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Synthesis and crystal structure of dinuclear and tetranuclear palladium dppm complexes. $[Pd_2(\mu\text{-dppm})_2(vpy)Cl]$ and $[Pd_4(\mu\text{-dppm})_4(\mu\text{-}X)_2](ClO_4)_2$ (X = Cl, Br and I)

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Abstract—Reaction of the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ which was prepared from $[Pd_2(\mu\text{-dppm})_2X_2]$ (X = Cl, Br and I) and $AgClO_4$ in ethanol with 2-vinylpyridine (vpy) afforded dinuclear Pd(I) dppm complex $[Pd_2(\mu\text{-dppm})_2(vpy)Cl]$ (**1**). When the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ was allowed to stand for a few days, tetranuclear Pd dppm complex $[Pd_4(\mu\text{-dppm})_4(\mu\text{-}X)_2](ClO_4)_2$ (X = Cl (**2**), Br (**3**) and I (**4**)) was systematically formed. The structure for **1** and **2** were crystallographically determined. On complex **1** two Pd atoms are doubly bridged by two dppm ligands to form an eight-membered $Pd_2P_4C_2$ framework in a twist-chair conformation. Each Pd atoms is also coordinated by the Cl atom and the N atom of vpy in unsymmetrical side-by-side mode. The Pd–Pd distance is 2.597(2) Å and the torsion angle between two Pd_2P_2 plane is 43.2°. On the other hand four Pd atoms on **2** are bridged by four dppm ligands to form a rectangular Pd_4 core, which is composed of the shorter Pd–Pd separations (2.590(1) Å) and the close Pd···Pd separations (3.818(2) Å). The later Pd···Pd separation is also bridged by the Cl atom. The Pd–P distance (2.351(1) Å) bridging the close Pd···Pd separation is rather longer than that (2.238(2) Å) bridging the shorter Pd–Pd separation. © 1998 Elsevier Science Ltd. All rights reserved. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: palladium complexes; dinuclear complexes; tetranuclear complexes; crystal structures; bidentate phosphine ligands; nitrogen donor ligands.

Bidentate phosphine ligands such as bis(diphenylphosphino)methane (dppm) and 2-(diphenylphosphino)pyridine (Ph_2Ppy) are useful bridging ligands to form homo- and heteronuclear Pd(I) complexes with a close metal-metal distance. There has been considerable interests in synthesis, structure and reaction of dinuclear Pt(I) and Pd(I) complexes [1–3], since these dinuclear complexes can provide unique properties for an unusual coordination mode of small molecules, their activation and catalytic transformation. Three typical coordination modes of (a) $[Pd_2(\mu\text{-dppm})_2L_2]$ (side-by-side) [4–9], (b) $[Pd_2(\mu\text{-}X)(\mu\text{-dppm})_2L_2]$ (A-frame) [10–18] and (c) $[Pd_2(\mu\text{-dppm})_2L_4]$ (face-to-face) [19, 20] have been known in dinuclear Pd(I) complexes. It has been reported that dinuclear Pd(I) dppm complexes in a side-by-side mode react with small molecules such as CO, SO_2, RCN, $CR{=}CR_2$ to afford those in A-frame mode via a insertion reaction into a Pd–Pd bond [14, 17, 21, 22]. Although crystal structures of several trinuclear [23–26] and tetranuclear Pd complexes [27–30] bridged by dppm ligands has been investigated, investigations to polynuclear Pd dppm complexes are relatively few and their structure, property and reactivity are not fully researched [2].

We have so far interested in the reactivity of the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ which was prepared from $[Pd_2(\mu\text{-dppm})_2X_2]$ and $AgClO_4$ in alcohol (Scheme) [31, 32]. It has been reported that reaction of

