Synthesis and Crystal Structure of Bis(diphenylphosphino)methane Dipalladium(I) Complex with 2-Vinylpyridine (vpy). $[Pd_2(\mu-dppm)_2(vpy)Cl]ClO_4$

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Abstract

The bis(diphenylphosphino)methane dipalladium(I) complex with 2-vinylpyridine, $[Pd_2(\mu dppm)_2(vpy)Cl]ClO_4$ (1) has been prepared and characterized crystallographically. 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. Each Pd atoms are also coordinated by Cl^- ion and N atom of vpy ligand to provide a side-by-side conformation. The Pd-Pd distance of 2.597(2)Å is rather shorter than that (2.75Å) in the Pd metal, indicative of the existence of a direct Pd-Pd bond. On the eight-membered $Pd_2C_2P_4$ ring, the torsion angle of 43.2° is close to 45° and the Pd-Pd bond of 2.597(2)Å is also shorter than those in other dipalladium(I) dppm complexes. It has been experimentally found that the closer torsion angle is to 45°, the shorter Pd-Pd distance is. Complex 1 has the following crystal data: orthorhombic, $P2_12_12_1$, a=11.882(5), b=11.909(7), c=38.676(5)Å, V=5473(3)Å³, Z=4, R=0.048 and $R_w=0.046$.

Key words: palladium complexes, bis(diphenylphosphino)methane, 2-vinylpyridine, crystal structures, metal-metal bond

1 Introduction

Although until 1971 only two Palladium(I) complexes had been identified due to their unstabilities, there has been recently interests in the synthesis, structure and reactivity of dipalladium(I) complexes owing to the remarkable and unique properties for the unusual coordination of small molecules, their activation and catalytic transformations.¹⁻³ A variety of dipalladium(I) complexes have been now prepared and their structures and properties have been characterized. The bidentate phosphorous ligands such as bis(diphenylphosphino)methane (dppm) and 2(diphenylphosphino)pyridine (Ph₂Ppy) are quite useful bridging ligands to provide the homo- and hetero-dipalladium(I) complexes having a close metal-metal distance. As the coordination modes on the dipalladium(I) complexes with dppm, it has been known that there are three coordination modes of (i) [Pd₂(dppm)₂L₂] (side-by-side),⁴⁻⁹ (ii) [Pd₂(μ -dppm)₂L₂] (A-frame)¹⁰⁻¹⁹ and (iii) [Pd₂(dppm)₂L₄] (face-to-face).^{20,21} In particular, the dipalladium(I) complexes with a side-by-side mode are highly reactive with the small molecules such as CO, SO₂, RCN, CR₂CR₂ and can be generally produced the dipalladium(I) complexes having a A-frame mode by the insertion reaction into the Pd-Pd bonds.

In this study novel dipalladium(I) complex,

2 Experimental

2.1 Generals

The dppm and vpy ligand were commercially purchased from Aldrich and were used without further purification. The $[Pd_2(\mu-dppm)_2Cl_2]$ complex was prepared according to the literature.²² All organic solvents were dried by general method and were distilled before use. Deuterium solvents were available from Merck and were used without further purfication. All operation were performed using standard Schlenk techniques under an argon atomsphere. IR and UV-VIS spectra were merasured by a JASCO FT/IR-8000 and Hitachi 150-20 spectrometer, respectively. ¹H and ³¹P NMR were also measured by a JEOL GSX 270 FT spectrometer. TMS and 85% H₃PO₄ in D₂O solution were used as an internal reference against ¹H and ³¹P NMR, respectively.

