Dinuclear Pd(I)−Pd(I) and Pt(II)···Pt(II) Complexes Supported by Tridentate Pyphos Ligands (Pyphos = 6-(Diphenylphosphino)-2-pyridonate)

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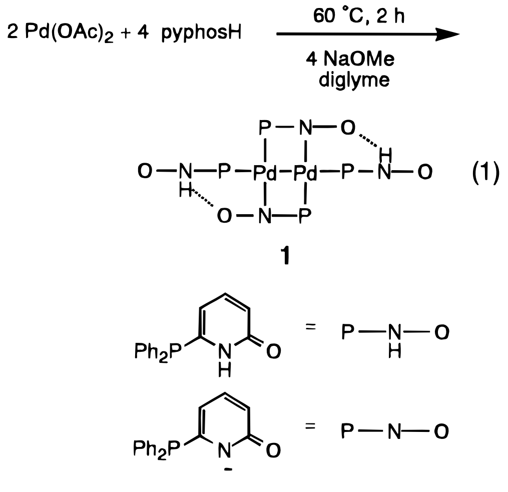
Two dinuclear complexes of palladium(I) and platinum(II) have been prepared by using a tridentate ligand containing three kinds of coordination sites, *i.e.* oxygen, nitrogen, and phosphorus atoms. Treatment of palladium(II) acetate with a mixture of 6-(diphenylphosphino)-2-pyridone (abbreviated as PyphosH) and sodium methoxide in diglyme produced a dimeric palladium(I) complex containing a metal−metal bond, $Pd_2(pyphos)_2(pyphosH)_2$ (**1**), in 43% yield. The dinuclear complex **1** has a Pd−Pd single bond [2.623(1) Å] surrounded by two pyphos ligands and two pyphosH ligands, where the pyphos ligand connected to pyphosH through an intramolecular hydrogen bond [**1**: monoclinic, space group $C2/c$ with $a = 19.794(7)$ Å, $b = 14.753(7)$ Å, $c = 25.626(5)$ Å, $\beta = 107.65(2)°$, $V = 7131(4)$ Å^3, $Z = 4$, and $R = 0.058$ for 4760 reflections with $I > 3\sigma(I)$ and 451 parameters]. In the case of platinum, a dinuclear platinum(II) complex, $Pt_2(pyphos)_4$ (**3**), was prepared in 84% yield by treatment of $PtCl_2(pyphosH)_2$ (**2**) with 2 equiv of sodium methoxide in ethanol. The dimeric structure of **3** was confirmed by X-ray analysis. The interatomic distance between the two platinum atoms of **3** is 4.3615(6) Å. Thus, complex **3** does not contain any metal−metal bond [**3**: monoclinic, space group $C2/c$ with $a = 19.646(2)$ Å, $b = 11.411(4)$ Å, $c = 30.368(3)$ Å, $\beta = 109.782(8)°$, $V = 6406(1)$ Å^3, $Z = 4$, $R = 0.046$ for 5844 reflections with $I > 3\sigma(I)$ and 425 parameters].

Introduction

In recent decades, a number of dinuclear complexes with a metal−metal bond have been prepared and studied with a view to the understanding of the bonding nature as well as model systems for heterogeneous catalysts.[1−4] Dinuclear complexes of palladium and platinum have mostly chelating diphosphine or monodentate phosphine ligands.[5−7] This is ascribed to the fact that the low oxidation state of group 10 metals is stabilized by coordinating phosphorus atoms. We have already reported trinuclear M···Mo−Mo (M = Pd, Pt) and tetranuclear M−Mo−Mo−M (M = Pd, Pt) complexes bearing a tridentate ligand, 6-(diphenylphosphino)-2-pyridonate (abbreviated as pyphos).[8,9] This ligand is rationally designed to coordinate to three different kinds of metals since it has three kinds of coordination sites, *i.e.* oxygen, nitrogen and phosphorus atoms. In these complexes, the pyphos ligand coordinated to a dimolybdenum moiety with O−N chelation and to palladium or platinum metal with the phosphorus site. Our interest in this area has focused on the synthesis of cluster compounds by using the pyphos ligand, and we have now applied this ligand to prepare cluster complexes of group 10 metals. Herein we report on the synthesis and characterization of dinuclear complexes of palladium(I), $Pd_2(pyphos)_2(pyphosH)_2$ (**1**), and platinum(II), $Pt_2(pyphos)_4$ (**3**), where the pyphos ligand coordinated to the metals by N−P chelation. Complex **1** has a Pd(I)−Pd(I) single bond, while complex **3** does not have any metal−metal bond.

