200 *Inorg. Chem.* **1997,** *36,* 200−203

Palladium(II) and Platinum(II) Complexes of a Tetraphosphamacrocycle. X-ray Crystal Structures of Phosphorus Analogs of a (Tetramethylcyclam)metal Complex[1]

Tsutomu Mizuta,[†] Akihiro Okano,[‡] Tsutomu Sasaki,[‡] Hiroshi Nakazawa,*[,†] and Katsuhiko Miyoshi*[,‡]

Coordination Chemistry Laboratory, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and
Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama,
Higashi-Hiroshima 739, Japan

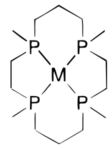
Received June 14, 1996[⊗]

Palladium(II) and platinum(II) complexes with 1,4,8,11-tetramethyl-1,4,8,11-tetraphosphacyclotetradecane were prepared by a template reaction in which $[M(MeHPCH_2CH_2PHMe)_2]Cl_2$ (M = Pd, Pt) reacts with 1,3-dibromopropane in the presence of K_2HPO_4 as a base. The bromide salts of the Pd^{2+}(**6a**) and Pt^{2+}(**6b**) complexes were isolated as crystals in a low yield. Their molecular structures were determined by X-ray crystallography. Both compounds have a square-planar geometry in which the configurations of the four asymmetric phosphorus atoms are of the trans III (RRSS) type. The M−P bond distances for **6a** and **6b** are 2.268(1) and 2.277(2) Å, respectively, which are slightly smaller than those of the complexes with noncyclic phosphines. Crystallographic data for **6a**: monoclinic, space group $C2/m$, $a = 8.4856(7)$ Å, $b = 17.273(1)$ Å, $c = 9.5712(7)$ Å, $\beta = 101.117(7)°$, $V = 1376.5(2)$ Å^3, $Z = 2$, and $R = 0.042$. Crystallographic data for **6b**: triclinic, space group $P\bar{1}$, $a = 9.538(3)$ Å, $b = 9.781(2)$ Å, $c = 8.719(1)$ Å, $\alpha = 115.34(2)°$, $\beta = 92.92(2)°$, $\gamma = 61.33(2)°$, $V = 632.6(3)$ Å^3, $Z = 1$, and $R = 0.041$.

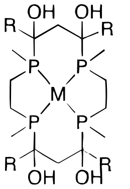
Introduction

There are numerous examples of macrocyclic metal complexes in which the macrocyclic ligand contains an N_4 donor set.[2−6] In contrast, the corresponding complexes with a P_4 donor set are limited in number. The first preparation of the macrocycle complex with a P_4 donor set was independently reported by DelDonno and Rosen[7] and Kyba et al.,[8] in 1977. In 1982, Stelzer et al. found an excellent synthetic method, where they used a metal template reaction for the cyclization.[9a] Their metal template method was applied to the preparation of several complexes in subsequent papers.[10−14]

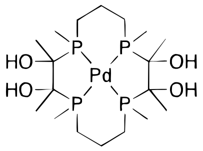
Chart 1



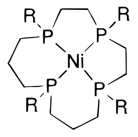
1



	M	R
2a	Ni	Me
2b	Pd	H
2c	Pd	Me



3



4

1 is a phosphorus analog of a tetramethylcyclam (tmc[1]) metal complex which is one of the typical N_4 macrocycle complexes whose structures and reactivities have been drawing considerable interest.[2−6,15] Although the first preparation of the macrocycle metal complexes with a 1,4,8,11-tetraphosphacyclotetradecane ([14]aneP$_4$)[1] framework, **2** and **3**, was carried out by Stelzer and co-workers, these complexes have the hydroxyl groups on the alkyl chains.[9] A 14-membered macrocycle complex **4** having no such hydroxyl group was prepared by the same group,[12] but its chain system is an unsymmetrical $C_3PC_3PC_2PC_2P$ type. In order to elucidate the structural properties of a tetraphosphamacrocycle complex, the preparation of **1** is still

---

[†] Institute for Molecular Science.