2.2 Preparation of $[Pd_2(\mu-dppm)_2-(vpy)Cl]ClO_4$ (1)

[Pd₂(μ -dppm)₂Cl₂] (21.1 mg, 4.0×10⁻⁴ mol) was mixed with AgClO₄ (8.3 mg, 8×10⁻³ mol) in methanol (3 ml) for three hours and the resultant reddish brown suspension was filtered. The vpy ligand (1.0 ml) was added to the filtrate and the reaction solution was mixed for two hours. The resultant orange suspension was filtered and the filtrate was sealed in a 5 mm diameter glass tube. The glass tube was allowed to stand for one week at room temperature and the yellow crystals were collected. Yield (17.1mg, 31.7%). IR (CsI, cm⁻¹) 1435(ν_{P-C}). ³¹P NMR (ppm from 85% H₃PO₄, ethanol, 23°C) -1.28. UV-VIS (nm(ϵ (M⁻¹cm⁻¹)), ethanol, 23°C) 332(1.7×10⁴), 395(7.0×10³).

2.3 X-ray crystallography of $[Pd_2-(\mu-dppm)_2(vpy)Cl]ClO_4$ (1)

A yellow crystal of 1 $(0.3 \times 0.3 \times 0.2 \text{ mm})$ was attached to the end of a glass fiber and mounted on a Rigaku AFC-5R automated diffractometer with graphite mono-chromated Mo-K_{α} radiation $[Pd_2(\mu-dppm)_2(vpy)Cl]ClO_4(1)$ has been synthesized from the reaction of $[Pd_2(\mu-dppm)_2]Cl_2$ with 2-vinylpyridine (vpy) and the structure has been characterized by a single crystal X-ray analysis.

 $(\lambda=0.71069\text{\AA})$. The detailed measurement conditions and crystal data are listed in Table 1. Intensity data were collected at 23°C using the ω scan technique to a maximum 2θ value of 55.0°. A total of 5721 reflections were collected. The intensities of three representative reflections, which were measured after every 150 reflections declined. The linear absorption coefficient for Mo-K_{\alpha} is 9.1cm⁻¹.

Table 1. Crystal data and measurement conditions of

Formula	Pd2P4C57NCl2O4H51
Formula weight	1221.64
crystal dememsions (mm)	0.3 X 0.3 X 0.2
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a (Å)	11.882(5)
b (Å)	11.909(7)
c (Å)	38.676(5)
V (Å ³)	5473(3)
Z	4
$D_{\rm cal} ({\rm g/cm^{-3}})$	1.482
F(000)	2472
λ (Mo K _α) (Å)	0.71069
μ (Mo K _{α}) (cm ⁻¹)	9.06
Scan type	ω
Scan rate (°/min)	2.0
Scan width (°)	0.76+0.30tan0
No. of reflections measured	5721
Reflections used in refiment	2579 ($I > 3\sigma(I_0)$)
maximum, manimum $\Delta \rho$ (eÅ ⁻³)	0.50, -0.50
R	0.048
R _w	0.046

 $R = \sum (|F_o| - |F_c|) / \sum |F_o|.$

 $R_w = \{\sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2 \}^{1/2}, \text{ where } w = 4F_o^2 / \sigma(F_o^2).$

Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structure was solved by a direct method $(MITHRIL)^{23}$ and the non-hydrogen atoms were refined by full-matrix least squares. Isotropic hydrogen atoms were located by Fourier difference synthesis. The final cycle of the full-matrix



Figure 1: Molecular structure of $[Pd_2(\mu-dppm)_2(vpy)Cl]^+$ cation (1). Only Pd(1), Pd(2), P(1), P(2), P(3), P(4), N(1) and Cl(1) in the coordination sphere are labeled.

least squares refinement was based on 2579 observed reflections $(I > 3\sigma(I))$ and 618 variable parameters. Reliability factors are defined as $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 / w |F_o|^2\}^{1/2}$, where $w = 4F_o^2 / \sigma(F_o^2)$. The final R and R_w values were 0.048 and 0.046, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and $-0.50 \text{ e}\mathring{A}^{-3}$, respectively. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, vol. IV.²⁴ All calculations were performed using the TEXSAN²⁵ crystallographic software package. Positional and equivalent isotropic parameters for 1 are given in Table 2.