Results and Discussion

Synthesis and Structure of $Pd_2(pyphos)_2(pyphosH)_2$ (1). Reaction of palladium acetate with a mixture of 6-(diphenylphosphino)-2-pyridone and sodium methoxide in diglyme produced a deep red solution, from which a dimeric palladium(I) complex, $Pd_2(pyphos)_2(pyphosH)_2$ (**1**), was obtained in 43%



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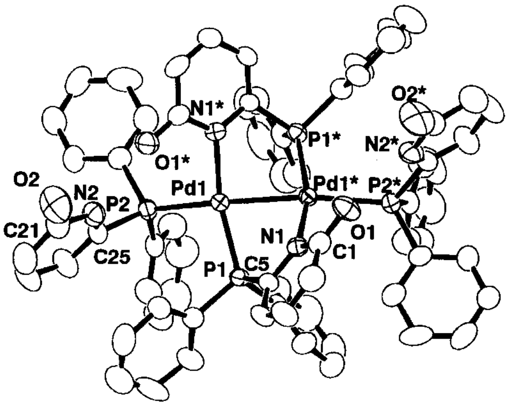

Figure 1. ORTEP drawing of **1** with a labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for **1**

Distances

Pd(1)−Pd(1*)	2.623(1)	Pd(1)−P(1)	2.262(3)
Pd(1)−P(2)	2.404(3)	Pd(1)−N(1*)	2.404(3)
P(1)−C(5)	1.819(9)	N(1)−C(5)	1.36(1)
N(1)−C(1)	1.36(1)	O(1)−C(1)	1.29(1)
P(2)−C(25)	1.821(9)	N(2)−C(25)	1.37(1)
N(2)−C(21)	1.40(1)	O(2)−C(21)	1.23(1)
O(1)···N(2*)	2.63(1)		

Angles

Pd(1)−Pd(1*)−N(1)	87.3(2)	Pd(1)−Pd(1*)−P(1*)	78.62(7)
Pd(1)−Pd(1*)−P(2*)	162.74(6)	N(1*)−Pd(1)−P(2)	97.9(2)
Pd(1)−P(1)−C(5)	105.6(3)	P(1)−C(5)−N(1)	111.3(6)
C(1)−N(1)−C(5)	119.2(8)	N(1)−C(1)−O(1)	119.3(9)
Pd(1*)−N(1)−C(1)	119.7(6)	Pd(1*)−N(1)−C(5)	121.0(6)
Pd(1)−P(2)−C(25)	118.6(3)	P(2)−C(25)−N(2)	112.2(6)
C(21)−N(2)−C(25)	125(1)	N(2)−C(21)−O(2)	121(1)

yield after crystallization from a solution of dichloromethane and hexane. Complex **1** can be also synthesized alternatively by treatment of PdCl$_2$(pyphosH)$_2$ with 2 equiv of sodium methoxide in ethanol, but the chemical yield was low (less than 5%).

The dinuclear complex **1** has two pyphos ligands and two pyphosH ligands. In the ^{1}H NMR spectrum of **1** at room temperature, we could not observe any signal assignable to the amido proton of pyphosH ligand. At −20 °C, however, the ^{1}H NMR spectrum of **1** displayed a broad singlet at δ 11.4 due to the amido proton. In the IR spectrum of **1** any band assignable to NH stretching frequency of the pyphosH coordinated to the Pd atom could not be detected, though that of the free ligand exhibited a broad strong band of NH stretching frequency at 2200−3110 cm^{-1}. This observation together with a crystallographic study (*vide infra*) indicated the presence of a hydrogen bonding in **1**. The ^{31}P{^{1}H} NMR spectrum of **1** in CDCl$_3$ showed complicated signals around δ −0.7, −2.3, −10.5, −15.7, and −20.7. The ^{31}P CPMAS of the solid sample showed also only very complicated unidentifiable signals. This might be due to the formation of monomeric species as well as transfer of hydrogen atoms between pyphos and pyphosH ligands, although the variable-temperature ^{31}P{^{1}H} NMR spectra of **1** measured in a temperature range of +30 to −40 °C did not show any change in chemical shift and the relative intensity of all resonances did not change.

