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A New Cationic Palladium(I) Dinuclear Complex with a Short Pd–Pd Bond Having P–O–N Tridentate Bridges. Preparation and Structure

Kazuhide Tani,* Shingo Nakamura, Tsuneaki Yamagata, and Yasutaka Kataoka

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560

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Introduction

Since the first report[1] of a palladium(I) complex, a number of dinuclear palladium(I) complexes with monodentate or bidentate bridging ligands containing metal–metal bonding have been reported.[2-4] Only one example of these complexes with tridentate bridging ligands,[5] however, is known to our knowledge. Here we report the isolation, the characterization, and the crystallographic structure of a new cationic palladium(I) dinuclear complex having P–O–N tridentate bridging ligands and containing an extremely short Pd–Pd bond. Recently we have reported the mononuclear palladium(II) complex with a *trans*-chelating bidentate hybrid ligand, *trans*-PdCl$_2$(PN) (**1**) (PN = *o*-PPh$_2$C$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N),[6] as the first example of a transition metal complex having a *trans*-chelating phosphine-pyridine ligand. In the course of our studies on the reactivity and properties of this complex we have isolated and characterized a cationic mononuclear solvento complex, *trans*-[Pd(PN)(CH$_3$CN)$_2$](PF$_6$)$_2$ (**2**), and the dinuclear palladium(I) complexes [Pd(PN)]$_2$X$_2$ (**3a**, X = BF$_4$; **3b**, X = PF$_6$). X-ray crystal structural analysis of **3a** revealed its dinuclear nature, containing a very short Pd–Pd bond; the hybrid ligands (PN) act as P–O–N tridentate bridges.

Experimental Section

The solvents were dried by standard methods and distilled under an inert gas atmosphere (N$_2$ or Ar) prior to use. ^{1}H NMR spectra were obtained at 270.05 MHz by using a JEOL GSX-270 spectrometer or at 399.65 MHz by using a JEOL GSX-400 spectrometer. ^{31}P NMR spectra were obtained at 40.25 MHz by using a JEOL FX-100 spectrometer or at 109.25 MHz by using the JEOL GSX-270 spectrometer. Infrared spectra were obtained on a Hitachi 295 infrared spectrophotometer. The hybrid ligand PN and *trans*-PdCl$_2$(PN) (**1**) were prepared according to the preceding procedure.[6]

Synthesis of [*trans*-Pd(*o*-Ph$_2$PC$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N)-(CH$_3$CN)$_2$](PF$_6$)$_2$ (2). To a solution of **1** (100 mg, 0.17 mmol) in CH$_3$-CN (5 mL) was added AgPF$_6$ (86 mg, 0.34 mmol) in the dark. After being stirred for 30 min at room temperature, the reaction suspension was filtered from AgCl, and the filtrate was concentrated *in vacuo* to give **2** as a yellow solid (124 mg, 90%), mp 118–120 °C dec. Anal. Calcd for C$_{29}$H$_{32}$N$_3$OP$_3$F$_{12}$Pd: C, 41.48; H, 3.62; N, 4.72. Found: C, 42.15; H, 3.92; N, 4.00. ^{1}H NMR (acetonitrile-d_3; 270 MHz): δ 2.06 (6H, s, C*H*$_3$CN), 2.41 (2H, m, C$_5$H$_4$NCH$_2$C*H*$_2$CH$_2$O), 3.29 (2H, m, C$_5$H$_4$-NC*H*$_2$CH$_2$CH$_2$O), 3.81 (2H, s, C$_5$H$_4$NCH$_2$CH$_2$C*H*$_2$O), 5.04 (2H, s, C$_6$H$_4$C*H*$_2$O), 6.94–8.22 (21H, m, arom), 8.79 (1H, m, 6-*H* of C$_5$H$_4$N). ^{31}P{^{1}H} NMR (acetonitrile-d_3, 109 MHz): δ 28.8 (1P, br s, *P*Ph$_2$–),

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(2) (a) Russell, M. J. H.; Barnard, C. F. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press Ltd.: Oxford, England, 1987; Vol. 5, p 1103. (b) Balch, A. L. *Comments Inorg. Chem.* **1984**, *3*, 51.
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(6) (a) Yabuta, M.; Nakamura, S.; Yamagata, T.; Tani, K. *Chem. Lett.* **1993**, 323. (b) Tani, K.; Nakamura, S.; Yabuta, M.; Yamagata, T. *J. Chem. Soc., Dalton Trans.*, in press.

