Crystal Structure of Bis(diphenylphosphino)methane Dipalladium(I) Nitrate Complex, $[\text{Pd}_2(\mu\text{-dppm})_2(\text{NO}_3)_2]$

Masahiko MAEKAWA^{*†}, Megumu MUNAKATA^{**†}, Takayoshi KURODA-SOWA^{**}
and Yusaku SUENAGA^{**}

^{*}Research Institute for Science and Technology, Kinki University,
Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

^{**}Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

There has recently been considerable interest in the synthesis, structure and reactivity of dipalladium(I) complexes owing to their remarkable and unique properties for the unusual coordination of small molecules, their activation and catalytic transformations.¹⁻³ In particular, the dipalladium(I) complexes bridged by a dppm ligand (dppm=bis(diphenylphosphino)methane) react with small molecules such as CO, SO₂, RCN, and CR₂=CR₂ to give a dinuclear structure in an A-frame mode *via* an insertion reaction into a Pd-Pd bond. The structure determinations on the dipalladium(I) dppm complexes are essential to understand their reactivities and properties. In this study the dipalladium(I) dppm complex $[\text{Pd}_2(\mu\text{-dppm})_2(\text{NO}_3)_2]$ (**1**) was prepared and crystallographically characterized.

$[\text{Pd}_2(\mu\text{-dppm})_2\text{Cl}_2]$ (63.0 mg, 6.0×10^{-5} mol) and AgNO₃ (22.1 mg, 1.3×10^{-4} mol) were stirred in methanol/tetrahydrofuran (10 ml, $v/v=1/1$) for 3 h and filtered. Reddish-orange filtrates were sealed in a 5 mm glass tube together with diethyl ether and allowed to stand for 2 d at an ambient temperature. Red brick single crystals of $[\text{Pd}_2(\mu\text{-dppm})_2(\text{NO}_3)_2]$ (**1**) were obtained.

A red crystal of **1** was attached to the end of a glass fiber and were mounted on a Rigaku AFC-6S diffractometer with a graphite monochromated Mo K α radiation ($\lambda=0.71069$ Å). The detailed measurement conditions and crystal data are listed in Table 1. The intensity data were collected at 23°C using the ω -2 θ scan technique to a maximum 2 θ of value of 55.1°. Of the 11833 reflections which were collected, 11371 were unique ($R_{\text{int}}=0.024$). 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. The linear absorption coefficient for Mo K α is 9.2 cm⁻¹. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.95 to 1.00. The data were corrected for Lorentz and polarization effects.

Table 1 Crystal and experimental data

Formula: Pd ₂ P ₄ O ₆ N ₂ C ₅₀ H ₄₄
Formula weight: 1105.60
Crystal system: monoclinic
Space group: $P2_1/c$ $Z=4$
$a=13.729(4)$ Å
$b=16.691(6)$ Å
$c=21.289(4)$ Å
$\beta=100.99(2)^\circ$
$V=4789(2)$ Å ³
$D_{\text{calc}}=1.533$ g/cm ³
$R=0.031$, $R_w=0.039$
No. of reflections used=11833 ($I>3\sigma(I)$)
Measurement: Rigaku AFC-6S
Program system: TEXSAN
Structure determination: direct method (MITHRIL)
Refinement: full-matrix least-squares

The structure was solved by a direct method (MITHRIL).⁴ The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at calculated positions with their isotropic thermal parameters fixed at values of 1.2-times those of their parent atoms. The final cycle of the full-matrix least squares refinement was based on 8948 observed reflections ($I>3\sigma(I)$), and 577 variable parameters. The reliability factors are defined as $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w=4F_o^2/\sigma(F_o^2)$. The final R and R_w values were 0.031 and 0.039. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.61 and -1.05 eÅ⁻³, respectively. The atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV.⁵ All of the calculations were performed using the program TEXSAN crystallographic software package.⁶ Selected positional parameters are listed in Table 2.

The molecular structure of **1** is shown in Fig. 1, together with the atomic labeling scheme. Selected bond distances and bond angles are listed in Table 3. The two groups of Pd and its four nearest neighbor

[†] To whom correspondence should be addressed.