Single crystals of **1** suitable for an X-ray diffraction study were obtained by recrystallization from a mixture of dichloromethane and hexane. Figure 1 shows an ORTEP diagram of **1**. Selected interatomic distances and angles are summarized in Table 1. Each palladium atom is related by a center of symmetry and thus the half of the molecule is crystallographically independent. Complex **1** has a dinuclear Pd−Pd moiety supported by four ligands, which are two pyphos N−P chelating ligands and two P-coordinating monodentate pyphosH ligands.

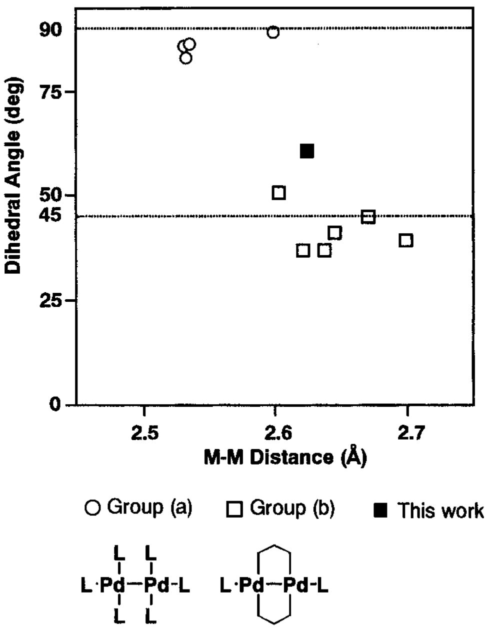

Figure 2. Plot of the dihedral angles and Pd−Pd bond distances for dinuclear palladium complexes. The dihedral angle is defined by the two coordination least-squares planes (PdP$_2$N planes) containing each palladium atoms.

The Pd−Pd distance of **1** is 2.623(1) Å, which lies in the range observed for the bond distances of common Pd^{I}−Pd^{I} single bonds, *i.e.* 2.500(1)−2.823(1) Å.[10,11] The bond length [2.404(3) Å] between the axial phosphorus atom and the palladium atom is longer than that [2.262(3) Å] between the equatorial phosphorus atom of the bridged pyphos and the palladium atom. This may be ascribed to the great *trans*-influence of the Pd−Pd σ-bond.[10,12−14] The Pd(1)−Pd(1*)−P(2*) angle is 162.74(6)° and this axial phosphorus atom is almost colinear with the Pd−Pd bond, whereas the Pd(1)−Pd(1*)−P(1*) bite angle is 78.62(7)°. The short interatomic distance between O(1) and N(2*) [2.63(1) Å] suggests the presence of an O···H−N hydrogen bonding.

It is noteworthy that the intramolecular hydrogen bonding between the NH group of pyphos-H and the carbonyl oxygen of the pyphos ligand stabilizes the dinuclear structure of **1**. The coordination geometry around each palladium atom is slightly distorted square plane comprised of two phosphorus atoms, one nitrogen atom and one palladium atom.

Angles of P(1)−Pd(1)−P(2) [99.63(9)°], P(1)−Pd(1)−Pd(1*) [78.62(7)°], N(1*)−Pd(1)−Pd(1*) [87.3(2)°], and N(1*)−Pd(1)−P(2) [97.9(2)°] deviate from 90°, indicating that the palladium atom is in a slightly distorted square planar environment. The dihedral angle between the two coordination least-squares planes around the palladium atoms is 60.7°, which is larger than the ideal angle of 45° for minimizing repulsive overlap of the out-of-plane metal dπ orbitals on adjacent metal centers.[5] For eight-membered ring systems comprised of two

