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Synthesis of organometallic dendrimers with a backbone composed of platinum-acetylide units[1]

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Abstract

Novel organometallic dendrimers containing platinum-acetylide units in the main chain have been synthesized up to a henicosanuclear complex (**12**) using triethynylmesitylene (**4**) as a bridging ligand. The molecular structure of trinuclear complex (**5b**), which is a model core of the dendrimer, has been established by an X-ray analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dendrimer; Platinum acetylides; Polynuclear metal complex

1. Introduction

Dendrimers are currently attracting widespread interest in many areas of science and technology because they may have unique physical and chemical properties applicable to a new material [1]. Dendrimers are nanosize compounds having a regularly branched structure and many functional end groups. In contrast with hyperbranched polymers which are synthesized by a one-pot reaction, dendrimers are synthesized in a stepwise way by a repetitive reaction sequence. Despite extensive studies on an organic dendrimer, organometallic dendrimers, whose redox, luminescent, and catalytic properties may be of interest, are still limited. Most of known organometallic dendrimers have a metal atom either only in the core or only at the periphery with the remainder based on organic chemistry [2]. Especially organometallic dendrimers containing metal atoms in the main chain [3] are remarkably rare except for some silane or siloxane dendrimers [4].

We have been studying transition metal poly-yne polymers which are rigid rod-like macromolecules consisting of metal-acetylide units with diynes such as 1,3-butadiyne and *p*-diethynylbenzene [5]. Now we have extended such a one-dimensional system to a three-dimensional dendritic poly-yne polymer by the use of a triyne as a bridging ligand. Here we wish to report in detail the synthesis and characterization of novel organometallic dendrimers containing platinum-acetylide units in the main chain. Some of the results have already been reported as a preliminary communication [6].

2. Results and discussion

In expectation of high solubility of platinum-acetylide dendrimers we have chosen triethynylmesitylene (**4**) as a bridging triyne ligand, and synthesized from mesitylene (**1**) in three steps. Iodination of **1** using iodine and periodic acid dihydrate gave triiodide (**2**) in 90% yield [7]. For transformation to a triethynyl derivative we employed a Pd–Cu catalyzed C_{sp}–C_{sp^2} coupling reaction which we previously developed [8]. Thus, treatment of **2** with trimethylsilylacetylene in the presence of

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[1] Dedicated to Professor Akira Nakamura upon his retirement from Osaka University in honour of his contributions to organometallic chemistry.

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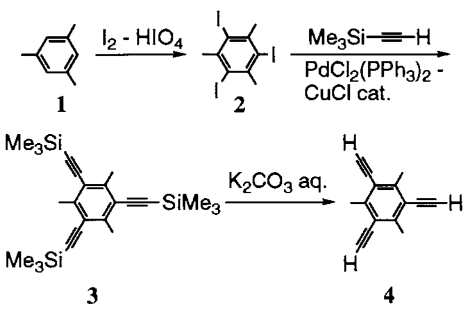
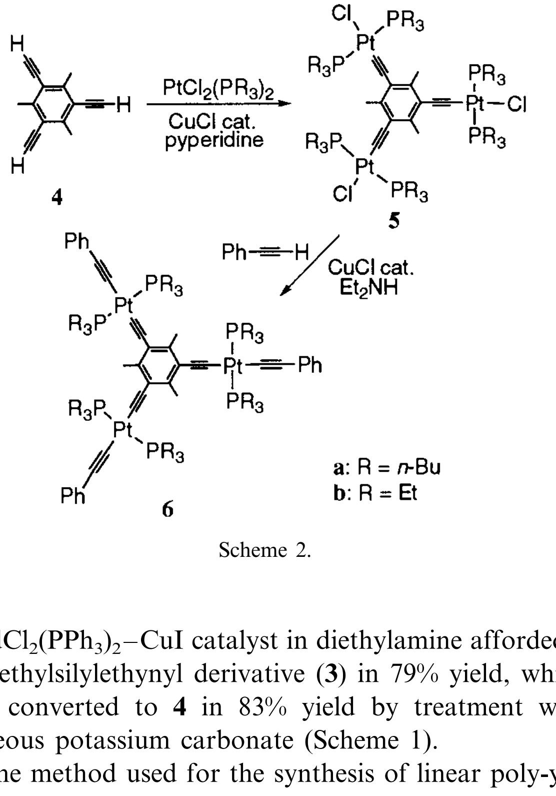


Scheme 1.



Scheme 2.

a $PdCl_2(PPh_3)_2$–CuI catalyst in diethylamine afforded a trimethylsilylethynyl derivative (**3**) in 79% yield, which was converted to **4** in 83% yield by treatment with aqueous potassium carbonate (Scheme 1).

The method used for the synthesis of linear poly-yne polymers has been successively applied to the synthesis of a platinum-acetylide dendrimer [5]. Thus, treatment of **4** with dichlorobis(tri-*n*-butylphosphine)platinum in the presence of a CuCl catalyst in piperidine under reflux for 48 h gave trinuclear complex (**5a**) in 92% yield [9]. Observation of a singlet signal attributed to the phosphine ligand at δ 7.35 ($J_{\text{Pt–P}} = 2390$ Hz) in $^{31}P\{^1H\}$-NMR as well as a singlet one of the methyl groups bound to aromatic ring at δ 3.08 in ^1H-NMR strongly suggests that complex **5a** has a symmetrical structure. Triethylphosphine analog **5b** was similarly prepared in 77% yield by the reaction of **4** with dichlorobis(triethylphosphine)platinum. In this reaction a little amount of a polymeric material was also generated as white precipitates because polynuclear complexes having triethylphosphine are less soluble than those having tri-*n*-butylphosphine, and the yield of **5b** was slightly lower than that of **5a**. Reactions of **5a** and **5b** with phenylacetylene in the presence of a CuCl catalyst gave phenylethynyl complexes (**6a**) and (**6b**) in 82 and 83% yields, respectively (Scheme 2).

