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

B. S. Balaji, Yasushi Obora, Daisuke Ohara, Shigehiro Koide, and Yasushi Tsuji*

Catalysis Research Center and Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0811, Japan

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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 $PtCl_2(COD)$ 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 $Pt(L-L)_2$ complexes (**13a,b**), respectively. Preliminary studies on oxidative addition of RI ($R = CH_3$ 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 divergent[2] and convergent[3] 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 core[8] 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

* To whom correspondence should be addressed. Fax: +81-11-706-3698. E-mail: tsuji@cat.hokudai.ac.jp.

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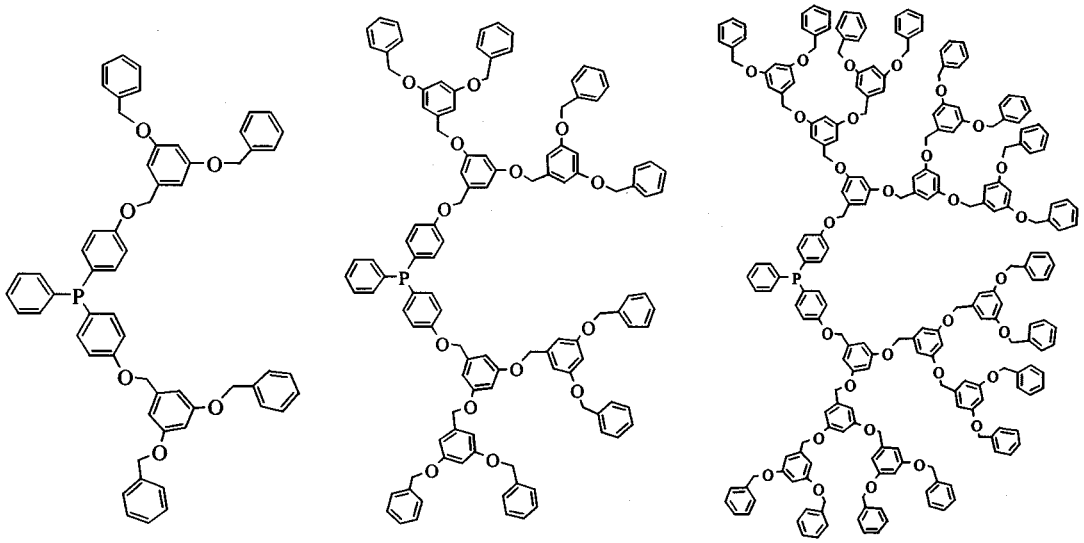
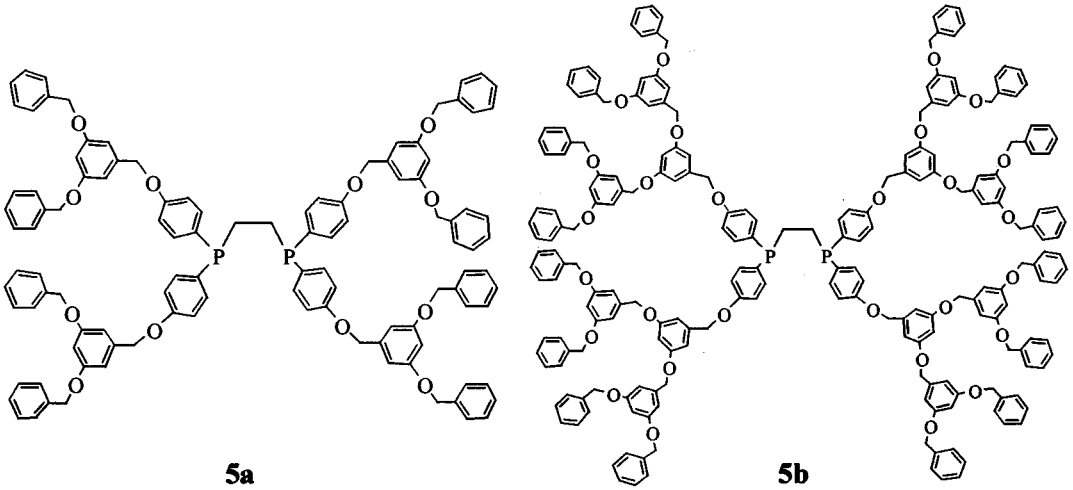
Chart 1. Compounds 1a−c, Monodentate Ligands, and 5a,b, Bidentate Ligands



