# Synthesis and Crystal Structure of Bis(diphenylphosphino)methane Dipalladium(I) Complex with 2-Vinylpyridine (vpy). $\left[\mathrm{Pd}_{2}(\mu \text {-dppm })_{2}(\right.$ vpy $\left.) \mathrm{Cl}\right] \mathrm{ClO}_{4}$ 

Masahiko Maekawa,*,a Megumu Munakata, ${ }^{*, b}$ Takayoshi Kuroda-Sowa ${ }^{b}$ and Yusaku Suenaga ${ }^{b}$<br>${ }^{a}$ Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan<br>${ }^{b}$ Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Jopan

(Received, November 25, 1996)


#### Abstract

The bis(diphenylphosphino)methane dipalladium(I) complex with 2-vinylpyridine, $\left[\mathrm{Pd}_{2}(\mu\right.$ dppm $)_{2}(\mathrm{vpy}) \mathrm{Cl} \mathrm{ClO}_{4}(1)$ has been prepared and characterized crystallographically. Two Pd atoms are doubly bridged by two dppm ligands to form an eight-membered $\mathrm{Pd}_{2} \mathrm{P}_{4} \mathrm{C}_{2}$ ring framework in a twist-chair conformation. Each Pd atoms are also coordinated by $\mathrm{Cl}^{-}$ion and N atom of vpy ligand to provide a side-by-side conformation. The Pd-Pd distance of $2.597(2) \AA$ is rather shorter than that $(2.75 \AA)$ in the Pd metal, indicative of the existence of a direct $\mathrm{Pd}-\mathrm{Pd}$ bond. On the eight-membered $\mathrm{Pd}_{2} \mathrm{C}_{2} \mathrm{P}_{4}$ ring, the torsion angle of $43.2^{\circ}$ is close to $45^{\circ}$ and the $\mathrm{Pd}-\mathrm{Pd}$ bond of $2.597(2) \AA$ is also shorter than those in other dipalladium( I ) dppm complexes. It has been experimentally found that the closer torsion angle is to $45^{\circ}$, the shorter $\mathrm{Pd}-\mathrm{Pd}$ distance is. Complex 1 has the following crystal data: orthorhombic, $P 2_{1} 2_{1} 2_{1}, a=11.882(5), b=11.909(7)$, $c=38.676(5) \AA, V=5473(3) \AA^{3}, Z=4, R=0.048$ 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 $\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)$ 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) $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2} \mathrm{~L}_{2}\right]$ (side-by-side), ${ }^{4-9}$ (ii) $\left[\mathrm{Pd}_{2}(\mu \text {-dppm })_{2} \mathrm{~L}_{2}\right]$ (A-frame) $)^{10-19}$ and (iii) $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2} \mathrm{~L}_{4}\right]$ (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 $\mathrm{CO}, \mathrm{SO}_{2}, \mathrm{RCN}, \mathrm{CR}_{2} \mathrm{CR}_{2}$ and can be gen-
erally produced the dipalladium(I) complexes having a A-frame mode by the insertion reaction into the $\mathrm{Pd}-\mathrm{Pd}$ 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 $\left[\mathrm{Pd}_{2}(\mu \text {-dppm })_{2} \mathrm{Cl}_{2}\right]$ 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 15020 spectrometer, respectively. ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR were also measured by a JEOL GSX 270 FT spectrometer. TMS and $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ in $\mathrm{D}_{2} \mathrm{O}$ solution were used as an internal reference against ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR, respectively.

### 2.2 Preparation of $\left[\mathrm{Pd}_{2}(\mu \text {-dppm })_{2^{-}}\right.$ (vpy) Cl$] \mathrm{ClO}_{4}$ (1)

$\left[\mathrm{Pd}_{2}(\mu-\mathrm{dppm})_{2} \mathrm{Cl}_{2}\right]\left(21.1 \mathrm{mg}, 4.0 \times 10^{-4} \mathrm{~mol}\right)$ was mixed with $\mathrm{AgClO}_{4}\left(8.3 \mathrm{mg}, 8 \times 10^{-3} \mathrm{~mol}\right)$ 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 ( $17.1 \mathrm{mg}, 31.7 \%$ ). IR (CsI, $\mathrm{cm}^{-1}$ ) $1435\left(\nu_{P-C}\right) .{ }^{31} \mathrm{P}$ NMR ( ppm from $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$, ethanol, $23^{\circ} \mathrm{C}$ ) -1.28 . UV-VIS ( $\mathrm{nm}\left(\epsilon\left(\mathrm{M}^{-1} \mathrm{~cm}^{-1}\right)\right.$ ), ethanol, $\left.23^{\circ} \mathrm{C}\right) 332\left(1.7 \times 10^{4}\right), 395\left(7.0 \times 10^{3}\right)$.