[‡] Hiroshima University.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

(1) Abbreviations: cyclam, 1,4,8,11-tetraazacyclotetradecane; tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; [14]aneP$_4$, 1,4,8,11-tetraphosphacyclotetradecane; Me$_4$[14]aneP$_4$, 1,4,8,11-tetramethyl-1,4,8,11-tetraphosphacyclotetradecane.

(2) Melson, G. A., Ed. *Coordination Chemistry of Macrocyclic Compounds*; Plenum: New York, 1979.

(3) Bernal, I., Ed. *Stereochemistry of Organometallic and Inorganic Compounds. Vol. 2: Stereochemical and Stereophysical Behavior of Macrocycles*; Elsevier: Amsterdam, 1987.

(4) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, UK, 1992.

(5) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.

(6) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87.

(7) (a) DelDonno, T. A.; Rosen, W. *J. Am. Chem. Soc.* **1977**, *99*, 8051. (b) DelDonno, T. A.; Rosen, W. *Inorg. Chem.* **1978**, *17*, 3714.

(8) Kyba, E. P.; Hudson, C. W.; McPhaul, M. J.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8053.

(9) (a) Bartsch, R.; Hietkanp, S.; Morton, S.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 375. (b) Bartsch, R.; Hietkanp, S.; Morton, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1983**, *22*, 3624.

(10) Bartsch, R.; Hietkanp, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1984**, *23*, 3304.

(11) Brauer, D. J.; Gol, F.; Hietkamp, S.; Peters, H.; Sommer, H.; Stelzer, O. *Chem. Ber.* **1986**, *119*, 349.

(12) (a) Brauer, D. J.; Lebbe, T.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 438. (b) Brauer, D. J.; Dörenbach, F.; Lebbe, T.; Stelzer, O. *Chem. Ber.* **1992**, *125*, 1785.

(13) Toulhoat, C.; Vidal, M.; Vincens, M. *Phosphorus Sulfur Silicon* **1992**, *71*, 127.

(14) Caminade, A.-M.; Majoral, J. P. *Chem. Rev.* **1994**, *94*, 1183.

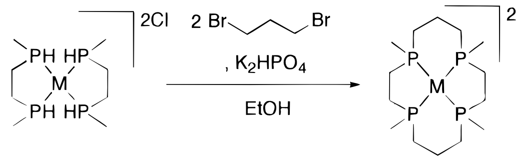
(15) For recent reports, see: (a) Waltz, L.; Lilie, J.; Chandrasekher, S.; Woo, D.; Brown, K. *Inorg. Chem.* **1996**, *35*, 124. (b) Ram, M. S.; Riordan, C. G.; Ostrander, R.; Rheingold, A. L. *Inorg. Chem.* **1995**, *34*, 5884. (c) Ram, M. S.; Riordan, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 2365.

S0020-1669(96)00700-8 CCC: $14.00

important, since the structure of a transition metal complex of **1** can be directly compared with well-known tmc−metal complexes. We now report here the preparation and X-ray crystal structures of the Pd^{2+} and Pt^{2+} complexes with the symmetrical $C_3PC_2PC_3PC_2P$-type macrocycle.

Results and Discussion

Preparation of Pd^{2+} and Pt^{2+} Complexes with Me_4[14]-aneP$_4$.[1] A template reaction is an excellent method for the construction of the phosphorus macrocycles.[7,9−14,16−19] Stelzer et al. reported that $[Pd(MeHPCH_2CH_2PHMe)_2]Cl_2$ (**5a**) reacts with diketones to form **2b** and **2c** in high yield. During the reaction, the deprotonated phosphorus atoms attack the carbonyl groups of the diketone, with the OH groups remaining at the position α to the phosphorus. If a dihalogeno alkane and/or alkene is used in place of the diketones, the resulting macrocycle should have no substituent on the alkyl chain. Actually, two research groups, Stelzer[11] and Vincens,[13] examined the reaction of **5a** with 1,4-dichloro-2-butene or with 1,2-bis(chloromethyl)-benzene in the presence of K_2CO_3 and obtained 16-membered ring complexes in good yield. However, a similar attempt with 1,3-dichloropropane to prepare the 14-membered ring complex has not been successful. We succeeded in the preparation of **1**, though the yield was low. The method we employed is the reaction of **5a** (Pd^{2+}) or **5b** (Pt^{2+}) with 1,3-dibromopropane in place of 1,3-dichloropropane in the presence of K_2HPO_4 (eq 1). The reason for the use of K_2HPO_4 in place of K_2CO_3 is that it can be readily removed from the reaction mixture as a precipitate of KH_2PO_4.