The molecular structure of **5b** was established by X-ray crystallography as shown in Fig. 1. The molecule of **5b** has a 2-fold symmetry axis passing through Cl(2), Pt(2), C(10), C(9), C(8), C(4) and C(5). Since platinum moieties are far apart from each other, bond lengths and angles of platinum-acetylide skelton are comparable with those of other platinum-acetylide complexes [10]. It is of interest that the three coordination planes around Pt atoms are twisted from the aromatic ring by about 60° but the twist direction of three coordination planes are not the same [11]. Crystallographic data and selected bond distances and angles for **5b** are shown in Tables 1 and 2.

When **4** was treated with excess **5a** in the presence of a CuCl catalyst in diethylamine, formation of complex **7** having a larger molecular weight was confirmed by gel permeation chromatography. However we could not isolate **7** as a pure form from the reaction mixture. Introduction of a phenylethynyl group as a terminal ligand by the reaction of **7** with phenylacetylene has enabled isolation of a nonanuclear complex (**8**) by column chromatography on alumina. The $^{31}P\{^1H\}$-NMR spectrum of **8** showed two singlet signals at δ 4.20 ($J_{\text{Pt–P}} = 2396$ Hz) and 3.80 ($J_{\text{Pt–P}} = 2375$ Hz) in a 1:2 intensity ratio. The former was assigned to the phosphine ligands bound to three inner platinum atoms and the latter to those bound to the six external platinum atoms. This data is consistent with the expected structure of **8**, which is also supported by IR, ^1H-NMR and elemental analyses (Scheme 3).

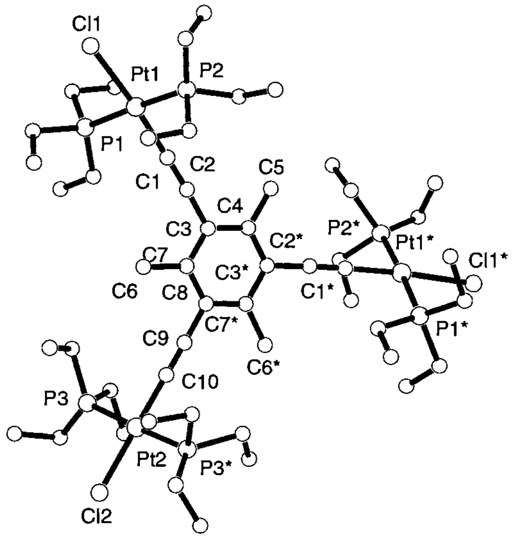


Fig. 1. Molecular structure of **5b**. Hydrogen atoms are omitted for clarity.

Table 1
Crystallographic data for **5b**

Emprical formula	$C_{51}H_{99}Cl_3P_6Pt_3$
Formula weight	1589.81
Crystal size (mm)	0.45 × 0.42 × 0.35
Color	Pale yellow
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	29.590(5)
b (Å)	14.679(9)
c (Å)	16.77(2)
β (°)	110.15(4)
V (Å^3)	6836(6)
Z	4
D_{calc} (g cm^{-3})	1.54
μ(Mo–K$_\alpha$) (cm^{-1})	63.8
F(000)	3120
Scan mode	$\omega-2\theta$
2θ range (°)	6–55
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
No. of reflections measured	8305
No. of unique reflections	8148
No. of data with $I > 3\sigma(I)$	3605
No. of variables	198
Goodness-of-fit	2.56
Residuals R, R_w	0.069, 0.071

Then we tried to synthesize dendrimer of a second generation which consists of henicosa platinum moieties. Thus, trinuclear platinum complex **9** was synthesized by the reaction of **5a** with a large excess of **4**. Complex **9** was characterized by spectral analyses; existence of a terminal acetylene group was confirmed by the IR spectrum showing an absorption at 3311 cm^{-1} as well as by the ^{1}H-NMR spectrum exhibiting an resonance at δ 2.78. In order to prepare a dendrimer of next generation, **9** was treated with a large excess of **5a**, but the reaction proceeded with low selectivity to give a complex mixture and the desired product could not be isolated. Then, we have chosen another synthetic route as shown in Scheme 6.