### 2.3 X-ray crystallography of [ $\mathrm{Pd}_{2}-$ ( $\mu$-dppm $\left.)_{2}(\mathrm{vpy}) \mathrm{Cl}\right] \mathrm{ClO}_{4}(1)$

A yellow crystal of $1(0.3 \times 0.3 \times 0.2 \mathrm{~mm})$ was attached to the end of a glass fiber and mounted on a Rigaku AFC-5R automated diffractometer with graphite mono-chromated Mo- $\mathrm{K}_{\alpha}$ radiation
$\left[\mathrm{Pd}_{2}(\mu \text {-dppm })_{2}(\mathrm{vpy}) \mathrm{Cl}^{2}\right] \mathrm{ClO}_{4}(\mathbf{1})$ has been synthesized from the reaction of $\left[\mathrm{Pd}_{2}(\mu-\mathrm{dppm})_{2}\right] \mathrm{Cl}_{2}$ with 2 -vinylpyridine (vpy) and the structure has been characterized by a single crystal X-ray analysis.
$(\lambda=0.71069 \AA$ ). The detailed measurement conditions and crystal data are listed in Table 1. Intensity data were collected at $23^{\circ} \mathrm{C}$ using the $\omega$ scan technique to a maximum $2 \theta$ value of $55.0^{\circ}$. 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 $\mathrm{Mo}-\mathrm{K}_{\alpha}$ is $9.1 \mathrm{~cm}^{-1}$.

Table 1. Crystal data and measurement conditions of 1

| Formula | $\mathrm{Pd}_{2} \mathrm{P}_{4} \mathrm{C}_{57} \mathrm{NCl}_{2} \mathrm{O}_{4} \mathrm{H}_{51}$ |
| :---: | :---: |
| Formula weight | 1221.64 |
| crystal dememsions (mm) | $0.3 \times 0.3 \times 0.2$ |
| Crystal system | Orthorhombic |
| Space group | $P 21_{121}{ }^{1}$ |
| $a(\AA)$ | 11.882(5) |
| $b(\AA)$ | 11.909(7) |
| $c(\AA)$ | 38.676(5) |
| $V\left(\AA^{3}\right)$ | 5473(3) |
| $\boldsymbol{Z}$ | 4 |
| $D_{\text {cal }}\left(\mathrm{g} / \mathrm{cm}^{-3}\right)$ | 1.482 |
| $\mathrm{F}(000)$ | 2472 |
| $\lambda\left(\mathrm{Mo} \mathrm{K} \mathrm{K}_{\alpha}\right)(\AA)$ | 0.71069 |
| $\mu\left(\mathrm{Mo} \mathrm{K} \mathrm{K}_{\alpha}\left(\mathrm{cm}^{-1}\right)\right.$ | 9.06 |
| Scan type | $\omega$ |
| Scan rate ( $/$ / min) | 2.0 |
| Scan width ( ${ }^{\circ}$ ) | $0.76+0.30 \tan \theta$ |
| No. of reflections measured | 5721 |
| Reflections used in refiment | 2579 (I>3 ${ }^{\text {( }}$ IO $)$ ) |
| maximum, manimum $\Delta \rho\left(\mathrm{e} \AA^{-3}\right)$ | 0.50, -0.50 |
| $R$ | 0.048 |
| $\boldsymbol{R}_{W}$ | 0.046 |

$R=\Sigma\left(\left|F_{o}\right|-\left|F_{c}\right|\right) / \Sigma\left|F_{o}\right|$.
$R_{w}=\left\{\Sigma w\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2} / \Sigma w\left|F_{o}\right|^{2}\right\}^{1 / 2}$, where $w=4 F_{o}^{2} / \sigma\left(F_{o}^{2}\right)$.

