

Dendrimer–Phosphine Complexes with Platinum(0) at the Core

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Preparation of novel mono- and bidentate phosphine ligands having dendrimer moiety is reported. Monodentate (**1a–c**) and bidentate ligands (**5a,b**) were synthesized from bis(4-hydroxyphenyl)phenylphosphine oxide (**3**) and 1,2-bis(dichlorophosphino)ethane, respectively, in high yields. The defect-free monodisperse nature of these compounds was confirmed by ^{31}P NMR and elemental analysis as well as by ESI mass spectra. Complexation of these ligands with $\text{PtCl}_2(\text{COD})$ followed by NaBH_4 reduction in a THF/ H_2O mixture gave Pt(0) complexes **10a,b** (having **1a,b** as the ligands) and **13a,b** (**5a,b** as the ligands). Monodentate ligands gave PtL_3 complexes (**10a,b**) and bidentate ligands gave $\text{Pt}(\text{L–L})_2$ complexes (**13a,b**), respectively. Preliminary studies on oxidative addition of RI ($\text{R} = \text{CH}_3$ or C_6H_5) to **10a,b** showed that the metal center is easily accessible. Further, molecular modeling of **13b** showed nanoscale flattened globular structure of the complex with an approximate diameter of 4.4 nm.

Introduction

Ever since the discovery of dendritic macromolecules,¹ considerable interest is focused on dendrimers. During the past decade, a vast variety of dendrimer molecules with different functional groups were synthesized both by divergent² and convergent³ methodologies. Owing to their unique physical and chemical properties,⁴ dendrimers have found use in many areas such as encapsulation of function,⁵ host–guest chemistry,⁶ and nanoscale technology.⁷

Recently, incorporation of metals into dendrimers has received much attention and is being studied extensively. There are mainly two ways to incorporate metals into dendrimers, namely, at core⁸ and at periphery.⁹ In the case of the incorporation at the periphery, there are many examples and a large number of metal atoms can be introduced within the same peripheral surface.⁹ On the contrary, in the case of the incorporation of a metal at core,⁸ the metal is surrounded by the dendrimer

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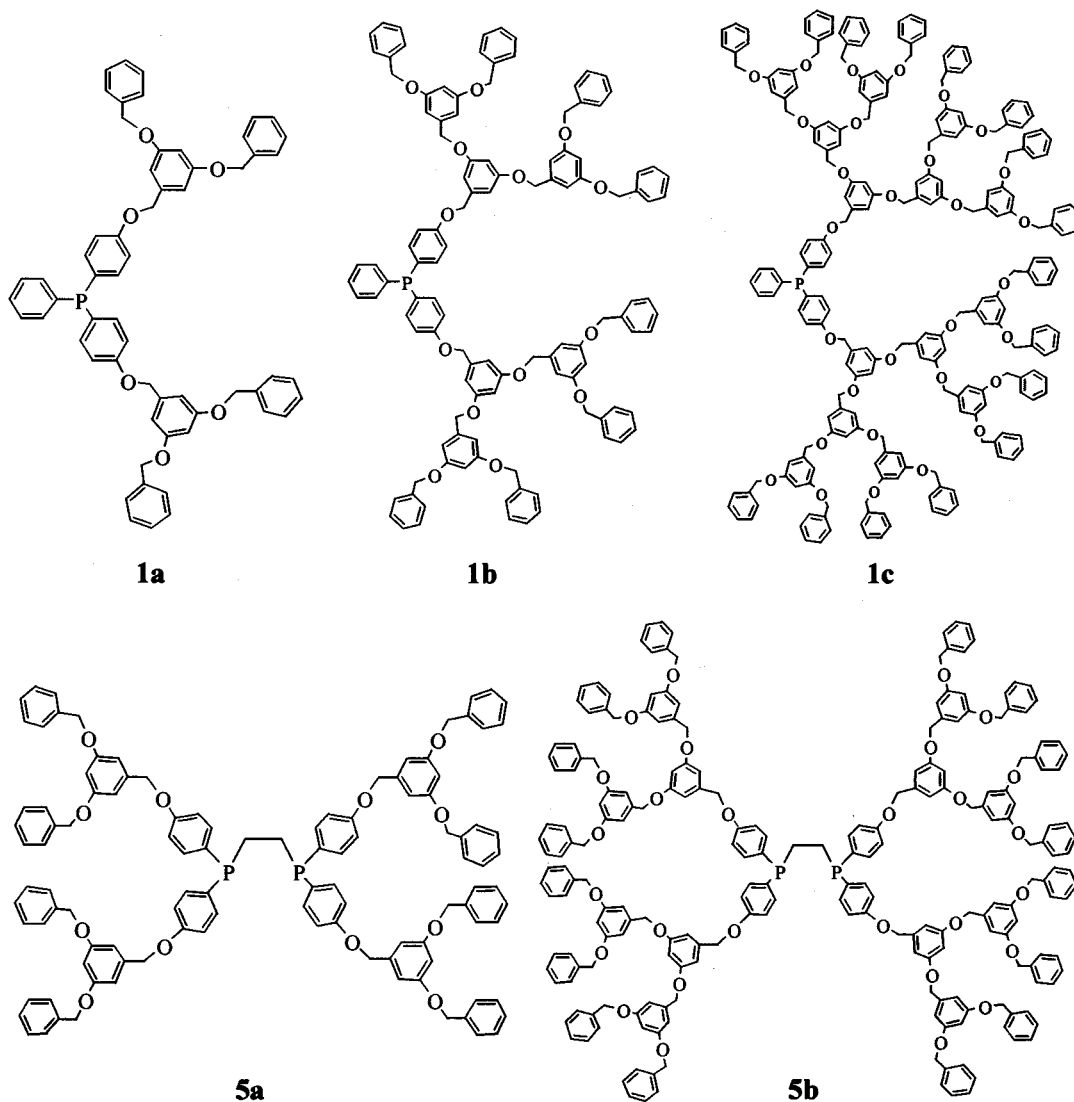
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Chart 1. Compounds 1a-c, Monodentate Ligands, and 5a,b, Bidentate Ligands



moiety and experience unique properties typical of dendrimers. However, the latter compounds are less addressed.

It is well-known that the strong coordinating ability of phosphines to transition metals is utilized in a wide variety of homogeneous catalytic reactions such as hydrogenation,¹⁰ hydroformylation,¹¹ and allylic substitution.¹² The beneficial feature of phosphines is their

ability to tune metal environment (steric and/or electronic) through coordination. Both mono- and bidentate phosphines are employed for this purpose.