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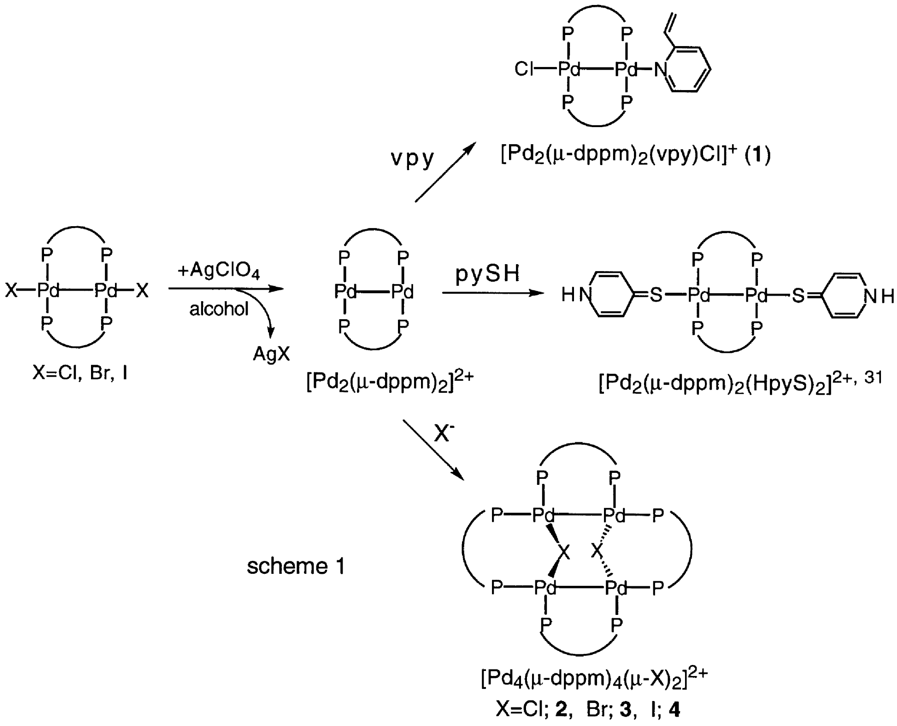

Scheme 1.

the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ with 4-mercaptopyridine (pySH) as a S-donor ligand afforded the dinuclear Pd(I) complex $[Pd_2(\mu\text{-dppm})_2(HpyS)_2](ClO_4)_2$ [31]. In this study, the reaction of the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ with 2-vinylpyridine (vpy) as a N donor ligand was furthermore attempted and dinuclear Pd(I) complex $[Pd_2(\mu\text{-dppm})_2(vpy)Cl]$ (1) was obtained. It was found that tetranuclear Pd complex $[Pd_4(\mu\text{-dppm})_4(\mu\text{-X})_2](ClO_4)_2$ (X = Cl(**2**), Br(**3**) and I(**4**)) were systematically constructed by the standing of the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ in ethanol. The structure for **1** and **2** were determined by a single crystal X-ray structure analysis.

EXPERIMENTAL

General

Dinuclear Pd(I) dppm complex $[Pd_2(\mu\text{-dppm})_2X_2]$ (X = Cl, Br and I) were prepared according to the literature [22]. Bis(diphenylphosphino)methane (dppm), 2-vinyl-pyridine (vpy) and $AgClO_4$ were purchased from Aldrich and used without further purification. All organic solvents were dried by general procedures and distilled before use. All operations were carried out using standard Schlenk techniques under Ar. IR spectra were measured with a JASCO 8000 FT IR spectrometer, using a CsI pellet. ^1H NMR and ^{31}P NMR spectra were obtained with a JEOL GSX 270 FT NMR spectrometer at 23°C. Deuterium solvents were available from Merck and were dried by molecular sieves before use. Tetramethylsilane and 85% H_3PO_4 in D_2O were used as a reference, respectively.

Synthesis of $[Pd_2(\mu\text{-dppm})_2(vpy)Cl]ClO_4$ (**1**)

$[Pd_2(\mu\text{-dppm})_2Cl_2]$ (21.0 mg, 0.02 mmol) and $AgClO_4$ (9.0 mg, 0.04 mmol) were mixed in ethanol (10 ml) for 3 hours. The reddish brown suspension was filtered. The vpy ligand (1.0 ml) was then added to the filtrate. After stirring for 2 hours, the orange suspension was filtered and the filtrate was sealed in a 5 mm diameter glass tube. The orange solution was allowed to stand for 1 week at an ambient temperature and the yellow crystals were collected. Yield. 17 mg (32%). Found: C, 55.83; H, 3.99; N, 1.09. Calc. for $Pd_2P_4C_{57}NCl_2O_4H_{51}$: C, 56.04H, 4.21; N, 1.15. IR (CsI, cm^{-1}): 1435($\nu_{P\text{–}C}$). ^1H NMR ($CDCl_3$): δ {7.92 and 7.40} (40 H, *br m*, Ph) and 4.39 (4 H, *br s*, CH_2) for dppm, 8.69 (1 H, *br s*, 2-H), 7.71 (1 H, *br s*, 4-H), 7.10 (1 H, *br s*, 5-H), 6.87 (1 H, *br s*, 3-H), 6.73 (1 H, *br s*, CH=), 6.40 (1 H, *br d*, $=CH_2$) and 5.80 (1 H, *br d*, $\text{–}CH_2$) for vpy. ^{31}P NMR (ethanol): −1.28. UV-VIS (nm ($\epsilon(M^{-1}cm^{-1})$), ethanol): 332 (1.7×10^4), 395 (7×10^3).

