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Hexanuclear Pt complexes composed of two cyclic triplatinum units connected with 1,4-diphenylene and 1,1′-ferrocenylene spacer

Masumi Itazaki, Osamu Kitami, Makoto Tanabe, Yasushi Nishihara, Kohtaro Osakada *

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

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Abstract

1,4-Bis(dimethylsilyl)benzene reacted with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ at room temperature to yield trinuclear Pt complex $[Pt_3(SiMe_2C_6H_4SiMe_2H)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**1a**). Heating a solution containing an equimolar mixture of $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ and **1a** at 60 °C produced a hexanuclear Pt complex $[(PEt_3)_2(\mu\text{-}PPh_2)_3Pt_3(SiMe_2C_6H_4SiMe_2)Pt_3(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**2a**). Complex **1a** was characterized by X-ray crystallography and NMR spectroscopy, while the structure of **2a** was determined by X-ray crystallography of single crystals containing **2a** and $[Pt_3H_2(PEt_3)_2(\mu\text{-}PPh_2)_4]$ in 1:1 ratio. $[Pt_3(SiMe_2fcSiMe_2H)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (fc = $Fe(\eta^5\text{-}C_5H_4)_2$) (**1b**) and $[(PEt_3)_2(\mu\text{-}PPh_2)_3Pt_3(SiMe_2fcSiMe_2)Pt_3(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**2b**) were obtained similarly from the reactions of 1,1′-bis(dimethylsilyl)ferrocene with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ and characterized by NMR spectroscopy and elemental analyses.

Keywords: Platinum; Phosphido; Ferrocene; Cluster; Si-ligands

1. Introduction

Many cyclic trinuclear Pt complexes were stabilized by electron-withdrawing bridging ligands such as CO and CNR. Phosphides (PR_2) are also employed as the bridging ligands of the cyclic triplatinum complexes having Pt(I) and Pt(II) centers [1–3]. Braunstein et al. reported a triplatinum complex, $[Pt_3Ph(PPh_3)_2(\mu\text{-}PPh_2)_3]$, with a Pt(I)–Pt(I)–Pt(II) core whose metal centers are bridged by PPh_2 ligands [4–7]. Recently, we reported that the reaction of PPh_2H with $[Pt(PEt_3)_3]$ afforded $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ as one of the products [8]. The hydride ligand of the 46-electron cyclic triplatinum complex reacts easily with various organic compounds. Addition of arylboronic acid to a solution of $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ induces elimination of H_2 to produce the cationic triplatinum complex and the boron-containing counter anion, $[Pt_3(PEt_3)_3(\mu\text{-}PPh_2)_3]$–$[HO\text{–}BAr\text{–}O\text{–}(BOAr)_3]$. A similar ionic complex, $[Pt_3(PEt_3)_3(\mu\text{-}PPh_2)_3]I$, was obtained from the reactions of MeI and of CuI with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$. H_2SiPh_2 and $HSiPh_3$ also reacted with the triplatinum complex to produce $[Pt_3(SiXPh_2)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (X = H, Ph). Analogous reaction of organic compound having two Si–H groups with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ would afford the complexes containing two cyclic Pt_3 units connected by the Si-containing spacer. In this paper, we report the preparation of new hexanuclear Pt complexes from the reaction of bis-silyl compounds with the cyclic triplatinum-hydrido complex.

2. Results and discussion

1,4-Bis(dimethylsilyl)benzene reacts with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ at room temperature to produce a trinuclear complex $[Pt_3(SiMe_2C_6H_4SiMe_2H)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**1a**), as shown in Eq. (1).

* Corresponding author. Tel.: +81 45 924 5222; fax: +81 45 924 5224/5276.
E-mail address: kosakada@res.titech.ac.jp (K. Osakada).

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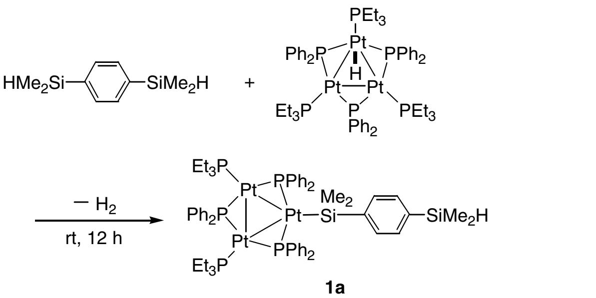
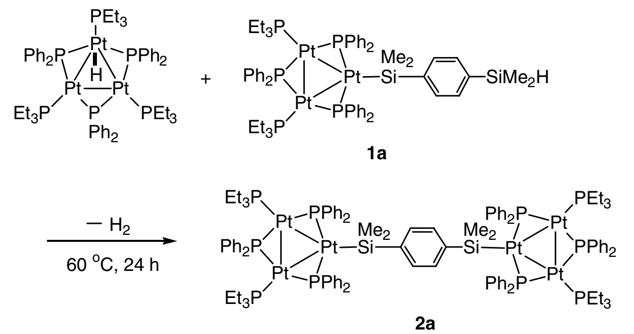


