

Synthesis, Characterization, and Absorption Spectra of Metallamacrocycles, [Pd{ α,ω -bis(diphenylphosphino)oligothienylene}Cl₂]₂

Dong Min Kang, Sam Gon Kim, Sung Joong Lee, Jong Keun Park,[†] Ki Min Park,[‡] and Sung Chul Shin^{*}

Department of Chemistry and Research Institute of Life Science, Gyeongsang National University, Jinju 660-701, Korea

**E-mail: scshin@nongae.gsnu.ac.kr*

[†]Department of Chemistry Education and Research Institute of Basic Science, Gyeongsang National University, Jinju 660-701, Korea

[‡]Research Institute of Basic Science, Gyeongsang National University, Jinju 660-701, Korea

Received May 17, 2005

Dimeric metallamacrocycles of 2 : 2 (metal-to-ligand) stoichiometry, [Pd{ α,ω -bis(diphenylphosphino)oligothienylene}Cl₂]₂ **1-3** were prepared from a self-assembly reaction of [Pd(CH₃CN)₂Cl₂] and α,ω -bis(diphenylphosphino)oligothienylene in 90-94% yields. The structures of metallamacrocycles **1-3** were determined by X-ray diffraction. **1** crystallizes in the monoclinic space group P2₁/n with $a/\text{\AA} = 12.0737(13)$, $b/\text{\AA} = 17.1993(18)$, $c/\text{\AA} = 13.0951(14)$ and $\beta/^\circ = 101.505(2)$. **2** crystallizes in the triclinic space group $P\bar{1}$ with $a/\text{\AA} = 10.2634(4)$, $b/\text{\AA} = 19.7855(9)$, $c/\text{\AA} = 21.0851(9)$, $\alpha/^\circ = 63.1010(10)$, $\beta/^\circ = 86.5880(10)$, $\gamma/^\circ = 81.2280(10)$. **3** crystallizes in the triclinic space group $P\bar{1}$ with $a/\text{\AA} = 10.4353(19)$, $b/\text{\AA} = 13.482(3)$, $c/\text{\AA} = 13.816(3)$, $\alpha/^\circ = 108.027(4)$, $\beta/^\circ = 90.461(4)$, $\gamma/^\circ = 93.261(4)$. The UV spectra of **1-3** were characterized.

Key Words : Metallamacrocycles, Self-assembly, Oligothiophenes, Palladium, Supramolecules

Introduction

Organic and inorganic functionalities incorporated into metallamacrocycles exhibits a variety of coupling phenomena between the localized d-electrons of transition metal and the mobile π -electrons of the organic ligand in a synergistic way.¹ There has been considerable interest in such phenomena of the metallamacrocycles owing to the potential applications in catalysis, sensing, molecular electronics, and facilitated small molecule transport.²⁻⁴ A number of synthetic strategies, including symmetry interaction, molecular library, weak-link approach and directional bonding approaches have been employed for building the metallamacrocycles.⁴⁻⁹ Amongst these strategies, the directional-bonding approach employs the directional binding constraint by conventionally-rigid ligands and the geometrical requirement by metal ions, combination of which dictates the overall structure.^{5,6,10} A fascinating variety of molecular squares,¹¹⁻¹⁴ triangles^{15,16} and boxes^{17,18} have been assembled *via* this synthetic strategy.

On the one hand, oligothiophenes functionalized with biting units at both α,ω -positions may be rigid or semirigid and of directional binding constraint. Therefore, they could lead to the construction of metallamacrocycles as edge linkers, together with appropriate metals as corners. Thus, their coupling either with two *cis* biting sites or two *trans* biting sites of the square planar palladium centers may result in the self-assembly of dimeric metallamacrocycles in a 2/2 (metal-to-ligand) stoichiometry. In order to investigate this possibility, we attempted to construct a series of the metallamacrocycles, [Pd{ α,ω -bis(diphenylphosphino)oligothienylene}Cl₂]₂. Very recently Gray reported that 2,5'-bis(diphenylphosphino)bithienylene reacted with Mo(CO)₄

as a corner in a 1 : 1 ratio, producing a cyclic oligomer with eight repeat units.¹⁹ The oligothiophenes exhibit some attractive properties that are applicable to biological studies, semiconductors, nonlinear optical materials and highly ordered molecular assemblies.^{20,21} Complexation of the oligothiophenes with the palladium metals into metallamacrocycles may show novel properties which can be distinguished from those of the conventional metallamacrocyclic systems of palladium with other aromatic ligands, as a result of the synergistic interaction between the components. This paper reports the synthesis, characterization and absorption spectra of the metallamacrocycles, [Pd{ α,ω -bis(diphenylphosphino)oligothienylene}Cl₂]₂ (**1-3**).