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Table I. Crystallographic Data for [Pd$_2${*o*-Ph$_2$PC$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N}$_2$](BF$_4$)$_2$·4H$_2$O (**3a**)

formula: C$_{54}$H$_{52}$B$_2$F$_8$N$_2$-O$_2$P$_2$Pd$_2$·4H$_2$O	μ = 67.73 cm^{-1}
	temp = 286 ± 1 K
fw = 1281.48	2θ limit = 120.0°
cryst syst: *P*2$_1$/*n*(No. 14)	no. of measd data: 8571
a = 12.742(2) Å	corr factors: 1.003–1.5033^d
b = 27.059(4) Å	no. of unique data (R_{sym}): 7971 (0.025)
c = 15.669(1) Å	no. of obsd data: 4453 (F_o > 8.0σ(F_o))
β = 94.906(7)°	no. of params: 581
V = 5383(1) Å^3	*R*; R_w:^{b} 0.0545; 0.0837
Z = 4	GOF:^{c} 1.770
d(calcd) = 1.581 g/cm^3	$\Delta\rho$(max); $\Delta\rho$(min):^{d}
λ(Cu Kα) = 1.541 78 Å	1.36; –1.01 e/Å^3
(40 kV, 200 mA)	Δ/σ(max); Δ/σ(av):^{e} 0.000; 0.000

^{a} Correction methods applied were those in: North, A. C. T.; Phillips, D. C.; Mathews, B. W. *Acta Crytallogr.* **1968**, *A24*, 351–359. Relative absorption correction coefficient on F_o. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{1/2}$, $w = 1/\sigma^2(F_o)$. ^{c} GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observs} - N_{params})]^{1/2}$. ^{d} Residual electron density of the final difference Fourier map. ^{e} In the final refinement cycle.

–143.4 (2P, septet, J_{PF} = 706.8 Hz, *P*F$_6$). IR spectrum (Nujol mull): 3050, 2940, 2850, 2300, 1610, 1480, 1440, 1100, 850, 750, 690, 565, 535 cm^{-1}.

Synthesis of [Pd$_2$(*o*-Ph$_2$PC$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N)$_2$](BF$_4$)$_2$ (3a). (i) To a solution of **1** (100 mg, 0.17 mmol) and *o*-Ph$_2$PC$_6$H$_4$CH$_2$O-(CH$_2$)$_3$-2-C$_5$H$_4$N (82 mg, 0.2 mmol) in dichloromethane (3 mL) was added AgBF$_4$ (66 mg, 0.34 mmol) in the dark. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was filtered from the precipitated AgCl, and the filtrate was concentrated *in vacuo* to give a red solid. The crude solid was purified by recrystallization from dichloromethane–hexane to give **3a** as red prisms which crystallized with hydrated water molecules (21 mg, 20%); mp 182–183 °C dec. Anal. Calcd for C$_{54}$H$_{52}$N$_2$O$_2$P$_2$Pd$_2$B$_2$F$_8$·4H$_2$O: C, 50.61; H, 4.72; N, 2.19. Found: C, 51.08; H, 4.55; N, 2.27. ^{1}H NMR (acetone-d_6; 270 MHz): δ 2.24 (2H, m, C$_5$H$_4$NCH$_2$C*H*$_2$CH$_2$O), 2.40 (2H, m, C$_5$H$_4$NCH$_2$C*H*$_2$-CH$_2$O), 3.36–3.62 (4H, m, C$_5$H$_4$NC*H*$_2$CH$_2$CH$_2$O), 3.94 (4H, m, C$_5$H$_4$-NCH$_2$CH$_2$C*H*$_2$O), 4.33 (2H, dd, *J* = 13.0, 9.2 Hz, C$_6$H$_4$C*H*$_2$O), 5.02 (2H, dt, *J* = 3.2, 12.7 Hz, C$_6$H$_4$C*H*$_2$O), 6.01 (2H, d, *J* = 4.5 Hz, arom), 6.80 (2H, t, *J* = 5.8 Hz, arom), 6.93 (6H, m, arom), 7.41–8.06 (26H, m, arom). ^{31}P{^{1}H} NMR (acetone-d_6, 109 MHz): δ 28.6 (s). IR spectrum (Nujol mull): 3620, 3550, 3060, 1630, 1605, 1570, 1480, 1100, 1060, 1000, 975, 915, 840, 760, 720, 695, 538, 515 cm^{-1}.