(1)

5a: M=Pd
5b: M=Pt

6a: M=Pd
6b: M=Pt

In the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, a sharp singlet is observed at 38.5 and at 36.0 ppm for the palladium and platinum complexes, respectively. In addition to the singlet for both cases, several broad multiplets are observed near the singlet with considerable integrated intensity. The separation of these complicated species was tried by means of recycling HPLC with a GPC column. The mixture could be separated into several bands which were separately collected. The $^{31}P\{^1H\}$ NMR spectra of these fractions indicated that only one fraction contained the product showing the sharp singlet, but it was still contaminated with small amounts of unknown products. The observed multiplets in the $^{31}P\{^1H\}$ NMR suggest that the species showing the multiplets are the metal complexes having at least three phosphorus atoms as ligands. Since further separation was unsuccessful, the identification of these species was abandoned. However, the product with the sharp singlet could only be isolated as colorless crystals by the slow evaporation of the aqueous solution of the reaction mixture, while the recrystallizations from the usual organic solvents gave the mixture with the other products. The obtained crystals were large enough for X-ray analysis in both cases, and have the formulas $[Pd(Me_4[14]aneP_4)]Br_2{\cdot}6H_2O$ (**6a**) and $[Pt(Me_4[14]aneP_4)]Br_2{\cdot}4H_2O$ (**6b**) (vide infra). The water of crystallization was readily lost in air, but it plays an important role in the crystal growth.

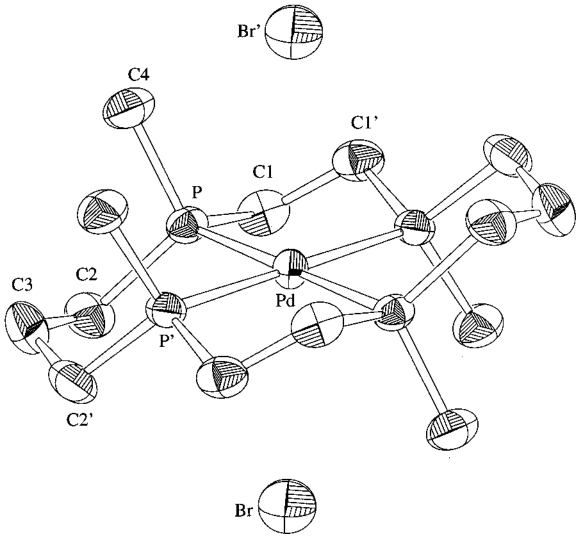
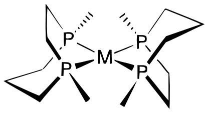
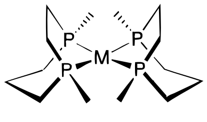


Figure 1. Crystal structure of **6a** with the numbering scheme. Thermal ellipsoids are drawn at 50% probability.

The spectroscopic data of **6a** and **6b** given in the Experimental Section show that the palladium and platinum complexes have a highly symmetrical structure. In the ^1H NMR, only one singlet is observed for the four methyl groups, indicating that they are equivalent. One singlet and three quintets are observed in the $^{13}C\{^1H\}$ NMR. The three quintets are assigned to the carbon atoms adjacent to the phosphorus, where the carbon atoms virtually couple with the four chemically equivalent phosphorus atoms coordinating to the metal ion. The $^{195}Pt\{^1H\}$ NMR spectrum for **6b** is also consistent with the expected structure; the signal observed is a quintet at −5283 ppm, which is similar to the quintet (−5263 ppm) reported for $[Pt(dmpe)_2]Br_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane).[20] Although all these observations are consistent with our expected structure, **1**, two ambiguous points still remain. First is the configurations of the four asymmetric phosphorus centers and second is that a structure with two seven-membered rings (**7a** and **7b**) is also consistent with the above spectroscopic data.[9] Thus, X-ray structural analyses were carried out for both crystals.