Synthesis of $[Pd_4(\mu\text{-dppm})_4(\mu\text{-Cl})_2](ClO_4)_2$ (**2**)

$[Pd_2(\mu-\text{dppm})_2Cl_2]$ (21.0 mg, 0.02 mmol) and $AgClO_4$ (9.0 mg, 0.04 mmol) were mixed in ethanol

(10 ml) for 3 hours. The reddish brown suspension was filtered and the filtrate was sealed in a 5 mm diameter glass tube. The reddish brown solution was allowed to stand at an ambient temperature for 3 days and the red prism crystals were collected. Yields. 15 mg (69%). Found: C, 53.21; H, 3.65. Calc. for $Pd_4Cl_4P_8O_8C_{100}H_{88}$: C, 53.79; H, 3.97. IR (CsI, cm^{-1}): 1437 ($\nu_{P\text{–}C}$), 1098 (ν_{ClO4}). ^1H NMR ($CDCl_3$): δ {7.98, 7.51 and 7.45} (80 H, m, Ph), 4.41 (8 H, tt, CH_2). ^{31}P NMR (ethanol): −4.91. UV-VIS (nm ($\epsilon(M^{-1}cm^{-1})$), THF): 358 (1.0×10^4), 431 (8.7×10^3), 512 (8.7×10^3). XPS (eV): 342.9 ($3d_{3/2}$), 337.5 ($3d_{5/2}$).

Synthesis of $[Pd_4(\mu\text{-dppm})_4(\mu\text{-X})_2](ClO_4)_2$ (X = Br(**3**) *and* I(**4**))

In a similar manner as **2**, red brick crystals of **3** or red needle crystals of **4** were obtained using $[Pd_2(\mu\text{-dppm})_2Br_2]$ (45.6 mg, 4.0×10^{-5} mol) or $[Pd_2(\mu\text{-dppm})_2I_2]$ (49.5 mg, 0.04 mmol) and $AgClO_4$ (18.0 mg, 0.08 mmol) in ethanol (10 ml). **3**: Yields. 17 mg (40%). Found: C, 51.25; H, 3.58. Calc. for $Pd_4Br_2P_8C_{100}H_{88}Cl_2O_8$: C, 51.73; H, 3.82. IR (CsI, cm^{-1}): 1437 ($\nu_{P\text{–}C}$), 1096 (ν_{ClO4}). ^1H NMR ($CDCl_3$): δ {7.97, 7.52 and 7.46} (80 H, *m*, Ph), 4.28 (8 H, *t*, CH_2). ^{31}P NMR (ethanol): −4.96. UV-VIS (nm ($\epsilon(M^{-1}cm^{-1})$), THF): 356 (8.3×10^3), 435 (7.8×10^3), 515(7.5×10^3). **4**: Yields. 11 mg (37%). Found: C, 49.37; H, 3.49. Calc. for $Pd_4I_2P_8C_{100}H_{88}Cl_2O_8$: C, 49.71; H, 3.67. IR (CsI, cm^{-1}): 1435 ($\nu_{P\text{–}C}$), 1096 (ν_{ClO4}). ^1H NMR ($CDCl_3$): δ {7.97, 7.48 and 7.46} (80 H, *m*, Ph), 4.39 (8 H, *br s*, CH_2). ^{31}P NMR (ethanol, 23°C): −4.91. UV-VIS (nm ($\epsilon(M^{-1}cm^{-1})$), THF): 342 (1.3×10^4), 444 (9.9×10^3), 512 (7.6×10^3).

