Heteroleptic Binuclear Palladium(II) Complexes with $P_2Pd(S_2)$ Cores: X-ray Crystal Structures of $(PdCl_2)_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2$ and $[Pd(MET)]_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2$ where MET is (Z)-1,4-Dimethoxy-1,4-dioxobut-2-ene-2,3-dithiolate

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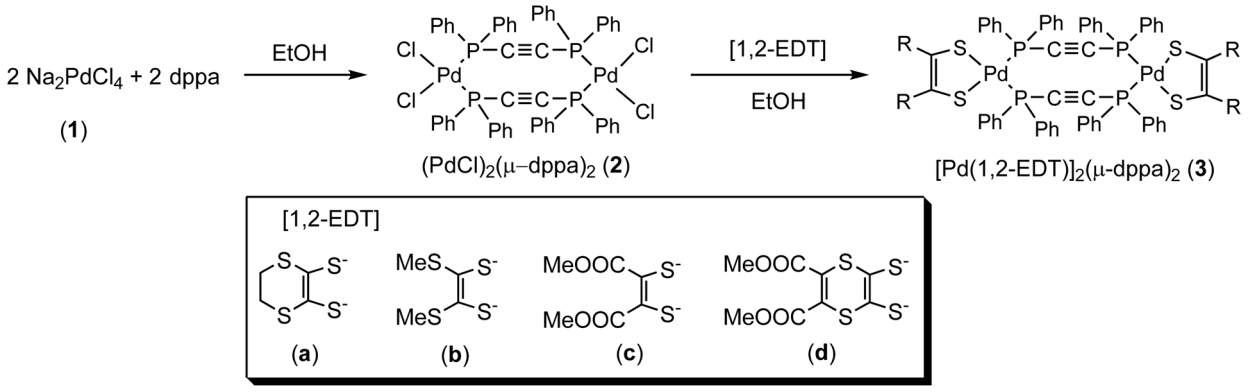
1,2-Bis(diphenylphosphino)acetylene (abbreviated as dppa: $Ph_2PCCPPh_2$) is a linear diphosphine ligand,[1] which has been used as a bridging ligand between metals or metal clusters such as Cu-chalcogenide,[2] Ru_3-cluster,[3] Ag(I),[4] $W_2(CO)_6$,[5] $Mo(CO)_4$,[6] $Pt(C_6F_5)_2$,[7] $Pt(SC_6F_5)_2$,[8] $Ru(acac)_2$ [9] and MX_2 (M = Pd, Pt; X = Cl, Br, I, SCN).[10-12] In these complexes, two phosphine groups in dppa coordinate to the metals. If the acetylenic group in dppa participates in the coordination of the metals, clusters such as the Cu-chalcogenide cluster[2] and Co-carbonyl cluster[13] can be formed. The dppa ligand shows more versatile modes of coordination chemistry than in the case where only two phosphines participate in the coordination. Previous studies on dppa-complexes mainly focused on their synthesis, X-ray crystal structure analysis and (in some cases) electrochemical properties. Metal-dppa complexes with a monothiolate terminating ligand also belong to this family, but only a few have been reported so far.[8]

Very recently, we reported the results of our systematic studies of $[M(1,2\text{-BDT})]_2(\mu\text{-dppa})_2$ (M = Pd(II), Pt(II); 1,2-BDT = 1,2-benzenedithiolate (BDT), 3,4-toluenedithiolate (TDT) and 1,4-dichloro-2,3-benzenedithiolate (Cl_2BDT))[14] and $[Pt(1,2\text{-EDT})]_2(\mu\text{-dppa})_2$ complexes (1,2-EDT = 5,6-dihydro-1,4-dithiine-2,3-dithiolate (DDDT: **a**), (Z)-1,2-bis-(methylthio)ethane-1,2-dithiolate (MTDT: **b**), (Z)-1,4-dimethoxy-1,4-dioxobut-2-ene-2,3-dithiolate (MET: **c**) and 5,6-bis(methoxycarbonyl)-1,4-dithiine-2,3-dithiolate (MDDT: **d**)).[15] Among these complexes, $[Pt(Cl_2BDT)]_2(\mu\text{-dppa})_2$ and $[Pt(MET)]_2(\mu\text{-dppa})_2$ showed luminescence properties in the solution state. These two complexes were regarded as the first luminescent metal-dppa complexes with a $P_2Pt(S_2)$ core. In this study, we present the synthesis, characterization and X-ray crystal structure of $[Pd(MET)]_2(\mu\text{-dppa})_2$, together with those of $(PdCl_2)_2(\mu\text{-dppa})_2$. We believe that these results will help provide a better understanding of the chemistry and crystal structure of metal-dppa systems.