3 Results and Discussion

The molecular structure of 1 is shown in Figure 1, together with the atomic labeling scheme. Selected bond distances and bond angles are listed in Table 3. 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. I n the coordinating vpy ligand the pyridyl group is only coordinate to Pd atom. Each Pd(1) and Pd(2) atom therefore have a three-coordinate geometry by the coordination of Cl ion and N atom of vpy to provide a side-by-side conformation. The Pd(2)-Pd(1)-Cl(1) and Pd(1)-Pd(2)-N(1) angle are 176.9(1) and 179.4(4)°, which angles are larger than those (169.1(3), 173(1)°) of the similar dipalladium(I) dppm complexes.^{4,8} The Cl(1)-Pd(1)-Pd(2)-N(1) axis is almost linear. The bond distances, bond angles, torsion angles and coordination modes of some dipalladium(I) complexes bridged by dppm are summarized in Table 4.

The average Pd-P distance of $2.291(3)\mathring{A}$ is within those $(2.274(2)-2.302(2)\mathring{A})$ of other dipalladium(I) dppm complexes having a side-by-

atom	r	y	7	Bas(22)
	<u>x</u>	<u>y</u>	4	$\frac{D_{eq}(\mathbf{R})}{2.11(6)}$
Pd(1)	1.0057(1)	0.1231(1)	0.38/1/(3)	3.11(0)
Pa(2)	0.7965(1)	0.1120(1)	0.30802(3)	3.08(0)
CI(1)	1.1952(4)	0.1420(4)	0.4063(1)	4.9(3)
CI(2)	0.6633(6)	0.6514(6)	0.3365(2)	7.2(2)
P(1)	0.9932(4)	-0.0612(4)	0.4053(1)	3.5(2)
P(2)	0.7620(3)	0.0117(5)	0.4180(1)	3.3(2)
P(3)	1.0052(4)	0.3082(4)	0.3695(1)	3.5(2)
P(4)	0.8566(4)	0.2020(4)	0.3191(1)	3.4(2)
O(1)	0.684(3)	0.744(4)	0.317(1)	13(1)
O(2)	0.623(3)	0.608(4)	0.368(1)	13(1)
O(3)	0.759(2)	0.577(2)	0.3302(7)	19(1)
O(4)	0.610(3)	0.602(3)	0.3092(8)	10.8(9)
O(5)	0.547(3)	0.675(3)	0.336(1)	7(1)
O(6)	0.693(4)	0.659(4)	0.370(1)	10(1)
O(7)	0.719(3)	0.756(3)	0.339(1)	4.7(8)
N(1)	0.622(1)	0.103(2)	0.3526(4)	5(1)
C (1)	0.847(1)	-0.110(2)	0.4116(4)	3.2(8)
C(2)	0.914(1)	0.339(1)	0.3322(4)	2.8(8)
C (3)	1.060(1)	-0.155(1)	0.3762(4)	3.2(9)
C(4)	1.169(1)	-0.140(2)	0.3688(5)	5(1)
C(5)	1.227(2)	-0.213(2)	0.3455(6)	6(1)
C(6)	1.171(2)	-0.295(2)	0.3284(6)	7(2)
C (7)	1.055(2)	-0.307(2)	0.3362(6)	7(1)
C(8)	1.005(2)	-0.241(2)	0.3586(5)	5(1)
C(9)	1.053(1)	-0.095(2)	0.4466(5)	4(1)
C (10)	1.080(2)	-0.008(2)	0.4695(5)	5(1)
C (11)	1.114(2)	-0.036(2)	0.5032(7)	8(2)
C(12)	1.119(2)	-0.142(3)	0.5149(7)	9(2)
C (13)	1.101(2)	-0.230(3)	0.4914(7)	9(2)
C(14)	1.069(2)	-0.206(2)	0.4572(7)	6(1)
C(15)	0.789(2)	0.067(2)	0.4606(5)	4(1)
C (16)	0.801(2)	0.182(2)	0.4656(5)	5(1)
C(17)	0.811(2)	0.222(2)	0.4989(8)	8(2)
C(18)	0.814(2)	0.154(3)	0.5262(6)	7(2)
C(19)	0.804(2)	0.037(3)	0.5219(7)	8(2)
C(20)	0.795(2)	-0.003(2)	0.4878(6)	5(1)
C(21)	0.618(1)	-0.039(2)	0.4240(5)	4(1)
C(22)	0.586(2)	-0.145(2)	0.4134(6)	5(1)
C(23)	0.475(2)	-0.182(2)	0.4179(6)	7(1)
C(24)	0.401(2)	-0.109(3)	0.4342(7)	8(2)
C(25)	0.431(2)	-0.007(2)	0.4427(6)	6(1)
C(26)	0.539(1)	0.028(2)	0.4387(6)	5(1)
C(27)	0.963(1)	0.400(1)	0.4047(4)	3.1(8)
C(28)	1.008(2)	0.376(2)	0.4367(5)	5(1)
C(29)	0.984(2)	0.445(2)	0.4647(5)	6(1)
C (30)	0.908(2)	0.528(2)	0.4616(6)	6(1)
C (31)	0.863(2)	0.547(2)	0.4298(6)	6(1)
C(32)	0.885(2)	0.485(2)	0.4013(5)	5(1)
C(33)	1.140(1)	0.369(2)	0.3546(5)	4(1)