7a



7b

Crystal Structures of 6a and 6b. The molecular structures of **6a** and **6b** are shown in Figures 1 and 2, respectively. The coordination sphere is square-planar for both complexes with the four phosphorus atoms of the 14-membered macrocycle coordinated to the Pd^{2+} and Pt^{2+}. In Figure 1, each Br^- anion is located almost just above and below the Pd^{2+} ion. The distance from the Pd^{2+} to the Br^- is 3.476(1) Å, which is almost comparable to the sum of the van der Waals radii, 3.4−3.6 Å,[21] indicating no bonding interaction between them. The Br^- anions in Figure 2 are also located at positions similar to those in Figure 1. The distance from the Pt^{2+} to the Br^- is 4.172(2)

---

(16) (a) Scanlon, L. G.; Tsao, Y.-Y.; Cummings, S. C.; Toman, K.; Meek, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6851. (b) Scanlon, L. G.; Tsao, Y.-Y.; Toman, K.; Cummings, S. C.; Meek, D. W. *Inorg. Chem.* **1982**, *21*, 1215.

(17) (a) Diel, B. N.; Haltiwanger, C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700. (b) Diel, B. N.; Brandt, P. F.; Haltiwanger, C.; Hackney, M. L. J.; Norman, A. D. *Inorg. Chem.* **1989**, *28*, 2811.

(18) Ansell, C. W.; Cooper, M. K.; Dancey, K. P.; Duckworth, P. A.; Henrick, K.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Chem. Commun.* **1985**, 439.

(19) Jones, T. L.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 1411.

(20) (a) Hope, E. G.; Levason, W.; Powell, N. A. *Inorg. Chim. Acta* **1986**, *115*, 187. (b) Hanton, L. R.; Levason, W.; Powell, N. A. *Inorg. Chim. Acta* **1986**, *160*, 205.

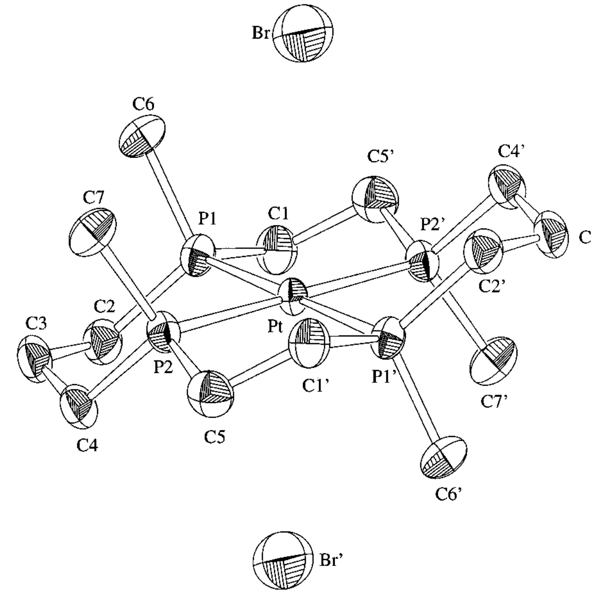


Figure 2. Crystal structure of **6b** with the numbering scheme. Thermal ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **6a** (Estimated Standard Deviations in Parentheses)