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Table 2. Comparison of Pd−Pd Bond Distances in Palladium(I) Complexes[a]

complex	d(M−M), Å	θ,[b] deg	ref
(a) Monodentate Dinuclear Complexes			
$[Pd_2(PMe_3)_6]^{2+}$	2.598(1)	89.0	27
$[Pd_2(MeNC)_6]^{2+}$	2.5310(9)	86.3	28
$Pd_2(MeNC)_4I_2$	2.533(1)	85.3	13
Pd_2(*tert*-BuNC)$_4Cl_2$	2.532(2)	82.7	12
(b) Dinuclear Complexes Supported with Bridging Ligands Forming 5-Membered Rings			
$Pd_2(pyhpos)_2(pyphosH)_2$	2.623(1)	60.7	this work
$Pd_2[PhN\{P(OPh)_2\}_2]Cl_2$	2.6196(9)	37	29
$[Pd_2(dppa)_2Cl_2]\cdot MeCOMe$	2.6378(6)	36.83(4)	7
$Pd_2(dppm)_2Br_2$	2.699(5)	39	30
$Pd_2(dmpm)_2Br_2$	2.603(1)	50.5	5
$Pd_2(dppm)_2(SnCl_3)Cl$	2.644(2)	41.3	31
$Pd_2(dppm)_2(C_6Cl_5)_2$	2.6704(21)	44.98(10)	6

[a] Abbreviations: dppa = bis(diphenylphosphino)amine, dppm = bis(diphenylphosphino)methane, and dmpm = bis(dimethylphosphino)methane. [b] The term θ denotes the dihedral angle between two coordination planes around the palladium atoms.

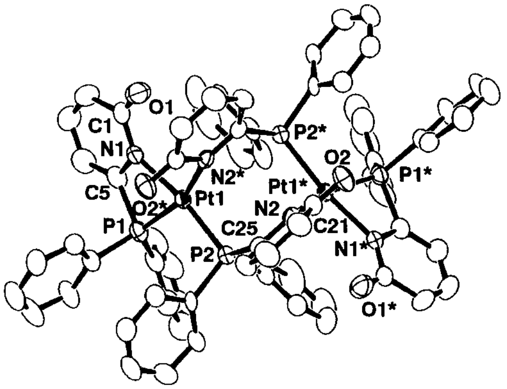


Figure 3. ORTEP drawing of **3** with a labeling scheme. Hydrogen atoms are omitted for clarity.

palladium atoms (group b shown in Figure 2), the dihedral angles lie in the range 36.83(4)−50.5° (Table 2). The presence of the intramolecular hydrogen bonding in **1** overcame the repulsion among the bulky ligands. The relation between the Pd−Pd bond distance and the dihedral angle is shown in Figure 2.

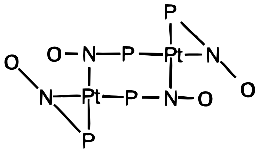
In sharp contrast to eight membered ring systems (group b), the dihedral angles of dipalladium complexes with non-bridging ligands (group a) are in the vicinity of 90°, at angles of which the repulsive interaction among monodentate ligands is minimized. Metal−metal bonds of group a complexes are shorter than those of group b complexes, indicating that the Pd−Pd bond distance is affected by bulkiness of monodentate ligand as well as the ring size effect of the chelating ligand.

Preparation and Structure of $Pt_2(pyphos)_4$ (3). A starting complex $PtCl_2(pyphosH)_2$ (**2**) was prepared by the reaction of $PtCl_2(PhCN)_2$ with 2 equiv of pyphosH. The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibited a singlet at δ 12.6 (J_{Pt-P} = 3592 Hz). A dinuclear platinum(II) complex, $Pt_2(pyphos)_4$ (**3**), was prepared in 84% yield by treatment of **2** with 2 equiv of sodium methoxide in ethanol. The $^{31}P\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ displayed two signals at δ −0.1 and −73.1 with satellites [J_{Pt-P} = 3520 and 2668 Hz, respectively] due to ^{195}Pt nuclei. The P−P coupling between two kinds of phosphorus nuclei is 4 Hz. The mass spectrum of **3** gave peaks attributable to the molecular ion of **3** and its fragmentation, and the most intense peak is at *m*/*e* 752 which corresponds to half of the molecule, $Pt(pyphos)_2$. These spectral data suggested that **3** is a dimeric Pt(II) complex, which is further confirmed by X-ray analysis (*vide infra*).

$$2\,PtCl_2(cod) + pyphosH \xrightarrow[CH_2Cl_2]{} \underset{\mathbf{2}}{PtCl_2(pyphosH)_2} \qquad (2)$$

cod = 1,5-cyclooctadiene

$$\underset{\mathbf{2}}{2\,PtCl_2(pyphosH)_2} + 4\,NaOMe \xrightarrow[EtOH]{} \qquad (3)$$