1a **1b** **1c**



5a **5b**

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 in 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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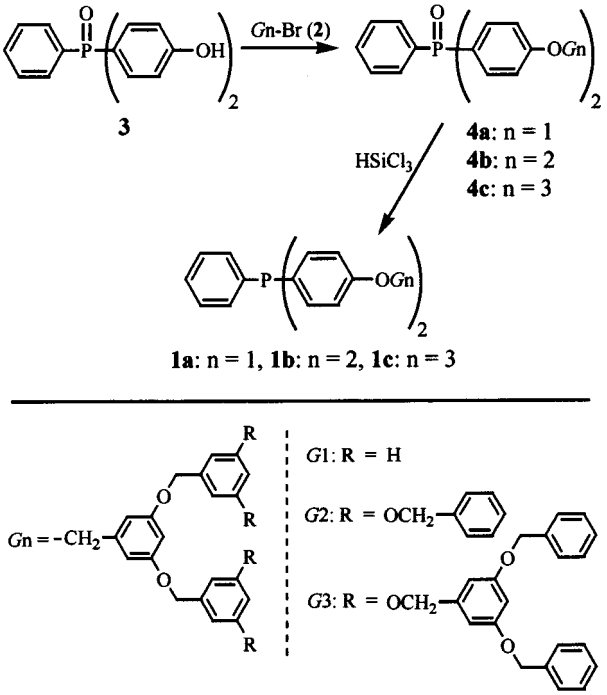
Scheme 1



been only three precedents (Ru,[8a] Ir,[13] and Au[14] 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 (*G*1-Br, **2a**; *G*2-Br, **2b**; *G*3-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 trichlorosilane[16] to the corresponding phosphines (**1a**−**c**, Scheme 1). ^{31}P 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 $(HOC_6H_4)_2PCH_2CH_2P(C_6H_4OH)_2$[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. ^{31}P 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 ^{13}C and ^{1}H 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**, $n = 2$).

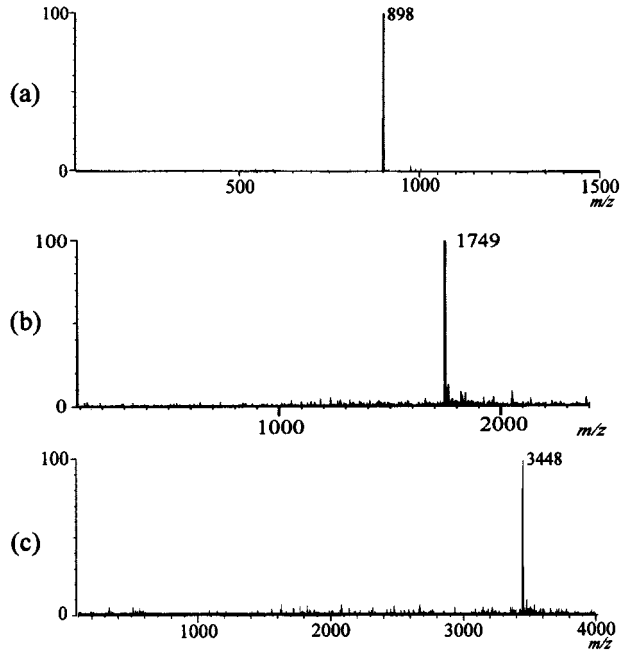
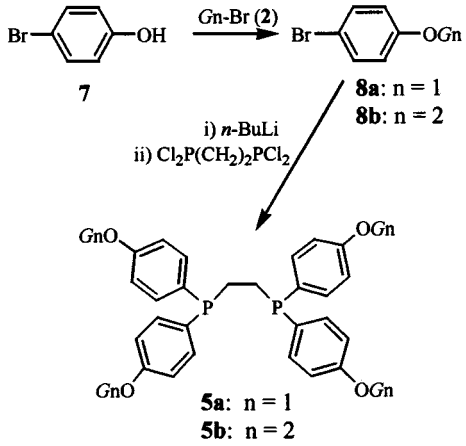


Figure 1. ESI MS spectra of monodentate ligands: (a) **1a**; (b) **1b**; (c) **1c**.