Lengths			
Pd−P	2.268(1)	P−C(1)	1.829(5)
P−C(2)	1.828(5)	P−C(4)	1.802(5)
C(1)−C(1)′	1.538(10)	C(2)−C(3)	1.519(7)
Angles			
P−Pd−P	92.63(6)	Pd−P−C(1)	105.5(2)
Pd−P−C(2)	111.5(2)	Pd−P−C(4)	117.4(2)
C(1)−P−C(2)	112.3(2)	C(1)−P−C(4)	103.6(2)
C(2)−P−C(4)	106.4(2)	P−C(1)−C(1)′	108.4(2)
P−C(2)−C(3)	112.9(4)	C(2)−C(3)−C(2)′	116.7(7)

Å, which is much larger than the sum of the van der Waals radii, 3.5−3.8 Å. In both structures, the configuration of the macrocycle with the four asymmetric phosphorus atoms is the trans III (RRSS).[22] The Pd^{2+} in **6a** is located on a crystallographic 2/*m* symmetry which relates the quarters of the macrocycle. The Pt^{2+} in **6b** is also located on an inversion center which relates the halves. Thus, all of the metal ion and the four phosphorus atoms are rigorously in the same plane in both cases. This high planarity observed is characteristic of the trans III configuration, as reported for many tmc and cyclam metal complexes.[23]

The hole size of a macrocyclic ligand is a fundamental structure parameter which usually influences the properties of the resultant metal complexes. In **6a**, ∠C(1)−P−C(2) in Table 1 is 112.3(2)°, which is significantly larger than the ideal value of 103.6° for the phosphorus.[24] ∠P−(C)2−C(3) of 112.9(4)° and ∠C(2)−C(3)−C(2) of 116.7(7)° are also larger than the ideal value of 109.5° for an sp^3 carbon atom. The corresponding angles in **6b** are also all larger than the ideal values: ∠C(1)−P(1)−C(2) 109.8°, ∠C(4)−P(2)−C(5) 112.9(5)°, ∠P(1)−C(2)−C(3) 115.0(6)°, ∠P(2)−C(4)−C(3) 116.4(6)°, and ∠C(2)−C(3)−C(4) 116.9(7)° (see Figure 2 and Table 2). These enlarged bond angles suggest that the Pd^{2+} and Pt^{2+} are larger in size than can be cozily incorporated into the hole of the macrocycle. The situation is depicted in Figure 3, where the too large ion is incorporated in the hole of the macrocycle whose puckering chelate ring has to be expanded. In addition, the M−P distances in **6a** and **6b**, 2.268(1) and 2.277(2) Å, respectively, are smaller by ∼0.04 Å than the M−P distances for the monodentate tertiary phosphine complexes, 2.312 Å for Pd−P and 2.315 Å for Pt−P.[25] It is a widely accepted interpretation for the shortening that an M−P bond is compressed by a macrocyclic ligand when the size of the metal ion is too large for the hole size.[26,27]

It is noteworthy that the M−N bond distances in the Pd^{2+} and Pt^{2+} complexes with the cyclam and tmc are, in contrast, close to those for the corresponding complex with a noncyclic ligand.[26,28−30] Thus, it can be said that the present phosphamacrocycle is smaller in cavity size than that of the cyclam and tmc. In general, the bonding cavity of the macrocycle tends to be reduced by the substitution of bulky donor atoms, though this effect may be appreciably offset by the corresponding increase in the "circumference" of the macrocyclic ring.[4] The smaller cavity size observed in **6a** and **6b** is interpreted in this way.

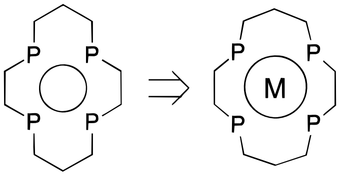


Figure 3. Deformation of the bond angles of a free macrocycle (left) on incorporation of a too-big ion (right).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6b** (Estimated Standard Deviations in Parentheses)