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 $\left[\mathrm{Pd}_{2}(\mu-\mathrm{dppm})_{2}(\mathrm{vpy}) \mathrm{Cl}\right]+$ cation (1). Only $\mathrm{Pd}(1), \mathrm{Pd}(2), \mathrm{P}(1), \mathrm{P}(2)$, $\mathrm{P}(3), \mathrm{P}(4), \mathrm{N}(1)$ and $\mathrm{Cl}(1)$ 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 $R=\sum\left(\left|F_{o}\right|-\left|F_{c}\right|\right) / \sum\left|F_{o}\right|$ and $R_{w}=\left\{\sum w\left(\left|F_{o}\right|-\right.\right.$ $\left.\left.\left|F_{c}\right|\right)^{2} / w\left|F_{o}\right|^{2}\right\}^{1 / 2}$, where $w=4 F_{o}^{2} / \sigma\left(F_{o}^{2}\right)$. 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 $-0.50 \mathrm{e}^{\circ} A^{-3}$, 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 TEXSAN ${ }^{25}$ 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 $\mathrm{Pd}_{2} \mathrm{P}_{4} \mathrm{C}_{2}$ ring framework in a twist-chair conformation: The $P(1)-P d(1)-P(4)$ and $P(2)-P d(2)-$ $P(3)$ angles are $176.2(2)$ and $171.6(2)^{\circ}$, respectively. I $n$ the coordinating vpy ligand the pyridyl group is only coordinate to Pd atom. Each $\mathrm{Pd}(1)$ and $\operatorname{Pd}(2)$ atom therefore have a three-coordinate geometry by the coordination of Cl ion and N atom of vpy to provide a side-by-side conforma-
tion. The $\operatorname{Pd}(2)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ and $\mathrm{Pd}(1)-\mathrm{Pd}(2)-$ $\mathrm{N}(1)$ angle are $176.9(1)$ and $179.4(4)^{\circ}$, which angles are larger than those (169.1(3), 173(1) ${ }^{\circ}$ ) of the similar dipalladium(I) dppm complexes. ${ }^{4,8}$ The $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Pd}(2)-\mathrm{N}(1)$ 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 $2.291(3) \AA$ is within those (2.274(2)-2.302(2) $\AA$ ) of other dipalladium(I) dppm complexes having a side-by-

| atom | $x$ | $y$ | 2 | $B_{e q}\left(\AA^{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Pd}(1)$ | 1.0057(1) | 0.1231(1) | 0.38717(3) | 3.11(6) |
| Pd(2) | 0.7965(1) | 0.1126(1) | 0.36802(3) | 3.08(6) |
| $\mathrm{Cl}(1)$ | 1.1952(4) | 0.1420(4) | 0.4063(1) | 4.9(3) |
| $\mathrm{Cl}(2)$ | 0.6633(6) | 0.6514(6) | 0.3365(2) | 7.2(2) |
| $\mathrm{P}(1)$ | 0.9932(4) | -0.0612(4) | 0.4053(1) | 3.5(2) |
| $\mathrm{P}(2)$ | 0.7620(3) | 0.0117(5) | 0.4180(1) | 3.3(2) |
| $\mathrm{P}(3)$ | 1.0052(4) | 0.3082(4) | 0.3695(1) | 3.5(2) |
| $\mathrm{P}(4)$ | 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) |
| $\mathrm{O}(3)$ | 0.759(2) | 0.577(2) | 0.3302(7) | 19(1) |
| $\mathrm{O}(4)$ | 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) |
| $\mathrm{O}(7)$ | 0.719(3) | 0.756(3) | 0.339(1) | 4.7(8) |
| $\mathrm{N}(1)$ | 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) |
| $\mathrm{C}(2)$ | 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(1) | 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) |


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

$B_{e q}=(4 / 3)\left\{\Sigma_{i} \Sigma_{i j} B_{i j} \mathrm{a}_{j} a_{j}\right\}$.
side mode, ${ }^{4-9,26}$ whereas the distance is shorter than those (2.307(2)-2.358(4) $\AA$ ) in a A-frame mode. ${ }^{10-19}$ The $\mathrm{Pd}(1)-\mathrm{Cl}(1)$ distance of $2.381(5) \AA$ is also similar to those of other dipalladium(I) dppm complexes ${ }^{7,8}$ and is rather shorter than the $\mathrm{Pd}-\mathrm{Br}$ distance in the $\left[\mathrm{Pd}_{2} \mathrm{~L}_{2} \mathrm{Br}_{2}\right]$ complex ( $\mathrm{L}=\mathrm{dppm} ; 2.535(6) \AA$, dmpm; 2.522(1) $\AA$ ). ${ }^{5,9}$