3

Single crystals of **3** grown from dichloromethane/diethyl ether were supplied for an X-ray diffraction study. An ORTEP drawing of **3** (Figure 3) shows the dinuclear structure of **3**. Selected interatomic distances and angles are shown in Table 3. The interatomic distance [4.3615(6) Å] between the two platinum atoms indicated that **3** has no metal−metal bond. The reported diplatinum(II) complexes have no metal−metal bonding except a few examples,[15] whereas diplatinum(III) complexes possess a Pt−Pt single bond comprised of a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration.[1,16−22] Each platinum atom is related by a center of symmetry and the coordination geometry around the platinum atom is a slightly distorted square. The platinum atom lies in this plane since the sum of the four angles around it is 360°. The two platinum atoms are bridged by two N−P pyphos ligands and each platinum atom is coordinated by another N−P chelating pyphos. The Pt−N bond distances [2.110(6) and 2.089(6) Å] and the Pt−P bond distances [2.264(2) and 2.241(2) Å] are in the range of similar diplatinum complexes with a Pt−N bond [1.963(8)−2.11(2) Å] or a Pt−P bonds [2.242(1)−2.349(10) Å].[4,15,17,18] The distances of the Pt(1)−N(1) bond [2.110(6) Å] and the Pt(1)−P(1) bond [2.264(2) Å] which belong to the N−P chelating pyphos ligands are about 0.02 Å longer than those of the Pt(1)−N(2*) bond [2.089(6) Å] and the Pt(1)−P(2) bond [2.241(2) Å] of the N−P-bridged pyphos ligands. A similar trend has been observed for the dipalladium complex, $Pd_2(pyphos)_2(pyphosH)_2$(**1**). The angle P(1)−Pt(1)−N(1) [68.4(2)°] of the P−N chelating ring is acute, while the angles P(1)−Pt(1)−P(2) [101.27(7)°], P(2)−Pt(1)−N(2*) [93.4(2)°], and N(1)−Pt(1)−N(2*) [96.7(2)°] are obtuse.

Experimental Section

General Data. All manipulations containing air- and moisture-sensitive compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. All solvents were purified by distillation under argon after drying over calcium hydride or benzophenone ketyl. The chelating ligand pyphosH was prepared according to

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **3**

Distances			
Pt(1)⋯Pt(1*)	4.3615(6)	Pt(1)−P(1)	2.264(2)
Pt(1)−P(2)	2.241(2)	Pt(1)−N(1)	2.110(6)
Pt(1)−N(2*)	2.089(6)	P(1)−C(5)	1.787(8)
N(1)−C(5)	1.370(10)	N(1)−C(1)	1.390(9)
O(1)−C(1)	1.24(1)	P(2)−C(25)	1.835(8)
N(2)−C(25)	1.371(9)	N(2)−C(21)	1.378(9)
O(2)−C(21)	1.245(8)		

Angles			
P(1)−Pt(1)−P(2)	101.27(7)	P(1)−Pt(1)−N(1)	68.4(2)
P(2)−Pt(1)−N(2*)	93.4(2)	N(1)−Pt(1)−N(2*)	96.7(2)
Pt(1)−P(1)−C(5)	85.3(3)	P(1)−C(5)−N(1)	101.6(5)
C(1)−N(1)−C(5)	122.7(7)	N(1)−C(1)−O(1)	122.4(8)
Pt(1)−N(1)−C(1)	134.0(6)	Pt(1)−N(1)−C(5)	103.2(5)
Pt(1)−P(2)−C(25)	114.7(2)	P(2)−C(25)−N(2)	117.1(6)
C(21)−N(2)−C(25)	119.5(7)	N(2)−C(21)−O(2)	119.3(8)

Table 4. Crystal Data and Data Collection Parameters for Complexes **1** and **3**