Table 2 Selective atomic coordinate and equivalent isotropic thermal parameters B_{eq} ($\text{\AA}^2$) of non-hydrogen atoms

Atom	x	y	z	B_{eq}
Pd(1)	0.39488(1)	0.10171(1)	1.81497(1)	2.561(8)
Pd(2)	0.21329(1)	0.07805(1)	0.75677(1)	2.540(8)
P(1)	0.17580(5)	0.05012(4)	0.85604(3)	2.64(3)
P(2)	0.32892(5)	0.17098(4)	0.88987(3)	2.76(3)
P(3)	0.44334(5)	0.03283(5)	0.73322(3)	2.95(3)
P(4)	0.25870(6)	0.09513(5)	0.65803(3)	2.98(3)
O(1)	0.0616(1)	0.0403(1)	0.7129(1)	3.80(9)
O(4)	0.5469(2)	0.1149(1)	0.8686(1)	4.2(1)
C(1)	0.1720(2)	-0.0568(2)	0.8703(1)	3.0(1)
C(7)	0.0542(2)	0.0845(2)	0.8687(1)	3.1(1)
C(13)	0.2392(2)	0.2504(2)	0.8668(1)	3.2(1)
C(19)	0.4159(2)	0.2122(2)	0.9577(1)	3.4(1)
C(24)	0.4611(2)	0.1631(2)	1.0068(2)	4.5(1)
C(31)	0.4071(2)	-0.0714(2)	0.7206(1)	3.5(1)
C(37)	0.2106(2)	0.0182(2)	0.5995(1)	3.8(1)
C(43)	0.2209(2)	0.1888(2)	0.6163(1)	3.6(1)
C(49)	0.2623(2)	0.0925(2)	0.9245(1)	3.1(1)
C(50)	0.3922(2)	0.0870(2)	0.6593(1)	3.6(1)

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} (a_i a_j).$$

Fig. 1 Molecular Structure of $[\text{Pd}_2(\mu\text{-dppm})_2(\text{NO}_3)_2]$ (**1**) and the atomic labeling scheme. Only Pd(1), Pd(2), P(1), P(2), P(3), P(4), O(1), O(4), C(49) and C(50) in the coordination sphere are labeled.

atoms, {Pd(1), Pd(2), P(2), O(4), P(3)} and {Pd(2), Pd(1), P(1), O(1), P(4)}, are nearly planar. The two Pd atoms are doubly bridged by two dppm ligands to form an eight-membered $\text{Pd}_2\text{P}_4\text{C}_2$ ring framework in a twist-chair conformation. The Pd(1)-O(4) and Pd(2)-O(1) distances were 2.190(2) and 2.206(2) $\text{\AA}$, respectively. The nitrate anion was weakly coordinated to a Pd atom. Each Pd atom therefore has a three-coordinate geometry in a side-by-side mode.

The Pd(1)-Pd(2) distance of 2.5940(7) $\text{\AA}$ is quite shorter than that (2.75 $\text{\AA}$) in Pd metal and is within

Table 3 Selected bond distances($\text{\AA}$) and bond angles($^\circ$)

Pd(1)-Pd(2)	2.5940(7)	Pd(1)-P(2)	2.2913(8)
Pd(1)-P(3)	2.2879(8)	Pd(1)-O(4)	2.190(2)
Pd(2)-P(1)	2.3159(8)	Pd(2)-P(4)	2.3214(8)
Pd(2)-O(1)	2.206(2)		
Pd(2)-Pd(1)-P(2)	86.43(2)	Pd(2)-Pd(1)-P(3)	87.28(3)
Pd(2)-Pd(1)-O(4)	176.06(6)	P(2)-Pd(1)-P(3)	173.58(3)
P(2)-Pd(1)-O(4)	92.88(6)	P(3)-Pd(1)-O(4)	93.48(6)
Pd(1)-Pd(2)-P(1)	87.44(2)	Pd(1)-Pd(2)-P(4)	90.82(3)
Pd(1)-Pd(2)-O(1)	171.77(6)	P(1)-Pd(2)-P(4)	174.80(3)
P(1)-Pd(2)-O(1)	88.44(6)	P(4)-Pd(2)-O(1)	92.66(6)

