Notes

A Sterically Enforced Bent Form of an Edge-Sharing Dipalladium(II) Complex Attained by a Linked-Bisphosphido Bridge

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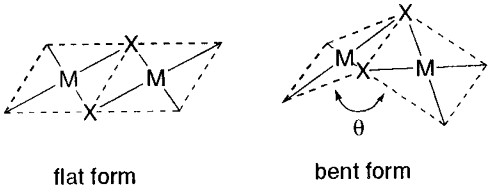
Many examples are known of edge-sharing square planar bimetallic complexes formed by d^8 transition-metal centers. In a recent report, Aullón et al. tentatively classified the structures of such complexes bridged with two X ligands (X = halogen anion, RO^-, RS^-, S^{2-}, or R_2P^-) into two possible groups, that is, flat and bent forms (Chart 1).[1] Of these two structures, the bent form is of interest, particularly because axial orbitals of the two metals are in close proximity under the hinged planes to interact cooperatively with a substrate. Such an interaction is expected to play a significant role in binding a substrate to a bimetallic complex.

For the bisphosphido-bridged complexes, most of them are regarded as the flat form,[2−14] though both forms often occur for other X ligands. Two limited exceptions are $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ and $[PtMe(\mu\text{-}CyPP)]_2$.[15] Since the examples of the bent bisphosphido bimetallic complexes are so far limited to these two Rh(I) and Pt(II) complexes,[16−20] it is worth preparing such bent complexes in searching for the factors responsible for the bent structure.

Chart 1



Very recently, Claver et al. used alkyl dithiolates $^-S(CH_2)_nS^-$ with a few methylene units as a bridging moiety to prepare linked-bisthiolato-bridged complexes, all of which have a bent structure,[21] implying that the linked bridge acts as an effective ligand to adopt a bent structure. On the other hand, to our knowledge, linked-bisphosphido groups have not been used as a bridging moiety in an edge-sharing square planar complex of d^8 transition metals. Of course some bimetallic complexes with linked-bisphosphido groups such as $\{RP-(linker)-PR\}^{2-}$ (linker = $(CH_2)_n$, 1,2-phenylene, or *o*-xylene) are known,[22−34] but they do not have edge-sharing square planar structures. In this paper, we describe the preparation and X-ray structure of linked-bisphosphido dipalladium(II) complexes with a formula $[Pd_2(\mu\text{-}RPCH_2CH_2PR)(DPPE)_2]Cl_2$ (R = Me and Ph), in which the linked-bisphosphido groups are employed as a ligand to enforce them sterically to adopt a bent structure.

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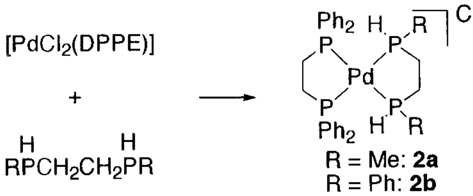
Table 1. Crystallographic Data for $[Pd_2(\mu\text{-MPE})(DPPE)_2]Cl_2$ (**3a**) and $[Pd_2(\mu\text{-PPE})(DPPE)_2]Cl_2$ (**3b**)

	3a	**3b**
empirical formula	$C_{57}H_{60}Cl_4P_6Pd_2$	$C_{67.5}H_{65}Cl_5P_6Pd_2$
fw	1285.56	1452.16
space group	$Pna2_1$ (No. 33)	$P2_1/n$ (No. 14)
a, Å	22.1960(4)	12.3700(2)
b, Å	22.5510(4)	24.2300(2)
c, Å	11.3940(1)	45.1860(6)
β, deg		92.242(1)
V, Å^3	5703.2(3)	13 530.6(3)
Z	4	8
T, °C	−73(1)	−73(1)
λ(Mo Kα), Å	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.497	1.426
μ, mm^{-1}	1.023	0.910
R^a	0.034	0.064
$R_w{}^b$	0.039	0.068

^{a} $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$.