Scheme 2



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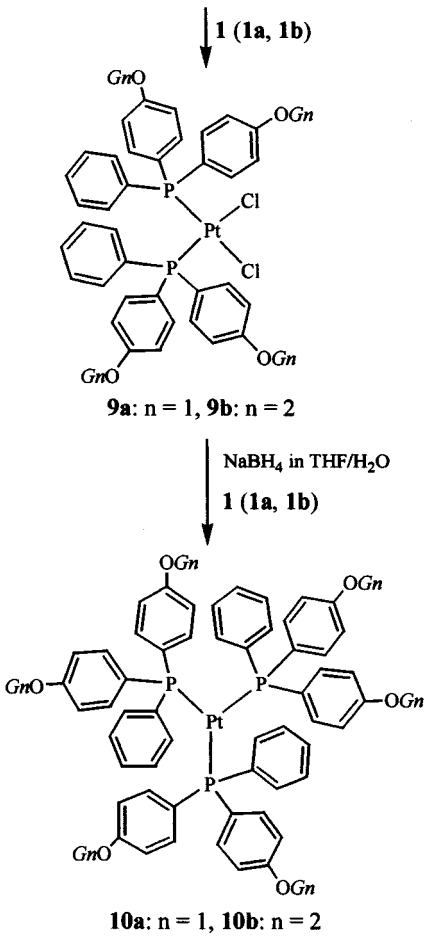
Scheme 3



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 $PtCl_2$(COD) at room temperature.[19] ^{31}P 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 ^{31}P NMR spectra of known Pt(II) TPP complexes (*cis*- and *trans*-$PtCl_2(PPh_3)_2$),[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 corresponding Pt(0) complexes (**10a** and **10b**) were successfully carried out with $NaBH_4$ in a THF/H_2O mixture, while other reducing agents reported for Pt(II) (*n*-Bu_4NF,[22a] *n*-Bu_4NHSO_4,[22b] and NH_2NH_2[22c]) were all unsuccessful. The ^{31}P 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 $Pt(PPh_3)_3$ (49.9 ppm, $^1J_{P-Pt}$ = 4438 Hz),[23] but not with $Pt(PPh_3)_4$ (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 $Pt(PPh_3)_3$ and $Pt(PPh_3)_4$ can be prepared selectively.[24a] Moreover, $Pt(PPh_3)_4$ can be generated by adding excess PPh_3 to $Pt(PPh_3)_3$.[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 PtL_4 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 $PtCl_2$(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 $[Pt^{2+}(DPPE)_2]$.[26] Thus, further addition of **5a,b** to **11a,b** afforded the cationic complex **12a,b** in high yields, respectively. ^{31}P NMR spectra of **12a,b** were almost identical with that of $[Pt(DPPE)_2]Cl_2$. Finally, reduction of **12a,b** with $NaBH_4$ in a THF/H_2O 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*-$PtCl_2$(DPPE) is almost insoluble.