Given the importance of dendrimers on one hand and phosphines on the other, the incorporation of dendrimers on a phosphine core must be a rational scheme for making potent ligands. Triphenyl phosphine (TPP) and 1,2-bis(diphenylphosphino)ethane (DPPE) are typical mono- and bidentate phosphine ligands, respectively, which are most frequently used in a wide variety of homogeneous catalysis.¹⁵ A good deal of knowledge about performance of TPP and DPPE as ligands has been accumulated for many transition metal catalyses. In this paper, we introduce dendrimer moieties to the phenyl rings of TPP and DPPE to obtain dendrimer-phosphine ligands (**1a-c** and **5a,b**, Chart 1) which might possess a nature similar to TPP and DPPE, but with additional dendrimer properties. Dendrimer-phosphine complexes having a metal at the core would be easily prepared with these ligands. Although these phosphine complexes might realize unique catalytic ability provoked by the dendrimer exterior, there have

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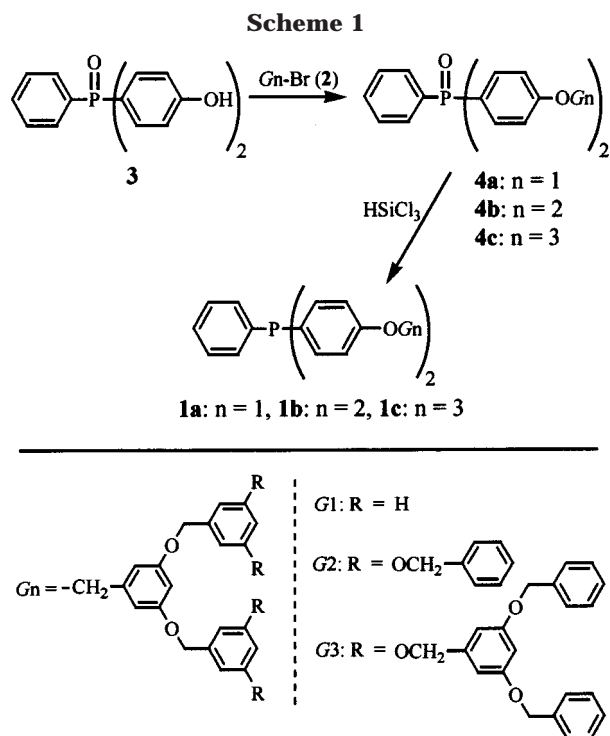
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been only three precedents (Ru,^{8a} Ir,¹³ and Au¹⁴ complexes) for such complexes. Herein, we report synthesis, characterization, and complexation of mono (**1a–c**) and bidentate (**5a,b**) dendrimer–phosphine ligands to provide novel metallo–dendrimer complexes with Pt(0) at the core.

Results and Discussion

Synthesis of Monodentate Phosphine Ligands

(1). Our basic strategy of the synthesis consists of connecting Fréchet type polybenzyl ether dendrimer unit (G1–Br, **2a**; G2–Br, **2b**; G3–Br, **2c**)^{3a} to bis(4-hydroxyphenyl)phenylphosphine oxide (**3**) to afford the corresponding dendrimer–phosphine oxides (**4a–c**) in high yields (Scheme 1).

The phosphine oxides (**4a–c**) were readily reduced using trichlorosilane¹⁶ to the corresponding phosphines (**1a–c**, Scheme 1). ³¹P NMR spectra of **1a–c** showed resonance at -7.6 , -7.6 , and -7.7 ppm, respectively, without any peaks in the phosphine oxide region (20–30 ppm). ESI mass spectrum of **1a–c** showed a single molecular ion peaks at m/z 898 (M^+), 1749 ($M + H^+$), and 3448 ($M + H^+$), respectively (Figure 1). These mass spectra as well as elemental analysis data clearly indicate that the products are monodisperse and with no incomplete substitution. Obtaining such a defect-free ligand is essential for synthesis of a metallo–dendrimer with definite structure and well-defined architecture.

Synthesis of Bidentate Phosphine Ligands (**5**).

To use the chelating nature of bidentate phosphines such as DPPE, a parallel synthetic route was envisioned. Synthesis similar to the one used for monodentate ligands (Scheme 1) could not be applied successfully due to the poor solubility of $(\text{HO}C_6H_4)_2PCH_2CH_2P(C_6H_4-$

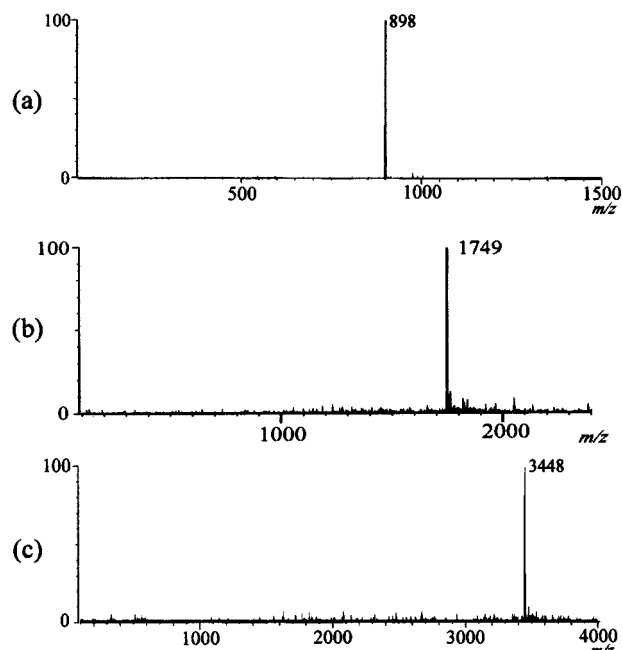
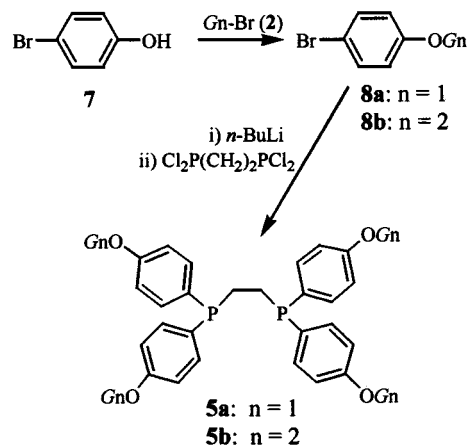


Figure 1. ESI MS spectra of monodentate ligands: (a) **1a**; (b) **1b**; (c) **1c**.