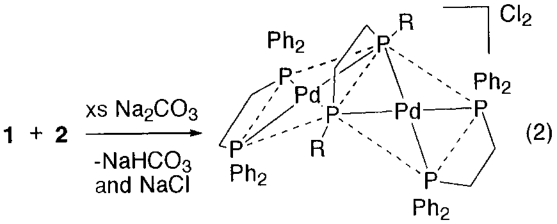
Results and Discussion

Preparation of the Linked-Bisphosphido Complexes. Synthesis of the bisphosphido dinuclear complexes is usually based on a one-pot reaction of a phosphine having a P−H bond with an appropriate metal fragment.[35,36] In the present study, stepwise reactions were employed, leading to a higher yield. First, 1,2-bis(methylphosphino)ethane (abbreviated as $MPEH_2$) or 1,2-bis(phenylphosphino)ethane (abbreviated as $PPEH_2$) was treated with 1 equiv of $[PdCl_2(DPPE)]$ (**1**) to coordinate to the first Pd(II) center (eq 1). Then, the $[Pd(MPEH_2$ or $PPEH_2)(DPPE)]Cl_2$ (**2a** or **2b**, respectively) thus formed was made to react with another 1 equiv of **1** to form the linked-bisphosphido complex $[Pd_2(\mu\text{-MPE}$ or $\mu\text{-PPE})(DPPE)_2]Cl_2$ (**3a** or **3b**, respectively) in a fairly high yield with the release of 2 equiv of HCl, which was trapped by a mild base, Na_2CO_3 (eq 2). $MPEH_2$ and $PPEH_2$ each have two chiral phosphorus atoms, and so the intermediates **2a** and **2b** should have been obtained as a mixture of racemic and meso isomers, but only one final product **3a** or **3b** was obtained.



(1)

R = Me: **2a**
R = Ph: **2b**



(2)

R = Me: **3a**
R = Ph: **3b**

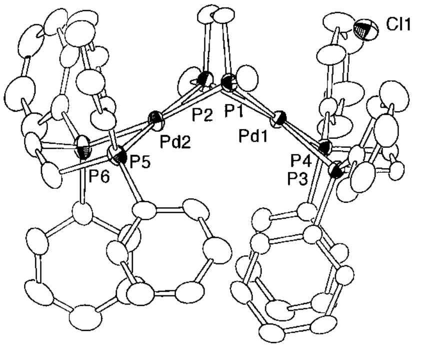


Figure 1. ORTEP drawing of the dipalladium complex $[Pd_2(\mu\text{-MPE})(DPPE)_2]Cl_2{\cdot}CH_2Cl_2$ (**3a**). One of the two counteranions, a solvent molecule, and hydrogen atoms have been omitted for clarity.

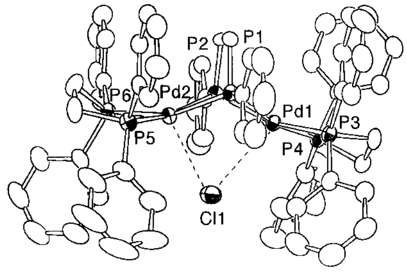


Figure 2. ORTEP drawing of one of the two independent dipalladium complexes in a crystal of $[Pd_2(\mu\text{-PPE})(DPPE)_2]Cl_2{\cdot}1.5CH_2Cl_2$ (**3b**). Counteranions, solvent molecules, and hydrogen atoms have been omitted for clarity.

Table 2. Listings of Geometrical Parameters for **3a**, **3b**

		3b	
	3a	molecule 1	molecule 2
	Distances/Å		
Pd(1)−P(1)	2.330(2)	2.332(2)	2.358(2)
Pd(1)−P(2)	2.332(2)	2.356(2)	2.336(2)
Pd(1)−P(3)	2.304(2)	2.300(2)	2.331(2)
Pd(1)−P(4)	2.322(2)	2.331(2)	2.303(2)
Pd(2)−P(1)	2.332(2)	2.342(2)	2.352(2)
Pd(2)−P(2)	2.361(2)	2.342(2)	2.340(2)
Pd(2)−P(5)	2.326(2)	2.313(2)	2.302(2)
Pd(2)−P(6)	2.311(2)	2.304(2)	2.311(2)
	Angles/deg		
P(1)−Pd(1)−P(2)	69.52(6)	67.76(6)	67.68(6)
P(1)−Pd(2)−P(2)	68.98(6)	67.82(6)	67.70(6)
P(3)−Pd(1)−P(4)	82.32(6)	85.01(6)	85.13(6)
P(5)−Pd(2)−P(6)	84.25(7)	84.77(6)	85.81(7)
Pd(1)−P(1)−Pd(2)	90.32(6)	96.50(6)	94.15(6)
Pd(1)−P(2)−Pd(2)	89.53(6)	95.82(6)	95.04(6)

X-ray Analysis of 3a and 3b. Suitable crystals of **3a** and **3b** both as methylene chloride solvates were grown by diffusion of Et_2O onto CH_2Cl_2 solutions. Crystal, data collection, and refinement parameters for **3a** and **3b** are given in Table 1. Atomic coordinates and equivalent temperature factors are included as Supporting Information. ORTEP diagrams are shown in Figures 1 and 2. Selected geometrical parameters for **3a** and **3b** are included in Table 2. Further details of the structure determinations are given in the Experimental Section and the Supporting Information.