Experimental

The HPLC grade organic solvents were purchased and used after drying them over a molecular sieve. Silica gel 60 (particle size 0.063-0.200 mm, MERCK) was used for the column chromatography. Na_2PdCl_4 (Kojima) and 1,2-bis-(diphenylphosphino)acetylene (Aldrich) were purchased and used for the synthesis. The element analyses were carried out at the National Center for Inter-University Research Facilities (NCIRF) at Seoul National University. The Infrared spectra were recorded by the KBr method on a MIDAC FT-IR spectrometer and the UV-vis spectra in acetonitrile on an HP 8452A diode array spectrometer. The Raman spectra were recorded with a Raman microscope spectrometer (Renishaw, Ltd.) equipped with a He-Ne laser (λ_0 = 6328 Å). A low laser power of *ca*. 0.06 mW focused on a 1 μm^2 area was applied. The mass spectrometric analyses were carried out at the NCIRF. The MALDI-TOF mass spectra were recorded using a Voyager-DETM STR Biospectrometry Workstation (Applied Biosystems Inc.). The ^1H and ^{31}P NMR spectra were measured on an Avance 500 (Bruker) and refer-



Scheme 1. Synthesis of complexes **2** and **3**.

enced to TMS and 85% H_3PO_4, respectively. The positive chemical shifts in the ^{31}P NMR spectra are downfield from the standard.

Bis[μ-{bis(diphenylphosphino)acetylene}] bis(dichloropalladium(II)) (2).[11] An ethanol solution (75 mL) of Na_2PdCl_4 (700 mg, 2.4 mmol) was added slowly to an ethanol solution (75 mL) of dppa (950 mg, 2.4 mmol) and stirred at room temperature for 1 hr. The yellow product was filtered, washed with cyclohexane and dried in air. Recrystallization from CH_2Cl_2/CH_3OH afforded yellow plate crystals. Yield: 1.1 g (80%). EA: calc for $C_{52}H_{40}C_{l4}P_4Pd_2{\cdot}2CHCl_3$ C 46.92, H 3.06; obsd C 46.57, H 3.01. ^1H NMR ($CDCl_3$, ppm): δ 7.53 (16H, m), 7.48 (8H, t, ^3J = 7.47), 7.26 (16H, t, ^3J = 7.47). ^{31}P NMR ($CDCl_3$, ppm): δ 4.873. FT-IR (KBr, cm^{-1}): 3056 (C-H str), 1480, 1437 (Ar ip str), 1185, 1161, 1097 (ip CH def), 1025, 998 (P-Ph str), 837, 743 (oop CH def), 689, 533, 511, 491, 475 (oop ring def). UV-vis (CH_3CN, nm, ε_{max} ($\times 10^4$ M^{-1} cm^{-1})): 266 (6.65), 326 (2.38). Raman (cm^{-1}): 2134 (C≡C), 351 (Pd-Cl).

Bis[μ-{bis(diphenylphosphino)acetylene}] bis(palladium(II)dithiolate) (3). To an ethanol suspension (10 mL) of the 4,5-ethylenedithio-1,3-dithiole-2-one precursors of the corresponding dithiolates (2 mmol; 417 mg (**a**), 421 mg (**b**), 469 mg (**c**), 645 mg (**d**)) was added potassium hydroxide (4 mmol, 210 mg) with stirring for 30 min under an argon atmosphere. $(PdCl_2)_2(\mu$-dppa$)_2$ (1 mmol, 1.14 g) dissolved in methylene chloride (40 mL) was then added, followed by stirring at room temperature for 4 h. The precipitate was filtered off and washed with methylene chloride, a small amount of *dil*. acid and H_2O, in sequence. The filtrate was dried under reduced pressure and then recrystallized from CH_2Cl_2/CH_3OH. Only a single crystal of **3c** was obtained as a brown plate.