	1	**3**
formula	$C_{71}H_{60}Cl_6N_4O_4P_4Pd_2$	$C_{70}H_{56}Cl_4N_4O_4P_4Pt_2$
fw	1580.68	1673.12
cryst system	monoclinic	monoclinic
space group	$C2/c$ (No.15)	$C2/c$ (No.15)
a, Å	19.794(7)	19.646(2)
b, Å	14.753(7)	11.411(4)
c, Å	25.626(5)	30.368(3)
β, deg	107.65(2)	109.782(8)
Z	4	4
V, Å^3	7131(4)	6406(1)
d_{calcd}, g cm^{-3}	1.472	1.735
diffractometer	Rigaku AFC 5R	Rigaku AFC 7R
cryst size, mm	0.3 × 0.4 × 0.5	0.2 × 0.2 × 0.2
abs coeff, cm^{-1}	8.61	46.7
scan mode	$\omega-2\theta$	$\omega-2\theta$
temp, °C	23	20
scan speed, deg/min	8.0	16.0
scan width, deg	$1.01 + 0.35 \tan\theta$	$0.79 + 0.30 \tan\theta$
$2\theta_{max}$, deg	60.2	55.0
no. of data collcd (unique data)	11162 (10868)	7950(7720)
no. of unique data [$I > 3\sigma(I)$]	4760	5844
no. of variables	451	425
R^a	0.058	0.046
$R_w{}^a$	0.080	0.037
GOF	2.24	3.28
Δ, e Å^{-3}	1.06 (max) −0.65 (min)	3.01 (max) −1.93 (min)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

the literature.[23] Palladium(II) acetate (Aldrich) and potassium tetrachloroplatinate(II) (Wako) were used without further purification. $PtCl_2(PhCN)_2$ was prepared according to the literature.[24] ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL EX-270 and GXS-270 instruments operating at 270 (^1H NMR) or 109 MHz ($^{31}P\{^1H\}$ NMR) using 5 mm NMR tubes. $^{31}P\{^1H\}$ NMR was measured against external 85% H_3PO_4. IR spectra were recorded on a HITACHI infrared spectrophotometer, Model 295. Mass spectrometric data were obtained using FAB techniques on a JEOL SX-102 spectrometer by using 3-nitrobenzyl alcohol as a matrix and by dissolving the sample in dichloromethane. UV−vis spectra were taken on a Jasco Ubest-30 in a sealed 1 mm cell. Elemental analysis was performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points were measured in sealed tubes and were not corrected.

Preparation of $Pd_2(pyphos)_2(pyphosH)_2$ (1). To a mixture of palladium acetate (0.062 g, 0.28 mmol) and pyphosH (0.199 g, 0.71 mmol) suspended in diglyme (20 mL) was added sodium methoxide (0.033 g, 0.61 mmol). The reaction mixture was stirred for a period of 2 h at 60 °C. The orange suspension of palladium acetate turned gradually to a dark red solution. Solid precipitates were removed by filtration, and then the filtrate was concentrated to give a dark red residue, which was washed with hexane (10 mL). Recrystallization from a mixture of dichloromethane and hexane afforded complex **1** as dark red crystals in 43% yield, mp 210.5 °C (dec). ^1H NMR ($CDCl_3$, 30 °C): δ 5.50−6.60 (m, 12H), 6.68−7.91 (m, 40H). ^{31}P-NMR ($CDCl_3$, 30 °C): δ −0.7 (d), −2.3 (d), −10.2 to −10.7 (m), −15.7 (d), −20.5 to −21.0 (m). Mass spectrum (FAB): m/z 1327 (MH^+). UV−vis (CH_2Cl_2): $\lambda_{max} = 317$ ($\epsilon = 3.5 \times 10^3$), 518 nm ($\epsilon = 2.4 \times 10^3$). Anal. Calcd for $C_{68}H_{54}N_4O_4P_4Pd_2 \cdot 3CH_2Cl_2$: C, 53.88; H, 3.82; N, 3.54. Found: C, 53.89; H, 3.90; N, 3.64.

Preparation of $PtCl_2(pyphosH)_2$ (2). To a Schlenk tube charged with $PtCl_2(PhCN)_2$ (0.138 g, 0.29 mmol) and pyphosH (0.160g, 0.57 mmol) was added dichloromethane (20 mL) via syringe. After the reaction mixture was stirred for a day at room temperature, all volatile components were removed under reduced pressure to yield white powder of **2** in quantitative yield, mp 240−243 °C dec. ^1H NMR ($CDCl_3$, 30 °C): δ 6.49 (t, 2H), 6.73 (d, 2H), 7.20−7.59 (m, 24H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30 °C): δ 12.6 (s, $J_{Pt-P} = 3592$ Hz). Anal. Calcd for $C_{34}H_{28}N_2O_2P_2PtCl_2$: C, 49.53; H, 3.42; N, 3.40. Found: C, 50.01; H, 3.85; N, 2.97.