C(34)	1.187(2)	0.330(2)	0.3248(6)	6(1)
C(35)	1.291(2)	0.376(2)	0.3140(6)	7(9)
C(36)	1.347(2)	0.446(2)	0.3326(8)	8(2)
C(37)	1.306(2)	0.484(2)	0.3639(7)	7(1)
C(38)	1.201(2)	0.447(2)	0.3754(5)	5(1)
C(39)	0.968(1)	0.144(2)	0.2920(4)	3.2(9)
C(40)	1.004(2)	0.202(2)	0.2631(5)	5(1)
C(41)	1.094(2)	0.161(2)	0.2437(5)	6(1)
C(42)	1.144(2)	0.059(3)	0.2555(7)	8(2)
C(43)	1.107(2)	-0.003(2)	0.2826(6)	8(2)
C(44)	1.020(2)	0.039(2)	0.3016(5)	5(1)
C(45)	0.744(1)	0.231(2)	0.2884(5)	4(1)
C(46)	0.711(2)	0.149(2)	0.2660(5)	6(1)
C(47)	0.616(2)	0.161(2)	0.2449(6)	6(1)
C(48)	0.561(2)	0.256(3)	0.2461(5)	6(1)
C(49)	0.593(2)	0.345(2)	0.2678(6)	6(1)
C(50)	0.681(2)	0.327(2)	0.2893(5)	4(1)
C(51)	0.587(2)	0.014(2)	0.3356(5)	4(1)
C(52)	0.483(2)	-0.010(2)	0.3266(7)	9(2)
C(53)	0.404(2)	0.075(3)	0.3368(8)	8(2)
C(54)	0.434(2)	0.165(3)	0.3552(7)	9(2)
C(55)	0.545(2)	0.177(2)	0.3623(6)	4(1)
C(56)	0.594(2)	0.275(2)	0.3809(8)	8(2)
C(57)	0.544(2)	0.343(2)	0.3994(8)	11(2)
		-		

 $B_{eq} = (4/3) \{ \Sigma_i \Sigma_{ij} B_{ij} \mathbf{a}_i \cdot \mathbf{a}_j \}.$

side mode,^{4-9,26} whereas the distance is shorter than those $(2.307(2)-2.358(4)\mathring{A})$ in a A-frame mode.¹⁰⁻¹⁹ The Pd(1)-Cl(1) distance of $2.381(5)\mathring{A}$ is also similar to those of other dipalladium(I) dppm complexes^{7,8} and is rather shorter than the Pd-Br distance in the [Pd₂L₂Br₂] complex (L=dppm; $2.535(6)\mathring{A}$, dmpm; $2.522(1)\mathring{A}$).^{5,9}