For **3a**: Yield: 74% (1.01 g). MALDI-TOF-MS (*m/z*, %): 961.28 (M^+-Pd(**a**)-(**a**)+2SH+1, 69.71), 883.23 (M^+-Pd(**a**)-(**a**)-Ph+2SH, 63.22), 807.17 (M^+-Pd(**a**)-(**a**)-2Ph+2SH+1, 100). ^{31}P NMR ($CDCl_3$, ppm): δ 1.460. FT-IR (KBr, cm^{-1}): 3053 (Ph C-H str), 2919, 2854 (CH_2CH_2), 2057 (C≡C), 1626 (C=C), 1480, 1436 (Ar ip str), 1161, 1098 (ip CH def), 1026, 999 (P-Ph str), 836, 744 (oop CH def), 691, 537, 514, 497 (oop ring def). UV-vis (CH_3CN, nm, ε_{max} ($\times 10^4$ M^{-1} cm^{-1})): 248 (3.38), 268 (4.29), 286 (4.07).

For **3b**: Yield: 60% (0.82 g). MALDI-TOF-MS (*m/z*, %): 1075.29 (M^+-Pd(**b**)-1, 13.4), 909.25 (M^+-Pd(**b**)-2Ph-CH_3+2, 35.65), 891.21 (M^+-Pd(**b**)-2Ph-2CH_3, 47.07), 816.18 (M^+-Pd(**b**)-3Ph-2CH_3+1, 92.62), 814.18 (M^+-Pd(**b**)-3Ph-2CH_3, 100). ^{31}P NMR ($CDCl_3$, ppm): δ 1.459. FT-IR (KBr, cm^{-1}): 3054 (Ph C-H str), 2946 (-CH_3), 2054 (C≡C), 1629, 1480, 1436 (Ar ip str), 1097 (ip CH def), 1025, 998 (P-Ph str), 839, 745 (oop CH def), 691, 528, 510, 490, 436 (oop ring def). UV-vis (CH_3CN, nm, ε_{max} ($\times 10^4$ M^{-1} cm^{-1})): 248 (4.25), 274 (6.24), 296 (6.58), 3.52 (0.83).

For **3c**: Yield: 72% (1.02 g). MALDI-TOF-MS (*m/z*, %): 1385.33 (M^+-2CH_3+2H+1, 27.2), 917.29 (M^+-Pd(**c**)-2Ph-2CH_3+1, 100). ^{31}P NMR ($CDCl_3$, ppm): δ 1.045. FT-IR (KBr, cm^{-1}): 3051 (Ph C-H str), 2917 (-CH_3), 2054 (C≡C), 1720 (C=O), 1654 (C=C), 1480, 1436 (Ar ip str), 1238 (C-O), 1185, 1131, 1098 (ip CH def), 1026, 998 (P-Ph str), 834, 744 (oop CH def), 691, 537, 514, 497, 436 (oop ring def). UV-vis (CH_3CN, nm, ε_{max} ($\times 10^4$ M^{-1} cm^{-1})): 260 (5.80), 390 (0.46).

Table 1. The crystal data and structure refinement parameters for $(PdCl_2)_2(\mu$-dppa$)_2{\cdot}CH_2Cl_2$ and $[Pd(MET)]_2(\mu$-dppa$)_2{\cdot}CH_3OH$.