Oxidative Addition Study. Oxidative addition[27] 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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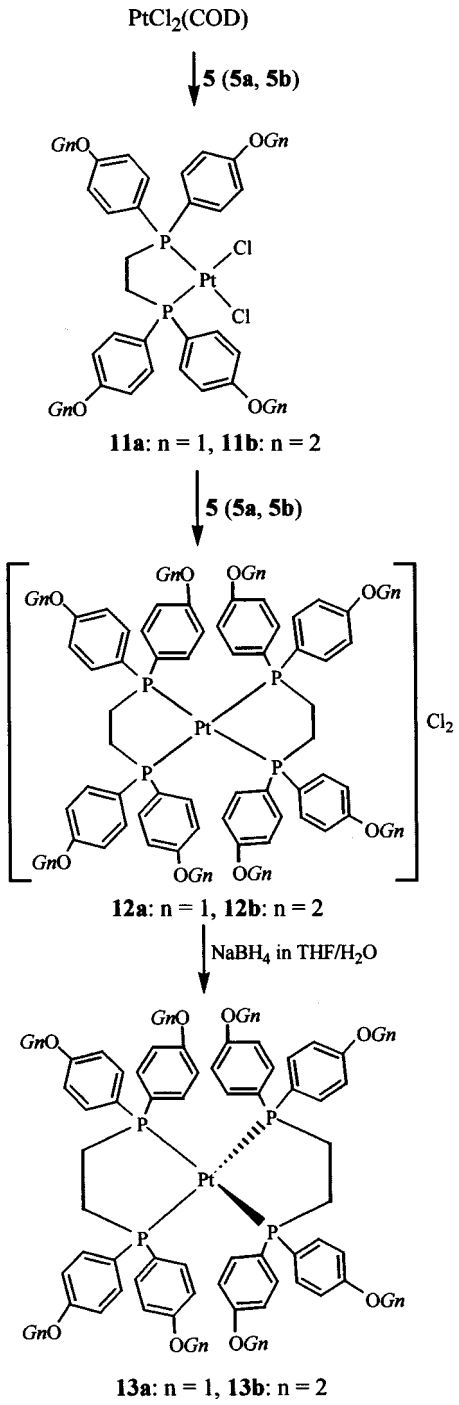
Scheme 4



CH_3I and C_6H_5I were carried out with monitoring the reaction by ^{31}P 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 $Pt(PPh_3)_3$ (**10c**) and **10a,b** were studied (Table 1). The reaction of CH_3I with **10c**,[29a,c] **10a** and **10b** was too fast and completed within 2 min (before the ^{31}P NMR measurement) to afford trans adducts **14c** (^{31}P 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 C_6H_5I was slower enough to be followed by ^{31}P NMR. Since C_6H_5I was used in excess (10 equiv), the reaction showed pseudo first order dependence on $[PtL_3]$: $-d[PtL_3]/dt = k_{obs}[PtL_3]$. Plots of $\ln[PtL_3]$ vs time showed a straight line ($R^2 = 0.97-0.99$) up to 80% conversion. In both benzene and 1,2-dichloroethane as a solvent, **10c** afforded trans adduct **14d** (^{31}P 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** (^{31}P 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 recrystalized 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 modeling[31] is developing as a reliable tool. Even a large molecule could be modeled properly, if nonempirical,[32] semiempirical,[33] and molecular mechanics[34] calculations are combined.

Among the Pt complexes obtained in this study, **13b** is the largest molecule ($C_{444}H_{384}O_{56}P_4Pt$, 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 *G*2 moiety, conformational analysis was carried out for *G*2-OC_6H_5 by CONFLEX[35]/MM3.[36] Then, to get an initial structure of **13b**, the optimized *G*2 moiety was introduced to $Pt(DPPE)_2$ whose structure had been optimized[37] by the DFT[38] method (B3LYP[39]/

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Table 1. Oxidative Addition of PtL_3 (10a−c) with CH_3I and C_6H_5I[a]

$$\underset{\mathbf{10}}{PtL_3} + RI \longrightarrow \underset{\mathbf{14}}{\textit{trans}\text{-}PtRIL_2}$$

entry	PtL_3	R	solvent	temp/°C	14 (L)	$k_{obs} \times 10^2$/min^{-1}
1	**10a**	CH_3	toluene-d_8	22	**14a** (**1a**)	large[b]
2	**10b**	CH_3	toluene-d_8	22	**14b** (**1b**)	large[b]
3	**10c**	CH_3	toluene-d_8	22	**14c** (TPP)	large[b]
4	**10c**	C_6H_5	benzene-d_6	49	**14d** (TPP)	10.97
5	**10c**	C_6H_5	$ClCH_2CH_2Cl$	49	**14d** (TPP)	5.29
6	**10b**	C_6H_5	benzene-d_6	49	**14e** (**1b**)	5.62
7	**10b**	C_6H_5	$ClCH_2CH_2Cl$	49	**14e** (**1b**)	2.73

[a] $[PtL_3]_0 = 1.5 \times 10^{-2}$ mol dm^{-3}; $[RI]_0/[PtL_3]_0 = 10$. [b] The oxidative addition was completed within 2 min.

