Preparation and Characterization of Mononuclear Palladium(II) and Dinuclear Palladium(I) Complexes Containing a New Phosphine-Imine-Type Didentate Ligand, 8-(Dimethylphosphino)quinoline (Me_2Pqn). Molecular Structures of *cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$ and $[Pd_2Cl_2(Me_2Pqn)_2]$

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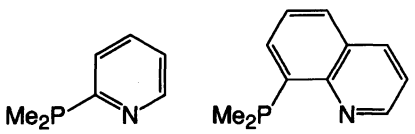
A new phosphine ligand, 8-(dimethylphosphino)quinoline (Me_2Pqn), and its palladium(I or II) complexes, $[PdX_2(Me_2Pqn)]$ (X = Cl (**1a**), Br (**1b**), and I (**1c**)), $[Pd(Me_2Pqn)_2](BF_4)_2$ (**2b**), and $[Pd_2Cl_2(Me_2Pqn)_2]$ (**3**), have been prepared and characterized. The structures of **2b** and **3** have been determined by X-ray analysis. The crystal data and final R values are: for **2b**, FW=658.42, monoclinic, $P2_1/n$, a=17.453(2), b=10.453(2), c=14.928(2) Å, β=105.63(1)°, V=2622.8(5) Å^3, D_x=1.667 Mg m^{-3}, and Z=4, R=0.071 for 3908 reflections ($|F_o| \geq 3\sigma(|F_o|)$); for **3**, MW=662.64, monoclinic, $P2_1/n$, a=16.429(1), b=12.191(1), c=12.821(1) Å, β=92.673(8)°, V=2565.1(4) Å^3, D_x=1.714 Mg m^{-3}, and Z=4, R=0.056 for 5136 reflections ($|F_o| \geq 3\sigma(|F_o|)$). In **2b** the square coordination plane formed by two long Pd–N (2.138(9) and 2.135(8) Å) and two Pd–P bonds (2.243(3) and 2.237(3) Å) is slightly distorted towards tetrahedral geometry, the dihedral angle between the two chelate planes formed by the Pd, P, and N atoms being 10.3(2)°. **3** is a dinuclear complex with a Pd–Pd bond (2.542(1) Å), Me_2Pqn chelates to one Pd(I) center, and the N donor atom occupies the *trans* position to the Pd–Pd bond. The dihedral angle between the two coordination planes linked by the Pd–Pd bond is nearly a right angle, 82.13(6)°.

In previous papers[1—3] we reported on the preparation and characterization of 2-(dimethylphosphino)-pyridine (Me_2Ppy; Scheme 1) complexes of palladium(I or II) and platinum(I or II), where Me_2Ppy acted as a monodentate phosphorus donating, chelating, or bridging ligand. The ligand readily bridges two M(I) (M=Pd and Pt) ions to form a stable dinuclear complex having a M(I)–M(I) bond,[2,3] while the four-membered chelate ring formed by chelation of Me_2Ppy is highly strained, as revealed by X-ray analyses.[1] The two Me_2Ppy ligands in *cis*-$[PdCl(Me_2Ppy\text{-}P,N)(Me_2Ppy\text{-}P)]^+$ exchange rapidly the coordination modes between these two ligands in solution.[1] These coordination behaviors seem to depend primarily on the steric factor of Me_2Ppy. As an extension of this work, we have studied palladium(I or II) complexes of an analogous phosphine-imine-type ligand, 8-(dimethylphosphino)quinoline (Me_2Pqn). The ligand is expected to form a stable five-membered ring upon chelate coordination; it could be interesting to see whether it can act as a bridging ligand to two Pd(I) ions to form a dinuclear complex.



Me_2Ppy Me_2Pqn

Scheme 1.

There have been known a quite large number of metal complexes with phosphine,[4—6] arsine,[4—7] and stibine[8] derivatives of 8-quinoline. To our knowledge, however, no report has been published on Me_2Pqn. This paper deals with the preparation of the new Me_2Pqn ligand and its palladium(I or II) complexes, together with X-ray structure analyses of the mononuclear *cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$ and the dinuclear $[Pd_2Cl_2(Me_2Pqn)_2]$ complexes.

Experimental

All preparative procedures were performed under an

atmosphere of nitrogen until air-stable complexes were formed. All of the solvents used in the preparation of Me_2Pqn and its complexes were bubbled with nitrogen for 20 min immediately before use. Tetramethyldiphosphane,[9] $[PdCl_2(PhCN)_2]$ (PhCN = benzonitrile),[10] and $[Pd_2(dba)_3]\cdot CHCl_3$[11] (dba=1,5-diphenyl-1,4-pentadien-3-one) were prepared by literature methods.