Lengths			
Pt−P(1)	2.273(1)	P(2)−C(5)	1.806(10)
Pt−P(2)	2.281(2)	P(2)−C(7)	1.820(8)
P(1)−C(1)	1.824(9)	C(1)−C(5)′	1.59(1)
P(1)−C(2)	1.798(10)	C(2)−C(3)	1.56(1)
P(1)−C(6)	1.825(8)	C(3)−C(4)	1.49(1)
P(2)−C(4)	1.809(10)		
Angles			
P(1)−Pt−P(2)	92.95(8)	Pt−P(2)−C(7)	117.5(3)
Pt−P(1)−C(1)	106.6(3)	C(4)−P(2)−C(5)	112.9(5)
Pt−P(1)−C(2)	112.2(3)	C(4)−P(2)−C(7)	105.9(4)
Pt−P(1)−C(6)	116.6(4)	C(5)−P(2)−C(7)	105.5(4)
C(1)−P(1)−C(2)	109.8(4)	P(1)−C(1)−C(5)′	107.7(6)
C(1)−P(1)−C(6)	103.8(4)	P(1)−C(2)−C(3)	115.0(6)
C(2)−P(1)−C(6)	107.4(4)	C(2)−C(3)−C(4)	116.9(7)
Pt−P(2)−C(4)	108.7(3)	P(2)−C(4)−C(3)	116.4(6)
Pt−P(2)−C(5)	106.5(3)	P(2)−C(5)−C(1)′	109.4(6)

---

(21) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Hapaer and Row: New York, 1978.

(22) Bosnich, B.; Poon, C. K.; Tobe, M. *Inorg. Chem.* **1965**, *4*, 1102.

(23) (a) Mochizuki, K.; Kondo, T. *Inorg. Chem.* **1995**, *34*, 6241. (b) Szalda, D. J.; Fujita, E.; Sanzenbacher, R.; Paulus, H.; Elias, H. *Inorg. Chem.* **1994**, *33*, 5855. (c) Po, H. N.; Brinkman, E.; Doedens, R. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *C47*, 2310. (d) Blake, A. J.; Reid, G.; Schroeder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1561. (e) BareField, E. K.; Freeman, G. M.; Van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 552. (f) Kato, M.; Ito, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 285. (g) Toriumi, K.; Yamashita, M.; Ito, H.; Ito, T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 963. (h) Kato, M.; Ito, T. *Inorg. Chem.* **1985**, *24*, 509. (i) Ito, T; Ito, H.; Toriumi, K. *Chem. Lett.* **1981**, 1101.

(24) The value estimated is an average of the angles in the complexes described in ref 25.

(25) The value estimated is an average of the M−P distances of 13 and 17 complexes for Pd^{2+} and Pt^{2+}, respectively. They are retrieved from the Cambridge Crystallographic Data Center data base on the basis of the following criteria: they have two PMe$_3$ or PEt$_3$ ligands in a trans position of a square-planar coordination sphere, and they have no hydride ligand since the M−P distances of the hydride complexes are 2.277 Å (an average of seven complexes), which is appreciably shorter probably because of the small size of the hydride ligand.

(26) Busch, D. H.; Farmery, K.; Goedken, V.; Katovic, V.; Melnyk, A. C.; Sperati, C. R.; Tokel, N. *Adv. Chem. Ser.* **1971**, *No. 100*, 44.

(27) Hancock, R. D. *Acc. Chem. Res.* **1990**, *23*, 253.

(28) Waknine, D.; Heeg, M. J.; Endicott, J. F.; Ochrymowycz, L. A. *Inorg. Chem.* **1991**, *30*, 3691.

(29) Martin, L. Y.; De Hayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4047.

(30) Thöm, V. J.; Fox, C. C.; Boeyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947.