Table 2
Selected bond distance (Å) and angles (°) for **5b**

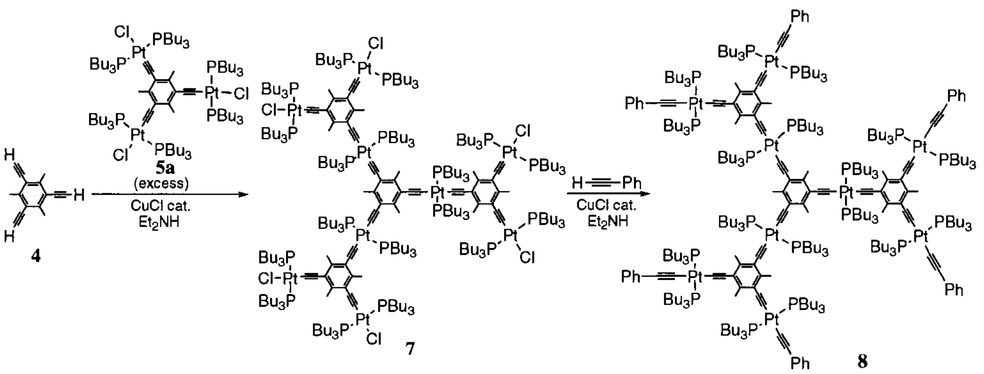
Pt(1)–P(1)	2.284(6)	Pt(1)–P(2)	2.291(6)
Pt(1)–Cl(1)	2.488(4)	Pt(1)–C(1)	1.93(2)
C(1)–C(2)	1.20(2)	C(2)–C(3)	1.47(2)
C(3)–C(7)	1.41(2)	C(7)–C(8)	1.39(2)
C(8)–C(9)	1.43(3)	C(9)–C(10)	1.19(3)
Pt(2)–C(10)	1.95(2)	Pt(2)–P(3)	2.254(8)
Pt(2)–Cl(2)	2.388(7)		
P(1)–Pt(1)–P(2)	176.9(2)	P(1)–Pt(1)–C(1)	90.3(5)
P(1)–Pt(1)–Cl(1)	87.2(2)	P(2)–Pt(1)–C(1)	88.0(5)
P(2)–Pt(1)–Cl(1)	94.4(2)	Pt(1)–C(1)–C(2)	177(1)
C(1)–C(2)–C(3)	175(1)	C(2)–C(3)–C(7)	119(1)
C(3)–C(7)–C(8)	119(1)	C(7)–C(8)–C(9)	119(1)
C(8)–C(9)–C(10)	180.0(1)	C(9)–C(10)–Pt(2)	180.0(1)
C(10)–Pt(2)–Cl(2)	180.0(1)	C(10)–Pt(2)–P(3)	88.8(2)
P(3)–Pt(2)–Cl(2)	91.2(2)		

Triethynylmesitylene **4** was treated with a large excess of **5a** followed by the reaction again with a large excess of **4** in a similar manner to that for the synthesis of **8** to give nonanuclear complex **10**. The complex is a precursor of the second generation dendrimer and has twelve ethynyl end groups at the outer shell. Although the ^{1}H-NMR spectrum detected a trace amount of an impurity in the product, we could obtain complex **10** which is pure enough to be consistent with the results of elemental and spectral analyses. The ^{31}P{^{1}H}-NMR spectrum of **10**, which is quite similar to that of **8**, showed two singlet signals at δ 4.14 ($J_{Pt-P} = 2382$ Hz) and 4.10 ($J_{Pt-P} = 2382$ Hz) in a 1:2 intensity ratio. Treatment of **10** with excess of chloro(phenylethynyl)bis(tri-n-butylphosphine)-platinum (**11**) gave henicosanuclear complex **12** as a second generation dendrimer. Although unreacted **11** was successfully removed from the reaction mixture by means of alumina column chromatography, product **12** concomitant with a small amount of an impurity having a molecular weight close to **12**, and unfortunately we could not obtain an analytically pure sample of **12**. The purity, however, is high enough to characterize **12** by spectral analyses. The ^{31}P{^{1}H}-NMR spectrum of **12** showed signals at δ 4.20 ($J_{Pt-P} = 2398$ Hz) assigned to the phosphine ligands bound to nine inner platinum atoms and at δ 3.79 ($J_{Pt-P} = 2376$ Hz) attributed to those bound to twelve exterior platinum atoms in the molecule with a 3:4 intensity ratio. The ^{31}P-NMR spectral pattern of **12** is quite similar to that of **8**, suggesting that **12** has a quite similar structure to **8**. The ^{1}H- and ^{13}C-NMR data also support the structure of **12** (Schemes 4–6)

In summary, a successful strategy for the step by step synthesis of a novel platinum-acetylide dendrimer has been developed using 1,3,5-triethynyl-2,4,6-trimethylbenzene **4** as a bridging triyne ligand, and a second generation dendrimer **12** built up by 21 Pt atoms, 22 benzene rings and 42 acetylenic bonds has been successfully synthesized. Complex **12** belongs to a class with high molecular weight as an organometallic dendrimer containing metal atoms in all generations. Since many stable acetylide complexes are known, the method presented here may allow syntheses of various metal-acetylide dendrimers.

3. Experimental section

All reactions to prepare platinum-acetylide complexes were carried out under an atmosphere of argon, but the workup was performed in air. NMR spectra were recorded on a JEOL EX-270 (270 MHz) and Bruker ARX-400 (400 MHz) spectrometer using $SiMe_4$ as an internal standard for ^{1}H- and ^{13}C-NMR, and an external 85% H_3PO_4 reference for ^{31}P-NMR. IR and



Scheme 3.

mass spectra were taken on a Perkin-Elmer System 2000 FT-IR and Shimadzu GCMS-QP-2000 instrument, respectively. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University.

*3.1. Preparation of triiodomesitylene **2***

A mixture of mesitylene **1** (12.02 g, 100 mmol), iodine (50.76 g, 100 mmol), periodic acid dihydrate (22.79 g, 100 mmol), and sulfuric acid (3.6 ml) in acetic acid (100 ml) was stirred at 100°C for 1 week. After unreacted iodine was removed by addition of aqueous sodium hydrogensulfite, the solvent was evaporated under reduced pressure. The residue was extracted with benzene and the benzene solution was dried over anhydrous sodium sulfate followed by filtration by alumina column chromatography. Purification by recrystallization from benzene gave **2** as colorless needles (44.59 g, 90%).