Preparation of 8-(Dimethylphosphino)quinoline (Me_2Pqn). A mixture of tetramethyldiphosphane (5.87 g, 48.1 mmol) and potassium metal (3.76 g, 96.2 mmol) in tetrahydrofuran (300 cm^3) was stirred for one day at 30—40 °C. The unreacted potassium metal was removed, and the resulting yellow-orange solution was cooled in an ice bath. To the solution was added a tetrahydrofuran solution (50 cm^3) of 8-chloroquinoline (15.74 g, 96.2 mmol) dropwise with stirring over 2 h. The mixture was stirred over night at room temperature, and then refluxed for 2 h. The solvent was removed by distillation under reduced pressure, and the residue was extracted with diethyl ether (200 cm^3). The dark-red extract was carefully distilled under reduced pressure (0.13 kPa). After distilling a colorless oil (unreacted 8-chloroquinoline; 51—58 °C, 4.67 g), a greenish yellow oil of Me_2Pqn (96—102 °C) was obtained. Yield 5.93 g (33.7%). ^1H NMR ($CDCl_3$) δ=1.44 (d, 6H, J=4.0 Hz), 6.72—7.61 (m, 1H), 7.11—7.61 (m, 4H), 8.72 (dd, 1H, J=4.0, 1.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=13.60 (d, J=12.2 Hz), 121.14 (s), 126.40 (s), 127.70 (s), 129.30 (s), 136.31 (s), 143.58 (d, J=16.7 Hz), 149.20 (s), 144.39 (d, J=15.2 Hz) $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ=−51.30.

Preparation of the Complexes. $[Ni(Me_2Pqn)_2](BF_4)_2$. An aqueous solution of $Ni(BF_4)_2$ (40 wt%, 4.96 g, 8.55 mmol) was evaporated to dryness under reduced pressure, and the residue was dissolved in ethanol (70 cm^3). To the solution was added an ethanol solution (20 cm^3) of Me_2Pqn (3.23 g, 7.10 mmol) with stirring; the mixture was refluxed for 1 h. After cooling in an ice bath for 3 h, the resulting brown precipitate was collected by filtration, washed with ice-cold ethanol (20 cm^3) and diethyl ether (50 cm^3), and dried in vacuo. Yield 3.97 g (75.9%). Anal. Found: C, 43.25; H, 4.63; N, 3.92%. Cacld for $C_{22}H_{24}B_2F_8N_2NiP_2$: C, 43.27; H, 4.59; N, 3.96%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ=22.52.

This complex is air-stable in the solid state, and can be used for storage of the air-sensitive Me_2Pqn ligand. The free Me_2Pqn ligand was recovered by the following method: The Ni(II) complex and excess KCN (ca. 8-fold) were dissolved in a small amount of deaerated water. The solution was mixed with the same volume of diethyl ether and stirred vigorously, and then allowed to stand for a while. The ethereal layer was separated, and the aqueous layer was washed with diethyl ether several times. The ethereal extracts were combined, and then evaporated under reduced pressure to give the ligand almost quantitatively.

$[PdCl_2(Me_2Pqn)]$ (1a). To a dichloromethane solution (10 cm^3) of $[PdCl_2(PhCN)_2]$ (1.03 g, 2.70 mmol) was added a methanol solution (10 cm^3) of Me_2Pqn (430 mg, 2.70 mmol) with stirring. After stirring for 2 h, the solution was concentrated to ca. 5 cm^3 under reduced pressure to yield a brown precipitate. It was collected by filtration, washed with diethyl ether (10 cm^3), and dried in air. The crude product was dissolved in hot acetonitrile (60 °C, 500 cm^3), and the solution was filtered while hot. The filtrate was cooled to room temperature, and concentrated to ca. 20 cm^3 under reduced pressure. The pale-yellow crystals formed were collected by filtration and dried in vacuo. Yield 760 mg (77.1%). Anal. Found: C, 36.05; H, 3.12; N, 3.83%. Cacld for $C_{11}H_{12}Cl_2NPPd$: C, 36.34; H, 3.30; N, 3.82%. ^1H NMR ($CDCl_3$) δ=2.04 (filled-in doublet 6H, J=14.1 Hz) 7.70—8.03 (m, 2H), 8.28—8.50 (m, 2H), 8.65—8.78 (m, 1H), 10.07 (dt, 1H, J=5.3, 1.3 Hz). $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ=14.90 (d, J=38.1 Hz), 124.71 (s), 130.06 (d, J=7.6 Hz), 131.56 (d, J=10.7 Hz), 133.60 (d, J=47.3 Hz), 134.50 (J=3.0 Hz), 136.73 (s), 141.92 (s), 153.28 (d, J=19.8 Hz), 157.06 (s). $^{31}P\{^1H\}$ NMR (CD_3NO_2) δ=39.80.

$[PdBr_2(Me_2Pqn)]$ (1b) and $[PdI_2(Me_2Pqn)]$ (1c). To a chloroform solution (50 cm^3) of **1a** (250 mg, 0.68 mmol) was added a methanol solution (50 cm^3) of KBr (200 mg, 1.68 mmol) or KI (250 mg, 1.52 mmol). The mixture was stirred at room temperature over night, and evaporated to dryness under reduced pressure. The residue was extracted with chloroform (300 cm^3), the extract was mixed with methanol (50 cm^3), and the mixture was concentrated to ca. 10 cm^3 under reduced pressure. Yellow crystals of **1b** or red-orange crystals of **1c** were formed, collected by filtration, and dried in vacuo. For **1b**, Yield 270 mg (90.9%). Anal. Found: C, 29.33; H, 2.69; N, 3.27%. Cacld for $C_{11}H_{12}Br_2NPPd$: C, 29.01; H, 2.50; N, 3.08%. For **1c**, Yield 302 mg (83.6%). Anal. Found: C, 24.14; H, 2.17; N, 2.50%. Cacld for $C_{11}H_{12}I_2NPPd$: C, 24.05; H, 2.20; N, 2.55%.

***cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$ (2b).** To a dichloromethane solution (25 cm^3) of $[PdCl_2(PhCN)_2]$ (1.00 g, 2.61 mmol) was added a dichloromethane solution (10 cm^3) of Me_2Pqn (1.04 g, 5.50 mmol) with stirring. Although immediate precipitation occurred, the precipitate was dissolved within several minutes after the addition was completed. After stirring was continued for an additional 2 h, the solvent was removed under reduced pressure. The resulting orange oily product gave a yellow powder (**2a**)[12] by vigorous stirring with diethyl ether (50 cm^3). The powder was collected by filtration and dried in vacuo. Compound **2a** was dissolved in methanol (5 cm^3) and the solution was filtered. The filtrate was mixed with a saturated methanol solution (5 cm^3) of NH_4BF_4 (or $LiBF_4$), stirred for 30 min, and then allowed to stand in a refrigerator over night. Colorless crystals were obtained, collected by filtration, and dried in vacuo. Yield 1.34 g (78.0%). Anal. Found: C, 40.13; H, 3.60; N, 4.31%. Cacld for $C_{22}H_{24}B_2F_8N_2P_2Pd$: C, 40.13; H, 3.67; N, 4.31%. ^1H NMR ($CDCl_3$) δ=2.18 (filled-in doublet, 6H, J=10.6 Hz), 7.93—8.13 (m, 2H), 8.40—8.53 (m, 2H), 8.82—8.90 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ=14.57 (virtually coupled quintet), 125.53 (s), 130.68 (t, J=4.5 Hz), 131.38 (t, J=5.5 Hz), 133.76 (t, J=6.2 Hz), 134.92 (s), 136.84 (s), 143.33 (s), 150.71 (virtually coupled triplet), 155.16 (s). $^{31}P\{^1H\}$ NMR (CD_3NO_2) δ=31.96.

Crystalline complex **2b** was also obtained from **2a** by the following method: To an acetonitrile solution (100 cm^3) of **2a** (200 mg) was added a methanol solution (8 cm^3) of $AgBF_4$ (140 mg, 0.12 mmol), and the mixture was stirred for 4 h in the dark to yield a white precipitate. After it was removed by filtration, the filtrate was evaporated to dryness under reduced pressure to give colorless crystals, which were collected by filtration and recrystallized from a mixture of acetonitrile and methanol (1:1). Yield 195 mg.

$[Pd_2Cl_2(Me_2Pqn)_2]$ (3). A dichloromethane solution (25 cm^3) of Me_2Pqn (378 mg, 2.00 mmol) was added

with stirring to a dichloromethane solution (25 cm^3) of $[PdCl_2(PhCN)_2]$ (326 mg, 0.85 mmol), giving a yellow solution. To the solution was added $[Pd_2(dba)_3]\cdot CHCl_3$ (436 mg, 0.42 mmol); the mixture was stirred for 7 h. The resulting orange-red solution was concentrated to ca. 10 cm^3 under reduced pressure, and the concentrate was cooled in an ice bath for a while to give an orange-red precipitate. It was collected by filtration, washed with diethyl ether, and dried in vacuo (412 mg). The second crop (118 mg) was obtained from the filtrate by the addition of diethyl ether (40 cm^3). Total yield: 530 mg (94.2%). Anal. Found: C, 39.81; H, 3.85; N, 4.11%. Calcd for $C_{22}H_{24}Cl_2N_2P_2Pd_2$: C, 39.91; H, 3.65; N, 4.23%. Dark-red prismatic crystals of **3** were formed by storing a methanol solution of the complex and diethyl ether in a vessel in a desiccator. A small amount of black precipitate (Pd black) was yielded together with the crystals. $^{31}P\{^1H\}$ NMR (CD_3NO_2) δ=4.42.

Measurements. Infrared spectra in the 700—200 cm^{-1} range were obtained with a Hitachi EPI-L spectrophotometer by the Nujol mull method using polyethylene films. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 23 °C on a Hitachi R-90HS (at 90.02, 22.66, and 36.46 MHz, respectively) or a JEOL GX400 (at 399.8, 100.5, and 161.9 MHz, respectively) spectrometer, using TMS as an internal reference for ^1H and ^{13}C NMR spectra, and 85% H_3PO_4 as an external reference for ^{31}P NMR spectra. Conductivity measurements were carried out on a TOA CM-6A conductometer with 1 mmol dm^{-3} nitromethane solutions at room temperature.

