_2(PPhMe_2)_2$

To an NMR tube containing $AgBF_4$ (25 mg, 0.13 mmol) was introduced $PtI_2(PPhMe_2)_2$ (28 mg, 0.038 mmol) and acetone-d_6 (0.7 cm^3) under Ar atmosphere. After the reaction for 1 h at r.t. the $^{31}P\{^1H\}$-NMR spectrum indicates disappearance of the signals of the starting complex (δ −10.78, *cis* form, J(Pt–P) = 3370 Hz and δ −16.84, *trans* form, J(Pt–P) = 2308 Hz) and existence of a new signal at δ −5.00 (J(Pt–P) = 3452 Hz) as the dominant signal. The signal is assigned to $[Pt(\mu\text{-}I)(PPhMe_2)_2](BF_4)_2$. Heating the reaction mixture for 72 h at 60°C did not cause a significant change of the NMR spectra.

3.6. Reaction of $HOSiMe_2(C_6H_4CF_3)$ with $PtI(Ph)(PPhMe_2)_2$

To an NMR tube containing $PtI(Ph)(PPhMe_2)_2$ (39 mg, 0.057 mmol) was introduced acetone-d_6 (0.7 cm^3), Ag_2O (13 mg, 0.057 mmol), and $HOSiMe_2(C_6H_4CF_3\text{-}4)$ (13 mg, 0.057 mmol) under Ar atmosphere. After the reaction for 24 h at r.t. the $^{31}P\{^1H\}$-NMR spectrum contains signals of $PtI(Ph)(PPhMe_2)_2$ (δ −11.27, J(Pt–P) = 2797 Hz) only. Heating of the reaction mixture for 6 h at 60°C did not cause change of the spectra.

3.7. Reaction of **4** with CH_2Cl_2 or $CHCl_3$

To complex **4** in an NMR tube was added $CDCl_3$ at r.t. under Ar. Complete dissolution of **4** required 10 min or longer. The $^{31}P\{^1H\}$-NMR spectrum obtained soon after dissolution contained the signals of **4** and **5** in ca. 1:2 peak area ratio.

Table 1
Crystallographic data and details of structure refinement

Complex	**1**	**4**
Formula	$C_{43}H_{34}F_3IP_2Pt$	$C_{51}H_{45}F_3OP_2$-$SiPt\cdot C_{3.5}H_4$
Formula weight	991.68	1108.03
Dimensions (mm)	0.43 × 0.35 × 0.33	0.55 × 0.30 × 0.20
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)
Unit cell dimensions		
a (Å)	25.285(2)	26.902(5)
b (Å)	13.736(2)	11.469(3)
c (Å)	11.549(2)	32.689(3)
β (°)	112.44(2)	105.69(1)
V (Å^3)	3707.5(8)	9710(3)
Z	4	8
ρ_c (g cm^{-3})	1.777	1.368
F(000)	1920	4264
μ (Mo–Kα) (mm^{-1})	4.735	3.056
Measured reflections	9053	11887
Used reflections [$I > 3.0\sigma(I)$]	3578	6532
Variables	227	545
R (R_w)	0.035 (0.036)	0.045 (0.036)

Recrystallization of **4** from CH_2Cl_2–hexane or $CHCl_3$–hexane afforded **5** as colorless crystals. The lattice parameters of the obtained crystals (orthorhombic, $a = 11.79(1)$, $b = 23.75(1)$, $c = 25.55(1)$ Å with $Pbca$) were the same as those reported previously (orthorhombic, $a = 11.800(4)$, $b = 23.705(2)$, $c = 25.549(5)$ Å with the same space group) [9]. Data for **5**. Anal. Found: C, 60.81; H, 4.35; Cl, 4.28. Calc. for $C_{42}H_{35}P_2ClPt$: C, 60.62; H, 4.24; Cl, 4.26%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.52 (m, 12H, $P(C_6H_5)_3$), 7.28 (m, 18H, $P(C_6H_5)_3$), 6.65 (d, 2H, J(H–H) = 7 Hz, J(Pt–H) = 48 Hz, C_6H_4-*o*), 6.27 (t, 1H, J(H–H) = 8 Hz, C_6H_4-*p*), 6.10 (t, 2H, J(H–H) = 7 Hz, C_6H_4-*m*). $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ = 25.03 (s, ^1J(Pt–P) = 3150 Hz).

3.8. X-ray crystallography

Crystals of **1** and **4** suitable for X-ray diffraction study were obtained by recrystallization from C_6H_5Me–hexane and mounted in glass capillaries under Ar. Data were collected at 23°C on a Rigaku AFC-5R or -7R automated four-circle diffractometer equipped with monochromated Mo–Kα radiation (λ = 0.71073 Å). Calculations were carried out using a program package TEXSAN for Windows. The structures were solved by a combination of heavy atom method and subsequent Fourier techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 148989 and 148990 for compounds **1** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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