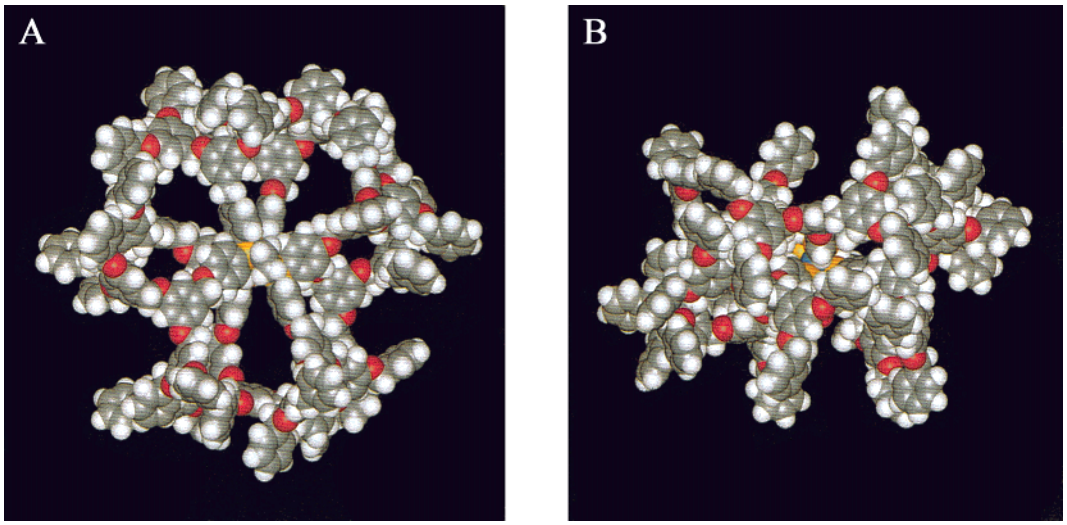

Figure 2. (a) Side and (b) top view of optimized **13b**.

LANL2DZ[40]). Finally, the resulting structure was further optimized by PM3[41]/MOZYME[42] method with fixing the PtP_4 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 room[6] 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. *G*1-Br,[3a] *G*2-Br,[3a] *G*3-Br,[3a] $C_6H_5(P{=}O)(C_6H_4OH)_2$ (**3**),[44] and $PtCl_2(COD)$[45] were prepared according to literature procedures. ^{1}H NMR (400.13 MHz), ^{13}C NMR (100.61 MHz), and ^{31}P NMR (161.98 MHz) spectra were recorded on a Bruker ARX 400 instrument. ^{31}P NMR data are given relative to external 85% H_3PO_4. 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 $CHCl_3$ as an eluent. Elemental analyses were performed at the Center for Instrumental Analysis of Hokkaido University.

$C_6H_5(P{=}O)(C_6H_4O$-*G*1$)_2$ (4a). To a refluxing solution of dry K_2CO_3 (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 *G*1-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%). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): δ 69.9, 70.1, 101.6, 106.3, 114.9 ($^3J_{C-P}$ = 7 Hz), 127.5, 128.3, 128.6, 132.0 ($^2J_{C-P}$ = 20

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Hz), 133.9 ($^2J_{C-P}$ = 20 Hz), 136.6, 138.7, 160.2. ^{31}P NMR (C_6D_6): δ 29.3. Anal. Calcd for $C_{60}H_{51}O_7P$: C, 78.76; H, 5.62. Found: C, 78.71; H, 5.65.