Crystal Structure Determination. The crystal data and experimental conditions are listed in Table 1. The X-ray intensities were measured at 23 °C with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) on an automated Rigaku four-circle diffractometer AFC-5. The ω–2θ scan technique was employed. Absorption corrections were made by the Gauss numerical integration method.[13] The final lattice constants were determined by least-squares treatments using setting angles of 47 and 25 reflections for **2b** and **3**, respectively, in the $25° < 2\theta < 30°$ range. The structure of **2b** was solved by the usual heavy-atom method, and that of **3** by a direct method using the SHELXS-86 program.[14] All of the hydrogen atoms were located by difference Fourier syntheses. The function $\Sigma w||F_o|-|F_c||^2$, with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ was minimized by block-diagonal least-squares methods using anisotropic and isotropic thermal parameters for all non-hydrogen and hydrogen atoms, respectively. Complex neutral-atom scattering factors[15] were used. All of the calculations were carried out on a HITAC M-680 computer at the Computer Center of Institute for Molecular Science using the computation program system UNICS-III.[16] The atomic parameters are listed in Table 2, and the selected bond lengths and angles in Table 3.[17]

Results and Discussion

The Palladium(II) Complexes. The Me_2Pqn ligand was prepared by a method similar to that for Me_2Ppy,[1] and purified by distillation under reduced pressure. Although the free ligand is easily oxidized in air, its Ni(II) and Pd(II) complexes are very stable. The reaction of $Ni(BF_4)_2$ with Me_2Pqn in ethanol yielded a brown precipitate of $[Ni(Me_2Pqn)_2](BF_4)_2$, from which the ligand was recovered almost quantitatively by treating with KCN in water and by extracting with diethyl ether.

Pale-yellow crystals of $[PdCl_2(Me_2Pqn)]$ (**1a**) were obtained by recrystallization of the reaction product between $[PdCl_2(PhCN)_2]$ and Me_2Pqn in a 1:1 molar ratio in dichloromethane. The complex is a non-electrolyte in nitromethane (Λ_m=2.35 Ω^{-1} mol^{-1} cm^2),[18] and can be assumed to be a monomeric, four-coordinate planar complex. In the infrared spectrum two bands due to the ν(Pd–Cl) are observed at 330 and 294 cm^{-1}, which are smaller wavenumbers than those of the corresponding 8-(diphenylphosphino)quinoline (Ph_2Pqn) complex, $[PdCl_2(Ph_2Pqn)]$ (334 and 325 cm^{-1}).[5] The red shift of the ν(Pd–Cl) in **1a** may be attributable to the stronger trans influence of the dimethylphosphino group of Me_2Pqn compared to that of the diphenylphosphino one of Ph_2Pqn. $[PdX_2(Me_2Pqn)]$ (X=Br (**1b**) and I (**1c**)) were obtained from **1a** by replacing Cl^- with Br^- or I^-. The infrared spectra of **1b** and **1c** are very similar to that of **1a**, except for the bands due to the ν(Pd–X).

The reaction of $[PdCl_2(PhCN)_2]$ and Me_2Pqn in a 1:2 molar ratio in dichloromethane gave a clear yellow solution, from which a yellow powder (**2a**) was obtained by treating with diethyl ether. Compound **2a** was very soluble in common organic solvents, except for ethers and hydrocarbons, and all attempts to crystallize it were unsuccessful. However, a methanol solution of **2a** afforded colorless crystals upon adding a methanol solution of NH_4BF_4 (or $LiBF_4$), or by treating with $AgBF_4$. Elemental analysis and conductivity measurements (Λ_m=182 Ω^{-1} mol^{-1} cm^2)[18] indicate that these crystals are $[Pd(Me_2Pqn)_2](BF_4)_2$ (**2b**). For this type of complex there are two possible isomers, *cis* and *trans*. From the steric repulsions among four methyl groups and between two *ortho*-hydrogen atoms of the quinolyl rings, the *trans*-isomer is expected to be more favorable than the *cis*-isomer. However, an isomer in which two strongly *trans*-labilizing ligands, such as phosphines, are in the trans positions is known to be unstable. In the ^1H and ^{13}C NMR spectra in CD_3CN solutions the complex shows a virtually coupled peak in the P–CH_3 region owing to the $^2J_{(P,P)}$ coupling, and the $^2J_{(P,P)}$ value calculated by spectral simulation is as small as that expected for a *cis*-isomer. The resonance of *ortho*-hydrogen of the quinolino group is observed at a higher field (δ=8.82—8.90, m) than that of the monochelate complex (**1a**; δ=10.07, dt, J=5.3, 1.3 Hz). The higher field shift is attributable to the effect of mutual shielding of Me_2Pqn ligands in the cis positions (vide infra). The *cis*-structure was confirmed by an X-ray analysis.

A perspective drawing of the complex cation in **2b** is shown in Fig. 1, together with the atom numbering scheme. The Pd–N bond lengths (2.138(9) and 2.135(8) Å) are remarkably long compared with those in analogous imine complexes, such as [Pd-

Table 1. Crystal Data of *cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$ (**2b**) and $[Pd_2Cl_2(Me_2Pqn)_2]$ (**3**)

Compound	*cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$	$[Pd_2Cl_2(Me_2Pqn)_2]$
Chemical formula	$C_{22}H_{24}B_2F_8N_2P_2Pd$	$C_{22}H_{24}Cl_2N_2P_2Pd_2$
Formula weight	658.42	662.64
Temperature/°C	23	23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Lattice constants a/Å	17.453(2)	16.429(1)
b/Å	10.453(2)	12.191(1)
c/Å	14.928(2)	12.821(1)
β/deg	105.63(1)	92.673(8)
V/Å^3	2622.8(5)	2565.1(4)
Z	4	4
D_x/Mg m^{-3}	1.667	1.714
μ(Mo $K\alpha$)/mm^{-1}	0.889	1.73
Transmission factor, A	0.717—0.832	0.639—0.767
Number of unique reflections[a)]	3908	5136
Number of parameters refined	431	368
R[b)]	0.071	0.056
R_w[c)]	0.072	0.067

a) $|F_o|>3\sigma(|F_o|)$. b) $R=\sum||F_o|-|F_c||/\sum|F_o|$. c) $R_w=(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2)^{1/2}$.