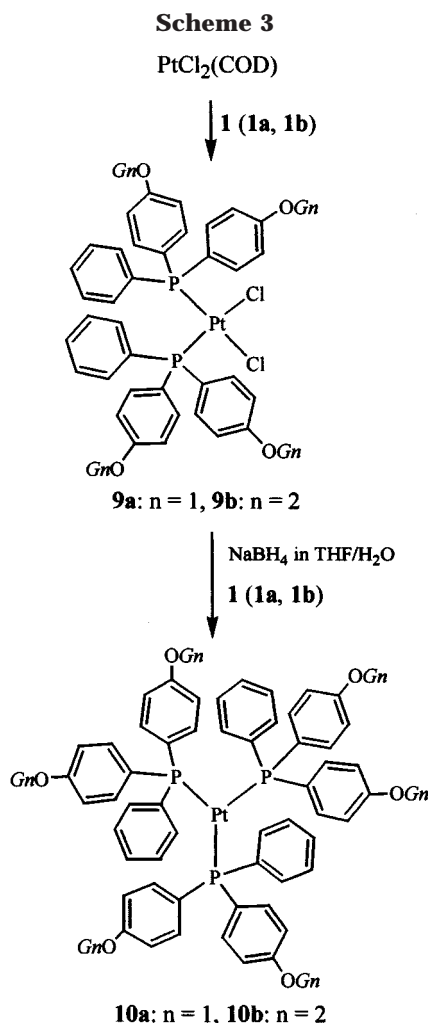
Scheme 2



$\text{OH})_2$ ¹⁷ and the corresponding phosphine oxide in common organic solvents. The reactions with these substrates only afforded an intractable mixture of products containing a varying number (1–4) of the dendrimer moieties (GPC and ESI mass spectra). As an alternate strategy, **2a** and **2b** were condensed with 4-bromophenol (**7**) to get the corresponding ethers **8a,b**, respectively, in high yields (Scheme 2). Then, lithiation of **8a** and **8b** with *n*-BuLi followed by reaction with 1,2-bis(dichlorophosphino)ethane gave the required products (**5a,b**) in a pure form. ³¹P resonance of **5a** and **5b** appeared as a single sharp peak at -14.8 and -15.0 ppm, and ESI mass spectra gave corresponding molecular ion peaks at m/z 1672 ($M + H^+$) and 3370 ($M + H^+$), respectively. Careful examination of ¹³C and ¹H NMR spectra indicated that **5a** and **5b** were obtained as a defect-free monodisperse material, which was supported by the elemental analysis data of the corresponding phosphine oxides (**6a**, $n = 1$; **6b**, $n = 2$).

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Complexation Studies. Our next aim was to study the coordination ability of **1a–c** and **5a,b**. Platinum was selected as the metal counterpart due to good stability and catalytic activity of its phosphine complexes.¹⁸

In the case of monodentate phosphines (Scheme 3), 2 equiv of **1a** was allowed to react with 1 equiv of PtCl₂(COD) at room temperature.¹⁹ ³¹P NMR analysis of the reaction mixture indicated all the **1a** coordinated to the Pt(II) center to show resonance at 12.5 ppm (¹J_{P–Pt} = 3682 Hz). The analytically pure **9a** was isolated in 97% yield from the reaction mixture. On the basis of comparison with ³¹P NMR spectra of known Pt(II) TPP complexes (*cis*- and *trans*-PtCl₂(PPh₃)₂),²⁰ the product obtained (**9a**) was formulated to be the *cis* complex as shown in Scheme 3. Similarly, starting from **1b**, the *cis*-complex **9b** was isolated in an analytically pure form.²¹ Subsequently, reduction of **9a** and **9b** to the correspond-

ing Pt(0) complexes (**10a** and **10b**) were successfully carried out with NaBH₄ in a THF/H₂O mixture, while other reducing agents reported for Pt(II) (*n*-Bu₄NF,^{22a} *n*-Bu₄NHSO₄,^{22b} and NH₂NH₂)^{22c} were all unsuccessful. The ³¹P resonances of **10a** and **10b** appeared only at 48.2 ppm (¹J_{P–Pt} = 4445 Hz) and 49.0 ppm (¹J_{P–Pt} = 4455 Hz), respectively. These chemical shifts as well as the ¹J_{P–Pt} values are very similar to those of Pt(PPh₃)₃ (49.9 ppm, ¹J_{P–Pt} = 4438 Hz),²³ but not with Pt(PPh₃)₄ (9.2 ppm, ¹J_{P–Pt} = 3829 Hz).²³ Thus, both **10a** and **10b** must have the three phosphine ligands on the platinum as shown in Scheme 3. This formula was further supported by the elemental analysis of **10a** and **10b**. In the case of Pt(0) TPP complex, both Pt(PPh₃)₃ and Pt(PPh₃)₄ can be prepared selectively.^{24a} Moreover, Pt(PPh₃)₄ can be generated by adding excess PPh₃ to Pt(PPh₃)₃.^{23,24b} In contrast, neither a use of excess **1** in the reduction of **9** (Scheme 3) nor adding excess **1** to **10** yielded the corresponding PtL₄ complex. This may be attributed to the voluminous size of **1**.^{25a–c}

As for the chelating phosphines, **11a** and **11b** were obtained in high yields by the reaction of PtCl₂(COD) with **5a** and **5b**, respectively (Scheme 4). It is well-known that, unlike the monodentate ligands, chelating phosphines such as DPPE afford cationic complexes [Pt²⁺(DPPE)₂].²⁶ Thus, further addition of **5a,b** to **11a,b** afforded the cationic complex **12a,b** in high yields, respectively. ³¹P NMR spectra of **12a,b** were almost identical with that of [Pt(DPPE)₂]Cl₂. Finally, reduction of **12a,b** with NaBH₄ in a THF/H₂O mixture gave Pt(0) complex **13a,b** respectively, as analytically pure materials in high yields (Scheme 4).

In line with Hawker's observation^{4b} of enhanced solubilities of dendritic units, the novel dendrimer-phosphine ligands (**1a–c**, **5a,b**) and their Pt complexes (**9a,b**, **10a,b**, **11a,b**, **12a,b**, and **13a,b**) obtained in the present study show high solubilities in benzene, THF, and dichloromethane, as compared with TPP, DPPE, and the corresponding Pt complexes. All the dendrimer-phosphines (**1a–c**, **5a,b**) are insoluble in hexane. However, addition of even a small amount of benzene or toluene caused a drastic change and gave a homogeneous solution. With TPP and DPPE, such a distinct phenomenon was not observed. Moreover, **11a** and **11b** are freely soluble in dichloromethane, whereas the corresponding *cis*-PtCl₂(DPPE) is almost insoluble.

Oxidative Addition Study. Oxidative addition²⁷ is one of the most important elementary steps in many catalytic cycles. Therefore, the reaction of the dendrimer-phosphine Pt(0) complexes (**10** and **13**) with