(ii) To a mixture of PdCl$_2$(PhCN)$_2$ (150 mg, 0.39 mmol) and *o*-Ph$_2$-PC$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N (400 mg, 0.97 mmol) in dichloromethane (15 mL) solution was added AgBF$_4$ (152 mg, 0.78 mmol) in the dark. A similar workup as above gave a red solid. The crude solid was purified by recrystallization from dichloromethane–hexane to give **3a** as red prisms (50 mg, 21%).

[Pd$_2$(*o*-Ph$_2$PC$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N)$_2$](PF$_6$)$_2$ (3b) was prepared in a manner similar to that used for the preparation of **3a** by using AgPF$_6$ instead of AgBF$_4$ as red prisms in 20% yield; mp 180–181 °C dec. Anal. Calcd for C$_{54}$H$_{52}$N$_2$O$_2$P$_4$Pd$_2$F$_{12}$: C, 48.92; H, 3.95; N, 2.11. Found: C, 49.48; H, 4.10; N, 2.25. ^{1}H NMR (acetone-d_6, 270 MHz) showed the same spectrum as that for complex **3a**. ^{31}P{^{1}H} NMR (acetone-d_6, 109 MHz): δ 28.6 (2P, s, Ph$_2$P–), –142.8 (2P, septet, *J* = 707 Hz, *P*F$_6$). IR spectrum (Nujol mull): 3060, 1605, 1570, 1483, 1100, 1080, 1070, 1035, 1000, 980, 915, 880, 840, 760, 720, 700, 565, 540, 515 cm^{-1}.

X-ray Structure Determination for [Pd$_2$(*o*-Ph$_2$PC$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N)$_2$](BF$_4$)$_2$·4H$_2$O (3a). A summary of the crystallographic data is given in Table I. Red crystals for X-ray measurements were obtained by recrystallization from a dichloromethane/hexane solution. A red crystal of approximate dimensions 0.40 × 0.30 × 0.25 mm^3 was mounted on a glass fiber with cyanoacrylate adhesives. Cell constants and an orientation matrix for data collection were determined by least-squares refinement, using the setting angles of 22 reflections in the range of 53° < 2θ < 59° on a Rigaku diffractometer(AFC-5R) equipped with a Rotaflex rotating anode X-ray generator (40 kV, 200 mA) with monochromated Cu Kα radiation. Systematic absences were consistent with the centric space group *P*2$_1$/*n* (No. 14). The data were collected at 13 ± 1 °C using the 2θ–ω scan method. As a check on the crystal stability, three representative reflections were measured every 200

Table II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) for the cationic part of $[Pd_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}2\text{-}C_5H_4N\}_2](BF_4)_2\cdot 4H_2O$ (3a)