C_6H_5(P=O)(C_6H_4O-*G*2)$_2$ (4b). This was prepared from *G*2-Br (**2b**) (5.0 g, 6.2 mmol) similarly, and obtained as a white solid (4.64 g, yield 87%).^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): δ 29.3. Anal. Calcd for $C_{116}H_{99}O_{15}P$: C, 78.98; H, 5.66. Found: C, 78.98; H, 5.72.

C_6H_5(P=O)(C_6H_4O-*G*3)$_2$ (4c). Similarly, **4c** was prepared from *G*3-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%). ^{1}H NMR ($CDCl_3$) : 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): δ 29.1; ESI-MS: m/z 3463 ([M + H]$^+$). Anal. Calcd for $C_{228}H_{195}O_{31}P$: C, 79.10; H, 5.68. Found: C, 78.93; H, 5.73.

C_6H_5P(C_6H_4O-*G*1)$_2$ (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 $HSiCl_3$ (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 Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluting with CH_2Cl_2) to give **1a** as a white solid (1.18 g, 93%). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): δ −7.6. ESI-MS: m/z 898 ([M]$^+$). Anal. Calcd for $C_{60}H_{51}O_6P$: C, 80.16; H, 5.72. Found: C, 80.41; H, 5.74.

C_6H_5P(C_6H_4O-*G*2)$_2$ (1b). In a similar manner, **1b** was prepared from **4b** (3.19 g, 1.8 mmol) as a white solid (2.70 g, 83%). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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.^{31}P NMR (C_6D_6): δ −7.6. ESI-MS: m/z 1749 ([M + H]$^+$). Anal. Calcd for $C_{116}H_{99}O_{14}P$: C, 79.71; H, 5.71. Found: C, 79.93; H, 5.77.

C_6H_5P(C_6H_4O-*G*3)$_2$ (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%). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): δ −7.7. ESI-MS: m/z 3448 ([M + H]$^+$). Anal. Calcd for $C_{228}H_{195}O_{30}P$: C, 79.47; H, 5.70. Found: C, 79.59; H, 5.85.

BrC_6H_4O-*G*1 (8a). A 100 mL two necked flask was charged with dry K_2CO_3 (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 *G*1-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 $MgSO_4$. 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%).^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$) 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]$^+$.

BrC_6H_4O-*G*2 (8b). Similarly, **8b** was prepared from *G*2-Br (**2b**) (3.00 g, 3.30 mmol) in 80% yield (2.67 g). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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]$^+$.

(*G*1-OC_6H_4)$_2$PCH_2CH_2P(C_6H_4O-*G*1)$_2$ (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 $MgSO_4$ (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 CH_2Cl_2 (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 CH_2Cl_2 (0.5 mL) and a flash filtration through Florisil using a THF/CH_2Cl_2 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. ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): δ −14.82. ESI-MS: m/z 1672 ([M + H]$^+$).

(*G*2-OC_6H_4)$_2$PCH_2CH_2P(C_6H_4O-*G*2)$_2$ (5b). Compound **5b** was similarly prepared from **8b** (1.5 g, 1.67 mmol) in 70% yield (0.985 g). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): δ −14.99. ESI-MS: m/z 3370 ([M + H]$^+$).

(*G*1-OC_6H_4)$_2$(P=O)CH_2CH_2(P=O)(C_6H_4O-*G*1)$_2$ (6a). H_2O_2 (10%, 0.5 mL) was added to **5a** (100 mg, 0.06 mmol) in 5 mL of CH_2Cl_2, 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 $MgSO_4$ followed by removal of the solvent under reduced pressure gave **6a** as a white glass like material. ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): 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.

(*G*2-OC$_6$H$_4$)$_2$(P=O)CH$_2$CH$_2$(P=O)(C$_6$H$_4$O-*G*2)$_2$ (6b). Compound **6b** was prepared similarly from **5b** (100 mg, 0.03 mmol). ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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. ^{31}P NMR (C_6D_6): δ 34.09. Anal. Calcd for $C_{222}H_{192}O_{30}P_2$: C, 78.38; H, 5.69. Found: C, 78.20; H, 5.89.