(1)

Fig. 1 displays the structure of **1a** determined by X-ray crystallography. One of the P atoms is slightly deviated from the Pt_3 plane. The Pt2–Pt3 bond (3.0440(5) Å) is slightly longer than the other Pt–Pt bonds (3.0203(4) and 2.9879(5) Å). The ^{1}H NMR spectrum of **1a** shows the signals due to Si–Me hydrogens at δ 0.91 and 0.33. The former signal is flanked with ^{195}Pt satellite signals ($J(PtH) = 34$ Hz) and is assigned to the Pt–$SiMe_2$ hydrogens. The latter signal is split as a doublet due to the coupling to the Si–H hydrogen ($J(HH) = 3.9$ Hz) and is assigned to the methyl hydrogens of the $SiHMe_2$ group. The Si–H hydrogen signal is observed as a septet ($J(HH) = 3.9$ Hz) at δ 4.75. The $J(SiH)$ value is determined as 183 Hz. The $^{13}C\{^{1}H\}$ NMR spectrum of **1a** also exhibits the signals due to $SiMe_2$ carbons at δ −3.4 and 6.8. The $^{31}P\{^{1}H\}$ NMR spectrum contains three signals at δ −3.6, 82.3, and 94.3, which are reasonably assigned to two PEt_3 ligands, one PPh_2 ligand bridging the Pt centers that are not bonded to the Si center, and two other unequivalent PPh_2 ligands, respectively, based on comparison of the spectrum with a computer simulated one [9].

Heating a toluene solution containing an equimolar mixture of **1a** and $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ at 60 °C leads to isolation of a hexanuclear complex, $[(PEt_3)_2(\mu\text{-}PPh_2)_3Pt_3(SiMe_2C_6H_4SiMe_2)Pt_3(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**2a**) (Eq. (2)).



(2)

Although crystals of **2a** suited for X-ray crystallography were not obtained from its solution, cooling the reaction mixture of **1a** and $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ containing a small amount of PPh_2H impurity caused separation of single crystals composed of equimolar **2a** and $[Pt_3H_2(PEt_3)_2(\mu\text{-}PPh_2)_4]$ [8]. Formation of the latter complex in the solution may be attributed to the reaction of PPh_2H with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$. Fig. 2 shows the structure of the complexes. The two points of crystallo-