M.p. 206.0–207.0°C; MS (EI) *m*/*z* 498 (M^+); ^{1}H-NMR ($CDCl_3$) δ 3.01 (s, 9H, Me); ^{13}C-NMR ($CDCl_3$) δ 144.12 (s, Ar), 101.18 (s, Ar), 39.56 (s, Ar*Me*)

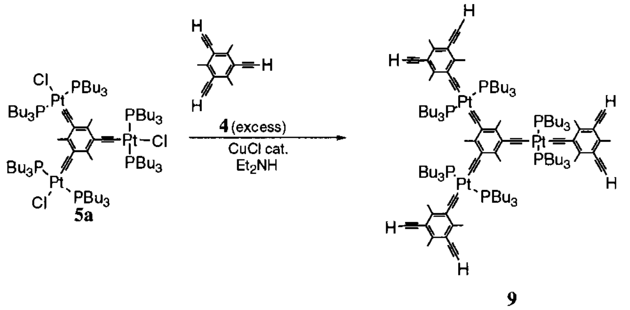
*3.2. Preparation of tris(trimethylsilylethynyl)mesitylene **3***

A mixture of triiodomesitylene **2** (9.958 g, 20 mmol) and trimethylsilylacetylene (11.788 g, 120 mmol) in 100 ml of diethylamine was stirred in the presence of dichlorobis(triphenylphosphine)palladium and copper iodide catalysts at room temperature for 72 h. The solvent was removed under reduced pressure, and the residue was extracted with benzene. After drying over anhydrous sodium sulfate, the benzene solution was passed through a short alumina column. The filtrate was concentrated and purified by chromatography on alumina with hexane/benzene (v/v = 19/1) as an eluent. Recrystallization from ethanol gave colorless needles of **3** (6.45 g, 79%).

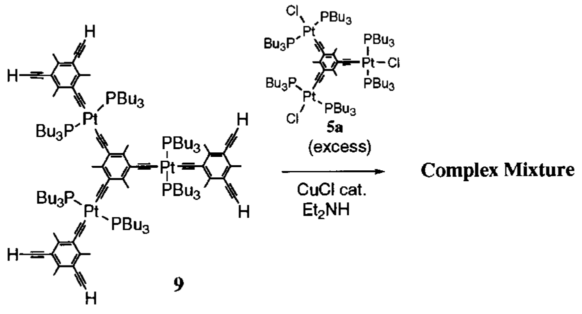
M.p. 245.0–246.0°C; MS (EI) *m*/*z* 408 (M^+); IR (KBr) 2147 cm^{-1} ($\nu_{C\equiv C}$); ^{1}H-NMR ($CDCl_3$) δ 2.55 (s, 9H, Ar*Me*), 0.26 (s, 27H, $SiMe_3$); ^{13}C-NMR ($CDCl_3$) δ 142.85 (s, Ar), 120.91 (s, Ar), 102.26 (s, *C*≡C), 102.22 (s, *C*≡C), 20.13 (s, Ar*Me*), 0.08 (s, $SiMe_3$); Anal. Calc. for $C_{24}H_{36}Si_3$: C, 70.51; H, 8.88%. Found: C, 70.34; H, 8.74%.

*3.3. Preparation of triethynylmesitylene **4***

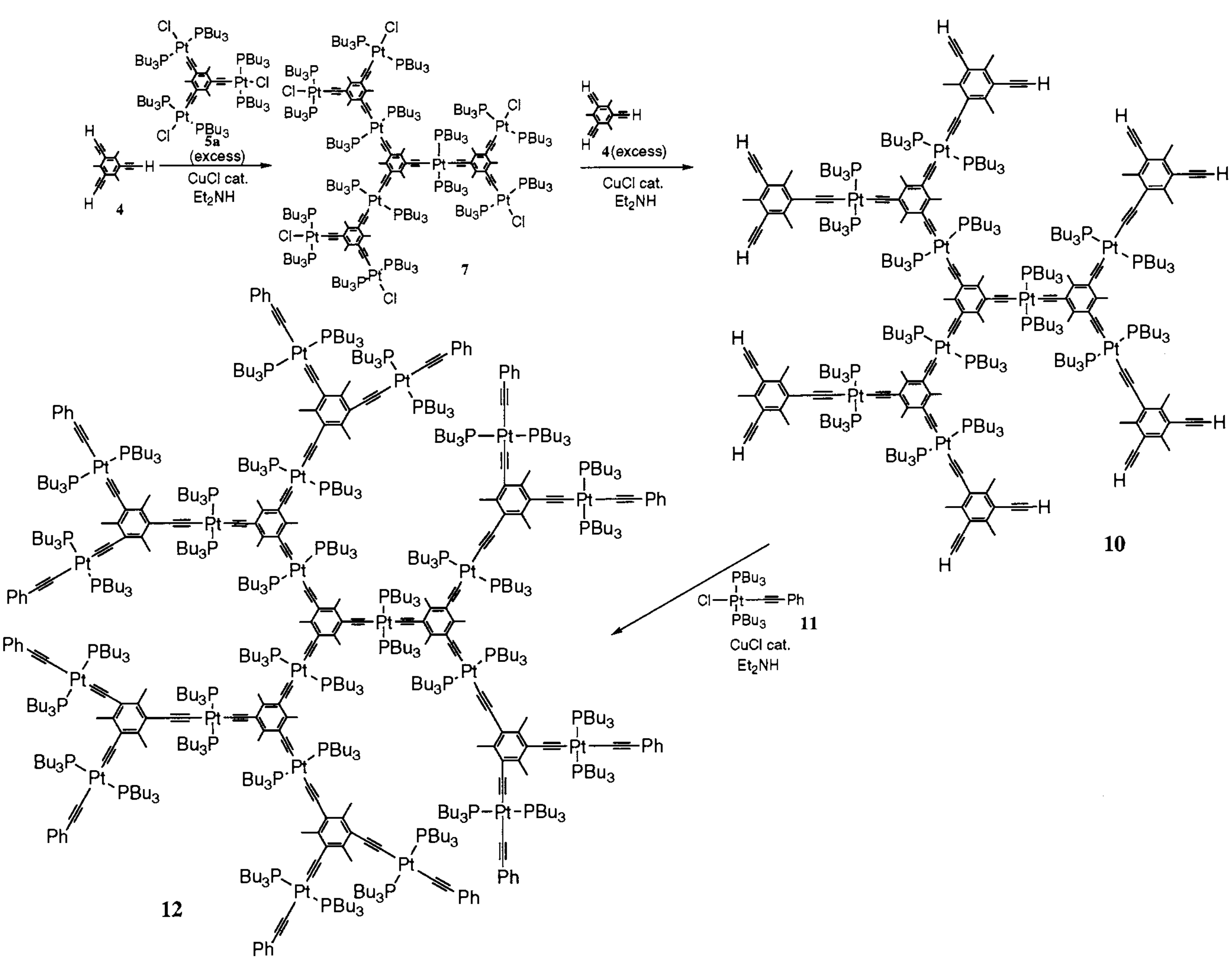
Tris(trimethylsilylethynyl)mesitylene **3** (2.454 g, 6.0 mmol) was treated with aqueous potassium carbonate (1.416 g, 10.2 mmol) in methanol (70 ml) at 50°C for 5 h. The solvent was removed under reduced pressure, and the residue was extracted with benzene. After drying over anhydrous sodium sulfate followed by evaporation of the solvent, the crude product was purified by sublimation under vacuum to give pale purple crystals (0.951 g, 83%).