those (2.594(2) – 2.699(5) $\text{\AA}$) of other dipalladium(I) dppm complexes^{7–11}, indicative of a direct Pd-Pd bond. The four Pd-P distances are also similar to those (2.274(2) – 2.302(2) $\text{\AA}$) found in other dipalladium(I) dppm complexes.^{7–11} The O(1)-Pd(1)-Pd(2)-O(4) axis is almost linear. The torsion angle between the plane defined by {P(1), Pd(1), P(4) and Pd(2) atom} and {P(2), Pd(2), P(3) and Pd(1) atom} is 40.6°, which is in the range of those (39 – 50.5°) in other dipalladium(I) dppm complexes.^{7–11}

In this study we also found another single crystal of $[\text{Pd}_2(\mu\text{-dppm})_2(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH}$ (**2**) as a methanol solvate. Complex **2** has formula $\text{Pd}_2\text{P}_4\text{O}_7\text{N}_2\text{C}_{51}\text{H}_{48}$, a formula weight 1137.64, triclinic, space group $P1$, $a=12.118(2)$, $b=18.894(3)$, $c=11.719(3)$ $\text{\AA}$, $\alpha=92.42(2)$, $\beta=109.87(2)$, $\gamma=74.77(1)^\circ$, $V=2432(1)$ $\text{\AA}^3$, $Z=2$, $D_{\text{calc}}=1.554$ g/cm^3 , $F(0\ 0\ 0)=1152$, $\mu(\text{Mo K}\alpha)=9.11$ cm^{-1} , scan type ω -2 θ , scan rate 4.0°/min, scan width 1.00+0.30tan θ , $R=0.033$, $R_w=0.043$. The structure, bond distance and bond angles for **2** are almost equal to those of **1**.

We thank Mr. Nobuhisa Shimada and Shin-ichi Akiyama for their assistances. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. Detailed crystallographic data for **1** and **2** are available from the Cambridge Crystallographic Data Centre and Professor M. Munakata upon request.

References

1. R. J. Puddephatt, *Chem. Soc. Rev.*, **12**, 99 (1983).
2. C. F. J. Barnard and M. J. H. Russell, "Comprehensive Coordination Chemistry", ed. G. Wilkinson, Vol. 5, Chap. 51, pp. 1099 – 1130, Pergamon Press, Oxford, 1987.
3. A. L. Balch, "Reactivity of Metal-Metal Bonds", ed. M. H. Chisholm, Chap. 8, pp. 167 – 185, ACS Symposium Series, 1981.
4. "MITHRIL", J. Gilmore, *J. Appl. Cryst.*, **17**, 42, Univ. of Glasgow, Scotland (1984).
5. "International Tables for X-ray Crystallography", vol. IV, The Kynoch Press, Birmingham, England, 1974.
6. "TEXSAN", TEXRAY structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, USA 1985.
7. T. E. Krafft, C. I. Hejna and J. S. Smith, *Inorg. Chem.*, **29**,

- 2682 (1990).
8. M. L. Kullberg, F. R. Lemke, D. R. Powell and C. P. Kubiak, *Inorg. Chem.*, **24**, 3589 (1985).
9. M. M. Olmstead, L. S. Benner, H. Hope and A. L. Balch, *Inorg. Chim. Acta*, **32**, 193 (1979).
10. P. Espinet, J. Fornies, C. Fortuno, G. Hidalgo, F. Martinez, M. Tomas and A. T. Welch, *J. Organomet. Chem.*, **317**, 105 (1986).
11. R. G. Holloway, B. R. Penfold, R. Colton and M. J. McCormick, *J. Chem. Soc., Chem. Commun.*, **1976**, 485.

(Received August 4, 1997)

(Accepted October 30, 1997)