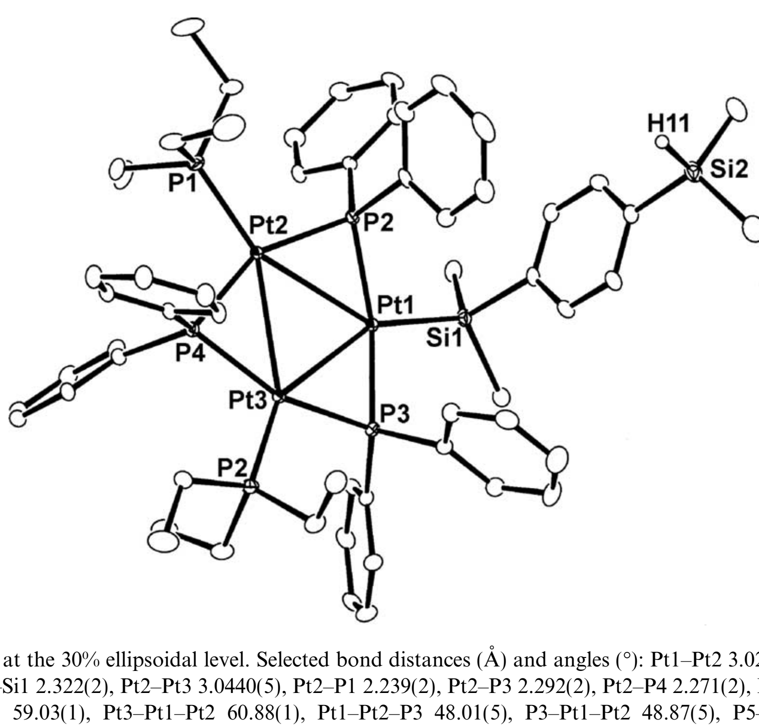


Fig. 1. ORTEP drawing of **1a** at the 30% ellipsoidal level. Selected bond distances (Å) and angles (°): Pt1–Pt2 3.0203(4), Pt1–Pt3 2.9879(5), Pt1–P3 2.261(2), Pt1–P5 2.250(2), Pt1–Si1 2.322(2), Pt2–Pt3 3.0440(5), Pt2–P1 2.239(2), Pt2–P3 2.292(2), Pt2–P4 2.271(2), Pt3–P2 2.242(2), Pt3–P4 2.276(2), Pt3–P5 2.315(2), Pt1–Pt2–Pt3 59.03(1), Pt3–Pt1–Pt2 60.88(1), Pt1–Pt2–P3 48.01(5), P3–Pt1–Pt2 48.87(5), P5–Pt1–Pt2 110.95(5), Si1–Pt1–Pt2 146.08(6), Pt1–Pt2–P1 150.97(6), Pt1–Pt2–P4 106.35(6), Pt1–Pt3–Pt2 60.09(1), P3–Pt1–Pt3 107.82(5), Pt1–Pt3–P5 48.17(5), P5–Pt1–Pt3 50.08(5), Si1–Pt1–Pt3 153.04(6), Pt1–Pt3–P4 107.26(5), Pt1–Pt3–P2 150.16(6), Pt1–P3–Pt2 83.12(6), P5–Pt1–P3 154.82(9), Si1–Pt1–P3 98.33(8), Si1–Pt1–P5 102.97(8), Pt1–Si1–C1 115.2(3), Pt1–Si1–C2 117.3(3), Pt1–Si1–C3 110.3(3), P3–Pt2–Pt3 105.19(6), Pt2–Pt3–P5 108.26(5), P1–Pt2–Pt3 149.92(5), Pt2–Pt3–P4 47.91(5), P4–Pt2–Pt3 48.04(6), Pt2–Pt3–P2 149.59(6), P3–Pt2–P1 104.39(8), P4–Pt2–P1 102.10(8), P4–Pt2–P3 153.15(8), P5–Pt3–P2 102.07(8), P4–Pt3–P2 102.51(8), P5–Pt3–P4 154.28(8).

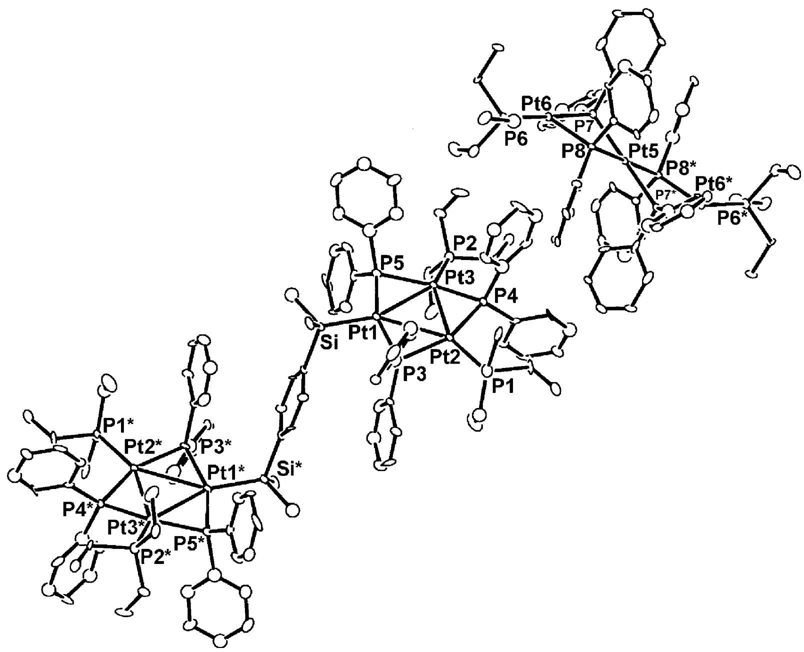
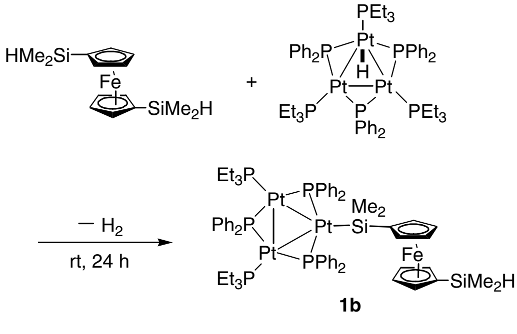