Data collection, structure solution and refinements for **1** and **2**

A suitable crystal for **1** or **2** was attached to the end of a glass fiber and were mounted on a Rigaku AFC-5R diffractometer with a graphite mono-chromated Mo Kα radiation ($\lambda = 0.71069$ Å). The detailed measurement conditions and crystal data are summarized in Table 1. The intensity data were collected at 23°C using the ω scan technique for **1** and ω-2θ scan technique for **2**. The reflection data of 5721 and 11222 reflections were collected. On **1** the intensities of three representative reflections which were measured after every 150 reflections remained constant through data collection, indicative of crystal and electronic stability. No decay correction was applied. On the other hand the intensities of three representative reflections on **2** which were measured after every 150 reflections declined by 8.1%. A linear correction factor was applied to the data to account for this phenomena. The linear absorption coefficient for Mo

Table 1. Crystal data and measurement conditions for **1** and **2**

Complex	**1**	**2**
Formula	$Pd_2P_4C_{57}NCl_2O_4H_{51}$	$Pd_4Cl_4P_8O_8C_{100}H_{88}$
M	1221.64	2233.0
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a (Å)	11.882(5)	14.256(6)
b (Å)	11.909(7)	15.348(9)
c (Å)	38.676(5)	13.366(5)
α (°)	90.0	114.65(3)
β (°)	90.0	105.90(3)
γ (°)	90.0	62.74(3)
U (Å^3)	5473(3)	2350(4)
Z	4	1
D_{calc} (gcm^{-3})	1.482	1.577
λ(Mo Kα) (Å)	0.71069	0.71069
μ(Mo Kα) (cm^{-1})	9.06	10.47
Scan type	ω	ω-2θ
Scan rate (°/min)	2.0	8.0
Scan width (°)	$0.76+0.30\tan\theta$	$1.30+0.30\tan\theta$
$2\theta_{max}$ (°)	55.0	55.0
No. of reflections measured	5721	11222
No. of observations	2579 ($I > 2\sigma(I_0)$)	7704 ($I > 3\sigma(I_0)$)
F(000)	2472	1124
R^a	0.048	0.035
$R_w{}^b$	0.046	0.041

$^aR = \|F_0| - F_c\|/|F_0|$.

$^bR_w = [(w(|F_0| - |F_c|)^2/w|F_0|^2)]^{1/2}$, $w = 4F_0^2/\sigma^2(F_0)^2$.

Kα is 9.1 and 10.5 cm^{-1} for **1** and **2**, respectively. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structures were solved by a direct method (MITHRIL) [33]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of the full-matrix least squares refinement was based on 2579 and 7704 observed reflections ($I > 3\sigma(I)$), and 618 and 559 variable parameters for **1** and **2**, respectively. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w\ (|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)$. The final R and R_w values were 0.048 and 0.046 for **1**, and 0.035 and 0.041 for **2**, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and -0.50 eÅ^{-3} for **1**, and 1.01 and -0.45 eÅ^{-3} for **2**, respectively. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV [34]. All calculations were performed using the program TEXSAN crystallographic software package [35].

RESULTS AND DISCUSSION

Crystal structure of $[Pd_2(\mu\text{-dppm})_2(vpy)Cl]ClO_4$ (1)

According to the Scheme, reaction of the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ with 2-vinylpyridine (vpy) gave the dinuclear Pd(I) complex $[Pd_2(\mu\text{-dppm})_2(vpy)Cl](ClO_4)$ (**1**). Crystal structure of **1** is shown in Fig. 1, together with the atomic labeling scheme. Selected bond distances and bond angles are listed in Table 2. The two Pd atoms are doubly bridged by two dppm ligands to form an eight-membered $Pd_2P_4C_2$ ring framework in a twist-chair conformation: The P(1)–Pd(1)–P(4) and P(2)–Pd(2)–P(3) angles are 176.2(2) and 171.6(2)°, respectively. Each Pd atoms is furthermore coordinated by the Cl atom and the N atom of the vpy ligand, providing an unsymmetrical side-by-side mode. The Cl(1)–Pd(1)–Pd(2)–N(1) axis is almost linear. The Pd(2)–Pd(1)–Cl(1) and Pd(1)–Pd(2)–N(1) angle are 176.9(1) and 179.4(4)°, respectively, which are slightly larger than those (169.1(3), 173(1)°) of other dinuclear Pd(I) dppm complexes [4, 8].