Scheme 4.



Scheme 5.



Scheme 6.

M.p. 128.2–129.0°C; MS (EI) *m*/*z* 192 (M^+); IR (KBr) 2101 cm^{-1} ($\nu_{C\equiv C}$), 3288 cm^{-1} ($\nu_{\equiv C-H}$); ^{1}H-NMR ($CDCl_3$) δ 3.50 (s, 3H, ≡CH), 2.61 (s, 9H, Ar*Me*); ^{13}C-NMR ($CDCl_3$) δ 143.84 (s, Ar), 120.26 (s, Ar), 85.27 (s, *C*≡C), 80.58 (s, *C*≡C), 20.10 (s, Ar*Me*); Anal. Calc. for $C_{15}H_{12}$: C, 93.71; H, 6.29%. Found: C, 93.47; H, 6.28%.

3.4. Synthesis of complex **5a**

A mixture of triethynylmesitylene **4** (10.059 g, 15.0 mmol) and dichlorobis(tri-*n*-butylphosphine)platinum (0.864 g, 4.5 mmol) in 240 ml of a solution of piperidine/toluene (v/v = 1/1) was stirred in the presence of a copper chloride catalyst under reflux for 48 h. The solvent was removed under reduced pressure, and the residue was extracted with benzene. After drying over anhydrous sodium sulfate, the solution was filtered on an alumina short column. The filtrate was concentrated and the residue was purified using alumina column chromatography with hexane/benzene (v/v = 1/1) as an eluent. The major pale yellow fraction was collected and concentrated under vacuum to give pale yellow oil (8.65 g, 92%).

IR (neat) 2106 cm^{-1} ($\nu_{C\equiv C}$); ^{1}H-NMR (C_6D_6) δ 3.08 (s, 9H, Ar*Me*), 2.11–2.01 (m, 36H, $PCH_2CH_2CH_2CH_3$), 1.76–1.63 (m, 36H, $PCH_2CH_2CH_2CH_3$), 1.49–1.36 (m, 36H, $PCH_2CH_2CH_2CH_3$), 0.95 (t, J = 7.3Hz, 54H, $PCH_2CH_2CH_2CH_3$); ^{13}C-NMR ($CDCl_3$) δ 135.95 (s, Ar), 125.13 (s, Ar), 98.56 (s, *C*≡CPt), 88.83 (t, J_{P-C} = 31 Hz, C≡*C*Pt), 26.27 (s, Ar*Me*), 24.30 (vt, N = 13 Hz, $PCH_2CH_2CH_2CH_3$), 21.89 (vt, N = 34 Hz, $PCH_2CH_2CH_2CH_3$), 20.53 (s, $PCH_2CH_2CH_2CH_3$), 13.90 (s, $PCH_2CH_2CH_2CH_3$); ^{31}P-NMR ($CDCl_3$) δ 7.35 (s, J_{Pt-P} = 2390 Hz); Anal. Calc. for $C_{87}H_{171}P_6Cl_3Pt_3$: C, 49.88; H, 8.23; P, 8.87; Cl, 5.08%. Found: C, 49.64; H, 8.26; P, 8.98; Cl, 4.88%.

3.5. Synthesis of complex **5b**

Complex **5b** was prepared from the reaction of **4** with dichlorobis(triethylphosphine)platinum by a method similar to that for **5a**. Recrystallization from ethanol gave pure **5b** as pale yellow crystals in 77% yield.