atom	x/a	y/b	z/c	$U_{eq},^a \text{Å}^2$
Pd(1)	5741.8(6)	6312.4(3)	7309.8(5)	38.6(5)
Pd(2)	3909.8(6)	6296.9(3)	7766.4(5)	39.1(5)
P(1)	6124(2)	6699(1)	8545(2)	41(2)
P(2)	3495(2)	6678(1)	6533(2)	40(2)
O(1)	4585(6)	5946(3)	8928(5)	47(5)
O(2)	5095(6)	5963(3)	6135(5)	47(5)
N(1)	2346(8)	6119(4)	8167(6)	47(6)
N(2)	7317(8)	6144(4)	6898(6)	48(6)
C(1)	6971(9)	7210(4)	8267(8)	46(8)
C(2)	6628(9)	7514(5)	7584(8)	48(8)
C(3)	7259(11)	7877(5)	7306(9)	63(10)
C(4)	8282(12)	7931(5)	7668(1)	70(11)
C(5)	8658(11)	7625(6)	8341(9)	62(9)
C(6)	8003(10)	7272(5)	8641(8)	54(8)
C(7)	6904(9)	6355(5)	9369(8)	42(7)
C(8)	7078(11)	6555(5)	10187(9)	60(9)
C(9)	7722(11)	6311(6)	10819(9)	65(9)
C(10)	8215(11)	5889(6)	10612(9)	62(9)
C(11)	8009(10)	5660(5)	9804(9)	56(9)
C(12)	7362(9)	5905(5)	9174(8)	49(8)
C(13)	5130(9)	7001(5)	9154(8)	49(8)
C(14)	5085(10)	7526(5)	9160(8)	51(8)
C(15)	4341(11)	7754(5)	9613(9)	59(9)
C(16)	3656(11)	7501(7)	10044(10)	72(11)
C(17)	3681(11)	6987(6)	10070(9)	71(10)
C(18)	4417(9)	6733(5)	9636(8)	51(8)
C(19)	4433(10)	6185(5)	9741(8)	55(9)
C(20)	4715(10)	5423(5)	8962(9)	55(9)
C(21)	3707(11)	5145(5)	8974(10)	63(9)
C(22)	2934(11)	5242(5)	8186(8)	56(9)
C(23)	2097(10)	5641(5)	8307(9)	56(9)
C(24)	1131(14)	5513(7)	8576(12)	96(14)
C(25)	421(14)	5870(8)	8724(14)	106(15)
C(26)	669(12)	6349(7)	8587(11)	83(12)
C(27)	1642(11)	6456(5)	8300(9)	57(9)
C(28)	2604(9)	7163(4)	6800(8)	40(7)
C(29)	1578(10)	7221(5)	6419(8)	52(8)
C(30)	928(11)	7586(6)	6708(11)	69(10)
C(31)	1267(11)	7887(6)	7395(11)	71(10)
C(32)	2290(11)	7831(5)	7794(9)	59(9)
C(33)	2941(10)	7474(5)	7505(9)	50(8)
C(34)	2753(9)	6324(5)	5713(8)	46(7)
C(35)	2532(12)	6521(6)	4889(8)	66(10)
C(36)	1955(15)	6248(6)	4275(9)	82(11)
C(37)	1572(15)	5795(7)	4453(11)	89(12)
C(38)	1756(13)	5586(6)	5244(11)	76(11)
C(39)	2370(11)	5857(5)	5882(9)	57(9)
C(40)	4460(9)	6993(4)	5911(7)	42(7)
C(41)	4470(10)	7516(5)	5928(8)	50(8)
C(42)	5180(11)	7775(5)	5471(9)	60(9)
C(43)	5873(11)	7534(6)	5033(9)	64(10)
C(44)	5905(10)	7020(6)	5013(9)	62(9)
C(45)	5191(9)	6745(5)	5454(8)	49(8)
C(46)	5231(11)	6198(5)	5335(8)	56(9)
C(47)	5032(11)	5419(5)	6090(9)	59(9)
C(48)	6060(11)	5170(5)	6092(9)	64(10)
C(49)	6794(11)	5272(5)	6900(9)	62(9)
C(50)	7592(10)	5680(5)	6777(8)	53(9)
C(51)	8595(14)	5575(7)	6535(12)	89(14)
C(52)	9265(14)	5949(8)	6383(15)	118(18)
C(53)	8999(12)	6422(6)	6528(11)	76(12)
C(54)	8016(11)	6515(5)	6771(8)	51(8)

^{a} Values for anisotropically refined atoms were given in the isotropic equivalent thermal parameters defined as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

reflections. No significant decay of intensities was indicated throughout the data collection. *Lp* correction and a relative absorption correction, using an empirical ϕ scan method, were applied to the data.

The positions of 58 atoms, including two Pd atoms of the cationic part, were determined by direct methods using SHELXS-86.[7] All non-hydrogen atoms of the cationic part were located on Fourier and difference Fourier

(7) Sheldrick, G. M. SHELXS-86. Universitat Göttingen, Göttingen, Germany, 1986.

Scheme I

a: X = BF₄; b: X = PF₆
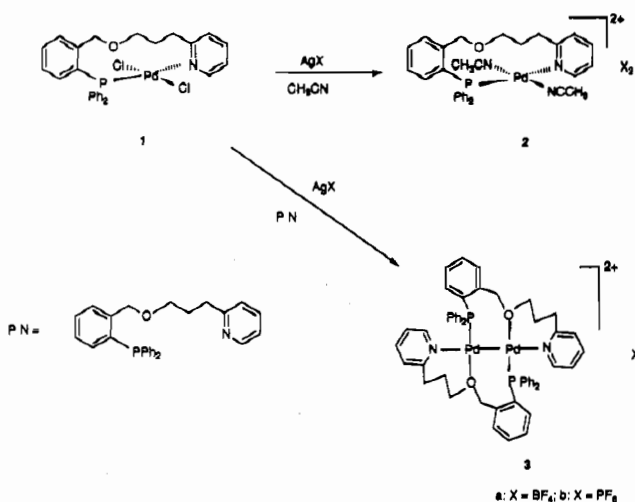
maps and assigned anisotropic thermal parameters. The structure was refined by using full-matrix least-squares techniques (ANYBLK[8]). At the stage where $R = 0.0686$, four oxygen atoms of solvate molecules and the hydrogen atoms of cationic part were located on a difference Fourier map. One oxygen atom of solvate molecules and the other oxygen atoms were assigned anisotropic and isotropic thermal parameters, respectively. The presence of the four solvate water molecules was also suggested from the IR spectrum (ν_{OH} 3620 and 3550 cm^{-1}) and the elemental analysis. We can eliminate the possibility of disordered molecules of dichloromethane because we could not find peaks at proper geometrical positions of dichloromethane as the solvate molecules in a difference Fourier map. ^{1}H NMR also showed only a tiny signal at δ 5.55 due to a trace of dichloromethane as impurities. The boron and fluorine atoms of two anionic parts were fixed contributions. The positions of hydrogen atoms, except the hydrogen atoms of the solvate molecules, were calculated (sp^2, C–H = 0.95 Å; sp^3, C–H = 1.08 Å) and were included in the refinements.