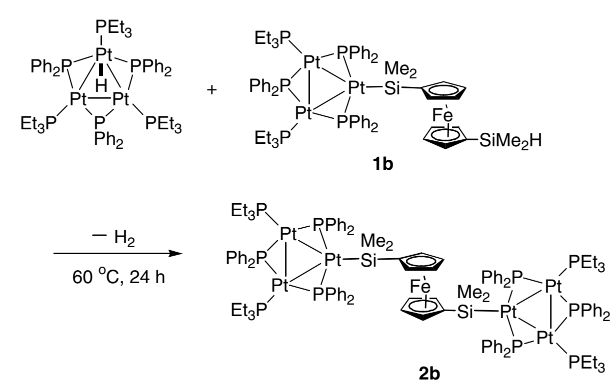
Fig. 2. ORTEP drawing of **2a** at the 30% ellipsoidal level. The peaks with asterisks are due to the atoms which are crystallographically equivalent to those with the same numbers without asterisks. Selected bond distances (Å) and angles (°): Pt1–Pt2 3.052(1), Pt1–Pt3 3.025(2), Pt1–P3 2.239(7), Pt1–P5 2.25(1), Pt1–Si1 2.33(1), Pt2–Pt3 2.966(2), Pt2–P1 2.235(6), Pt2–P3 2.304(9), Pt2–P4 2.26(1), Pt3–P2 2.25(1), Pt3–P4 2.262(6), Pt3–P5 2.310(8), Pt1–Pt2–Pt3 60.33(4), Pt3–Pt1–Pt2 58.43(4), Pt1–Pt2–P3 46.9(2), P3–Pt1–Pt2 48.7(2), P5–Pt1–Pt2 107.4(2), Si1–Pt1–Pt2 146.9(2), Pt1–Pt2–P1 149.0(3), Pt1–Pt2–P4 108.6(2), Pt1–Pt3–Pt2 61.23(4),P3–Pt1–Pt3 106.4(2), Pt1–Pt3–P5 47.6(2), P5–Pt1–Pt3 49.3(2), Si1–Pt1–Pt3 154.4(2), Pt1–Pt3–P4 109.6(3), Pt1–Pt3–P2 147.2(2), Pt1–P3–Pt2 84.4(3), P5–Pt1–P3 155.6(3), Si1–Pt1–P3 98.3(3), Pt1–P5–Pt3 83.1(2), Si1–Pt1–P5 105.7(3), Pt1–Si1–C1 114(1), Pt1–Si1–C2 112(1), Pt1–Si1–C3 115.2(9), P3–Pt2–Pt3 106.5(2), Pt2–Pt3–P5 108.5(3), P1–Pt2–Pt3 150.3(3), Pt2–Pt3–P4 49.1(3), P4–Pt2–Pt3 49.0(2), Pt2–Pt3–P2 148.3(2), P3–Pt2–P1 102.1(3), P4 Pt2–P1 102.4(3), P4–Pt2–P3 155.4(2), Pt2–P4–Pt3 81.9(3), P5–Pt3–P2 102.2(3), P4–Pt3–P2 102.6(3), P5–Pt3–P4 153.5(3).

graphic symmetry in the unit cell are located at the center of phenylene group of **2a** and at the central Pt atom of $[Pt_3H_2(PEt_3)_2(\mu\text{-}PPh_2)_4]$, respectively. Bond parameters of the triplatinum core of **2a** are similar to those of **1a**, although the Pt2–Pt3 bond (2.966(2) Å) is shorter than the other Pt–Pt bonds (3.052(1) and 3.025(2) Å). The structure and the bond parameters of $[Pt_3H_2(PEt_3)_2(\mu\text{-}PPh_2)_4]$ in the crystals are similar to those obtained from its single crystals [8]. The ^{1}H NMR spectrum of isolated **2a** exhibits the signals due to hydrogens of the Pt–SiMe$_2$ groups at δ 0.96 (J(PtH) = 32 Hz).

1,1′-Bis(dimethylsilyl)ferrocene also reacts with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ to yield the trinuclear and hexanuclear Pt complexes as depicted in Eqs. (3) and (4).