***cis*-PtCl$_2$[PC$_6$H$_5$(C$_6$H$_4$O-*G*1)$_2$]$_2$ (9a).** To $PtCl_2$(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). ^{31}P NMR (C_6D_6): δ 12.5 ($^1J_{P-Pt}$ = 3682 Hz). ESI-MS: *m*/*z* 2028.7 ([M − Cl]$^+$). Anal. Calcd for $C_{120}H_{102}O_{12}Cl_2P_2Pt$: C, 69.83; H, 4.98. Found: C, 69.68; H, 5.13.

***cis*-PtCl$_2$[PC$_6$H$_5$(C$_6$H$_4$O-*G*2)$_2$]$_2$ (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). ^{31}P NMR (C_6D_6): δ 13.3 ($^1J_{P-Pt}$ = 3657 Hz). ESI-MS: *m*/*z* 3727.7 ([M − Cl]$^+$). Anal. Calcd for $C_{232}H_{198}O_{28}Cl_2P_2Pt$: C, 74.07; H, 5.30. Found: C, 74.00; H, 5.36.

Pt[PC$_6$H$_5$(C$_6$H$_4$O-*G*1)$_2$]$_3$ (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 H_2O. Then, solid $NaBH_4$ 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). ^{13}C and ^{1}H NMR spectra were very similar to those of **1a**. ^{31}P NMR (C_6D_6): δ 48.2 ($^1J_{P-Pt}$ = 4445 Hz). ESI-MS: *m*/*z* 2893 ([M + H]$^+$). Anal. Calcd for $C_{180}H_{153}O_{18}P_3Pt$: C, 74.75; H, 5.33. Found: C, 75.23; H, 5.60.

Pt[PC$_6$H$_5$(C$_6$H$_4$O-*G*2)$_2$]$_3$ (10b). In a manner similar to **10a**, **10b** was prepared from the reaction between **9b** and **1b**. ^{13}C and ^{1}H NMR spectra were very similar to those of **1b**. ^{31}P NMR (C_6D_6): δ 49.0 ($^1J_{P-Pt}$ = 4455 Hz). ESI-MS: *m*/*z* 5456 ([M + H + H_2O]$^+$). Anal. Calcd for $C_{348}H_{297}O_{42}P_3Pt$: C, 76.85; H, 5.50. Found: C, 76.90; H, 5.88.

***cis*-PtCl$_2$[(*G*1-OC$_6$H$_4$)$_2$PCH$_2$CH$_2$P(C$_6$H$_4$O-*G*1)$_2$] (11a).** At room temperature, **5a** (225 mg, 0.134 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 1 min to $PtCl_2$(COD) (50 mg, 0.134 mmol) in CH_2Cl_2 (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 CH_2Cl_2 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/CH_2Cl_2 mixture (1:9 in volume) as an eluent to afford a white solid in 96% yield (250 mg). ^{31}P NMR (C_6D_6): δ 39.73 ($^1J_{P-Pt}$ = 3641 Hz). ESI-MS: *m*/*z* 1902.3 ([M − Cl]$^+$), 1866.9 ([M − 2Cl]$^+$).

***cis*-PtCl$_2$[(*G*2-OC$_6$H$_4$)$_2$PCH$_2$CH$_2$P(C$_6$H$_4$O-*G*2)$_2$] (11b).** In a manner analogous to **11a**, **11b** was prepared from **5b** (200 mg, 0.059 mmol) in 95% yield (205 mg). ^{31}P (C_6D_6): δ 40.00 ($^1J_{P-Pt}$ = 3628 Hz). Anal. Calcd for $C_{222}H_{192}O_{28}Cl_2P_2Pt\cdot 0.5\ CH_2Cl_2$:[46] C, 72.65; H, 5.29. Found: C, 72.62; H 6.00.