The average Pd–P distance of 2.291(3) Å is within those (2.274(2)–2.302(2) Å) of other dinuclear Pd(I) dppm complexes in a side-by-side mode [4–9, 36], whereas the distance is rather shorter than those (2.307(2)–2.358(4) Å) in a A-frame mode [10–18]. The Pd(1)–Cl(1) distance of 2.381(5) Å is similar to those in other dinuclear Pd(I) dppm complexes [7, 8].

The Pd(1)–Pd(2) distance of 2.597(2) Å is rather shorter than that (2.75Å) in Pd metal and those (2.594(2)–2.699(5) Å) of other dinuclear Pd(I) dppm complexes with Pd–Pd bond [4–9], indicative of a direct Pd–Pd bond. It has been theoretically reported on dinuclear Pd(I) dppm complexes that the twist

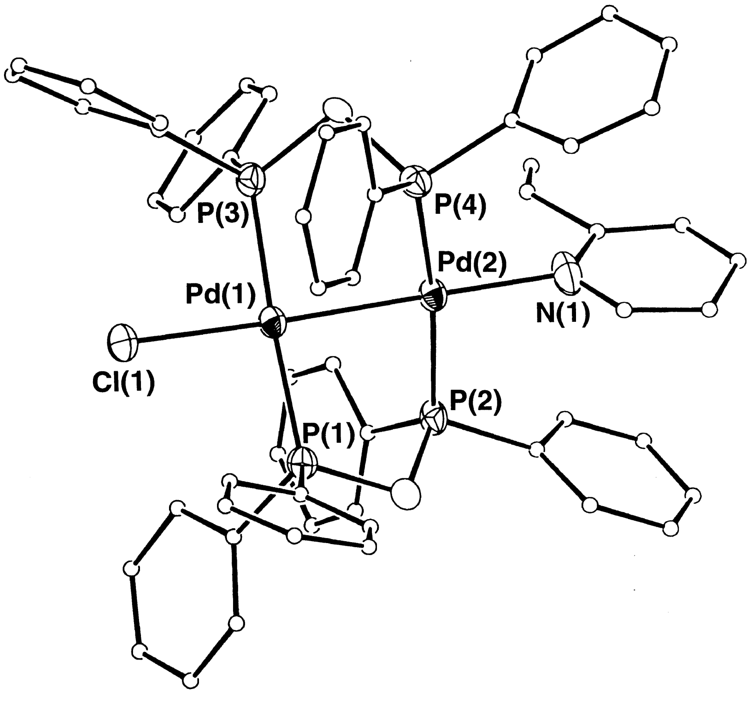

Fig. 1. Molecular structure of $[Pd(\mu\text{-dppm})_2(vpy)Cl]^+$ (**1**) and the atomic labeling scheme. Only Pd(1), Pd(2), P(1), P(2), P(3), Pd(4), Cl(1) and N(1) in the coordination sphere are labeled.

Table 2. Selected bond distance (Å) and bond angles (°) of **1**

Pd(1)–Pd(2)	2.597(2)	Pd(1)–Cl(1)	2.381(5)
Pd(1)–P(1)	2.309(5)	Pd(1)–P(3)	2.308(5)
Pd(2)–P(2)	2.312(5)	Pd(2)–P(4)	2.285(5)
Pd(2)–N(1)	2.16(1)		
Pd(2)–Pd(1)–Cl(1)	176.9(1)	Pd(2)–Pd(1)–P(1)	88.8(1)
Pd(2)–Pd(1)–P(3)	87.7(1)	P(1)–Pd(1)–Cl(1)	93.2(2)
P(3)–Pd(1)–Cl(1)	90.2(2)	P(1)–Pd(1)–P(3)	176.2(2)
Pd(1)–Pd(2)–P(2)	87.5(1)	Pd(1)–Pd(2)–P(4)	85.1(1)
Pd(1)–Pd(2)–N(1)	179.4(4)	P(2)–Pd(2)–P(4)	171.6(2)
P(2)–Pd(2)–N(1)	91.9(4)	P(4)–Pd(2)–N(1)	95.5(4)
P(1)–C(1)–P(2)	107(1)	P(3)–C(2)–P(4)	104.8(8)