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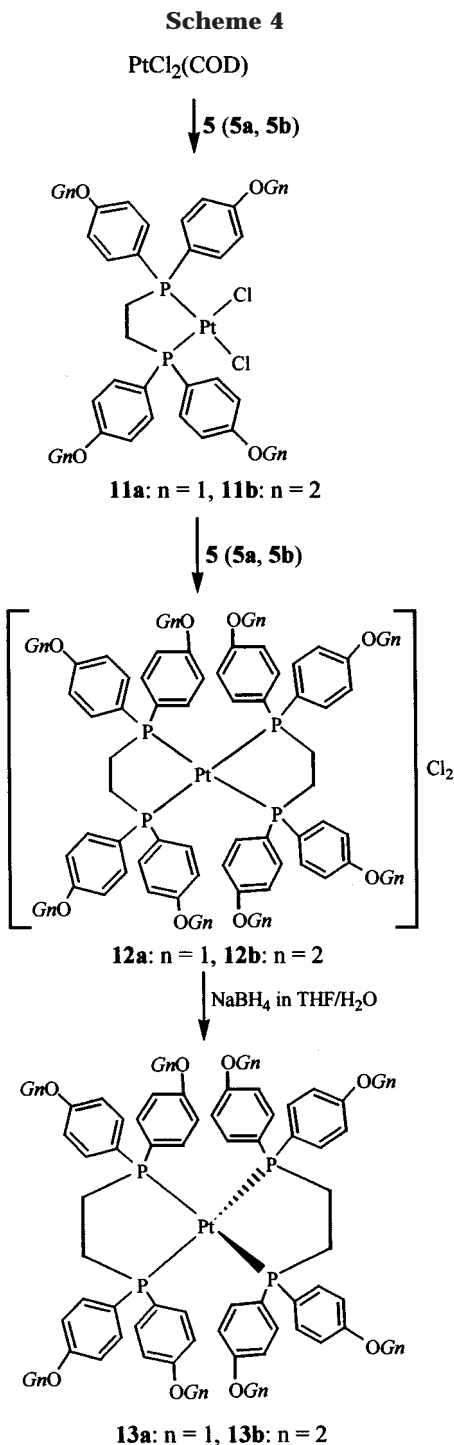
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CH₃I and C₆H₅I were carried out with monitoring the reaction by ³¹P NMR. Just like Pt(DPPE)₂,²⁸ **13a** and **13b** (stable 18-electron complexes) did not show any reactivity in the reaction. So, the reactions of Pt(PPh₃)₃ (**10c**) and **10a,b** were studied (Table 1). The reaction of CH₃I with **10c**,^{29a,c} **10a** and **10b** was too fast and completed within 2 min (before the ³¹P NMR measurement) to afford trans adducts **14c** (³¹P resonance at 27.7

ppm with ¹J_{P-Pt} = 3063 Hz: lit.^{29c} 26.8 ppm, ¹J_{P-Pt} = 3064 Hz), **14a** (26.4 ppm with ¹J_{P-Pt} = 3050 Hz), and **14b** (26.3 ppm with ¹J_{P-Pt} = 3039 Hz), respectively, in quantitative yields (entries 1–3). On the other hand, the reaction of **10c**^{29b} and **10b** with C₆H₅I was slower enough to be followed by ³¹P NMR. Since C₆H₅I was used in excess (10 equiv), the reaction showed pseudo first order dependence on [PtL₃]: -d[PtL₃]/dt = k_{obs}[PtL₃]. Plots of ln[PtL₃] vs time showed a straight line (R² = 0.97–0.99) up to 80% conversion. In both benzene and 1,2-dichloroethane as a solvent, **10c** afforded trans adduct **14d** (³¹P resonance at 22.9 ppm with ¹J_{P-Pt} = 3086 Hz: lit.^{29b} 21.2 ppm with ¹J_{P-Pt} = 3097 Hz) quantitatively (entries 4 and 5), while **10b** reacted two times slower to afford trans adduct **14e** (³¹P resonance at 20.8 ppm with ¹J_{P-Pt} = 3050 Hz) (entries 6 and 7). Thus, the Pt center of **10b** is still easily accessible in the reaction. The dendrimer–phosphine ligands might work as a potent ligand in a catalytic reaction.³⁰

Molecular Modeling of 13b. All the Pt complexes (**9a,b**, **10a,b**, **11a,b**, **12a,b**, and **13a,b**) obtained in this study could not be recrystallized due to their high solubility in common organic solvent systems: only amorphous or glassy materials were obtained. Thus, the so extremely low crystallinity nature of the complexes prevented us from obtaining single crystals suitable for X-ray crystallographic analysis. On the other hand, recently molecular modeling³¹ is developing as a reliable tool. Even a large molecule could be modeled properly, if nonempirical,³² semiempirical,³³ and molecular mechanics³⁴ calculations are combined.

Among the Pt complexes obtained in this study, **13b** is the largest molecule (C₄₄₄H₃₈₄O₅₆P₄Pt, MW = 6934.7) and relatively rigid since it contains the chelate ligand **5b**. So we performed calculations to visualize a molecular shape of **13b**. First, to search a low-energy conformer of the G₂ moiety, conformational analysis was carried out for G₂-OC₆H₅ by CONFLEX³⁵/MM3.³⁶ Then, to get an initial structure of **13b**, the optimized G₂ moiety was introduced to Pt(DPPE)₂ whose structure had been optimized³⁷ by the DFT³⁸ method (B3LYP³⁹/

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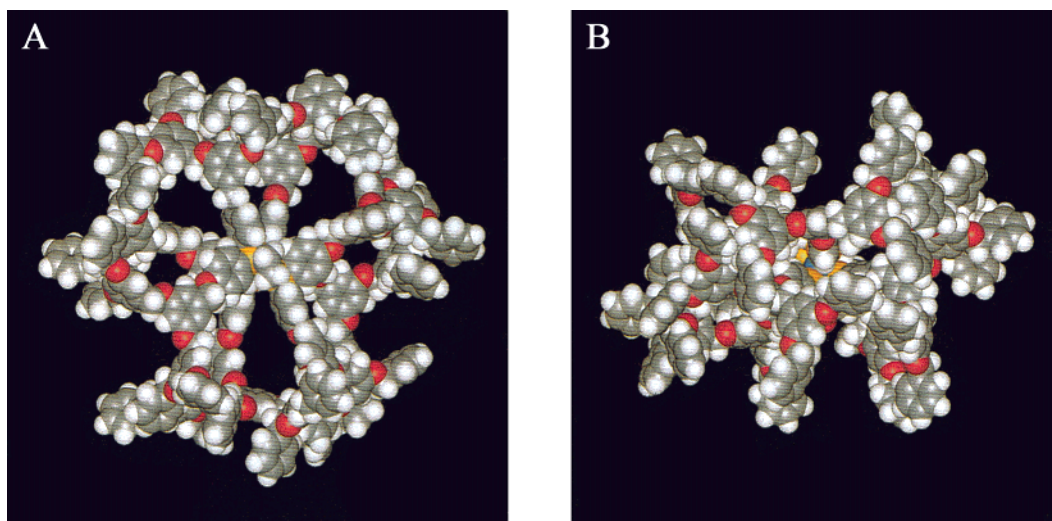
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Table 1. Oxidative Addition of PtL₃ (10a–c) with CH₃I and C₆H₅I^a

entry	PtL ₃ + RI		→ <i>trans</i> -PtRIL ₂		14 (L)	<i>k</i> _{obs} × 10 ² /min ⁻¹
	10	R	solvent	temp/°C		
1	10a	CH ₃	toluene- <i>d</i> ₈	22	14a (1a)	large ^b
2	10b	CH ₃	toluene- <i>d</i> ₈	22	14b (1b)	large ^b
3	10c	CH ₃	toluene- <i>d</i> ₈	22	14c (TPP)	large ^b
4	10c	C ₆ H ₅	benzene- <i>d</i> ₆	49	14d (TPP)	10.97
5	10c	C ₆ H ₅	ClCH ₂ CH ₂ Cl	49	14d (TPP)	5.29
6	10b	C ₆ H ₅	benzene- <i>d</i> ₆	49	14e (1b)	5.62
7	10b	C ₆ H ₅	ClCH ₂ CH ₂ Cl	49	14e (1b)	2.73

^a [PtL₃]₀ = 1.5 × 10⁻² mol dm⁻³; [RI]₀/[PtL₃]₀ = 10. ^b The oxidative addition was completed within 2 min.