Empirical formula	$C_{53}H_{42}P_4Cl_6Pd_2$	$C_{130}H_{114}P_8O_{19}Pd_4S_8$
Formula weight	1228.25	2910.05
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	18.7287(4)	13.9109(5)
b (Å)	19.2294(5)	15.6357(6)
c (Å)	14.0517(3)	16.4604(6)
α (°)	90.00	76.826(1)
β (°)	91.007(1)	75.876(1)
γ (°)	90.00	67.516(1)
V (Å^3)	5059.8(2)	3171.7(2)
Z	4	1
μ (mm^{-1})	1.191	0.856
F (000)	2456	1478
2θ range	$1.52 < 2\theta < 28.33$	$1.29 < 2\theta < 28.37$
Reflections collected	50097	51147
Unique	12568 [R(int) = 0.0554]	15471 [R(int) = 0.0626]
Completeness to θ	28.33°, 99.6%	28.37°, 97.6%
GOF on F^2	1.054	1.200
$R1$(wR2) [I>2σ(I)]	0.0388 (0.0852)	0.0826 (0.1481)

For **3d**: Yield: 63% (1.00 g). MALDI-TOF-MS (*m/z*, %): 1574.41 (M^+-CH_3+2, 31.3), 1572.42 (M^+-CH_3, 27.6), 1358.42 ((M^+-4$COOCH_3$+4H+2, 55.5). FT-IR (KBr, cm^{-1}): 3051 (Ph C-H str), 2945 (-CH_3), 2052 (C≡C), 1722 (C=O) 1625 (C=C), 1479, 1436 (Ar ip str), 1245 (C-O), 1098 (ip CH def), 1022 (P-Ph str), 840, 744 (oop CH def), 691, 555, 526, 511, 491 (oop ring def). UV-vis (CH_3CN, nm, ε_{max} ($\times 10^4$ M^{-1} cm^{-1})): 248 (4.37), 268 (4.86).

X-ray crystal structural analysis. The X-ray structure analyses for $(PdCl_2)_2(\mu$-dppa$)_2$ (**2**) and $[Pd(MET)]_2(\mu$-dppa$)_2$ (**3c**) were performed at 130(2) K on a Bruker SMART APEXII diffractometer equipped with graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The preliminary orientation matrix and cell parameters were determined from three sets of ω/ψ or ω scans at different starting angles. The data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS.[16] The structures were solved by direct methods and refined by full matrix least-squares analysis using the anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program.[17] The phenyl carbon atoms (C56, C57 and C58) of complex **3c** were disordered and assigned with an occupancy factor of 0.57:0.43. The crystal data and structural refinement parameters are shown in Table 1.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (Deposition No. CCDC-

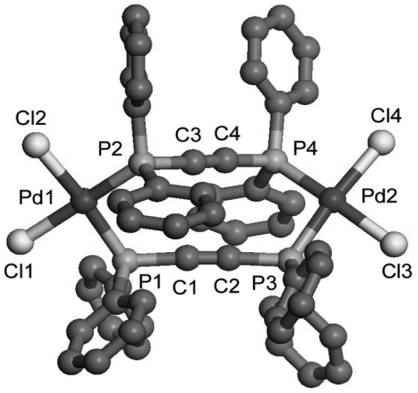


Figure 1. The molecular structure of $(PdCl_2)_2(\mu$-dppa$)_2$ (**2**). The hydrogen atoms are omitted for clarity.

701474 for $(PdCl_2)_2(\mu$-dppa$)_2 \cdot CH_2Cl_2$ and CCDC-701475 for $[Pd(MET)]_2(\mu$-dppa$)_2 \cdot CH_2OH$). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/perl/catreq.cgi (*or* from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The heteroleptic Pd(II) complexes of $[Pd(1,2\text{-EDT})]_2(\mu$-dppa$)_2$[15] were prepared by the ring-opening reaction of their oxo-analogues using KOEt (Scheme 1). The FT-IR spectra of the complexes show the characteristic vibrational peaks of each ligand: The symmetric ν(C≡C) vibration is known to be IR inactive but Raman active in group theory.[18] Therefore, the ν(C≡C) vibrational band was not observed in the IR spectrum of **2**, but was observed in the Raman spectrum at 2134 cm^{-1}. However, it appears in the IR spectra of **3** at around 2054 cm^{-1}. This suggests that the molecular structures of complex **3c** are dynamically unsymmetrical, even though their schematic structures appear to be symmetrical, as shown in Scheme 1, possibly because of the relatively bulky and dynamic MET ligands, as can be seen in the X-ray structure analysis result. The 1,2-EDT ligands also exhibit the characteristic bands: ν(C=C) of 1,4-dithiine at 1626 cm^{-1} for **3a**, ν(C-H) of the -CH_3 moiety at *ca.* 2946 cm^{-1} for **3b**, and ν(C=O) and ν(C-O) of the ester moiety at 1720 cm^{-1} and 1238 cm^{-1} for **3c** and 1722 cm^{-1} and 1245 cm^{-1} for **3d**, respectively. The MALDI-TOF mass spectra of the complexes show very rich fragmentations. The fragmentation patterns in the low-molecular-weight region involve the consecutive loss of the 1,2-EDT ligand and phenyl groups on the dppa bridging ligand. The ^{31}P NMR spectra of complex **3** show a singlet with an approximately 3.4 ppm up-field shift compared to that of complex **2**. This means that the 1,2-EDT ligands are better electron donors than the chloride ligand, which influences the electron density of the P atom through the Pd(II) ion, resulting in the higher-field resonance.