along the Pd–Pd axis is due to anti-bonding interactions of filled metal *d* orbitals which are minimized when the torsion angle equals 45° [4, 5]. The twisted conformation allows the ligands to span a shorter metal-metal bond. The crystallographic data for **1** reveal that the torsion angle between the plane defined by {P(1), Pd(1), P(3) and Pd(2)} and {P(2), Pd(2), P(4) and Pd(2)} is 43.2° and the Pd–Pd distance is 2.597(2) Å. The torsion angle is more close to 45° and the Pd–Pd distance is correspondingly more short, compared with other dinuclear Pd(I) dppm complexes {$[Pd_2(\mu\text{-dppm})_2Br_2]$ (39°, 2.699(5) Å) [9], $[Pd_2(\mu\text{-dppm})_2(SnCl_3)Cl]$ (41.3°, 2.644(2) Å) [6], $[Pd_2(\mu\text{-dppm})_2(OCOF_3)_2]$ (44.5°, 2.594(2) Å) [4], $[Pd_2(\mu\text{-dppm})_2(C_6Cl_5)_2]$ (44.98°, 2.6704(21) Å) [8], $[Pd_2(\mu\text{-dmpm})_2Br_2]$ (50.5°, 2.603(1) Å)[5]}. This facts illustrate that the smaller deviation from 45° leads to the shortening of Pd–Pd distance.

Crystal structure of $[Pd_4(\mu\text{-dppm})_4(\mu\text{-Cl})_2](ClO_4)_2$

When the intermediate $[Pd_2(\mu\text{-dppm})_2]^{2+}$ was allowed to stand in ethanol according to the Scheme, tetranuclear Pd complex $[Pd_4(\mu\text{-dppm})_4(\mu\text{-X})_2](ClO_4)_2$ (X = Cl(**2**), Br(**3**) and I(**4**)) was systematically formed. This facts indicate that if no other suitable ligands (or higher affinity solvents and counter anion) were present in solution, tetranuclear Pd complex $[Pd_4(\mu\text{-dppm})_4(\mu\text{-X})_2](ClO_4)_2$ was constructed from $[Pd_2(\mu\text{-dppm})_2]^{2+}$ and dissolving halogen anions. It has been reported that the similar complex $[Pd_4(\mu\text{-dppm})_4(\mu\text{-Cl})_2]Y_2$ (Y = BF_4 and PF_6) was obtained from reaction of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ with copper or gold complexes [27]. Crystal structure of **2** was shown in Fig. 2, together with the atomic labeling scheme. Selected bond distances and bond angles are listed in Table 3. Complex **2** has the center of inversion at the midpoint of Pd(1)···P(1′). Four Pd atoms are bridged by four dppm ligands to form the rectangular Pd_4 core, which consists of the shorter Pd–Pd separations and the close Pd···Pd separations. The close Pd···Pd separations are moreover bridged by the Cl atom, which is situated 1.45 Å from the mean Pd_4 plane. All the Pd atoms are coplanar. The similar Pd_4 core has been known in $[Pd_4(\mu\text{-dppm})_4(\mu\text{-Cl})_2](BF_4)_2\bullet (CH_3)_2CO$ [27, 28] and $[Pd_4(\mu\text{-dppm})_4(\mu\text{-Cl})_2](ClO_4)_2\bullet$bpe [29].

The shorter Pd(1)–Pd(2) distance of 2.590(1) Å is rather shorter than that (2.75 Å) in Pd metal and those (2.53–2.77 Å) of other dinuclear Pd(I) complexes [2,

Table 3. Selected bond distances and bond angles for **2**

Pd(1)–Pd(2)	2.590(1)	Pd(1)···Pd(2′)	3.818(2)
Pd(1)–Cl(1)	2.427(2)	Pd(2)–Cl(1)	2.414(2)
Pd(1)–P(1)	2.237(2)	Pd(1)–P(3)	2.331(1)
Pd(2)–P(2)	2.240(2)	Pd(2)–P(4)	2.372(2)
P(1)–C(49)	1.814(4)	P(2)–C(49)	1.848(4)
P(3)–C(50)	1.828(4)	P(4)–C(50)	1.833(4)
P(1)–Pd(1)–P(3)	100.14(6)	P(3)–Pd(1)–Cl(1)	91.33(5)
Pd(2)–Pd(1)–Cl(1)	88.70(5)	Pd(2)–Pd(1)–P(1)	82.23(5)
P(2)–Pd(2)–P(4)	110.64(6)	P(4)–Pd(2)–Cl(1′)	90.77(6)
Pd(1)–Pd(2)–Cl(1′)	76.16(5)	Pd(1)–Pd(2)–P(2)	82.44(5)
Pd(1)–Cl(1)–Pd(2′)	104.14(6)	P(1)–C(49)–P(2)	105.2(2)
P(3)–C(50)–P(4′)	121.6(2)		