(3)



(4)

The reaction at room temperature produces complex **1b** which is isolated from the reaction mixture by recrystallization. Isolation of complex **2b** was carried out by the reaction of 1,1′-bis(dimethylsilyl)ferrocene with **1b** on heating. Both complexes gave satisfactory NMR data and elemental analyses. Complex **1b** exhibits the ^{1}H NMR signals of SiMe$_2$ hydrogens at δ 0.21 (doublet) and δ 0.29 (singlet), while the SiMe$_2$ hydrogen signals of **2b** are observed as a singlet at δ 0.97. The Si–H hydrogen signal for **1b** is observed at δ 4.31. The $^{13}C\{^1H\}$ NMR signals due to the methyl carbons appear at δ −2.91 and 7.28 for **1b** and at δ 7.22 for **2b**. All these data are consistent with the structures in Eqs. (3) and (4).

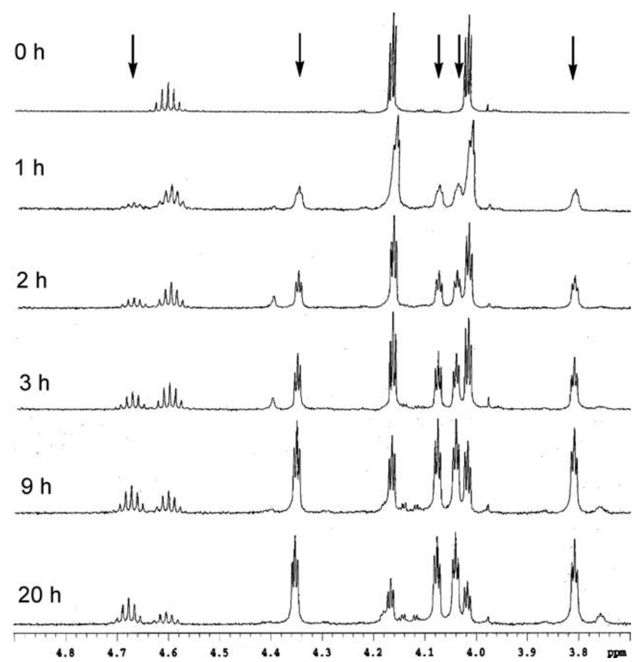


Fig. 3. Change of the ^{1}H NMR spectra during the reaction of 1,1′-bis(dimethylsilyl)ferrocene with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ at 40 °C in C_6D_6. Peaks with arrows are due to **1b** formed by the reaction.

Fig. 3 depicts change of the ^{1}H NMR spectra during the 2:1 reaction of 1,1′-bis(dimethylsilyl)ferrocene with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ at 40 °C. Amount of complex **1b** increases gradually at this temperature. Further coupling of the formed **1b** with $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ is not observed under the conditions.

In summary, this paper presented preparation of new hexanuclear Pt complexes via coupling of the trinuclear Pt complex having a hydride ligand by the spacers. Smooth reaction of the Si–H group of the trinuclear Pt complex with another triplatinum molecule suggests possible synthesis of many multinuclear complexes containing the cyclic Pt_3-phoshpido units.

3. Experimental

3.1. General

All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a nitrogen atmosphere. Hexane and toluene were distilled from sodium benzophenone ketyl and stored under nitrogen. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian Mercury 300 or JEOL Lamda 500 spectrometers. Peak position of the ^{31}P{^{1}H} NMR spectrum was referenced to an external 85% H_3PO_4. $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ was prepared according to the literature [8]. 1,4-Bis(dimethylsilyl)benzene and 1,1′-bis(dimethylsilyl)ferrocene were obtained from Aldrich and were purified before use. IR absorption spectra were recorded with Shimadzu FT/IR-8100 spectrometers. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

3.2. Preparation of $[Pt_3(SiMe_2C_6H_4SiMe_2H)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (*1a*) and $[Pt_3(SiMe_2fcSiMe_2H)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ ($fc = Fe(\eta^5\text{-}C_5H_4)_2$) (*1b*)