The molecular structure of **3a** shown in Figure 1 indicates that the two Pd(II) atoms are bridged by the linked-bisphosphido group, $MePCH_2CH_2PMe$, to form a rare butterfly structure. The dihedral angle (bent angle) formed by the Pd1−P1−P2 and Pd2−P1−P2 planes is 118.3°, which is substantially reduced compared with 133.4° in $[Rh(\mu\text{-PPh}_2)(DPPE)]_2$ with a butterfly structure.[16] Thus, the ethylene backbone of the linked-bisphosphido group effectively imposes the sterical constraint on the doubly bridged square planes, as we expected.

In the crystal structure of **3b**, two crystallographically independent **3b** molecules are present, forming a considerably

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(35) For example, see: Hayter, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 3046.
(36) Another example: Brandon, J. B.; Dixson, K. B. *Can. J. Chem.* **1981**, *59*, 1188.

large unit cell. Since each possesses geometrical parameters comparable to those of the other, one of the two is depicted in Figure 2, where the linked-bisphosphido ligand PPE doubly bridges the two Pd(II) atoms to form a butterfly structure similar to that found for **3a**. However, a striking difference is found between the molecular structures of **3a** and **3b**. In **3a**, a Cl^- anion approaches only one of the two Pd(II) centers from a top direction as shown in Figure 1, where the Cl1−Pd1 distance is 3.268(2) Å. In **3b**, on the other hand, it approaches the two Pd(II) atoms simultaneously from the bottom so as to form a third bridge. Interatomic distances from the Cl^- to each palladium(II) are 3.102(2) Å for Cl1−Pd1 and 2.981(2) Å for Cl1−Pd2, and in the other independent molecule, the corresponding distances are 3.063(2) and 2.962(2) Å. Though they are all greater than a normal single bond length of 2.30 Å for a Pd−Cl bond in $PdCl_4^{2-}$,[37−40] they are smaller than 3.30 Å, a sum of van der Waals radii.[41] In addition, the two Pd(II) centers in Figure 2 (**3b**) are displaced toward the Cl^- anion by 0.24 and 0.34 Å from their respective ideal square coordination plane, whereas those in Figure 1 (**3a**) are both almost in a square plane with a displacement similar in magnitude to those of the four phosphorus atoms. Concerning the Pd(II) square planar complexes having four phosphorus donor atoms, two examples were reported for a similar axial coordination of the counterion.[42−44] In both cases, the ligands are tetraphosphamacrocycles, and the Pd−Cl distances are 2.831 and 3.107 Å. Thus, the comparable Pd−Cl distances and displacement of the Pd(II) centers toward the Cl^- found in **3b** demonstrate the presence of a weak bonding interaction between the Pd(II) and Cl atoms,[45] whereas the interaction in **3a** is considered to be negligible or much weaker than in **3b**.

The presence of the additional Cl^- bridge in **3b** may be responsible for the hinged structure opened more widely in **3b** than in **3a**. The dihedral angles formed by the two P(bridge)−Pd−P(bridge) triangular planes are 127.4° and 124.5° for the two independent molecules in **3b**, which are significantly wider than 118.3° in **3a**. The Pd···Pd separation is greater in **3b**, 3.4866(7) and 3.4487(7) Å, than in **3a**, 3.3054(7) Å.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were purified by distillation: CH_2Cl_2 was distilled from P_2O_5, and Et_2O and THF were distilled from sodium metal. These were stored under an N_2 atmosphere. $[PdCl_2(DPPE)]$ was prepared from $[PdCl_2(cod)]$[46] and DPPE. $PPEH_2$ was prepared according to the literature method.[47] $MPEH_2$ was also prepared by the reported method[48] and used as a ca. 0.16 M THF solution.

^1H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL LA-300 and -500 spectrometers. ^1H and ^{13}C NMR data were referred to $Si(CH_3)_4$ as an internal standard. ^{31}P NMR data were referred to 85% H_3PO_4 as an external standard.

[Pd(MPEH$_2$)(DPPE)]Cl$_2$, 2a. $[PdCl_2(DPPE)]$ (160 mg, 0.278 mmol) was dissolved in CH_2Cl_2 (35 mL), to which a 0.16 M THF solution of $MPEH_2$ was added until the disappearance of $[PdCl_2(DPPE)]$ was confirmed by ^{31}P NMR spectra. The total amount of $MPEH_2$ added was 1.9 mL (0.30 mmol). After the solvent was completely removed under reduced pressure, the residue was redissolved into 2 mL of CH_2Cl_2, and then 30 mL of Et_2O was added to precipitate **2a**. After the separation of the precipitate by decantation, it was washed twice with 2 mL of Et_2O and then dried in vacuo to give 165 mg of **2a** (0.237 mmol, 85%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.26 and 1.49 (m, 6H, CH_3), 2.4−3.2 (8H, CH_2), 4.91 and 5.60 (d, $^1J_{P-H} = 384$ and 383 Hz, respectively, 2H, P−H), 7.2−8.2 (Ph, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 6.2 and 6.5 (d, $^1J_{P-C} = 36$ and 35 Hz, respectively, CH_3), 24.2 (m, CH_2 of $MPEH_2$), 30.7 (m, CH_2 of DPPE), 127.2−134.5 (m, Ph). $^{31}P\{^1H\}$ ($CDCl_3$): δ 17.3 (m, $MPEH_2$), 54.8 (m, DPPE); the other isomer, 19.3 (m, $MPEH_2$), 54.3 (m, DPPE).