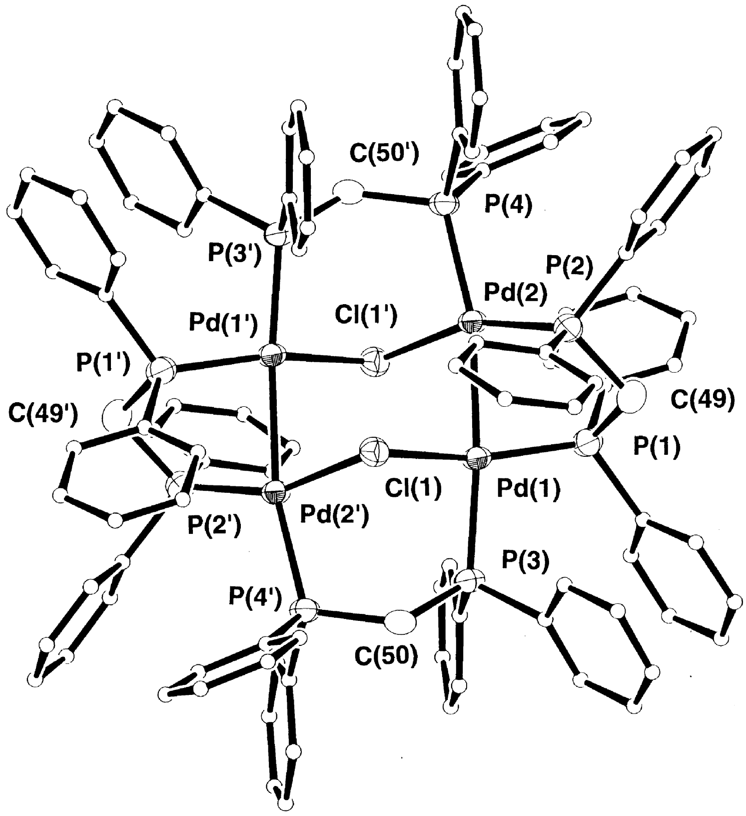

Fig. 2. Molecular structure of $[Pd_4(\mu\text{-dppm})_4(\mu\text{-Cl})_2]^{2+}$ (**2**) and the atomic labeling scheme. Only Pd(1), Pd(2), P(1), P(2), P(3), Pd(4), Cl(1), C(49), C(50), Pd(1′), Pd(2′), P(1′), P(2′), P(3′), P(4′), Cl(1′), C(49′) and C(50′) in the coordination sphere are labeled.

4, 5, 37], indicative of a direct Pd–Pd bond. On the other hand the close Pd(1)···Pd(2′) separation of 3.818(2) Å are longer than that in Pd metal, no indicative of a direct Pd–Pd bond. The shorter Pd–Pd distance is shorter than those (2.594(2)–3.332(1) Å) of other tetranuclear Pd complexes with the rectangular Pd_4 core [27–43]. The close Pd···Pd separation is longer than those (2.831(1)–3.742(2) Å) [27–43]. Consequently the Pd_4 core is rather rectangular.

The average Pd–P distance of 2.295(2) Å is within those (2.220(5)–2.353(7) Å) of dinuclear [4, 5, 37], trinuclear [24–26] and tetranuclear Pd complexes [27–30] bridged by dppm ligands. It is interesting that the Pd–P distance of 2.351(1) Å bridging the close Pd···Pd separation is very longer than that (2.238(2) Å) bridging the shorter Pd–Pd bond. The difference is considered due to both steric and electronic factors arising from the *trans* influence of the Pd–Pd bond and the bulk of the phenyl substituents. The average Pd–Cl of 2.420(2) Å is close to those (2.406(5)–2.430(1) Å) in other tetranuclear Pd complexes [27, 30, 39]. The Pd(1)–Cl(1)–Pd(2′) of 104.14(6)° is rather larger than those (78.1(1)° [30] and 93.15(3)° [39]) in other tetranuclear Pd complexes.

SUPPLEMENTARY MATERIALS

Complete listings of the atomic coordinates, bond distances, bond angles, hydrogen atomic coordinates, anisotropic thermal parameters, and a listing of observed and calculated structure factors for **1** and **2** are available from the Cambridge Crystallographic Data Centre and the author.

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