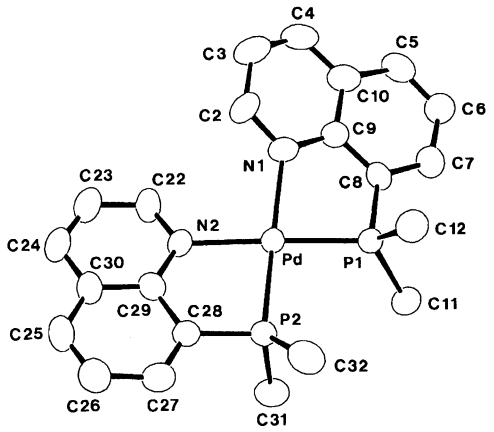


Fig. 1. A perspective view of the complex cation in *cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$ (**2b**).

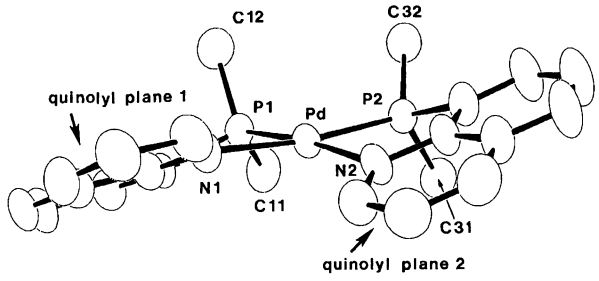


Fig. 2. A side view of *cis*-$[Pd(Me_2Pqn)_2]^{2+}$.

$(bpy)_2]^{2+}$ (bpy=2,2′-bipyridine, av 2.034(1) Å)[19] or $[Pd(phen)_2]^{2+}$ (phen=1,10-phenanthroline, av 2.051(3) Å).[20] The elongation of the Pd–N bond in **2b** indicates a large trans influence of the dimethylphosphino donor group. The Pd–P bond lengths (2.243(3) and 2.237(3) Å) and the chelate P–Pd–N angles of Me_2Pqn (82.5(2) and 83.6(2)°) are similar to those of the related Pd(II) complexes.[4,7,21]

Two planes of the quinolyl rings in **2b** are not in coplanar, but twisted around the Pd atom towards a tetrahedral geometry, probably due to the steric repulsion between the *ortho*-hydrogen atoms of two quinolyl rings. Similar twisted structures have been observed for the planar complexes with analogous heteroaromatic ligands, such as $[Pd(bpy)_2]^{2+}$[19] and $[M(phen)_2]^{2+}$ (M=Pd[20] and Pt[22]). As Table 4 shows, the dihedral angle (ϕ_L) between the two quinolyl planes of Me_2Pqn in **2b** (27.2(2)°) is similar to those in the bpy and phen complexes. The distance between the two *ortho*-hydrogen atoms (H2···H22) in **2b** is slightly longer than those in the bpy and phen complexes. On the other hand, the dihedral angle (ϕ_C) between the two chelate planes defined by the metal ion and the two chelating donor atoms, which represents a tetrahedral distortion of the coordination geometry around the metal ion, is small in **2b** (10.3(2)°) compared with those in the bpy and phen complexes (Table 4). The better planar structure of **2b** is attained by forming a puckered chelate ring with a deviation of the phosphino group from the quinolyl ring, as shown in Fig. 2. The deviation from the quinolyl ring is 0.45(1) Å for P1 and 0.35(1) Å for P2. The structure in Fig. 2 indicates the *ortho*-hydrogen atom shielded by the other quinolyl ring. Complex **2b** would have a similar structure in solution to give a resonance due to the *ortho*-hydrogen atom at the high field in the ^{1}H NMR spectrum.

The Dinuclear Palladium(I) Complex, $[Pd_2Cl_2(Me_2Pqn)_2]$ (3). Complex **3** was obtained almost quantitatively by a conproportionation reaction among $[Pd^{II}Cl_2(PhCN)_2]$, Me_2Pqn, and $[Pd^0_2(dba)_3]\cdot CHCl_3$ in dichloromethane. Red crystals of **3** were formed by storing a methanol solution of the reaction product and diethyl ether in a desiccator, but were contaminated by a small amount of black precipi-