To a toluene (8 mL) solution of $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ (147 mg, 0.10 mmol) was added 1,4-bis(dimethylsilyl)benzene (28.7 mg. 0.15 mmol) at room temperature. Stirring the reaction mixture at room temperature turned color of the solution from orange to dark red. The solvent was removed under reduced pressure. The residual material was washed with 3 mL of hexane twice at −70 °C and dried in vacuo to give $[Pt_3(SiMe_2C_6H_4SiMe_2H)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**1a**) (137 mg, 87%) as a red solid. Anal. Calc. for $C_{58}H_{77}P_5Pt_3Si_2$: C, 44.36; H, 4.94. Found: C, 44.55; H, 4.80%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.33 (d, 6H, HSiCH_3, ^{3}J(HH) = 3.9 Hz), 0.37 (dt, 18H, PCH$_2$CH_3, ^{3}J(HP) = 17 Hz, ^{3}J(HH) = 8 Hz), 0.91 (s, 6H, PtSiCH_3, ^{3}J(HPt) = 34.2 Hz), 1.50 (m, 12 H, PCH_2CH$_3$, ^{3}J(HH) = 8 Hz), 4.75 (sep, 1H, SiH, ^{3}J(HH) = 3.9 Hz, ^{3}J(HSi) = 183 Hz), 7.00, (m, 12H, PC$_6H_5$-*meta*), 7.11 (t, 6H, PC$_6H_5$-*para*, ^{3}J(HH) = 7.5 Hz), 7.23 (d, 2H, SiC$_6H_4$, ^{3}J(HH) = 7.8 Hz), 7.34 (d, 2H, SiC$_6H_4$, ^{3}J(HH) = 7.8 Hz), 7.84 (m, 8H, PC$_6H_5$-*ortho*), 7.90 (d, 2H, PC$_6H_5$-*ortho*, ^{3}J(HH) = 7.5 Hz), 7.91 (d, 2H, PC$_6H_5$-*ortho*, ^{3}J(HH) = 7.5 Hz). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 25 °C): δ −3.4 (HSiCH$_3$), 6.8 (PtSiCH$_3$), 8.0 (PCH$_2$$CH_3$), 19.0 (vt, ^{1+4}J(CP) = 16 Hz, PCH$_2$CH$_3$), 126.9 (vt, PC_6H$_5$-*meta*, ^{3+5}J(CP) = 5.2 Hz), 127.0 (PC_6H$_5$-*meta*), 127.3 (PC_6H$_5$-*para*), 127.4 (br, PC_6H$_5$-*para*), 131.1 (SiC_6H$_4$-*ipso*), 132.0 (SiC_6H$_4$), 133.4 (SiC_6H$_4$-*ipso*), 133.6 (d, PC_6H$_5$-*ortho*, ^{2}J(CP) = 12 Hz), 133.7 (SiC_6H$_4$), 134.0 (vt, ^{2+4}J(CP) = 6 Hz, PC_6H$_5$-*ortho*), 140.3 (vt, ^{1+3}J(CP) = 19 Hz, PC_6H$_5$-*ipso*), 140.5 (d, J(CP) = 15 Hz, PC_6H$_5$-*ipso*). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C): δ −3.62 (PEt$_3$, ^{3}J(PP) = 119 Hz, ^{2}J(PPt) = 177 Hz, J(PPt) = 4135 Hz), 82.3 (PPh$_2$, ^{2}J(PP) = 193 Hz, ^{2}J(PPt) = −57 Hz, J(PPt) = 2391 Hz), 94.3 (PPh$_2$, ^{2}J(PP) = 193, 247 Hz, ^{2}J(PPt) = −102 Hz, J(PPt) = 2120, 2321 Hz). IR (KBr): ν(SiH) = 2109 cm^{-1}.

Complex $[Pt_3(SiMe_2fcSiMe_2H)(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**1b**) was obtained from a similar reaction using 1,1′-bis(dimethylsilyl)ferrocene. Yield: 43%. Anal. Calc. for $C_{62}H_{81}FeP_5Pt_3Si_2$: C, 44.37; H, 4.86. Found: C, 44.12; H, 4.62%. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 0.21 (d, 6H, HSiCH_3, ^{3}J(HH) = 4.0 Hz), 0.29 (s, 6H, PtSiCH_3, ^{3}J(HPt) = 33 Hz), 0.40 (dt, 18H, PCH$_2$CH_3, ^{3}J(HH) = 7.5 Hz, ^{3}J(HP) = 17 Hz), 1.49 (br m, 12H, PCH_2CH$_3$, ^{3}J(HH) = 7.5 Hz), 3.37 (s, 2H, C$_5H_4$), 3.85 (s, 2H, C$_5H_4$), 3.89 (s, 2H, C$_5H_4$), 4.15 (s, 2H, C$_5H_4$), 4.31 (sep, 1H, SiH, ^{3}J(HH) = 4.0 Hz), 7.14-7.19