**Figure 2.** (a) Side and (b) top view of optimized 13b.

LANL2DZ⁴⁰). Finally, the resulting structure was further optimized by PM3⁴¹/MOZYME⁴² method with fixing the PtP₄ core structure, and the results are shown in Figure 2. The complex has nanoscale flattened globular structure with an approximate diameter of 4.4 nm. Noteworthy is that as the optimization proceeded, several cavities appeared around the Pt (Figure 2a), which might be utilized as a guest room⁶ in some catalytic transformations.

Experimental Section

General Experimental Procedures. All manipulations were performed under an argon atmosphere using standard Schlenk-type glassware on a dual-manifold Schlenk line. The reagents and the solvents were dried and purified before use by usual procedures.⁴³ 3,5-Dihydroxybenzyl alcohol and 1,2-

bis(dichlorophosphino)ethane were purchased from Aldrich. G1-Br,^{3a} G2-Br,^{3a} G3-Br,^{3a} C₆H₅(P=O)(C₆H₄OH)₂ (**3**),⁴⁴ and PtCl₂(COD)⁴⁵ were prepared according to literature procedures. ¹H NMR (400.13 MHz), ¹³C NMR (100.61 MHz), and ³¹P NMR (161.98 MHz) spectra were recorded on a Bruker ARX 400 instrument. ³¹P NMR data are given relative to external 85% H₃PO₄. Column chromatography was performed on silica gel (Wako Chemicals, Wakogel C-200HG; particle size 75–150 μm) or Florisil (Kanto Chemicals, granularity 150–250 μm). ESI mass spectra were recorded on a JEOL JMS-SX102A instrument. Recycling preparative-scale GPC (RP-GPC) was carried out on a Japan Analytical Industry LC-918 system equipped with Jaigel-1H and Jaigel-2H columns using CHCl₃ as an eluent. Elemental analyses were performed at the Center for Instrumental Analysis of Hokkaido University.

C₆H₅(P=O)(C₆H₄O-G1)₂ (4a). To a refluxing solution of dry K₂CO₃ (2.2 g, 15.8 mmol) and bis(4-hydroxyphenyl)phenylphosphine oxide (**3**) (1.95 g, 6.3 mmol) in 50 mL of DMF and 50 mL of THF were added dropwise a mixture of 18-crown-6 ether (800 mg, 3.0 mmol) and G1-Br (**2a**) (5.3 g, 13.9 mmol) in THF (100 mL) with stirring. After 48 h, this solution was allowed to cool to room temperature and then filtrated using Celite. The Celite was washed with THF (10 mL × 3). The combined organic solvent was concentrated and purified by column chromatography on silica gel (ethyl acetate: toluene = 1:2 in volume). Removal of the solvent gave **4a** as a white glass like solid, 5.6 g (yield > 99%). ¹H NMR (CDCl₃): δ 5.01 (s, 12H), 6.56 (t, *J* = 2 Hz, 2H), 6.63 (d, *J* = 2 Hz, 4H), 6.98 (dd, *J* = 9 Hz, 2 Hz, 4H), 7.24–7.40 (m, 22H), 7.51–7.57 (m, 5H), 7.62–7.65 (m, 2H). ¹³C NMR (CDCl₃): δ 69.9, 70.1, 101.6, 106.3, 114.9 (³*J*_{C-P} = 7 Hz), 127.5, 128.3, 128.6, 132.0 (²*J*_{C-P} = 20

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H_z), 133.9 (²J_{C-P} = 20 Hz), 136.6, 138.7, 160.2. ³¹P NMR (C₆D₆): δ 29.3. Anal. Calcd for C₆₀H₅₁O₇P: C, 78.76; H, 5.62. Found: C, 78.71; H, 5.65.

C₆H₅(P=O)(C₆H₄O-G₂)₂ (4b). This was prepared from G₂-Br (2b) (5.0 g, 6.2 mmol) similarly, and obtained as a white solid (4.64 g, yield 87%). ¹H NMR (CDCl₃): δ 4.95 (s, 8H), 5.01 (s, 20H), 6.54 (t, *J* = 2 Hz, 2H), 6.56 (t, *J* = 2 Hz, 4H), 6.64 (d, *J* = 2 Hz, 4H), 6.66 (d, *J* = 2 Hz, 8H), 7.00 (dd, *J* = 9 Hz, 2 Hz, 4H), 7.16 (m, 2H), 7.28–7.50 (m, 42H), 7.53–7.67 (m, 5H). ¹³C NMR (CDCl₃): δ 70.0, 70.1, 101.5, 101.6, 106.4, 114.8 (³J_{C-P} = 7 Hz), 127.5, 128.0, 128.5, 131.9 (²J_{C-P} = 20 Hz), 133.9 (²J_{C-P} = 20 Hz), 136.7, 138.6, 139.1, 160.1. ³¹P NMR (C₆D₆): δ 29.3. Anal. Calcd for C₁₁₆H₉₉O₁₅P: C, 78.98; H, 5.66. Found: C, 78.98; H, 5.72.

C₆H₅(P=O)(C₆H₄O-G₃)₂ (4c). Similarly, 4c was prepared from G₃-Br (2c) (356 mg, 0.21 mmol) and further purified by the RP-GPC. The product was freeze-thaw dried to get a white solid (256 mg, 74%). ¹H NMR (CDCl₃): δ 4.90–4.94 (br, 28H), 4.97 (s, 32H), 6.51 (t, *J* = 2 Hz, 4H), 6.53 (t, *J* = 2 Hz, 10H), 6.62 (d, *J* = 2 Hz, 14H), 6.63 (d, *J* = 2 Hz, 14H), 6.96 (dd, *J* = 9 Hz, 2 Hz, 9 Hz, 4H), 7.24–7.52 (m, 89H). ¹³C NMR (CDCl₃): δ 69.9, 70.0, 101.5, 106.3, 106.4, 114.8 (³J_{C-P} = 7 Hz), 127.5, 128.0, 128.4, 134.0, 136.7, 138.6, 139.0, 139.1, 160.0, 160.1. ³¹P NMR (C₆D₆): δ 29.1; ESI-MS: *m/z* 3463 ([M + H]⁺). Anal. Calcd for C₂₂₈H₁₉₅O₃₁P: C, 79.10; H, 5.68. Found: C, 78.93; H, 5.73.