M.p. 235.5–236.0°C (decomp.); IR (KBr) 2102 cm^{-1} ($\nu_{C\equiv C}$); ^{1}H-NMR (C_6D_6) δ 3.16 (s, 9H, Ar*Me*), 1.95–1.84 (m, 36H, PCH_2CH$_3$), 1.10 − 0.97 (dt, J_{P-H} = 16Hz, J_{H-H} = 8Hz, 54H, PCH$_2$CH_3); ^{13}C-NMR (CDCl$_3$) δ 135.37 (s, Ar), 125.22 (s, Ar), 99.53 (s, *C*≡CPt), 88.70 (t, J_{P-C} = 30 Hz, C≡*C*Pt), 20.40 (s, Ar*Me*), 14.36 (vt, *N* = 34 Hz, P*C*H$_2$CH$_3$), 8.02 (s, PCH$_2$*C*H$_3$); ^{31}P-NMR (CDCl$_3$) δ 15.34 (s, J_{Pt-P} = 2407 Hz); Anal. Calc. for $C_{51}H_{99}P_6Cl_3Pt_3$: C, 38.53; H, 6.28; P, 11.69; Cl, 6.71%. Found: C, 38.32; H, 6.12; P, 11.45; Cl, 6.71%.

3.6. Synthesis of complex 6a

Complex **5a** (1060 mg, 0.506 mmol) was reacted with phenylacetylene (207 mg, 2.024 mmol) in 25 ml of diethylamine in the presence of a copper chloride catalyst at room temperature for 3 h. The solvent was then removed under reduced pressure. After the residue was extracted with benzene, the solution was dried over anhydrous sodium sulfate followed by filtration using alumina short column. The pale yellow filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave pale yellow crystals of **6a** (951 mg, 82%).

M.p. 77.5–78.0°C; IR (KBr) 2106 cm^{-1} ($\nu_{C\equiv C}$); ^{1}H-NMR (CD$_2$Cl$_2$) δ 7.26–7.07 (m, 15H, Ph), 2.57 (s, 9H, Ar*Me*), 2.18–2.04 (m, 36H, PCH_2CH$_2$CH$_2$CH$_3$), 1.66–1.57 (m, 36H, PCH$_2$CH_2CH$_2$CH$_3$), 1.50–1.36 (m, 36H, PCH$_2$CH$_2$CH_2CH$_3$), 0.92 (t, *J* = 7.3Hz, 54H, PCH$_2$CH$_2$CH$_2$CH_3); ^{13}C-NMR (CDCl$_3$) δ 135.45 (s, Ar), 130.93 (s, Ar), 129.22 (s, Ar), 127.78 (s, Ar), 125.40 (s, Ar), 124.68 (s, Ar), 113.95 (t, J_{P-C} = 31 Hz, C≡*C*Pt), 109.47 (s, *C*≡CPt), 108.56 (t, J_{P-C} = 28 Hz, C≡*C*Pt), 106.41 (s, *C*≡CPt), 26.55 (s, Ar*Me*), 24.39 (vt, *N* = 13 Hz, P*C*H$_2$CH$_2$CH$_2$CH$_3$), 23.78 (vt, *N* = 34 Hz, PCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.81 (s, PCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.91 (s, PCH$_2$CH$_2$CH$_2$*C*H$_3$); ^{31}P-NMR (CDCl$_3$) δ 3.77 (s, J_{Pt-P} = 2375 Hz); Anal. Calc. for $C_{111}H_{186}P_6Pt_3$: C, 58.17; H, 8.18; P, 8.11%. Found: C, 58.03; H, 8.00; P, 8.05%.

3.7. Synthesis of complex 6b

Complex **6b** was prepared from the reaction of **5b** with phenylacetylene by a method similar to that for **6a** in 83% yield.

M.p. 237.0–237.5°C (decomp.); IR (KBr) 2106 cm^{-1} ($\nu_{C\equiv C}$); ^{1}H-NMR(CDCl$_3$) δ 7.30–7.17 (m, 15H, Ph), 2.58 (s, 9H, Ar*Me*), 2.18–2.09 (m, 36H, PCH_2CH$_3$), 1.25–1.14 (dt, J_{P-H} = 16Hz, J_{H-H} = 8Hz, 54H, PCH$_2$CH_3); ^{13}C-NMR (CDCl$_3$) δ 135.67 (s, Ar), 130.92 (s, Ar), 129.09 (s, Ar), 127.87 (s, Ar), 125.43 (s, Ar), 124.82 (s, Ar), 114.19 (t, J_{P-C} = 30 Hz, C≡*C*Pt), 109.45 (s, *C*≡CPt), 108.22 (t, J_{P-C} = 29 Hz, C≡*C*Pt), 107.56 (s, *C*≡CPt), 20.65 (s, Ar*Me*), 16.30 (vt, *N* = 35 Hz, P*C*H$_2$CH$_3$), 8.39 (s, PCH$_2$*C*H$_3$); ^{31}P-NMR (CDCl$_3$) δ 11.78 (s, J_{Pt-P} = 2390 Hz); Anal. Calc. for $C_{75}H_{114}P_6Pt_3$: C, 50.41; H, 6.43; P, 10.40%. Found: C, 50.31; H, 6.42; P, 10.21%.

3.8. Synthesis of complex 8

A mixture of **4** (8.2 mg, 0.042 mmol) and **5a** (800 mg, 0.382 mmol) in 70 ml of diethylamine was stirred at room temperature in the presence of a copper chloride catalyst for 1 h. Then a solution of phenylacetylene (143 mg, 1.400 mmol) in 30 ml of diethylamine was added to the reaction mixture. After stirred at room temperature for 2 h, workup similar to that of **6a** gave **8** as pale yellow oil (56 mg, 20%).