The $\operatorname{Pd}(1)-\operatorname{Pd}(2)$ distance of $2.597(2) \AA$ is rather shorter among those (2.594(2)-2.699(5) $\AA$ A) of the dipalladium(I) dppm complexes with a side-by-side mode ${ }^{4-9}$ and that $(2.75 \AA)$ in the Pd metal, indicative of the existence of a strong $\mathrm{Pd}-\mathrm{Pd}$ bond. On the eight-membered $\mathrm{Pd}_{2} \mathrm{C}_{2} \mathrm{P}_{4}$ ring, it has been theoretically reported that the twist along the PdPd axis is due to anti-bonding interactions of filled metal $d$ orbitals that are minimized when the torsion angle equals $45^{\circ} .4,5$ The twisted conformation also allows the ligands to span a shorter metalmetal bond. In the complex 1 the tortion angle ( $\tau$ ) which is between the mean plane $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{P}(3)$ $\mathrm{Pd}(2)$ and $\mathrm{P}(2)-\mathrm{Pd}(2)-\mathrm{P}(4)-\mathrm{Pd}(2)$ of $43.2^{\circ}$ is close to $45^{\circ}$ and the $\mathrm{Pd}-\mathrm{Pd}$ bond of $2.597(2) \AA$ is also shorter than those in other dipalladium(I) dppm
complexes $\left\{\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2} \mathrm{Br}_{2}\right]\left(39^{\circ}, 2.699(5) \AA\right){ }^{\circ}{ }^{9}\right.$
$\left.\left[\mathrm{Pd}_{2}(\mathrm{dppm})\right)_{2}\left(\mathrm{SnCl}_{3}\right) \mathrm{Cl}\right] \quad\left(41.3^{\circ}, \quad 2.644(2) \AA{ }_{\circ}\right)^{6}{ }^{6}$ $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2}\left(\mathrm{OCOF}_{3}\right)_{2}\right] \quad\left(44.5^{\circ}, \quad 2.594(2) \stackrel{\circ}{A}\right),{ }^{4}$ $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2}\left(\mathrm{C}_{6} \mathrm{Cl}_{5}\right)_{2}\right] \quad\left(44.98^{\circ}, \quad 2.6704(21) \AA\right)^{\circ},^{8}$ $\left.\left[\mathrm{Pd}_{2}(\mathrm{dmpm}){ }_{2} \mathrm{Br}_{2}\right]\left(50.5^{\circ}, 2.603(1) \AA\right)^{5}\right\}$. In this study it has been experimentally demonstrated that the closer torsion angle is to $45^{\circ}$, the shorter $\mathrm{Pd}-\mathrm{Pd}$ distance is.

Table 3. Selected bond distance $(\AA)$ and bond angles $\left({ }^{\circ}\right)$ of 1

| $P d(1)-\mathrm{Pd}(2)$ | $2.597(2)$ | $\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $2.381(5)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pd}(1)-\mathrm{P}(1)$ | $2.309(5)$ | $\mathrm{Pd}(1)-\mathrm{P}(3)$ | $2.308(5)$ |
| $\mathrm{Pd}(2)-\mathrm{P}(2)$ | $2.312(5)$ | $\mathrm{Pd}(2)-\mathrm{P}(4)$ | $2.285(5)$ |
| $\mathrm{Pd}(2)-\mathrm{N}(1)$ | $2.16(1)$ |  |  |
|  |  |  |  |
| $\mathrm{Pd}(2)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $176.9(1)$ | $\mathrm{Pd}(2)-\mathrm{Pd}(1)-\mathrm{P}(1)$ | $88.8(1)$ |
| $\mathrm{Pd}(2)-\mathrm{Pd}(1)-\mathrm{P}(3)$ | $87.7(1)$ | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $93.2(2)$ |
| $\mathrm{P}(3)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $90.2(2)$ | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{P}(3)$ | $176.2(2)$ |
| $\mathrm{Pd}(1)-\mathrm{Pd}(2)-\mathrm{P}(2)$ | $87.5(1)$ | $\mathrm{Pd}(1)-\mathrm{Pd}(2)-\mathrm{P}(4)$ | $85.1(1)$ |
| $\mathrm{Pd}(1)-\mathrm{Pd}(2)-\mathrm{N}(1)$ | $179.4(4)$ | $\mathrm{P}(2)-\mathrm{Pd}(2)-\mathrm{P}(4)$ | $171.6(2)$ |
| $\mathrm{P}(2)-\mathrm{Pd}(2)-\mathrm{N}(1)$ | $91.9(4)$ | $\mathrm{P}(4)-\mathrm{Pd}(2)-\mathrm{N}(1)$ | $95.5(4)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)-\mathrm{P}(2)$ | $107(1)$ | $\mathrm{P}(3)-\mathrm{C}(2)-\mathrm{P}(4)$ | $104.8(8)$ |