Table 3. Crystal and Refinement Data for **6a** and **6b**

	6a	**6b**
empirical formula	$C_{14}H_{44}Br_2O_6P_4Pd$	$C_{14}H_{40}Br_2O_4P_4Pt$
fw	698.60	751.26
crystal system	monoclinic	triclinic
a, Å	8.4856(7)	9.538(3)
b, Å	17.273(1)	9.781(2)
c, Å	9.5712(7)	8.719(1)
α, deg		115.34(2)
β, deg	101.117(7)	92.92(2)
γ, deg		61.33(2)
V, Å^3	1376.5(2)	632.6(3)
space group	*C*2/*m* (No. 12)	$P\bar{1}$ (No. 2)
Z	2	1
D_{obs}, g cm^{-3}	1.69	1.97
D_{calc}, g cm^{-3}	1.685	1.972
radiation	Mo Kα (*λ* = 0.710 69 Å) (graphite monochromated)	Mo Kα (*λ* = 0.710 69 Å) (graphite monochromated)
μ(Mo, Kα), cm^{-1}	38.42	89.59
temp, deg	23	23
R^a	0.042	0.041
$R_w{}^a$	0.050	0.043

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, and $w = 4F_o{}^2/\sigma^2(F_o)$).

Table 4. Listing of Final Fractional Coordinates and Thermal Parameters for **6a**

atom	*x*	*y*	*z*	B_{eq},^{a} Å^2
Pd	$^1/_2$	$^1/_2$	$^1/_2$	2.14(1)
Br	0.7594(1)	$^1/_2$	0.2598(1)	5.08(3)
P	0.3562(1)	0.59495(7)	0.3699(1)	2.40(2)
O(1)	0.7776(5)	0.3187(3)	0.1648(4)	5.7(1)
O(2)	1	0.2595(3)	0	3.8(1)
C(1)	0.4697(6)	0.6841(3)	0.4189(5)	3.3(1)
C(2)	0.3271(7)	0.5749(3)	0.1791(5)	3.7(1)
C(3)	0.236(1)	$^1/_2$	0.1373(8)	4.1(2)
C(4)	0.1606(6)	0.6166(3)	0.4068(6)	3.7(1)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Table 5. Listing of Final Fractional Coordinates and Thermal Parameters for **6b**

atom	*x*	*y*	*z*	B_{eq},^{a} Å^2
Pt	$^1/_2$	$^1/_2$	$^1/_2$	1.82(1)
Br	0.1473(2)	0.6751(2)	0.2276(1)	6.17(4)
P(1)	0.6684(3)	0.5824(3)	0.4416(3)	2.35(5)
P(2)	0.6222(3)	0.2375(3)	0.2563(3)	2.35(5)
O(1)	0.161(1)	0.289(1)	0.016(1)	6.5(3)
O(2)	0.192(1)	1.028(1)	0.4495(9)	5.9(2)
C(1)	0.643(1)	0.770(1)	0.640(1)	3.1(2)
C(2)	0.878(1)	0.408(1)	0.375(1)	3.0(2)
C(3)	0.914(1)	0.236(1)	0.216(1)	3.0(2)
C(4)	0.842(1)	0.136(1)	0.238(1)	3.1(2)
C(5)	0.547(1)	0.107(1)	0.277(1)	3.3(2)
C(6)	0.624(1)	0.662(1)	0.280(1)	3.7(3)
C(7)	0.584(1)	0.237(1)	0.050(1)	3.7(2)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. EtOH was distilled from $Mg(OEt)_2$ and stored under a nitrogen atmosphere.

JEOL EX-270 and LA-500 spectrometers were used to obtain the ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra. ^1H and ^{13}C NMR data were referenced to a methyl signal of $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$, ^{31}P NMR data to 85% H_3PO_4, and ^{195}Pt NMR data to H_2PtCl_6.