Table 2. Fractional Coordinates ($\times10^4$:$\times10^5$ for Pd) and Equivalent Isotropic Temperature Factors (B_{eq}[a)]$\times10/Å^2$)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
cis-[Pd(Me$_2$Pqn)$_2$](BF$_4$)$_2$ (**2b**)					[Pd$_2$Cl$_2$(Me$_2$Pqn)$_2$] (**3**)				
Pd	49389(4)	3525(6)	24758(5)	28	Pd1	73704(4)	51610(5)	52264(5)	24
P1	5602(1)	1774(2)	3527(2)	30	Pd2	82948(4)	43393(5)	66678(5)	24
P2	4376(1)	1777(2)	1376(2)	32	C11	6246(1)	4031(2)	5609(2)	41
F11	6838(5)	−3366(8)	2073(5)	70	C12	8864(1)	2950(2)	5596(2)	35
F12	6887(8)	−5474(10)	1794(7)	139	P1	8443(1)	6036(2)	4717(2)	29
F13	6275(10)	−4370(10)	756(6)	181	P2	7710(1)	5507(2)	7690(2)	31
F14	5861(9)	−4598(16)	1926(15)	260	N1	6728(4)	5988(6)	3922(5)	31
F21	3008(5)	−3453(7)	2978(5)	67	N2	8938(4)	3779(6)	8084(6)	32
F22	3126(8)	−5612(9)	3159(7)	141	C2	5950(5)	5837(8)	3635(7)	36
F23	3291(8)	−4337(8)	4385(6)	118	C3	5573(7)	6352(10)	2743(9)	48
F24	4125(7)	−4268(11)	3624(12)	163	C4	6013(7)	7043(10)	2160(9)	48
N1	5610(5)	−989(8)	3461(5)	38	C5	7316(7)	7992(9)	1888(9)	47
N2	4204(5)	−981(7)	1544(5)	33	C6	8087(8)	8179(10)	2227(10)	55
C2	5772(7)	−2194(9)	3258(7)	44	C7	8454(7)	7648(9)	3129(9)	45
C3	6148(8)	−3067(11)	3958(8)	53	C8	8003(6)	6902(8)	3668(7)	34
C4	6385(7)	−2680(11)	4844(8)	50	C9	7185(5)	6717(7)	3356(7)	32
C5	6570(6)	−841(11)	4014(7)	46	C10	6831(6)	7252(8)	2455(7)	38
C6	6496(7)	430(11)	6186(6)	45	C11	9166(6)	5222(9)	3996(8)	39
C7	6157(6)	1222(11)	5439(7)	44	C12	9085(6)	6976(9)	5501(8)	43
C8	5865(5)	755(9)	4534(6)	33	C22	9455(6)	2953(8)	8140(7)	38
C9	5914(5)	−552(9)	4364(6)	34	C23	9852(8)	2580(10)	9077(9)	52
C10	6293(6)	−1391(10)	5086(7)	41	C24	9712(8)	3116(11)	9970(9)	57
C11	5084(7)	3183(10)	3792(7)	47	C25	8977(9)	4592(11)	10865(8)	61
C12	6540(7)	2321(11)	3398(8)	49	C26	8429(10)	5422(12)	10818(9)	71
C22	4053(6)	−2149(10)	1775(7)	44	C27	8044(9)	5731(11)	9872(9)	59
C23	3633(7)	−3048(10)	1124(8)	50	C28	8207(7)	5185(9)	8951(7)	40
C24	3367(7)	−2720(10)	207(8)	50	C29	8775(6)	4306(8)	9009(6)	33
C25	3211(8)	−1045(11)	−980(7)	56	C30	9157(7)	4000(9)	9976(7)	43
C26	3342(8)	163(12)	−1194(7)	62	C31	7821(8)	6986(8)	7608(9)	49
C27	3733(8)	1096(11)	−513(7)	55	C32	6628(7)	5329(11)	7914(10)	55
C28	3997(6)	721(9)	395(7)	39					
C29	3914(6)	−593(9)	631(6)	36					
C30	3498(6)	−1460(11)	−69(7)	43					
C31	3531(6)	2707(11)	1483(8)	47					
C32	5016(7)	2925(12)	1039(8)	55					
B1	6499(9)	−4434(18)	1621(12)	70					
B2	3336(9)	−4500(13)	3475(9)	57					

a) $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

tate (Pd black). Although complex **3** seems to decompose slowly both in the solid state and in solution, no appreciable decomposition was observed during spectroscopic measurements and X-ray diffraction data collection. The ^{31}P NMR spectrum of **3** shows a single resonance at a relatively higher field ($\delta=4.42$) than that of the Pd(II) complexes of Me$_2$Pqn (**1a**: $\delta=39.80$, **2b**: $\delta=31.96$). The high-field shift of the ^{31}P resonance has been observed for the dinuclear Pd(I) complexes of Me$_2$Ppy,[2] Ph$_2$Ppy,[23] and dppm.[24]

Figure 3 is a perspective drawing of **3** together with the atom numbering scheme. A large number of papers have been published concerning the preparation and structures of Pd(I)–Pd(I) dinuclear complexes of the side-by-side type.[2,3,23—37] Most of these complexes can be classified into two types. One involves complexes in which a didentate or tridentate ligand bridges two Pd(I)