Table 4. Summary of bond distances, bond angles and coordination mode of some dipalladium(1) complexes bridged by the dppmligands

| Compound | $\operatorname{Pd}-\mathrm{Pd}(\AA)$ | Pd-Pav. ( $\AA$ ) | Pd-Xav. ( $\AA$ ) | $\mathrm{Pd}-\mathrm{Pd}-\mathrm{X}\left({ }^{\circ}\right)$ | torsion angle | coordination mode | refs. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2} \mathrm{CO}_{2}(\mathrm{CO})_{7}\right]$ | 2.586(1) | 2.274(2) |  |  |  |  | 26 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2}\left(\mathrm{OCOCF}_{3}\right)_{2}\right]$ | 2.594(2) | 2.302(2) | 2.191(4) | 173(1) | 44.5 | side-by-side | 4 |
| [ $\left.\mathrm{Pd}_{2}(\mathrm{dppm})_{2}(\mathrm{vpy}) \mathrm{Cl}\right]$ | 2.597(2) | 2.291(3) | 2.381(5) | $\begin{aligned} & \text { 176.9(1), } \\ & \text { 179.4(4) } \end{aligned}$ | 43.2 | side-by-side | this work |
| $\left.{ }^{1} \mathrm{Pd}_{2}(\mathrm{dmpm})_{2} \mathrm{Br}_{2}\right]$ | 2.603(1) | 2.283(3) | 2.522(1) |  | 50.5 | side-by-side | 5 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm}) 2\left(\mathrm{SnCl}_{3}\right) \mathrm{Cl}\right]$ | 2.644 |  |  |  | 41.3 |  | 6 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2} \mathrm{Cl}_{2}\right]$ | 2.652(2) |  |  |  |  | side-by-side | 7 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2}\left(\mathrm{C}_{6} \mathrm{Cl}_{5}\right)_{2}\right]$ | 2.6704(21) | 2.292(6) | 2.145(12) | 169.1(3) | 44.98(10) | side-by-side | 8 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2} \mathrm{Br}_{2}\right]$ | 2.699(5) | 2.287 | 2.535(6) |  | 39 | side-by-side | 9 |
| $\mathrm{Pd}-\mathrm{Pd}$ in Pd metal | 2.751 |  |  |  |  |  |  |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2}\left(\mathrm{OCOCF}_{3}\right)(\mathrm{CO})\right]$ | 2.896(2) |  |  |  |  |  | 27 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm}) 2(\mu-\mathrm{I})\left(\mathrm{CH}_{3}\right)\right]_{\mathrm{BF}_{4}}$ | $\begin{aligned} & 2.976(6), \\ & 3.01(1) \end{aligned}$ | 2.33(2) | 2.577(6)(1) |  |  | A-frame | 10 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm}) 2(\mu-\mathrm{Cl})\left(\mathrm{CH}_{3}\right)(\mathrm{H})\right]$ | 3.031(1) | 2.307(2) | 2.050(11) |  |  | A-frame | 11 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2}(\mu-\mathrm{CO}) \mathrm{Cl}_{2}\right]$ | 3.169(1) |  |  |  |  | A-frame | 12 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm})_{2}(\mu-\mathrm{CNR}) \mathrm{Cl}_{2}\right]$ | 3.198(4) | 2.341(9) | 2.457(9) |  |  | A-frame | 13 |
| [ $\left.\mathrm{Pd}_{2}(\mathrm{dppm})_{2}\left(\mathrm{CNMM}_{3}\right]^{(1)} \mathrm{PF}_{6}\right)_{2}$ | 3.215(2) |  |  |  |  | A-frame | 14, 15 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm}) 2\left(\mu-\mathrm{C}=\mathrm{CCl}_{2}\right) \mathrm{Cl}_{2}\right]$ | 3.248(2) |  |  |  |  | A-frame | 16 |
| [ $\left.\mathrm{Pd}_{2}(\mathrm{dppm}) 2(\mu-\mathrm{S}) \mathrm{Cl}_{2}\right]$ | 3.258(2) | 2.316 (5) | 2.371(5) |  |  | A-frame | 17, 18 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm}) 2\left(\mu-\mathrm{SO}_{2}\right) \mathrm{Cl}_{2}\right]$ | $\begin{aligned} & 3.383(4), \\ & 3.220(4) \end{aligned}$ | $\begin{aligned} & 2.343(4), \\ & 2.358(4) \end{aligned}$ | $\begin{aligned} & 2.381(4), \\ & 2.381(4) \end{aligned}$ |  |  | A-frame | 17, 18 |
| $\left[\mathrm{Pd}_{2}(\mathrm{dppm}) 2\left(\mu-\mathrm{C}_{4} \mathrm{~F}_{6}\right)^{\text {c }} \mathrm{Cl}_{2}\right]$ | 3.492(1) |  |  |  |  | A-frame | 19 |

## Acknowledgment

We thank Mr. Akifumi Ohnishi and Mr. Youichi Nozaka for thier assistances with X-ray crystallography. This work was partially supported by a Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture in Japan.