[Pd(PPEH$_2$)(DPPE)]Cl$_2$, 2b. Complex **2b** was prepared from $[PdCl_2(DPPE)]$ and $PPEH_2$ similarly to **2a**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.7−3.0 (8H, CH_2), 5.91 and 6.53 (P−H, each pair of these signals due to a P−H coupling was overlaid with the phenyl signals), 6.9−7.8 (Ph, 30H). $^{31}P\{^1H\}$ ($CDCl_3$): a major isomer, δ 34.3 (m, $PPEH_2$), 56.3 (m, DPPE); a minor isomer, δ 32.8 (m, $PPEH_2$), 57.1 (m, DPPE).

[Pd$_2$(*μ*-MPE)(DPPE)$_2$]Cl$_2$, 3a. **2a** (148 mg, 0.212 mmol) was dissolved in 8 mL of CH_2Cl_2, to which Na_2CO_3 (680 mg, 6.42 mmol) and $[PdCl_2(DPPE)]$ (121 mg, 0.212 mmol) in CH_2Cl_2 were added. After vigorous stirring for 2 h, the solution was filtered to remove the salts formed. The volume of the filtrate was reduced to 2 mL, and then 20 mL of Et_2O was added to precipitate **3a**. After the separation of the yellow powder by decantation, it was washed with 2 mL of Et_2O three times and then dried in vacuo to give 185 mg of **3a** (0.154 mmol, 73%). ^1H NMR (300 MHz, $CDCl_3$): δ 0.55 (m, 6H, CH_3), 2.5−2.8 (12H, CH_2), 7.3−7.7 (Ph, 40H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 6.4 (br, CH_3), 29.6 (m, CH_2 of DPPE), 30.0 (m, CH_2 of MPE), 129.4−133.2 (m, Ph). $^{31}P\{^1H\}$ ($CDCl_3$): δ −9.5 (m, MPE), 47.8 (m, DPPE).

[Pd$_2$(*μ*-PPE)(DPPE)$_2$]Cl$_2$, 3b. The procedure for the synthesis of **3b** was similar to that for **3a**. The quantities used were as follows: **2b** (66 mg, 0.080 mmol), Na_2CO_3 (242 mg, 2.29 mmol), and $[PdCl_2(DPPE)]$ (40 mg, 0.070 mmol); 82 mg of **3b** (0.062 mmol, 66%) was obtained. ^1H NMR (300 MHz, $CDCl_3$): δ 2.1−2.6 (12H, CH_2), 6.2−8.1 (Ph, 50H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.6 (m, CH_2 of DPPE), 30.0 (m, CH_2 of PPE), 129.4−133.2 (m, Ph). $^{31}P\{^1H\}$ ($CDCl_3$): δ −13.3 (m, MPE), 44.4 (m, DPPE).

X-ray Crystallography. Suitable crystals of **3a** and **3b** were mounted on a glass fiber. All measurements were made on a Mac Science DIP2030 imaging plate area detector at 200 K to prevent efflorescence due to the loss of CH_2Cl_2 in the crystals. The crystal-to-detector distance was 100 mm; readout was performed in the 0.050 mm pixel mode for the 300 mm diameter detector. The data were collected to a maximum 2θ value of 55.8°. For **3a**, a total of 60 oscillation images were collected, each being exposed for 4.0 min with an oscillation angle of 3.0°. For **3b**, 120 images were collected, each being exposed similarly but with an oscillation angle of 1.5°. Cell parameters and intensities for the reflection were estimated by the program packages of MacDENZO.[49]

For **3a**, a total of 7375 reflections were collected, and 4849 reflections ($I > 3.00\sigma(I)$ and $2.7° < 2\theta < 49.1°$) were used for the final refinement, whereas, for **3b**, 23 575 reflections were collected, and 20 018 ($I > 3.00\sigma(I)$ and $2.7° < 2\theta < 50.2°$) were used. The structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms except for the disordered CH_2Cl_2 were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. Absorption correction

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was not applied for either case.[50] All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation.[51]

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Supporting Information Available: Listings of ^{31}P NMR data and experimental and simulated ^{31}P{^{1}H} NMR spectra. CIF files containing data for the structures of **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) MacDENZO corrects absorption effect upon estimation of intensities.

(51) *teXsan: Single-Crystal Structure Analysis Software*, version 1.6; Molecular Structure Corporation: The Woodlands, TX, 1993.