The comparison of the observed and calculated structure factors of the strong reflections showed an obvious effect of extinction, and the extinction parameter γ was introduced in the refinement as $|F_c(cor)| = |F_c(raw)|/(1 + \gamma Lp|F_c(raw)|^2)^{1/2}$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized and weight w is given by $w = 1.0/\sigma^2(|F_o|)$. Neutral atom scattering factors were taken from ref 9. Real and imaginary[10] contributions of Pd and P atoms were included in the calculations. The largest four peaks of a difference Fourier map had the electron density in the range 0.85–1.36 e/Å^3. These peaks were located near the BF$_4$ anions. All calculations were carried out on an NEC ACOS S930 computer at the Research Center Protein Engineering Institute for Protein Research, Osaka University.

The positional and equivalent thermal parameters for the cationic part are given in Table II.

Results and Discussion

Synthesis and Characterization of Complexes. Reaction of the *trans*-chelate PN complex, *trans*-PdCl$_2$(PN) (**1**), with an excess of AgPF$_6$ in acetonitrile gave the solvento complex *trans*-[Pd(PN)(CH$_3$CN)$_2$](PF$_6$)$_2$ (**2**) as a yellow powder, mp 118–120 °C dec, in a nearly quantitative yield. The complex is fairly stable in air in solid state but decomposed gradually in a chlorinated solvent, such as chloroform or dichloromethane, even under an inert atmosphere. The acetonitrile solution is stable under an inert gas atmosphere but decomposes gradually in air. Although there are some discrepancies in the elemental analyses from the above formulation, the spectral data indicated unambiguously the complex to be a mononuclear palladium(II) solvento complex, *trans*-[Pd(PN)(CH$_3$CN)$_2$](PF$_6$)$_2$. The IR spectrum

(8) The program (ANYBLK) was written by Dr. Hideo Imoto in 1990 (Department of Chemistry, Faculty of Science, The University of Tokyo 113, Japan).

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

(10) Cromer, D. T.; Ibers, J. A. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.
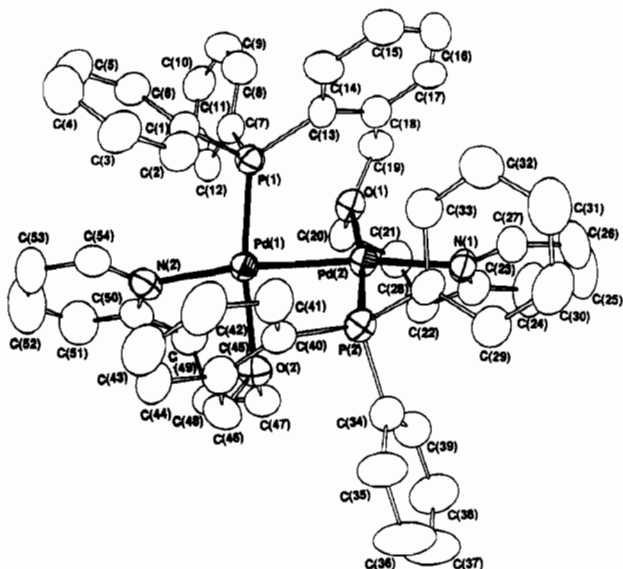
Figure 1. ORTEP drawing of the cationic part of complex **3a** with hydrogen atoms omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for [Pd$_2$[o-Ph$_2$PC$_6$H$_4$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N]$_2$](BF$_4$)$_2$·4H$_2$O (**3a**)