## References

[1] R. J. Puddephatt, Chem. Soc. Rev., 12 (1983) 99.
[2] C. F. J. Barnard and M. J. H. Russell, "Comprehensive Coordination Chemistry", ed. by G. Wilkinson, Pergamon Press, Oxford, 1987, Vol. 5. Chap. 51, pp. 1099-1130.
[3] A. L. Balch, "Reactivity of Metal-Metal Bonds", ed. by M. H. Chisholm, ACS Symposium Series, 1981, Chap. 8, pp. 167-185.
[4] T. E. Krafft, C. I. Hejna and J. S. Smith, Inorg. Chem., 29 (1990) 2682.
[5] M. L. Kullberg, F. R. Lemke, D. R. Powell and C. P. Kubiak, Inorg. Chem., 24 (1985) 3589.
[6] M. M. Olmstead, L. S. Benner, H. Hope and A. L. Balch, Inorg. Chim. Acta, 32 (1979) 193.
[7] M. P. Brown, R. J. Puddephatt, M. Rashidi, L. Manojlovic-Muir, K. W. Muir, T. Solomuin and K. R. Seddon, Inorg. Chim. Acta, 23 (1977) L33.
[8] P. Espinet, J. Fornies, C. Fortuno, G. Hidalgo, F. Martinez, M. Tomas and A. T. Welch, J. Organomet. Chem., 317 (1986) 105.
[9] R. G. Holloway, B. R. Penfold, R. Colton and M. J. McCormick, J. Chem. Soc., Chem. Comm., (1976) 485.
[10] M. M. Olmstead, J. P. Farr and A. L. Balch, Inorg. Chim. Acta, 52 (1981) 47.
[11] S. J. Young, B. Kellenberger, J. H. Reibenspies, S. E. Himmel, M. Manning, O. P. Anderson and J. K. Stille, J. Am. Chem. Soc., 110 (1988) 5744.
[12] M. L. Kullberg and C. P. Kubiak, Organometallics, 3 (1984) 632.
[13] A. W. Hanson, A. J. McAlees and A. Taylor, J. Chem. Soc., Perkin Trans., Part I (1985) 441.
[14] M. M. Olmstead, H. Hope, L. S. Benner and A. L. Balch, J. Am. Chem. Soc., 99 (1977) 5502.
[15] M. M. Olmstead, L. S. Benner and A. L. Balch, J. Chem. Soc., Chem. Comm., (1977) 823.
[16] J. A. Davies, A. A. Pinkerton, R. Syed and M. Vilmer, J. Chem. Soc., Chem. Comm., (1988) 47.
[17] A. L. Balch, L. S. Benner and M. M. Olmstead, Inorg. Chem., 18 (1979) 2996.
[18] G. Besenyei, C. Lee, J. Gullga, Inorg. Chem., 26 (1987) 3622.
[19] A. L. Balch, C. L. Lee, C. H. Lindsay and M. M. Olmstead, J. Organomet. Chem., 177 (1979) C22.
[20] C. T. Hunt and A. L. Balch, Inorg. Chem., 20 (1981) 2267.
[21] ref. 5 and references therein.
[22] L. D. Benner and A. L. Balch, J. Am. Chem. Soc., 100 (1978) 6099.
[23] C. J. Gilmore, MITHRIL, an intergated direct methods computer program; J. Appl. Crystallogr., University of Glasgow, Scotland, UK., 17 (1984) 42.
[24] International Tables for X-ray Crystallography, Kynoch, Birmingham, UK., 1974, Vol. IV.
[25] TEXSAN-TEXARAY, Structure analysis package, Molecular Structure Corporation, The Woodlands, TX, USA, 1985.
[26] P. Braunstein, J. Jud, Y. Dusausoy and J. Fischer, Organometallics, 2 (1983) 180.
[27] D. J. Wink, B. T. Creagan and S. Lee, Inorg. Chim. Acta, 180 (1991) 183.