(m, 12H, C_6H_5-*meta*), 7.20 (t, 2H, C_6H_5-*para*, ^3J(HH) = 7.0 Hz), 7.25 (t, 4H, C_6H_5-*para*, ^3J(HH) = 7.0 Hz), 7.55 (m, 8H, C_6H_5-*ortho*), 7.65 (d, 2H, C_6H_5-*ortho*, ^3J(HH) = 7.0 Hz), 7.67 (d, 2H, C_6H_5-*ortho*, ^3J(HH) = 7.0 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ −2.91 (HSiCH_3), 7.28 (PtSiCH_3), 7.99 (PCH_2CH_3), 18.9 (vt, ^{1+3}J(CP) = 15.6 Hz, PCH_2CH_3), 69.3 (C_5H_4), 71.7 (C_5H_4), 72.9 (C_5H_4), 73.5 (C_5H_4), 127.3 (PC_6H_5-*meta*), 127.4 (vt, PC_6H_5-*meta*, ^{3+5}J(CP) = 4.6 Hz), 127.8 (PC_6H_5-*para*), 127.9 (PC_6H_5-*para*), 133.6 (d, PC_6H_5-*ortho*, ^2J(CP) = 12 Hz), 134.1 (vt, PC_6H_5-*ortho*, ^{2+4}J(CP) = 6.7 Hz), 140.5 (m, PC_6H_5-*ipso*), 140.7 (d, PC_6H_5-*ipso*, ^2J(CP) = 3.0 Hz). The C_5H_4-*ipso* signals were not observed due to small intensity. IR (KBr): ν(SiH) = 2103 cm^{-1}.

3.3. Preparation of $[(PEt_3)_2(\mu\text{-}PPh_2)_3Pt_3(SiMe_2C_6H_4SiMe_2)Pt_3(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (2a) and $[(PEt_3)_2(\mu\text{-}PPh_2)_3Pt_3(SiMe_2fcSiMe_2)Pt_3(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (fc = $Fe(\eta^5\text{-}C_5H_4)_2$) (2b)

A toluene (8 mL) solution of a mixture of **1a** (118 mg, 0.075 mmol) and $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ (112 mg, 0.075 mmol) was heated at 60 °C with stirring. Color of the solution changed from orange to red during the reaction. After stirring for 24 h, the solvent was removed under reduced pressure. The resulting material was washed with 3 mL of hexane twice at room temperature and dried in vacuo to yield $[(PEt_3)_2(\mu\text{-}PPh_2)_3Pt_3(SiMe_2C_6H_4SiMe_2)Pt_3(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**2a**) (157 mg, 71%). Crystals of **2a** suitable for X-ray crystallography were not obtained from recrystallization of the solution. Anal. Calc. for $C_{106}H_{136}P_{10}Pt_6Si_2$: C, 43.21; H, 4.65. Found: C, 43.26; H, 4.67%. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.39 (dt, 36 H, PCH_2CH_3, ^3J(HH) = 7.5 Hz, ^3J(HP) = 16 Hz), 0.96 (s, 12H, Si(CH_3), ^3J(HPt) = 32 Hz), 1.50 (dq, 24H, PCH_2CH_3, ^3J(HH) = 7.5 Hz, ^2J(HP) = 7.3 Hz), 6.98 (s, 4H, SiC_6H_4), 7.02 (t, 24H, PC_6H_5-*meta*, ^3J(HH) = 7.5 Hz), 7.11 (t, 12H, PC_6H_5-*para*, ^3J(HH) = 7.5 Hz), 7.80 (br d, 16H, PC_6H_5-*ortho*, ^3J(HH) = 6 Hz), 7.91 (d, 4H, PC_6H_5-*ortho*, ^3J(HH) = 7.5 Hz), 7.95 (d, 4H, PC_6H_5-*ortho*, ^3J(HH) = 7.5 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 25 °C): δ −3.77 (PEt_3, ^3J(PP) = 130 Hz, ^2J(PPt) = 174 Hz, J(PPt) = 4147 Hz), 81.2 (PPh_2, ^2J(PP) = 193 Hz, ^2J(PPt) = −57 Hz, J(PPt) = 2399 Hz), 95.0 (PPh_2, ^2J(PP) = 172, 193 Hz, ^2J(PPt) = −102 Hz, J(PPt) = 2194, 2339 Hz).