Pd(1)–Pd(2)	2.500(1)	Pd(1)–P(1)	2.218(3)
Pd(1)–O(2)	2.169(8)	Pd(1)–N(2)	2.21(1)
Pd(2)–P(2)	2.214(3)	Pd(2)–O(1)	2.165(8)
Pd(2)–N(1)	2.19(1)	P(1)–C(1)	1.83(1)
P(1)–C(7)	1.82(1)	P(1)–C(13)	1.84(1)
P(2)–C(28)	1.81(1)	P(2)–C(34)	1.80(1)
P(2)–C(40)	1.84(1)	O(1)–C(19)	1.46(2)
O(1)–C(20)	1.43(2)	O(2)–C(46)	1.43(2)
O(2)–C(47)	1.47(2)	N(1)–C(23)	1.35(2)
N(1)–C(27)	1.31(2)	N(2)–C(50)	1.32(2)
N(2)–C(54)	1.37(2)	C(13)–C(18)	1.43(2)
C(18)–C(19)	1.49(2)	C(20)–C(21)	1.49(2)
C(21)–C(22)	1.53(2)	C(22)–C(23)	1.54(2)
C(40)–C(45)	1.39(2)	C(45)–C(46)	1.50(2)
C(47)–C(48)	1.47(2)	C(48)–C(49)	1.53(2)
C(49)–C(50)	1.52(2)		
Pd(2)–Pd(1)–P(1)	84.2(1)	Pd(2)–Pd(1)–O(2)	86.5(2)
Pd(2)–Pd(1)–N(2)	167.1(3)	P(1)–Pd(1)–O(2)	170.4(2)
P(1)–Pd(1)–N(2)	102.4(3)	O(2)–Pd(1)–N(2)	87.2(4)
Pd(1)–Pd(2)–P(2)	84.32(9)	Pd(1)–Pd(2)–O(1)	86.3(2)
Pd(1)–Pd(2)–N(1)	168.2(3)	P(2)–Pd(2)–O(1)	170.4(2)
P(2)–Pd(2)–N(1)	101.4(3)	O(1)–Pd(2)–N(1)	88.2(4)
Pd(1)–P(1)–C(1)	103.8(4)	Pd(1)–P(1)–C(7)	116.4(4)
Pd(1)–P(1)–C(13)	123.5(5)	Pd(2)–P(2)–C(28)	104.1(4)
Pd(2)–P(2)–C(34)	116.4(4)	Pd(2)–P(2)–C(40)	123.9(4)
Pd(2)–O(1)–C(19)	117.9(7)	Pd(2)–O(1)–C(20)	120.2(6)
Pd(2)–O(1)–C(21)	105.3(5)	Pd(1)–O(2)–C(46)	119.0(6)
Pd(1)–O(2)–C(47)	119.4(6)	Pd(1)–O(2)–C(48)	104.3(5)
Pd(2)–N(1)–C(23)	119.2(6)	Pd(2)–N(1)–C(27)	123(1)
Pd(1)–N(2)–C(50)	119.8(6)	Pd(1)–N(2)–C(54)	120.8(8)
P(1)–C(1)–C(2)	118.5(7)	P(1)–C(1)–C(6)	123(1)
P(1)–C(7)–C(8)	119.3(6)	P(1)–C(7)–C(12)	120.3(7)
P(1)–C(13)–C(14)	118.4(7)	P(1)–C(13)–C(18)	123(1)
P(2)–C(28)–C(29)	124.4(8)	P(2)–C(28)–C(33)	117(1)
P(2)–C(34)–C(35)	120.3(8)	P(2)–C(34)–C(39)	121(1)
P(2)–C(40)–C(41)	117.3(9)	P(2)–C(40)–C(45)	123.7(9)
C(19)–O(1)–C(20)	116(1)	C(46)–O(2)–C(47)	114.3(9)
C(23)–N(1)–C(27)	118(1)	C(50)–N(2)–C(54)	119.5(8)
C(13)–C(18)–C(19)	124(1)	C(17)–C(18)–C(19)	116(1)
O(1)–C(19)–C(18)	110(1)	O(1)–C(20)–C(21)	113.8(8)
C(20)–C(21)–C(22)	113.5(8)	C(21)–C(22)–C(23)	115(1)
N(1)–C(23)–C(22)	118.4(9)	C(2)–C(1)–C(6)	118(1)
C(1)–C(2)–C(3)	121(1)	C(2)–C(3)–C(4)	120(1)
C(3)–C(4)–C(5)	119.9(9)	C(4)–C(5)–C(6)	119.4(9)
C(1)–C(6)–C(5)	121(1)	C(8)–C(7)–C(12)	120.3(9)
C(7)–C(8)–C(9)	121(1)	C(8)–C(9)–C(10)	119.0(9)
C(9)–C(10)–C(11)	122(2)	C(10)–C(11)–C(12)	119(1)
C(7)–C(12)–C(11)	119.4(8)	C(14)–C(13)–C(18)	118.4(9)
C(13)–C(14)–C(15)	118.8(9)	C(14)–C(15)–C(16)	123(2)
C(15)–C(16)–C(17)	121(1)	C(16)–C(17)–C(18)	120(1)
C(13)–C(18)–C(17)	119.7(9)	C(40)–C(45)–C(44)	119.3(8)
C(40)–C(45)–C(46)	124.9(8)	O(2)–C(46)–C(45)	109(1)
O(2)–C(47)–C(48)	114.4(9)	C(47)–C(48)–C(49)	113.4(8)
C(48)–C(49)–C(50)	113.1(7)	N(2)–C(50)–C(49)	118.8(8)