Preparation of $Pt_2(pyphos)_4$ (3). To a mixture of **2** (0.181 g, 0.22 mmol) and sodium methoxide (0.025 g, 0.46 mmol) was added ethanol (15 mL). The reaction mixture was stirred for a day at room temperature. This white suspension turned gradually to a pale yellow one. Dichloromethane was added to this mixture and the precipitating solids were removed by filtration. The filtrate was condensed to give a yellow residue, which was washed with diethyl ether (20 mL). Recrystallization from a mixture of dichloromethane and diethyl ether afforded complex **3** as yellow crystals in 84% yield, mp 270−273 °C dec. ^1H NMR ($CDCl_3$, 30 °C): δ 5.40 (t, 2H), 6.17 (t, 2H), 6.33 (t, 4H), 6.71(t, 4H), 6.91−7.83 (m, 40H). $^{31}P\{^1H\}$ NMR (109 MHz, 30 °C, $CDCl_3$): δ −0.1 ($J_{Pt-P} = 3520$ Hz, $J_{P-P} = 4$ Hz), −73.1 ($J_{Pt-P} = 2668$ Hz, $J_{P-P} = 4$ Hz). Mass spectrum (FAB): m/z 1503 (MH^+). UV−vis (CH_2Cl_2): $\lambda_{max} = 342$ ($\epsilon = 2.5 \times 10^4$). Anal. Calcd for $C_{68}H_{52}N_4O_4P_4Pt_2 \cdot CH_2Cl_2$: C, 50.25; H, 3.37; N, 3.35. Found: C, 50.25; H, 3.58; N, 3.44.

Structure Determination of 1. A crystal of **1** was sealed in a glass capillary under argon atmosphere and then transferred to a goniometer on a Rigaku AFC-5R diffractometer. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 18 carefully centered reflections in the range $29.10 < 2\theta < 29.96°$, corresponded to a monoclinic cell with the following dimensions: $a = 19.794(7)$ Å, $b = 14.753(7)$ Å, $c = 25.623(3)$ Å, and $\beta = 107.65(2)°$. Of the 11162 reflections, collected 10868 were unique ($R_{int} = 0.044$). The intensities of three representative reflections which were measured after every 100 reflections declined by 0.70%. A linear correction factor was applied to the data to compensate for this phenomena. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.85 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure of **1** was solved by the direct method (MITHRIL,[25] TEXSAN crystallographic software package). A series of standard full-matrix least-squares refinement and Fourier synthesis revealed the remaining atoms as anisotropic temperature factor. Hydrogen atoms bound to aromatic carbon atoms were located as fixed contributions after idealization (C−H = 0.95 Å). All non-hydrogen atoms of the complex **1** were refined anisortropically to $R = 0.058$ and $R_w = 0.080$. Complex **1** contained three molecules of dichloromethane as the solvent of crystallization. The details of the data collection and the solution are summarized in Table 4. Positional parameters for **1** are given as Supporting Information.

Structure Determination of 3. A crystal of **3** was sealed in a glass capillary under argon atmosphere and then transferred to a goniometer on a Rigaku AFC-7R diffractometer. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range

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$49.37 < 2\theta < 50.00°$ and the details of data collection are shown in Table 4. The 11162 reflections were collected and the 7720 reflections were unique ($R_{\mathrm{int}} = 0.049$). Three standard reflections were chosen and monitored every 150 reflections, indicating the standards decreased by 4.1%. A linear correction factor was applied to the data to account for this decay. An absorption correction was applied based on azimuthal scans of several reflections.

The structure of **3** was solved by the direct method (SHELXS86,[26] TEXSAN crystallographic software package) and refined by the full-matrix least-squares method. Measured nonequivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. The positions of all non-hydrogen atoms for all complexes were found from a difference Fourier electron density map and refined anisotropically to reach to the values of $R = 0.046$ and $R_w = 0.037$. Hydrogen atoms bound to aromatic carbon atoms were located as fixed contributions after idealization (C−H = 0.95 Å). Complex **3** contained two molecules of dichloromethane as the solvent of crystallization. The details of the data collection and the solution are summarized in Table 4. Positional parameters for **3** are are given as Supporting Information.

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Supporting Information Available: Tables of atomic positional parameters, anisotropic displacement parameters, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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