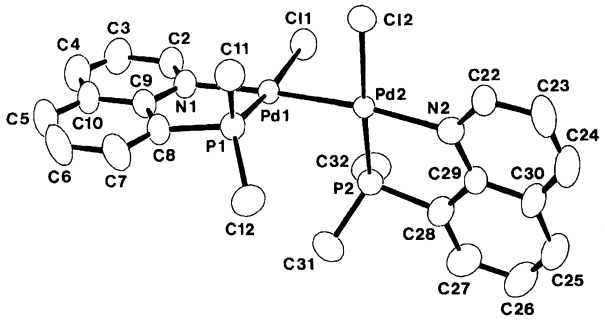


Fig. 3. A perspective view of [Pd$_2$Cl$_2$(Me$_2$Pqn)$_2$] (**3**).

ions of the Pd–Pd bond;[23—32] the other is those formed with monodentate isocyanides[32,33] or with mixed ligands of isocyanides and halide ions.[34,35] Recently, a few dinuclear Pd(I) complexes of the new type have

Table 3. Selected Bond Lengths (l/Å), Angles (ϕ/°), and Dihedral Angles (τ/°)

cis-$[Pd(Me_2Pqn)_2](BF_4)_2$ (**2b**)			
Pd–P1	2.243(3)	Pd–P2	2.237(3)
Pd–N1	2.138(9)	Pd–N2	2.135(8)
P1–Pd–P2	96.6(1)	P1–Pd–N1	82.5(2)
P1–Pd–N2	173.8(2)	P2–Pd–N1	172.6(2)
P2–Pd–N2	83.6(2)	N1–Pd–N2	98.1(3)
Plane(Pd,P1,N1) vs. plane(Pd,P2,N2)			10.3(2)
Plane(quinolyl ring 1)[a] vs. plane(quinolyl ring 2)[b]			27.2(2)
$[Pd_2Cl_2(Me_2Pqn)_2]$ (**3**)			
Pd1–Pd2	2.542(1)		
Pd1–C11	2.375(3)	Pd2–C12	2.398(2)
Pd1–P1	2.185(2)	Pd2–P2	2.187(3)
Pd1–N1	2.182(7)	Pd2–N2	2.168(7)
Pd2–Pd1–C11	93.75(7)	Pd1–Pd2–C12	95.59(6)
Pd2–Pd1–P1	86.96(6)	Pd1–Pd2–P2	85.11(7)
Pd2–Pd1–N1	172.0(2)	Pd1–Pd2–N2	169.8(2)
C11–Pd1–P1	172.32(9)	C12–Pd2–P2	175.46(9)
C11–Pd1–N1	94.2(2)	C12–Pd2–N2	94.0(2)
P1–Pd1–N1	85.0(2)	P2–Pd2–N2	85.1(2)
Plane(Pd1,Pd2,C11,P1,N1) vs. plane(Pd2,Pd1,C12,P2,N2)			82.13(6)
Plane(Pd1,Pd2,C11,P1,N1) vs. plane(quinolyl ring 1)[a]			2.7(2)
Plane(Pd2,Pd1,C12,P2,N2) vs. plane(quinolyl ring 2)[b]			3.6(2)
Plane(quinolyl ring 1)[a] vs. plane(quinolyl ring 2)[b]			80.9(2)

a) Plane(quinolyl ring 1) is defined by N1, C2, C3, C4, C5, C6, C7, C8, C9, and C10. b) Plane(quinolyl ring 2) is defined by N2, C22, C23, C24, C25, C26, C27, C28, C29, and C30.

Table 4. Selected Bond Lengths (l/Å), Dihedral Angles (τ/°), Non-Bonded Distances (l/Å) for the Me_2Pqn, bpy, and phen Complexes

Complex	M–N	ϕ_L[a]	ϕ_C[b]	H···H[c]	Ref.
cis-$[Pd(Me_2Pqn)_2](BF_4)_2$	2.138(9)	27.2(2)	10.3(2)	2.9(1)	d)
	2.135(8)				
$[Pd(bpy)_2(H_2O)](NO_3)_2$	2.026(1)	33.2	24.6(4)	2.0	19,20
	2.029(1)				
	2.030(1)				
	2.049(1)				
$[Pd(phen)_2](ClO_4)_2$	2.043(4)	22.5	18.7(2)	2.0(1)	20
	2.059(4)				
$[Pt(phen)_2]Cl_2$	2.026(8)	27.1	20.9(5)	1.95	20,22
	2.039(8)				

a) The dihedral angle between the planes of two heteroaromatic ligands. b) The dihedral angle between the planes defined by a metal and two donor atoms of a chelated ligand. c) The interligand *ortho*-hydrogen distance. d) This work.

been reported: $[Pd_2(dppp)_2](PF_6)_2$ (dppp=1,3-bis(diphenylphosphino)propane) by Budzelaar et al.[36] and $[Pd_2(CNR)_2(diphos)_2](PF_6)_2$ (R=aryl; diphos=bis(diphenylphosphino)ethane, -propane, -butane, or -ethene) by Tanase et al.[37] In these complexes the didentate phosphine ligand does not bridge two Pd(I) ions, but chelates to one Pd(I) ion. The Pd(I) ion in $[Pd_2(dppp)_2]^{2+}$ is coordinatively unsaturated, since it forms three bonds with two P and one Pd donor atoms. In $[Pd_2(CNR)_2(diphos)_2]^{2+}$ an additional isocyanide ligand coordinates at the cis position to the Pd–Pd bond, and the Pd(I) ion has a square-planar geometry. The structure of **3** is similar to those of the isocyanide complexes, having a chloride ion instead of an isocyanide at the cis position to the Pd–Pd bond. All of the dinuclear halogeno Pd(I) complexes so far known[23—28,34,35] have the halide ligand at the trans position to the Pd–Pd bond. Complex **3** is the first example in which the chloride ion coordinates at the cis position to the Pd–Pd bond.