showed the presence of the coordinated pyridyl group from ν-(C≡N) at 1610 cm^{-1}, which is a 20 cm^{-1} higher frequency shift compared to that of the free ligand at 1590 cm^{-1}. The IR spectrum also showed only one ν(C≡N) at 2300 cm^{-1} for coordinating acetonitrile, which suggests the *trans*-geometry is maintained in the solvento complex. Consistently, ^{1}H NMR showed the signal for the 6-H of the pyridyl ring at δ 8.79 as a complex multiplet with a characteristic shape, which showed also the presence of the *trans*-chelating PN ligand.[6] The ^{31}P{^{1}H} NMR showed a singlet signal at δ 28.8 for the coordinating PN ligand and a septet at δ −143.4 for PF$_6^-$. The peak ratio of these signals was 1:2. The results indicated that complex **2** is a cationic mononuclear palladium(II) complex with a *trans*-chelating PN ligand.

When the reaction of *trans*-PdCl$_2$(PN) with AgX (X = BF$_4$, PF$_6$) was performed in the presence of an equimolar amount of the PN ligand in a noncoordinating solvent, dichloromethane, attempting to isolate a bis-*trans*-PN complex, [Pd(*trans*-PN)$_2$]-X$_2$, a reddish solid of a complex mixture was obtained; the ^{31}P-{^{1}H} NMR spectrum indicated that the red solid is mainly comprised of five species. Recrystallization of the crude solid from dichloromethane–hexane afforded the palladium(I) dinuclear complex [Pd(PN)]$_2$X$_2$ (**3**) in an about 20% yield as air-stable red prisms. The other species could not be isolated in pure state. The complex **3** was also isolated in a similar yield by the direct reaction from PdCl$_2$(PhCN)$_2$ with 2 equiv of the PN ligand. The elemental analyses support the formulation **3**. The IR spectrum indicates the presence of a coordinating pyridyl group from ν(C≡N) at 1605 cm^{-1} and the absence of the coordinating acetonitrile. The ^{31}P{^{1}H} NMR showed a singlet signal at δ 28.6 for the cationic part. The 1:1 ratio of the signal for the PN ligand and that for the counteranion PF$_6^-$ of **3b** also indicated the complex to be a palladium(I) compound. During these reactions reduction of palladium(II) to palladium(I) has been accomplished. What the reducing agent is, however, is not clear at moment. The ligand itself may act as a reducing agent, because the phosphine oxide could be detected in the byproducts. Addition of a mixture of PPh$_3$ and pyridine or o-PPh$_2$CH$_2$O(CH$_2$)$_n$-2-C$_5$H$_4$N (n = 1, 2) instead of the PN ligand in the reaction did not produce the palladium(I) complex. Palladium(I) dinuclear complexes are generally prepared by the disproportionation reaction between appropriate palladium(0) and palladium(II) complexes.[5b] The reaction of *trans*-[Pd(PN)(MeCN)$_2$]$^{2+}$ and 0.5 equiv of Pd$_2$-(dba)$_3$ in the presence of 1 equiv of the PN ligand, however, did not give the complex **3** in an isolable yield. For the production of the palladium(I) complex **3** from palladium(II) complexes, 2

equiv of the PN ligand per palladium would be essential. In the above reactions affording the palladium(I) complex, the yield of complex **3** remains as low as 20% and several unidentifiable products containing phosphorus compounds are detected in the byproducts. In these byproducts decomposition products of the PN ligand by cleavage of the benzylic ether linkage and the phosphine oxide, o-P(O)Ph$_2$CH$_2$O(CH$_2$)$_3$-2-C$_5$H$_4$N, were also detected by ^{1}H NMR. Thus, the PN ligand may play a specific role for the reduction of palladium(II) to palladium(I) in the present reaction (Scheme I).