[Pt{(*G*1-OC$_6$H$_4$)$_2$PCH$_2$CH$_2$P(C$_6$H$_4$O-*G*1)$_2$}$_2$]Cl$_2$ (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 CH_2Cl_2, 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/CH_2Cl_2 mixture (1:1 in volume) as an eluent and **12a** was afforded as a white solid in 96% yield (357 mg). ^{31}P NMR (C_6D_6): δ 46.97 ($^1J_{P-Pt}$ = 2383 Hz). ESI-MS: *m*/*z* 3574.5 ([M − Cl]$^+$), 1769.5 ([M − 2Cl]$^{2+}$). Anal. Calcd for $C_{220}H_{192}O_{24}Cl_2P_4Pt\cdot CH_2Cl_2$: C, 71.84; H, 5.29. Found: C, 71.93; H, 5.48.

[Pt{(*G*2-OC$_6$H$_4$)$_2$PCH$_2$CH$_2$P(C$_6$H$_4$O-*G*2)$_2$}$_2$]Cl$_2$ (12b). In a manner similar to **12a**, **12b** was prepared from **11b** (150 mg, 0.041 mmol) in 92% yield (266 mg). ^{31}P NMR (C_6D_6): δ 46.45 ($^1J_{P-Pt}$ = 2370 Hz). ESI-MS: *m*/*z* 3684.6 ([M + 2H + 3$CHCl_3$]$^{+2}$). Anal. Calcd for $C_{444}H_{384}O_{56}Cl_2P_4Pt\cdot CH_2Cl_2$: C, 75.38; H 5.49. Found: C, 75.24; H 6.07

Pt[(*G*1-OC$_6$H$_4$)$_2$PCH$_2$CH$_2$P(C$_6$H$_4$O-*G*1)$_2$]$_2$ (13a). Compound **12a** (50 mg) was dissolved in a mixture of 0.47 mL of THF and 0.03 mL of H_2O. Then, solid $NaBH_4$ 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 CH_2Cl_2, 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). ^{13}C and ^{1}H NMR spectra were very similar to those of **5a**. ^{31}P NMR (C_6D_6): δ 27.86 ($^1J_{P-Pt}$ = 3746 Hz). ESI-MS: *m*/*z* 1769 ([M + 2H]$^{2+}$). Anal. Calcd for $C_{220}H_{192}O_{24}P_4Pt\cdot CH_2Cl_2$: C, 73.25; H, 5.40. Found: C, 72.81; H 5.76.

Pt[(*G*2-OC$_6$H$_4$)$_2$PCH$_2$CH$_2$P(C$_6$H$_4$O-*G*2)$_2$]$_2$ (13b). In a similar manner, **13b** was prepared from **12b** (50 mg) in 70% yield as a yellow glassy solid (35 mg). ^{13}C and ^{1}H NMR spectra were very similar to those of **5b**. ^{31}P NMR (C_6D_6): δ 29.46 ($^1J_{P-Pt}$ = 3741 Hz). ESI-MS: *m*/*z* 3467 ([M + 2H]$^{2+}$), 3512 ([M + AcOEt]$^{2+}$). Anal. Calcd for $C_{444}H_{384}O_{56}P_4Pt\cdot 2CH_2Cl_2$: C, 75.40; H 5.50. Found: C, 75.12; H 5.96.

PdCl$_2$(PC$_6$H$_5$(C$_6$H$_4$O-*G*3)$_2$)$_2$. To a mixture of $PdCl_2(PhCN)_2$ (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. ^{31}P NMR (C_6D_6): δ 22.08, 31.17.

Oxidative Addition of RI (R = CH$_3$ or C$_6$H$_5$) 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 C_6D_6 or 1,2-dichloroethane). Then, excess RI (10 equiv; R = CH_3 or C_6H_5) was added to the solution by a syringe. The sample was immediately analyzed with ^{31}P NMR. When 1,2-dichloroethane was used as the solvent, C_6D_6 in a sealed capillary was used for locking. For all the oxidative addition studies, H_3PO_4 in D_2O in a small sealed capillary was used as an internal standard for integrating the ^{31}P resonance. ^{31}P 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 98[47] and MOPAC2000 (Ver 1.32, Fujitsu), respec-

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tively, on an HP Exemplar V2500 at the Hokkaido University Computing Center.

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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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