The Pd(1)-Pd(2) distance of 2.597(2)Å is rather shorter among those $(2.594(2)-2.699(5)\mathring{A})$ of the dipalladium(I) dppm complexes with a sideby-side mode⁴⁻⁹ and that $(2.75\mathring{A})$ in the Pd metal, indicative of the existence of a strong Pd-Pd bond. On the eight-membered $Pd_2C_2P_4$ ring, it has been theoretically reported that the twist along the Pd-Pd axis is due to anti-bonding interactions of filled metal d orbitals that are minimized when the torsion angle equals 45°.4,5 The twisted conformation also allows the ligands to span a shorter metalmetal bond. In the complex 1 the tortion angle (τ) which is between the mean plane P(1)-Pd(1)-P(3)-Pd(2) and P(2)-Pd(2)-P(4)-Pd(2) of 43.2° is close to 45° and the Pd-Pd bond of 2.597(2)Å is also shorter than those in other dipalladium(I) dppm

complexes {[Pd₂(dppm)₂ Br₂] (39°, 2.699(5)Å),⁹ [Pd₂(dppm)₂(SnCl₃)Cl] (41.3°, 2.644(2)Å),⁶ [Pd₂(dppm)₂(OCOF₃)₂] (44.5°, 2.594(2)Å),⁴ [Pd₂(dppm)₂(C₆Cl₅)₂] (44.98°, 2.6704(21)Å),⁸ [Pd₂(dmpm)₂Br₂] (50.5°, 2.603(1)Å)⁵}. In this study it has been experimentally demonstrated that the closer torsion angle is to 45°, the shorter Pd-Pd distance is.

Table 3. 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)		

Table 4. Summary of bond distances, bond angles and coordination mode of some dipalladium(I) complexes bridged by the dppm ligands

Compound	Pd-Pd (Å)	Pd-Pav. (Å)	Pd-Xav. (Å)	Pd-Pd-X (°)	torsion angle	coordination	refs.
						mode	
[Pd2(dppm)2Co2(CO)7]	2.586(1)	2.274(2)					26
[Pd2(dppm)2(OCOCF3)2]	2.594(2)	2.302(2)	2.191(4)	173(1)	44.5	side-by-side	4
[Pd2(dppm)2(vpy)Cl]	2.597(2)	2.291(3)	2.381(5)	176.9(1),	43.2	side-by-side	this work
				179.4(4)			
[Pd2(dmpm)2Br2]	2.603(1)	2.283(3)	2.522(1)		50.5	side-by-side	5
[Pd2(dppm)2(SnCl3)Cl]	2.644				41.3		6
[Pd2(dppm)2Cl2]	2.652(2)					side-by-side	7
[Pd2(dppm)2(C6Cl5)2]	2.6704(21)	2.292(6)	2.145(12)	169.1(3)	44.98(10)	side-by-side	8
[Pd2(dppm)2Br2]	2.699(5)	2.287	2.535(6)		39	side-by-side	9
Pd-Pd in Pd metal	2.751						
[Pd2(dppm)2(OCOCF3)(CO)]	2.896(2)						27
[Pd2(dppm)2(µ-I)(CH3)I]BF4	2.976(6),	2.33(2)	2.577(6)(I)			A-frame	10
	3.01(1)						
[Pd2(dppm)2(µ-Cl)(CH3)(H)]	3.031(1)	2.307(2)	2.050(11)			A-frame	11
[Pd2(dppm)2(µ-CO)Cl2]	3.169(1)					A-frame	12
[Pd2(dppm)2(µ-CNR)Cl2]	3.198(4)	2.341(9)	2.457(9)			A-frame	13
[Pd2(dppm)2(CNMe)3](PF6)2	3.215(2)					A-frame	14, 15
[Pd2(dppm)2(µ-C=CCl2)Cl2]	3.248(2)					A-frame	16
[Pd2(dppm)2(µ-S)Cl2]	3.258(2)	2.316(5)	2.371(5)			A-frame	17, 18
[Pd2(dppm)2(µ-SO2)Cl2]	3.383(4),	2.343(4),	2.381(4),			A-frame	17, 18
	3.220(4)	2.358(4)	2.381(4)				
[Pd2(dppm)2(µ-C4F6)Cl2]	3.492(1)					A-frame	19

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