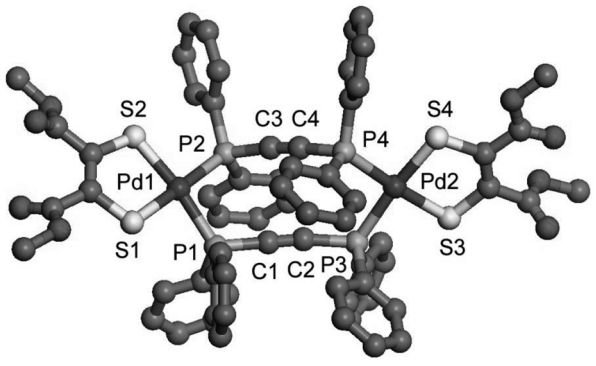


Figure 2 The molecular structure of $[Pd(MET)]_2(\mu$-dppa$)_2$ (**3c**). The hydrogen atoms are omitted for clarity.

Table 2. The selected bond distances (Å) and angles (deg) for (**2**)·CH_2Cl_2 and (**3c**)·CH_3OH

	(**2**)·CH_2Cl_2 (X = Cl)	(**3c**)·CH_3OH (X = S)
Pd1-P1	2.2648(9)	2.2881(15)
Pd1-P2	2.2429(8)	2.2846(15)
Pd2-P3	2.2694(9)	2.3097(15)
Pd2-P4	2.2456(8)	2.2865(15)
Pd1-X1	2.3382(8)	2.2848(15)
Pd1-X2	2.3250(9)	2.2860(15)
Pd2-X3	2.3362(8)	2.2994(15)
Pd2-X4	2.3048(9)	2.2880(15)
C1-C2	1.191(4)	1.176(8)
C3-C4	1.200(4)	1.176(8)
P1-Pd1-P2	96.55(3)	94.19(5)
P1-Pd1-X2	172.17(3)	170.88(6)
P2-Pd1-X2	85.74(3)	90.06(5)
P1-Pd1-X1	84.77(3)	86.91(5)
P2-Pd1-X1	173.29(3)	178.05(6)
X2-Pd1-X1	92.11(3)	89.08(5)
P3-Pd2-P4	96.74(3)	95.78(5)
P3-Pd2-X4	174.72(3)	171.07(6)
P4-Pd2-X4	88.38(3)	86.89(6)
P3-Pd2-X3	82.62(3)	88.62(5)
P4-Pd2-X3	173.75(3)	175.53(6)
X4-Pd2-X3	92.14(3)	88.65(5)

The molecular structures of (**2**)·CH_2Cl_2 and (**3c**)·CH_3OH were determined by the X-ray diffraction technique and are shown in Figures 1 and 2, respectively. The selected bond lengths (Å) and angles (°) are compared in Table 2.