Crystal Structure of Complex 3b. Crystals of [Pd(PN)]$_2$-(BF$_4$)$_2$·4H$_2$O consists of [Pd(PN)]$_2^{2+}$ cations, BF$_4$ anions, and four water solvate molecules. An ORTEP drawing of the cationic part is shown in Figure 1. This drawing illustrates the dimeric structure of the cation and the presence of two bridging PN ligands, which behave as tridentate ligands coordinating through P,O,N donor atoms. Selected bond distances and angles for the [Pd-(PN)]$_2^{2+}$ cation are shown in Table III. The coordination

geometry around palladium atoms is a slightly distorted square plane. Each bridging PN ligand forms a characteristic fused ring system that is comprised of two seven-membered rings. No unusual strain, however, is detected in the bond lengths and angles. A similar structure is found in the palladium(I) dinuclear complex with tridentate bridges $[Pd\{PhP(CH_2CH_2PPh_2)_2\}]_2(BF_4)_2$.[5b] In this case, however, the triphosphine bridges form fused rings that are comprised of a five- and a six-membered rings. The most striking aspect of the structure is the extremely short Pd–Pd bond at 2.500(1) Å. It is clearly shorter than the Pd–Pd distance of 2.5310(9) Å found in $[Pd_2(CNMe)_6](PF_6)_2$,[11] reported as the shortest one so far observed in the Pd(I) dinuclear system. The Pd–Pd bond lengths in the dinuclear palladium complexes lie normally in the range 2.57–2.699 Å.[3] This short Pd–Pd bond found in complex **3a** is partially due to the small *trans* influence of the pyridyl group coordinating at the *trans* position.[12] Another factor such as conformational demands of the bridging ligands, however, may play a significant role for shortening the Pd–Pd bond. The average Pd–N(py) distance (2.20(1) Å) is longer than Pd–N(py) distances for the bonds *trans* to phosphorus atoms observed in complex **1** (2.104(4) Å)[6] or in a structurally related palladium(I) complex, $RuPd(Ph_2PPy)_2(CO)_2Cl_2$, (2.126(5) Å).[13] This suggests that the *trans* influence of palladium is greater than that of phosphorus, consistent with previous observation.[5b] The average Pd–P distance is 2.216(3) Å. This value is shorter than the distance of Pd–P bond *trans* to pyridyl nitrogen (2.259-

(1) Å) found in complex **1** or that *trans* to chlorine atom (2.254-(1) Å) found in *cis*-$PdCl_2(o-Ph_2PC_6H_4CH_2OCH_2-2-C_5H_4N)$.[6b] This result suggests that the *trans* influence of the oxygen is smaller than nitrogen or chlorine. The dihedral angle between the best fit planes of the two square-planar units is 58.0(1)°. That reported for $[Pd\{PhP(CH_2CH_2PPh_2)_2\}]_2^{2+}$ is 67°. Dimers with no bridging ligands exhibit a wide range of angles between 60 and 90°.[14-17] This dihedral angle is considered to be responsible for the release of the strain. The average value for the two dihedral angles between the coordination plane and the plane of the coordinating pyridine ring is 57.0(2)°, which is smaller than the dihedral angle of 102.0(2)° found in complex **1**.[6b] This indicates more ring strain is present in complex **3** than in complex **1** due to the coordination of the oxygen of the PN ligand. By adjusting the dihedral angles, the inherent ring strain made by the specific fused ring systems may be released and the formation of complex **3** became possible.

Supplementary Material Available: Tables listing detailed experimental data for X-ray diffraction, fractional atomic coordinates and isotropic thermal parameters for the solvate atoms, the fixed BF_4^- and fixed hydrogen atoms, final anisotropic thermal parameters, interatomic distances, interatomic angles, and details of computation of dihedral angles used in the text and a figure indicating the characteristic ^1H NMR signal shapes for 6-H of the pyridyl ring in complexes **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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