C₆H₅P(C₆H₄O-G₁)₂ (1a). To a solution of 4a (1.27 g, 1.4 mmol) in degassed xylene (10 mL) was added triethylamine (0.41 mL, 2.94 mmol) and HSiCl₃ (0.28 mL, 2.8 mmol) at room temperature with stirring. The mixture was stirred at 120 °C for 48 h. Then, the suspension was cooled to room temperature and poured into 5 mL of 2 N NaOH(aq). The organic layer was washed with water and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluting with CH₂Cl₂) to give 1a as a white solid (1.18 g, 93%). ¹H NMR (CDCl₃): δ 4.98 (s, 4H), 5.01 (s, 8H), 6.55 (t, *J* = 2 Hz, 2H), 6.64 (d, *J* = 2 Hz, 4H), 6.92 (d, *J* = 9 Hz, 4H), 7.26–7.41 (m, 29H). ¹³C NMR (CDCl₃): δ 69.9, 70.1, 101.6, 106.3, 115.2 (³J_{C-P} = 7 Hz), 127.5, 128.0, 128.5, 133.2 (²J_{C-P} = 20 Hz), 135.3 (²J_{C-P} = 20 Hz), 136.7, 139.1, 160.2. ³¹P NMR (C₆D₆): δ -7.6. ESI-MS: *m/z* 898 ([M]⁺). Anal. Calcd for C₆₀H₅₁O₆P: C, 80.16; H, 5.72. Found: C, 80.41; H, 5.74.

C₆H₅P(C₆H₄O-G₂)₂ (1b). In a similar manner, 1b was prepared from 4b (3.19 g, 1.8 mmol) as a white solid (2.70 g, 83%). ¹H NMR (CDCl₃): δ 5.00 (br, 8H), 5.05 (br, 20H), 6.61 (br, 6H), 6.70–6.72 (br, 12H), 6.98 (d, *J* = 9 Hz, 4H), 7.20 (m, 1H), 7.29–7.46 (m, 48H). ¹³C NMR (CDCl₃): δ 69.9, 70.0, 101.5, 106.3, 114.9 (³J_{C-P} = 7 Hz), 127.5, 128.2, 128.5, 133.1 (²J_{C-P} = 20 Hz), 135.2 (²J_{C-P} = 20 Hz), 136.7, 138.3, 139.1, 160.0, 160.1. ³¹P NMR (C₆D₆): δ -7.6. ESI-MS: *m/z* 1749 ([M + H]⁺). Anal. Calcd for C₁₁₆H₉₉O₁₄P: C, 79.71; H, 5.71. Found: C, 79.93; H, 5.77.

C₆H₅P(C₆H₄O-G₃)₂ (1c). This was prepared from 4c (255 mg, 0.074 mmol) in an analogous manner and obtained as a white solid after freeze-thaw drying (172 mg, 67%). ¹H NMR (CDCl₃): δ 4.90–4.94 (br, 28H), 4.96 (s, 26H), 5.00 (s, 6H), 6.50–6.57 (m, 15H), 6.62 (d, *J* = 2 Hz, 10H), 6.63 (d, *J* = 2 Hz, 14H), 6.65 (d, *J* = 2 Hz, 3H), 6.88 (d, *J* = 9 Hz, 3H), 7.17–7.39 (m, 90H). ¹³C NMR (CDCl₃): δ 69.9, 70.0, 101.5, 106.3, 106.4, 127.5, 128.0, 128.6, 136.7, 139.1, 160.0, 160.1. ³¹P NMR (C₆D₆): δ -7.7. ESI-MS: *m/z* 3448 ([M + H]⁺). Anal. Calcd for C₂₂₈H₁₉₅O₃₀P: C, 79.47; H, 5.70. Found: C, 79.59; H, 5.85.

BrC₆H₄O-G₁ (8a). A 100 mL two necked flask was charged with dry K₂CO₃ (2.16 g, 15.65 mmol) and *p*-bromo phenol (7) (2.26 g, 13.05 mmol) in THF (20 mL). To this well-stirred suspension under reflux were added a mixture of G₁-Br (2a) (5.00 g, 13.05 mmol) and 18-crown-6 ether (345 mg, 1.30 mmol) in THF (40 mL) over 1 h. The rate of the addition is maintained in such a way that a brisk effervescence is observed for every drop addition. After the addition was over the reaction mixture

was refluxed for 48 h. Then the reaction mixture was cooled to room temperature. The mixture was filtered through a short pad of Celite. Celite was then washed with THF (10 mL × 5). The combined organic phase was evaporated to dryness under reduced pressure. The crude residue was taken in ethyl acetate which was washed with 5% NaOH (10 mL × 5), water, and brine successively. The organic layer was dried over MgSO₄. Removal of the solvent under reduced pressure yielded crude product. It was purified by column chromatography on silica gel using a EtOAc/hexane mixture (1:9 in volume) as an eluent: yield 5.27 g (85%). ¹H NMR (CDCl₃): δ 4.97–5.02 (m, 24H), 6.58 (s, 8H), 6.67 (s, 12H), 6.91 (s, 8H), 7.32–7.39 (m, 40H); ¹³C NMR (CDCl₃): δ 70.1, 101.6, 106.3, 113.2, 116.7, 127.6, 128.1, 128.6, 132.3, 136.9, 139.0, 157.7, 160.2. ESI-MS: *m/z* 474 [M]⁺, 476 [M]⁺.

BrC₆H₄O-G₂ (8b). Similarly, 8b was prepared from G₂-Br (2b) (3.00 g, 3.30 mmol) in 80% yield (2.67 g). ¹H NMR (CDCl₃): δ 4.99–5.08 (m, 24H), 6.62–6.74 (m, 8H), 6.86–6.88 (m, 8H), 7.26–7.46 (m, 40H). ¹³C NMR (CDCl₃): δ 70.5, 70.6, 102.0, 102.1, 106.8, 106.9, 113.7, 117.2, 127.7, 128.1, 128.7, 132.8, 137.2, 139.5, 139.7, 158.2, 160.6, 160.7. ESI-MS: *m/z* 898 [M]⁺, 900 [M]⁺.

(G₁-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G₁)₂ (5a). A 100-mL single necked round-bottom flask fitted with three-way stopcock was charged with 8a (1.5 g, 3.16 mmol) and 20 mL of THF. The reaction flask was cooled to -78 °C. To this cooled solution, *n*-BuLi (202 mg, 3.16 mmol) was added drop by drop over 5 min, keeping the temperature below -78 °C. After the addition was over, the reaction mixture was stirred at that temperature for 60 min. Then, 1,2-bis(dichlorophosphino)ethane (183 mg, 0.79 mmol) in toluene (2.5 mL) was added at -78 °C over 5 min. The reaction mixture was further stirred at that temperature for 90 min, and at room temperature overnight. The solvent was removed under reduced pressure, and the residue was dissolved in toluene (20 mL). Water (5 mL) was added to the solution, and the resulting suspension was stirred for 30 min. It was filtered through a short column containing a mixture of Celite and MgSO₄ (2:1 in volume), and the column was washed with toluene (5 mL × 4). The combined filtrate was concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ (1.5 mL), and MeOH (10 mL) was added to precipitate the crude 5a. After the crude 5a was dried under high vacuum, it was dissolved CH₂Cl₂ (0.5 mL) and a flash filtration through Florisil using a THF/CH₂Cl₂ mixture (1:99 in volume) as an eluent gave pure product in 75% yield (0.989 g). Alternatively, the crude 5a can be purified by column chromatography on silica gel using a EtOAc/hexane mixture (2:3 in volume) as an eluent. ¹H NMR (CDCl₃): δ 1.8–2.2 (m, 4H), 4.97–5.02 (m, 24H), 6.58 (s, 8H), 6.67 (s, 12H), 6.91 (s, 8H), 7.32–7.39 (m, 40H). ¹³C NMR (CDCl₃): δ 22.6, 69.7, 70.2, 101.6, 106.4, 115.1, 127.7, 128.1, 128.7, 134.2, 136.8, 139.3, 159.3, 160.2. ³¹P NMR (C₆D₆): δ -14.82. ESI-MS: *m/z* 1672 ([M + H]⁺).