Two coordination planes in **3** are nearly perpendicular to each other, the dihedral angle between them being 82.13(6)°. The perpendicular structure is in common for the unbridged dinuclear complexes.[33—35,37] However, a twisting structure with a dihedral angle of 45° is suggested to be the most favorable based on a con-

sideration of overlapping between the d orbitals of two Pd(I) ions, if there is no steric factors to prevent free rotation around the Pd–Pd bond.[27,37] Further studies will be needed to elucidate the structures of dinuclear Pd(I)–Pd(I) complexes.

The Pd–Pd bond length (2.542(1) Å) in **3** is rather shorter than those in the analogous unbridged diphosphine complexes, such as $[Pd_2(CNMes)_2(dppp)_2](PF_6)_2$ (2.617(2) Å; Mes=2,4,6-$Me_3C_6H_2$–)[37] and $[Pd_2(CNXyl)_2(Ph_2PCH{=}CHPPh_2)_2](PF_6)_2$ (2.602(1) Å; Xyl=2,6-$Me_2C_6H_3$–),[37] while being similar or slightly longer than those in $[Pd_2Cl_2(CNBu^t)_4]$ (2.532(2) Å)[34] and $[Pd_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}2\text{-}C_5H_4N\}_2](BF_4)_2$ (2.500(1) Å).[30] The Pd–Pd bond length seems to vary with the kind of ligand trans to the Pd(I) ion. It is interesting to compare the Pd–N and Pd–Cl bond lengths in **3** with those in *HT*-$[Pd_2Cl_2(\mu\text{-}Me_2Ppy)_2]$,[3] in which the arrangement of N and Cl donor atoms with respect to the Pd–Pd bond are different from those in **3** (Fig. 4). The Pd–N bond length (av 2.175(7) Å; *trans* to the Pd–Pd bond) in **3** is longer than that (av 2.158(6) Å; *trans* to the $-PMe_2$ donor) in the Me_2Ppy complex, while the Pd–Cl bond length (av 2.387(2) Å; *trans* to the $-PMe_2$ donor) in **3** is shorter than that (av 2.432(3) Å; *trans* to the Pd–Pd bond) in the Me_2Ppy complex. Thus, the trans influence of the Pd(I)–Pd(I) group seems to be stronger than that of the $-PMe_2$ group, which is known to give a strong trans influence.[1,3,38] The other structural parameters in **3** are normal. For the chelated Me_2Pqn moiety, the bite angle and the bond lengths and angles are very similar to those found in **2b**.

For the present non-bridging Me_2Pqn dinuclear complex, a geometrical isomer where the $-PMe_2$ donor group coordinates at the position trans to the Pd(I)–Pd(I) bond is possible. However, the ^{31}P NMR spectrum of the reaction product showed no signal indicative of other isomers than **3**. As stated above, both the $-PMe_2$ and Pd(I)–Pd(I) groups have a strong trans influence, and the isomer involving the mutually trans configuration for these ligands might be less stable than **3** where the nitrogen donor atom occupies the position trans to the Pd(I)–Pd(I) group. Complex **3** in solution decomposed slowly (Experimental), while *HT*-$[Pd_2Cl_2(\mu\text{-}Me_2Ppy)_2]$ was stable under similar conditions.[3] The bridging coordination of Me_2Ppy to two Pd(I) ions seems to stabilize the Pd(I)–Pd(I) bond to give a stable dinuclear complex. The Me_2Pqn ligand can form a stable five-membered chelate ring with a Pd(II) ion, as revealed by an X-ray analysis of *cis*-$[Pd(Me_2Pqn)_2]^{2+}$ (**2b**), but would be large to form a stable bridging structure with two Pd(I) ions. The $Ph_2P(CH_2)_nPPh_2$ ($n\geq2$) and $Ph_2PCH{=}CHPPh_2$ ligands also act as a chelate ligand to form non-bridging dinuclear Pd(I) complexes.[37]

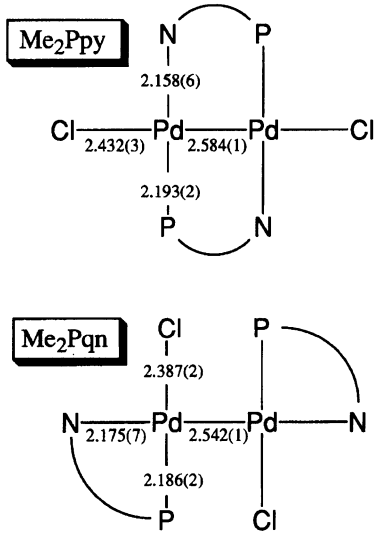


Fig. 4. Comparison of the bond lengths between in $[Pd_2Cl_2(Me_2Pqn)_2]$ (**3**) and in *HT*-$[Pd_2Cl_2(\mu\text{-}Me_2Ppy)_2]$ (all averaged values).

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