The average lengths of the Pd-P (2.2922(15) Å) and Pd-S (2.2896(15) Å) bonds in complex **3c** are very close to those in $[Pd(BDT)]_2(\mu$-dppa$)_2$ (2.2928(12) and 2.2818(13) Å, respectively).[14] The P-Pd-S *trans* angles of complex **3c** deviate from linearity, falling in the range from 170.88(6)° to 178.05(6)°. Compared to the large variation of the *trans* angles (7.2°), those of P-Pd-Cl for complex **2** vary within a narrow range (172.17(3)°-174.72(3)°). This suggests that the MET ligand is more flexible than the chloride ligand, due to the highly disordered atoms (O1, O3 and C19) in the former, resulting in the P_2PdS_2 core being more distorted than the P_2PdCl_2 one. This disordered structure was also observed in the MET ligand of the $[Pt(MET)]_2(\mu$-dppa$)_2$ complex.[15] The

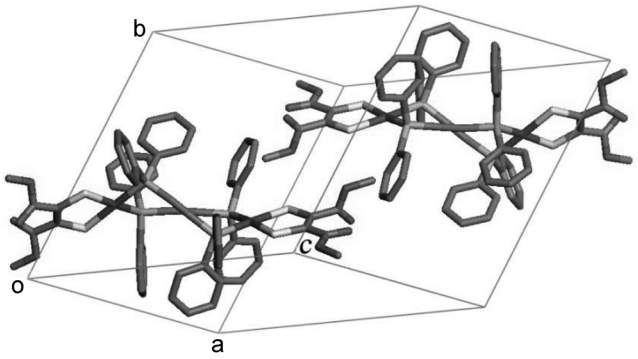


Figure 3. The close packing diagram of $[Pd(MET)]_2(\mu$-dppa$)_2$ (**3c**) showing its racemic structure. The hydrogen atoms and solvated methanol are omitted for clarity.

relatively high *R*-value of complex **3c** can be ascribed mainly to the disordering of the methyl ester groups in the MET ligand, as well as that of the phenyl groups connected to the P1 atom. This might be one of the reasons why single crystals suitable for X-ray structure analysis of neither $[Pd(MET)]_2(\mu$-dppa$)_2$, nor the other Pd(II)-dithiolate complexes prepared in this study, were able to be obtained for a long period of time, even though many attempts were made to crystallize them using various solvent pairs.

The average C≡C bond length of complex **3c** (1.176(8) Å) is slightly shorter than that of complex **2** (1.196(4) Å), $[Pd(BDT)]_2(\mu$-dppa$)_2$ (1.191(6) Å)[14] and $[Pt(MET)]_2(\mu$-dppa$)_2$ (1.195(13) Å).[15] The two acetylenic moieties in a single molecule of complex **3c** are staggered relative to each other. Moreover, they are distorted in right- and left-handed modes and its crystal has a racemic structure (Fig. 3). These structural characteristics were also observed in the X-ray crystal structure of $(ML_n)_2(\mu$-dppa$)_2$ complexes where ML_n is $Mo(CO)_4$,[6] $Pt(C_6F_5)_2$,[7] $Pt(SC_6F_5)_2$,[8] $Ru(acac)_2$,[9] Pd(BDT),[14] and Pt(MET).[15]

In conclusion, the heteroleptic binuclear Pd(II) complexes, $(PdCl_2)_2(\mu$-dppa$)_2$ (**2**) and $[Pd(1,2\text{-EDT})]_2(\mu$-dppa$)_2$ (**3**) (1,2-EDT = 1,2-ethylenedithiolates), were successfully prepared and characterized by elemental analysis and MALDI-TOF, ^{31}P NMR, FT-IR and UV-vis spectroscopies. Among them, the X-ray crystal structures of $(PdCl_2)_2(\mu$-dppa$)_2$ (**2**) and $[Pd(MET)]_2(\mu$-dppa$)_2$ (where MET = 1,4-dimethoxy-1,4-dioxobut-2-ene-2,3-dithiolate) (**3c**) were determined. Their structures are similar to those of the previously reported $[M(1,2\text{-benzenedithiolates})]_2(\mu$-dppa$)_2$ (M = Pt(II) and Pd(II)) and $[Pt(MET)]_2(\mu$-dppa$)_2$ complexes. These results will contribute to our understanding of the chemistry of binuclear dppa complexes with a 1,2-dithiolate terminal ligand, which have not been extensively investigated.

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