IR (neat) 2096 cm^{-1} ($\nu_{C\equiv C}$); ^{1}H-NMR (CD$_2$Cl$_2$) δ 7.26–7.09 (m, 30H, Ph), 2.58–2.56 (m, 36H, Ar*Me*), 2.10–2.08 (m, 108H, PCH_2CH$_2$CH$_2$CH$_3$), 1.61–1.59 (m, 108H, PCH$_2$CH_2CH$_2$CH$_3$), 1.49–1.38 (m, 108H, PCH$_2$CH$_2$CH_2CH$_3$), 0.94–0.86 (m, 162H, PCH$_2$CH$_2$CH$_2$CH_3); ^{13}C-NMR (CDCl$_3$) δ 135.53 (s, Ar), 135.28 (s, Ar), 135.13 (s, Ar), 130.93 (s, Ar), 129.28 (s, Ar), 127.79 (s, Ar), 125.70 (s, Ar), 125.42 (s, Ar), 125.29 (s, Ar), 124.67 (s, Ar), 114.58 (t, J_{P-C} = 30 Hz, C≡*C*Pt), 113.54 (t, J_{P-C} = 29 Hz, C≡*C*Pt), 113.45 (t, J_{P-C} = 31 Hz, C≡*C*Pt), 109.42 (s, *C*≡CPt), 108.69 (t, J_{P-C} = 28 Hz, C≡*C*Pt), 107.40 (s, *C*≡CPt), 106.93 (s, *C*≡CPt), 106.69 (s, *C*≡CPt), 26.54 (s, Ar*Me*), 24.40 (vt, *N* = 14 Hz, P*C*H$_2$CH$_2$CH$_2$CH$_3$), 24.27 (s, Ar*Me*), 23.84 (vt, *N* = 34 Hz, PCH$_2$*C*H$_2$CH$_2$CH$_3$), 23.76 (s, Ar*Me*), 20.97 (s, PCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.91 (s, PCH$_2$CH$_2$CH$_2$*C*H$_3$); ^{31}P-NMR (CDCl$_3$) δ 4.20 (s, J_{Pt-P} = 2396Hz, 3P), 3.80 (s, J_{Pt-P} = 2375Hz, 6P); Anal. Calc. for $C_{324}H_{552}P_{18}Pt_9$: C, 57.56; H, 8.23; P, 8.25%. Found: C, 57.65; H, 8.11; P, 7.99%.

3.9. Synthesis of complex 9

The reaction of **4** (826 mg, 4.297 mmol) with **5a** (1000 mg, 0.477 mmol) by a procedure similar to that for **6a** gave **9** (850 mg, 70%) as pale yellow crystals.

M.p. 133.5–134.5°C; IR (KBr) 2090 cm^{-1} ($\nu_{C\equiv C}$), 3311 cm^{-1} ($\nu_{\equiv C-H}$); ^{1}H-NMR (C_6D_6) δ 3.13–3.10 (m, 36H, Ar*Me*), 2.78 (s, 6H, ≡CH), 2.12–2.09 (m, 36H, PCH_2CH$_2$CH$_2$CH$_3$), 1.71–1.67 (m, 36H, PCH$_2$CH_2CH$_2$CH$_3$), 1.47–1.33 (m, 36H, PCH$_2$CH$_2$CH_2CH$_3$), 0.93 (t, *J* = 7.3Hz, 54H, PCH$_2$CH$_2$CH$_2$CH_3); ^{13}C-NMR (CDCl$_3$) δ 141.64 (s, Ar), 138.91 (s, Ar), 135.40 (s, Ar), 127.03 (s, Ar), 125.33 (s, Ar), 119.30 (s, Ar), 118.86 (t, J_{P-C} = 29 Hz, C≡*C*Pt), 113.17 (t, J_{P-C} = 30 Hz, C≡*C*Pt), 107.17 (s, *C*≡CPt), 105.80 (s, *C*≡CPt), 84.02 (s, *C*≡C), 81.85 (s, *C*≡C), 26.55 (s, Ar*Me*), 24.34 (vt, *N* = 13 Hz, P*C*H$_2$CH$_2$CH$_2$CH$_3$), 23.94 (vt, *N* = 34 Hz, PCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.99 (s, Ar*Me*), 20.61 (s, PCH$_2$CH$_2$*C*H$_2$CH$_3$), 19.75 (s, Ar*Me*), 13.90 (s,

$PCH_2CH_2CH_2CH_3$); ^{31}P-NMR ($CDCl_3$) δ 4.10 ($J_{Pt-P} =$ 2382Hz); Anal. Calc. for $C_{132}H_{204}P_6Pt_3$: C, 61.88; H, 8.03; P, 7.25%. Found: C, 61.68; H, 7.83; P, 7.33%.

3.10. Synthesis of complex **10**

Complex **10** was prepared from the reaction of **7** with **4** by the procedure similar to that for **9** using **4** instead of phenylacetylene (pale yellow oil, 66% yield).