(G₂-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G₂)₂ (5b). Compound 5b was similarly prepared from 8b (1.5 g, 1.67 mmol) in 70% yield (0.985 g). ¹H NMR (CDCl₃): δ 2.0–2.2 (m, 4H), 5.06 (s, 56H), 6.66 (s, 16H), 6.76 (s, 36H), 7.26–7.46 (m, 80H). ¹³C NMR (CDCl₃): δ 22.6, 70.0, 70.1, 101.6, 106.4, 115.2, 127.6, 128.0, 128.6, 132.7, 136.8, 139.1, 160.2. ³¹P NMR (C₆D₆): δ -14.99. ESI-MS: *m/z* 3370 ([M + H]⁺).

(G₁-OC₆H₄)₂(P=O)CH₂CH₂(P=O)(C₆H₄O-G₁)₂ (6a). H₂O₂ (10%, 0.5 mL) was added to 5a (100 mg, 0.06 mmol) in 5 mL of CH₂Cl₂, and the reaction mixture was stirred for 30 min. The resulting mixture was transferred to a separating funnel and washed with water and brine successively. The organic layer was dried over MgSO₄ followed by removal of the solvent under reduced pressure gave 6a as a white glass like material. ¹H NMR (CDCl₃): δ 1.8–2.2 (m, 4H), 4.97–5.02 (m, 24H), 6.63–6.73 (m, 20H), 6.91 (s, 8H), 7.32–7.39 (m, 40H). ¹³C NMR (CDCl₃): δ 22.7, 69.8, 70.2, 101.5, 106.4, 114.9, 127.6, 128.1, 128.6, 134.3, 136.8, 139.6, 158.7, 160.2. ³¹P NMR (C₆D₆): δ

34.46. Anal. Calcd for $C_{110}H_{96}O_{14}P_2$: C, 77.54; H, 5.68. Found: C, 77.98; H, 5.88.

(**G2-OC₆H₄**)₂(P=O)CH₂CH₂(P=O)(C₆H₄O-G2)₂ (**6b**). Compound **6b** was prepared similarly from **5b** (100 mg, 0.03 mmol). ¹H NMR (CDCl₃): δ 1.8–2.1 (m, 4H), 4.9–5.02 (m, 56H), 6.58–6.69 (m, 52H), 7.25–7.41 (m, 80H). ¹³C NMR (CDCl₃): δ 22.6, 70.0, 70.1, 101.6, 106.4, 115.2, 127.6, 128.1, 128.6, 132.7, 136.8, 139.2, 160.2. ³¹P NMR (C₆D₆): δ 34.09. Anal. Calcd for C₂₂₂H₁₉₂O₃₀P₂: C, 78.38; H, 5.69. Found: C, 78.20; H, 5.89.

cis-PtCl₂[PC₆H₅(C₆H₄O-G1)₂]₂ (**9a**). To PtCl₂(COD) (75 mg, 0.2 mmol) and **1a** (360 mg, 0.4 mmol) was added THF (1 mL) at room temperature. The reaction mixture was stirred for 6 h, and crude **9a** was precipitated by adding 5 mL of hexane. This light ivory product was purified by RP-GPC to afford **9a** as a white glass like solid in 97% yield (401 mg). ³¹P NMR (C₆D₆): δ 12.5 (¹J_{P-Pt} = 3682 Hz). ESI-MS: *m/z* 2028.7 ([M - Cl]⁺). Anal. Calcd for C₁₂₀H₁₀₂O₁₂Cl₂P₂Pt: C, 69.83; H, 4.98. Found: C, 69.68; H, 5.13.

cis-PtCl₂[PC₆H₅(C₆H₄O-G2)₂]₂ (**9b**). In the same manner as **9a**, **9b** was obtained from **1b** (87.5 mg, 0.05 mmol) as a white solid in 70% yield (66 mg). ³¹P NMR (C₆D₆): δ 13.3 (¹J_{P-Pt} = 3657 Hz). ESI-MS: *m/z* 3727.7 ([M - Cl]⁺). Anal. Calcd for C₂₃₂H₁₉₈O₂₈Cl₂P₂Pt: C, 74.07; H, 5.30. Found: C, 74.00; H, 5.36.

Pt[PC₆H₅(C₆H₄O-G1)₂]₃ (**10a**). Compound **9a** (81.3 mg, 0.0394 mmol) and **1a** (35.4 mg, 0.0394 mmol) were dissolved in a mixture of 3.8 mL of THF and 0.2 mL of H₂O. Then, solid NaBH₄ was added in one portion to the solution with stirring. After 1 min, 10 mL of hexane was added to the resulting yellow solution to precipitate crude **9a**. The crude **9a** was purified by a short Florisil column with THF as an eluent to afford an yellow solid in 50% yield (57 mg). ¹³C and ¹H NMR spectra were very similar to those of **1a**. ³¹P NMR (C₆D₆): δ 48.2 (¹J_{P-Pt} = 4445 Hz). ESI-MS: *m/z* 2893 ([M + H]⁺). Anal. Calcd for C₁₈₀H₁₅₃O₁₈P₃Pt: C, 74.75; H, 5.33. Found: C, 75.23; H, 5.60.