Preparation of $[(PEt_3)_2(\mu\text{-}PPh_2)_3Pt_3(SiMe_2fcSiMe_2)Pt_3(PEt_3)_2(\mu\text{-}PPh_2)_3]$ (**2b**) was carried out similarly to the preparation of **2a**. Yield: 54%. Anal. Calc. for $C_{110}H_{140}FeP_{10}Pt_6Si_2$: C, 43.25; H, 4.62. Found: C, 43.54; H, 4.83%. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.37 (dt, 18H, PCH_2CH_3, ^3J(HH) = 6.9 Hz, ^3J(HP) = 16 Hz), 0.97 (s, 12H, SiCH_3, ^3J(HPt) = 31 Hz), 1.46 (br t, 24H, PCH_2CH_3), 3.76 (s, 4H, C_5H_4), 4.22 (s, 4H, C_5H_4), 7.00 (t, 24H, PC_6H_5-*meta*, ^3J(HH) = 7.5 Hz), 7.09 (t, 12H, PC_6H_5-*para*, ^3J(HH) = 7.5 Hz), 7.84 (m, 16H, PC_6H_5-*ortho*), 7.87 (d, 4H, PC_6H_5-*ortho*, ^3J(HH) = 7.5 Hz), 7.90 (d, 4H, PC_6H_5-*ortho*, ^3J(HH) = 7.5 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ 7.22 (s, SiCH_3), 7.98 (s, PCH_2CH_3), 18.9 (t, ^{1+3}J(CP) = 14 Hz, PCH_2CH_3), 69.4 (C_5H_4), 72.5 (C_5H_4), 127.3 (br, PC_6H_5-*meta*), 127.4 (br, PC_6H_5-*meta*), 127.7 (PC_6H_5-*para*), 128.1 (PC_6H_5-*para*), 133.6 (d, PC_6H_5-*ortho*, J(CP) = 13 Hz), 134.2 (br, PC_6H_5-*ortho*), 140.7 (m, PC_6H_5-*ipso*). The C_5H_4-*ipso* signal was not observed due to small intensity.

3.4. Crystal structure determination

Recrystallization of **1a** from hexane–CH_2Cl_2 yielded the crystals suitable for X-ray crystallography. Cooling a solution formed by the reaction of 1,4-bis(dimethylsilyl)benzene and $[Pt_3H(PEt_3)_3(\mu\text{-}PPh_2)_3]$ resulted in separation of single crystals containing **2a** and $[Pt_3H_2(PEt_3)_2(\mu\text{-}PPh_2)_4]$ in equal amounts. These crystals were mounted in glass capillary tubes under Ar. Data of were collected at −160 °C on Rigaku Saturn CCD diffractometer equipped with monochromated Mo Kα radiation (λ = 0.71073 Å), and an empirical absorption correction (Ψ scan) was applied. Calculations were carried out with a program package Crystal Structure for Windows. Atomic scattering factors were obtained from the literature. A full matrix least-squares refinement was used for non-hydrogen atoms with

Table 1
Crystal data and details of structure refinement of **1a** and **2a** involving $[Pt_3H_2(PEt_3)_2(\mu\text{-}PPh_2)_4]$

	1a	**2a** + $[Pt_3H_2(PEt_3)_2(\mu\text{-}PPh_2)_4]$
Empirical formula	$C_{58}H_{77}P_5Pt_3Si_2$	$C_{166}H_{208}P_{16}Pt_9Si_2$
Formula weight	1570.56	4510.88
Color	Dark red	Dark red
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	21.893(5)	12.626(4)
b (Å)	13.649(3)	14.563(3)
c (Å)	22.543(5)	26.827(8)
α (°)		77.32(2)
β (°)	118.422(3)	86.01(2)
γ (°)		60.52(1)
V (Å^3)	5924(2)	4185(2)
Z	4	1
μ (mm^{-1})	7.249	7.674
F(000)	3048	2250
D_{calc} (g cm^{-1})	1.761	1.790
Crystal size (mm)	0.52 × 0.15 × 0.14	0.15 × 0.12 × 0.11
No. of unique reflections	13,535	17,753
No. of used reflections [$I > 3\sigma(I)$]	10,737	9497
No. of variables	693	954
$R(F_0)$	0.045	0.090
$R_w(F_0)$	0.060	0.119
GOF	1.058	1.347

anisotoropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters [10]. Crystallographic data and details of refinement of the complexes are summarized in Table 1. Crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 264878-264879. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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