IR (neat) 2090 cm^{-1} ($\nu_{C\equiv C}$), 3312 cm^{-1} ($\nu_{\equiv C-H}$); ^{1}H-NMR ($CDCl_3$) δ 3.44 (s, 12H, $\equiv CH$), 2.65–2.57 (m, 90H, ArMe), 2.07–2.05 (m, 108H, $PCH_2CH_2CH_2CH_3$), 1.59–1.55 (m, 108H, $PCH_2CH_2CH_2CH_3$), 1.41–1.32 (m, 108H, $PCH_2CH_2CH_2CH_3$), 0.87 (t, 162H, $J = 7.3$ Hz, $PCH_2CH_2CH_2CH_3$); ^{13}C-NMR ($CDCl_3$) δ 141.66(s, Ar), 138.92 (s, Ar), 136.97 (s, Ar), 135.43 (s, Ar), 135.29 (s, Ar), 127.05 (s, Ar), 126.25(s, Ar), 125.46 (s, Ar), 125.30 (s, Ar), 119.30 (s, Ar), 118.92 (t, $J_{P-C} = 28$ Hz, $C\equiv CPt$), 116.08 (t, $J_{P-C} = 31$ Hz, $C\equiv CPt$), 113.71 (t, $J_{P-C} = 28$ Hz, $C\equiv CPt$), 113.02 (t, $J_{P-C} = 28$ Hz, $C\equiv CPt$), 107.23 (s, $C\equiv CPt$), 107.13 (s, $C\equiv CPt$), 106.59 (s, $C\equiv CPt$), 105.79 (s, $C\equiv CPt$), 84.06 (s, $C\equiv C$), 81.87 (s, $C\equiv C$), 26.56 (s, ArMe), 24.34 (vt, $N = 13$ Hz, $PCH_2CH_2CH_2CH_3$), 23.95 (vt, $N = 34$ Hz, $PCH_2CH_2CH_2CH_3$), 21.30 (s, ArMe), 21.01 (s, ArMe), 20.61 (s, $PCH_2CH_2CH_2CH_3$), 20.35 (s, ArMe), 19.75 (s, ArMe), 13.90 (s, $PCH_2CH_2CH_2CH_3$); ^{31}P-NMR ($CDCl_3$) δ 4.14 (s, $J_{Pt-P} = 2382$ Hz, 3P), 4.10 (s, $J_{Pt-P} =$ 2382 Hz, 6P); Anal. Calc. for $C_{366}H_{588}P_{18}Pt_9$: C, 60.20; H, 8.12; P, 7.63%. Found: C, 59.94; H, 7.95; P, 7.56%.

3.11. Synthesis of complex **12**

A mixture of **10** (122 mg, 0.0167 mmol) and chloro(phenylethynyl)bis(tri-*n*-butylphosphine) platinum **11** (221 mg, 0.3008 mmol) in diethylamine (50 ml) was stirred at room temperature in the presence of a copper chloride catalyst for 24 h. Similar workup to that for **8** gave complex **12** as pale yellow oil (240 mg, 92%).

IR (neat) 2106 cm^{-1} ($\nu_{C\equiv C}$); ^{1}H-NMR ($CDCl_3$) δ 7.30–7.07 (m, 60H, Ph), 2.62–2.58 (m, 90H, ArMe), 2.12–2.08 (m, 252H, $PCH_2CH_2CH_2CH_3$), 1.61–1.58 (m, 252H, $PCH_2CH_2CH_2CH_3$), 1.44–1.36 (m, 252H, $PCH_2CH_2CH_2CH_3$), 0.92–0.85 (m, 378H, $PCH_2CH_2CH_2CH_3$); ^{13}C-NMR ($CDCl_3$) δ 135.52 (s, Ar), 135.27 (s, Ar), 135.13 (s, Ar), 130.93 (s, Ar), 129.26 (s, Ar), 127.78 (s, Ar), 125.69 (s, Ar), 125.41 (s, Ar), 125.27 (s, Ar), 124.66 (s, Ar), 114.59 (t, $J_{P-C} = 30$ Hz, $C\equiv CPt$), 113.45 (t, $J_{P-C} = 31$ Hz, $C\equiv CPt$), 109.41 (s, $C\equiv CPt$), 108.69 (t, $J_{P-C} = 28$ Hz, $C\equiv CPt$), 107.38 (s, $C\equiv CPt$), 106.90 (s, $C\equiv CPt$), 106.66(s, $C\equiv CPt$), 26.56 (ArMe), 24.40 (vt, $N = 14$ Hz, $PCH_2CH_2CH_2CH_3$), 24.26 (s, ArMe), 23.82 (vt, $N = 34$ Hz, $PCH_2CH_2CH_2CH_3$), 23.74 (s, ArMe), 20.96 (s, $PCH_2CH_2CH_2CH_3$), 13.90 (s, $PCH_2CH_2CH_2CH_3$); ^{31}P-NMR ($CDCl_3$) δ 4.20 (s, $J_{Pt-P} = 2398$Hz, 9P), 3.79 (s, $J_{Pt-P} = 2376$Hz, 12P)

3.12. X-ray structure determination of **5b**

A single-crystal suitable for an X-ray study was grown by slow evaporation of a dichloromethane/hexane solution of **5b** and mounted on a glass fiber using epoxy resin. Data were measured on a Rigaku AFC5R diffractmeter in the range of $6° < 2\theta < 55°$ with $\omega - 2\theta$ scan technique. The reflections were corrected for Lorentz-polarization effect, decay, and absorption using Ψ scan technique. The structure was solved by the Patterson method and refined by full-matrix least-squares method using anisotropic thermal parameters for all non-H atoms except for carbon atoms of triethylphosphine, which are refined isotropically. The hydrogen atoms were located at calculated positions. The final agreement factors are $R = 0.069$ and $R_w = 0.071$ for 198 parameters against 3605 reflections with $I > 3.0\sigma(I)$ out of 8148 unique reflections.

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