Pt[PC₆H₅(C₆H₄O-G2)₂]₃ (**10b**). In a manner similar to **10a**, **10b** was prepared from the reaction between **9b** and **1b**. ¹³C and ¹H NMR spectra were very similar to those of **1b**. ³¹P NMR (C₆D₆): δ 49.0 (¹J_{P-Pt} = 4455 Hz). ESI-MS: *m/z* 5456 ([M + H + H₂O]⁺). Anal. Calcd for C₃₄₈H₂₉₇O₄₂P₃Pt: C, 76.85; H, 5.50. Found: C, 76.90; H, 5.88.

cis-PtCl₂[(G1-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G1)]₂ (**11a**). At room temperature, **5a** (225 mg, 0.134 mmol) in CH₂Cl₂ (1 mL) was added dropwise over 1 min to PtCl₂(COD) (50 mg, 0.134 mmol) in CH₂Cl₂ (3 mL). The resulting solution was stirred for 10 h. The solution was concentrated under reduced pressure to half of the initial volume, and **11a** was precipitated by adding 10 mL of hexane. The **11a** thus obtained was dissolved in 1 mL of CH₂Cl₂ again, and **11a** was precipitated by adding 10 mL of MeOH. Finally, the crude **11a** was purified by a short Florisil column with a THF/CH₂Cl₂ mixture (1:9 in volume) as an eluent to afford a white solid in 96% yield (250 mg). ³¹P NMR (C₆D₆): δ 39.73 (¹J_{P-Pt} = 3641 Hz). ESI-MS: *m/z* 1902.3 ([M - Cl]⁺), 1866.9 ([M - 2Cl]⁺).

cis-PtCl₂[(G2-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G2)]₂ (**11b**). In a manner analogous to **11a**, **11b** was prepared from **5b** (200 mg, 0.059 mmol) in 95% yield (205 mg). ³¹P (C₆D₆): δ 40.00 (¹J_{P-Pt} = 3628 Hz). Anal. Calcd for C₂₂₂H₁₉₂O₂₈Cl₂P₂Pt·0.5 CH₂Cl₂: C, 72.65; H, 5.29. Found: C, 72.62; H 6.00.

[Pt{(G1-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G1)}₂]₂Cl₂ (**12a**). At room temperature, **11a** (200 mg, 0.103 mmol) was dissolved in THF (3 mL), and **5a** (175 mg, 0.104 mmol) in THF (1 mL) was added dropwise over 1 min. The resulting solution was stirred for 10 h. The solution was concentrated under reduced pressure to half of the initial volume, and **12a** was precipitated

by adding 10 mL of hexane. The precipitate was dissolved in 1 mL of CH₂Cl₂, and **12a** was precipitated once again by adding 10 mL of MeOH. Finally, the crude **12a** was purified through a short Florisil column with a THF/CH₂Cl₂ mixture (1:1 in volume) as an eluent and **12a** was afforded as a white solid in 96% yield (357 mg). ³¹P NMR (C₆D₆): δ 46.97 (¹J_{P-Pt} = 2383 Hz). ESI-MS: *m/z* 3574.5 ([M - Cl]⁺), 1769.5 ([M - 2Cl]²⁺). Anal. Calcd for C₂₂₀H₁₉₂O₂₄Cl₂P₄Pt·CH₂Cl₂: C, 71.84; H, 5.29. Found: C, 71.93; H, 5.48.

[Pt{(G2-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G2)}₂]₂Cl₂ (**12b**). In a manner similar to **12a**, **12b** was prepared from **11b** (150 mg, 0.041 mmol) in 92% yield (266 mg). ³¹P NMR (C₆D₆): δ 46.45 (¹J_{P-Pt} = 2370 Hz). ESI-MS: *m/z* 3684.6 ([M + 2H + 3CHCl₃]²⁺). Anal. Calcd for C₄₄₄H₃₈₄O₅₆Cl₂P₄Pt·CH₂Cl₂: C, 75.38; H 5.49. Found: C, 75.24; H 6.07

Pt[(G1-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G1)]₂ (**13a**). Compound **12a** (50 mg) was dissolved in a mixture of 0.47 mL of THF and 0.03 mL of H₂O. Then, solid NaBH₄ was added in one portion to the solution with stirring. After 5 min, 10 mL of hexane was added to the resulting yellow solution to precipitate **13a**. The **13a** thus obtained was dissolved in 1 mL of CH₂Cl₂, and diethyl ether (10 mL) was added to precipitate crude **13a**. The crude **13a** was purified by a short Florisil column with THF as an eluent to afford a yellow solid in 80% yield (36 mg). ¹³C and ¹H NMR spectra were very similar to those of **5a**. ³¹P NMR (C₆D₆): δ 27.86 (¹J_{P-Pt} = 3746 Hz). ESI-MS: *m/z* 1769 ([M + 2H]²⁺). Anal. Calcd for C₂₂₀H₁₉₂O₂₄P₄Pt·CH₂Cl₂: C, 73.25; H, 5.40. Found: C, 72.81; H 5.76.

Pt[(G2-OC₆H₄)₂PCH₂CH₂P(C₆H₄O-G2)]₂ (**13b**). In a similar manner, **13b** was prepared from **12b** (50 mg) in 70% yield as a yellow glassy solid (35 mg). ¹³C and ¹H NMR spectra were very similar to those of **5b**. ³¹P NMR (C₆D₆): δ 29.46 (¹J_{P-Pt} = 3741 Hz). ESI-MS: *m/z* 3467 ([M + 2H]²⁺), 3512 ([M + AcOEt]²⁺). Anal. Calcd for C₄₄₄H₃₈₄O₅₆P₄Pt·2CH₂Cl₂: C, 75.40; H 5.50. Found: C, 75.12; H 5.96.

PdCl₂(PC₆H₅(C₆H₄O-G3)₂)₂. To a mixture of PdCl₂(PhCN)₂ (5 mg, 0.01 mmol) and **1c** (100 mg, 0.03 mmol) was added benzene (2 mL) at room temperature. After stirring for 22 h, the reaction mixture was concentrated under reduced pressure. ³¹P NMR (C₆D₆): δ 22.08, 31.17.

Oxidative Addition of RI (R = CH₃ or C₆H₅) to 10 (Table 1). An NMR tube was charged with 0.45 mL of 1.5 × 10⁻² mol dm⁻³ solution of **10** (in C₆D₆ or 1,2-dichloroethane). Then, excess RI (10 equiv; R = CH₃ or C₆H₅) was added to the solution by a syringe. The sample was immediately analyzed with ³¹P NMR. When 1,2-dichloroethane was used as the solvent, C₆D₆ in a sealed capillary was used for locking. For all the oxidative addition studies, H₃PO₄ in D₂O in a small sealed capillary was used as an internal standard for integrating the ³¹P resonance. ³¹P resonances of **14a–e** were as follows: **14a**, 26.4 ppm (¹J_{P-Pt} = 3050 Hz); **14b**, 26.3 ppm (¹J_{P-Pt} = 3039 Hz); **14c**,^{29c} 27.7 ppm (¹J_{P-Pt} = 3063 Hz); **14d**,^{29b} 20.8 ppm (¹J_{P-Pt} = 3050 Hz); **14e**, 22.9 ppm (¹J_{P-Pt} = 3086 Hz).

Molecular Modeling of 13b. The CONFLEX/MM3 conformational analysis was carried out with CACHE 3.2 (Oxford Molecular) on a DELL Precision 610 WorkStation. The DFT and PM3/MOZYME calculations were performed with the Gaussian 98⁴⁷ and MOPAC2000 (Ver 1.32, Fujitsu), respec-

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Supporting Information Available: Cartesian coordinates of optimized **13b** (Figure 2). This material is available free of charge via Internet at <http://pubs.acs.org>.

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