Preparation of 6a. $[Pd(MeHPCH_2CH_2PHMe)_2]Cl_2$ (**5a**) was prepared according to the method described in the literature.[9b] **5a** (2.16 g, 5.10 mmol) was dissolved in 200 mL of EtOH, and K_2HPO_4 (4.45 g, 25.6 mmol) was added to the solution. The pale yellow color of the solution immediately turned to deep orange. 1,3-Dibromopropane was added to the solution, which was stirred at 55 °C. The reaction was monitored by $^{31}P\{^1H\}$ NMR analysis. After disappearance of the signals from the secondary phosphine coordinating to the metal, which took 4 days, the solution was filtered, and the solvent was removed. The residue was dissolved in water and was loaded on a column packed with the bromide form of QAE-Sephadex anion exchanger in air. After elution with water, the eluent was evaporated in vacuo. The remaining solid was extracted with MeOH, dried, and recrystallized from water. The colorless crystals thus obtained weighed ~301 mg (10% yield on average) and were highly hygroscopic at room temperature. ^1H NMR (500 MHz, D_2O): *δ* 1.66 (singlet, 12H, CH_3), 1.90−2.80 (multiplet, 20H, CH_2). $^{13}C\{^1H\}$ (D_2O): *δ* 11.0 (quintet, $^1J_{C-P} = 8$ Hz, CH_3), 22.5 (singlet, $CH_2CH_2CH_2$), 26.1 (quintet, $^1J_{C-P} = 9$ Hz), 29.9 (quintet, $^1J_{C-P} = 13$ Hz). $^{31}P\{^1H\}$ (D_2O): *δ* 38.5.

Preparation of 6b. **6b** was prepared and isolated by a method similar to that for **6a** from $[Pt(MeHPCH_2CH_2PHMe)_2]Cl_2$ (**5b**) as the starting material. The yield was also low, ~10%. **6b** was also hygroscopic at room temperature. ^1H NMR (500 MHz, D_2O): *δ* 1.75 (singlet,[31] $^3J_{H-Pt} = 30.0$ Hz, 12H, CH_3), 1.80−2.80 (multiplet, 20H, CH_2). $^{13}C\{^1H\}$ (D_2O): *δ* 10.9 (quintet,[31] $^1J_{C-P} = 9$ Hz, $^2J_{C-Pt} = 33$ Hz, CH_3), 22.9 (singlet,[31] $^3J_{C-Pt} = 14$ Hz, $CH_2CH_2CH_2$), 25.9 (quintet,[31] $^1J_{C-P} = 10$ Hz, $^2J_{C-Pt} = 40$ Hz), 29.6 (quintet,[31] $^1J_{C-P} = 14$ Hz, $^2J_{C-Pt} = 44$ Hz). $^{31}P\{^1H\}$ (D_2O): *δ* 36.0 ($^1J_{P-Pt} = 1968$ Hz).[32] ^{195}Pt $\{^1H\}$ (D_2O): *δ*−5283 ($^1J_{P-Pt} = 1976$ Hz).[32]

X-ray Structure Analyses of 6a and **6b.** The crystallographic and experimental data of X-ray crystal structure analyses are given in Table 3. Final atomic coordinates for non-hydrogen atoms are listed in Tables 4 and 5 for **6a** and **6b**, respectively.

Suitable crystals of **6a** and **6b** were sealed in a capillary with a small tip of wet filter paer and mounted on an Enraf-Nonuis CAD-4 and Rigaku AFC-5S automatic diffractometers, respectively. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. The structures were solved by a combination of direct methods[33] and Fourier synthesis[34] and refined by full-matrix least-squares calculations. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated isotropically. Final values of $R = 0.042$ and $R_w = 0.050$ for **6a** and $R = 0.041$ and $R_w = 0.043$ for **6b** were obtained ($R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$ and $w = 4F_o{}^2/\sigma^2(F_o)$). All calculations were performed using teXsan[35] with neutral atom scattering factors from Cromer and Waber,[36] Δ*f′* and Δ*f″* values,[37] and mass attenuation coefficients.[38] Anomalous dispersion coefficients were included in F_{calc}.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 07404037) and by Priority Area of Reactive Organometallics (No. 07216276) from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Full linstings of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

IC960700Y

---

(31) A signal with satellites by ^{195}Pt.

(32) The difference is for instrumental reasons.

(33) SAPI91: Fan, H.-F. *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, Japan, 1991.

(34) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

(35) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

(36) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(37) Creagh, D. C.; McAuley, W. J. In *International Tables for Crystallography*; Vol C, Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, Table 4.2.6.8, pages 219−222.

(38) Creagh, D. C.; Hubbell, J. H. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, Table 4.2.4.3, pages 200−206.