Experimental Section

General Remarks. Benzene was distilled and degassed over Na and under nitrogen prior to use. All other chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed on Kiesel gel 60 (230-400 mesh). 2,5-bis(diphenylphosphino)thiophene,²² 5,5'-bis(diphenylphosphino)-2,2'-bithiophene, 5,5''-bis(diphenylphosphino)-2,2':5',2''-terthiophene²³ were prepared using the methods reported in the literature. ¹H-NMR spectra at 300 MHz and ³¹P-NMR spectra at 202.40 MHz were recorded on a Bruker Avance-300 spectrometer and Bruker DRX-500 spectrometer, respectively, using SiMe₄ as an internal standard and CDCl₃ as a solvent. Infrared spectra were recorded on a Hitachi 270-50 spectrometer with KBr disc of the metallamacrocycles. Absorption spectra were obtained on a Perkin Elmer Lambda 900 spectrophotometer. Elemental analyses were performed on an Elementar Analysen systeme GmbH Vario EL.

X-ray Crystallography. Crystals suitable for X-ray diffraction were mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation source and a CCD detector. The frames of two-dimensional diffraction images were collected and processed in order to determine the cell parameters and orientation matrix. The frame data were processed to give the structure factors using the program SAINT.²⁴ The intensity data were corrected for Lorentz and polarization effects. Using the SADABS program,²⁵ the empirical absorption corrections were also applied. The structures were solved by a combination of the direct and the difference Fourier methods using the SHELXTL program package.²⁶ The structures were refined using a full matrix least squares against F^2 for all the data. All the non-H atoms were refined anisotropically. All hydrogen atoms were included in the calculated positions with the isotropic thermal parameters 1.2 times those of the attached atoms.

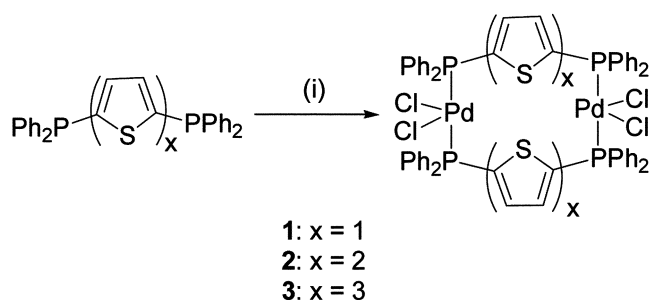
[Pd{2,5-bis(diphenylphosphino)thienylene}Cl₂]₂ (1). To a solution of 2,5-bis(diphenylphosphino)thienylene (1.4 g, 3.0 mmol) in benzene (20 mL) under N₂ atmosphere at room temperature was added [Pd(CH₃CN)₂Cl₂] (0.8 g, 3.0 mmol). After stirring for 4 h at room temperature, the precipitated yellow solids were filtered and washed with ethyl ether. Pure [Pd{2,5-bis(diphenylphosphino)thienylene}Cl₂]₂ (**1**) was obtained from diffusion of ethyl acetate into the CH₂Cl₂ solution of the crude **1** as yellow rhombic crystals. Yield: 1.7 g (94%). Mp: 268.3–268.5 °C (decomp). IR: 357 cm⁻¹. ¹H NMR: δ 7.62–7.38 (m, 60H), 7.22 (s, 4H). ³¹P{¹H} NMR: δ 12.86(s). Anal. Calcd for C₅₆H₄₄Cl₄P₄Pd₂S₂: C, 53.40; H, 3.52. Found: C, 53.32; H, 3.58%.

[Pd{5,5'-bis(diphenylphosphanyl)[2,2']bithienylene}Cl₂]₂ (2). The title compound was prepared in the same manner as described for the preparation of **1** by replacing 2,5-bis(diphenylphosphino)thienylene with 5,5'-bis(diphenylphosphanyl)[2,2']bithienylene (1.6 g, 3.0 mmol). The product was obtained as yellow rhombic crystals. Yield: 1.9 g (90%). Mp: 273.5–274.5 °C (decomp.). IR: 357 cm⁻¹. ¹H NMR: δ 7.77–7.10 (m, 68H). ³¹P{¹H} NMR: δ 22.30(s). Anal. Calcd for C₆₄H₄₈Cl₄P₄Pd₂S₄: C, 53.99; H, 3.40. Found: C, 53.86; H, 3.53%.

[Pd{5,5''-bis(diphenylphosphanyl)[2,2':5',2'']terthienylene}Cl₂]₂ (3). The title compound was prepared in the same manner as described for the preparation of **1** by replacing 2,5-bis(diphenylphosphino)thienylene with 5,5''-bis(diphenylphosphanyl)[2,2':5',2'']terthienylene (1.9 g, 3.0 mmol). The product was obtained as yellow rhombic crystals. Yield: 2.2 g (92%). Mp: 275.0–275.1 °C (decomp.). IR: 357 cm⁻¹. ¹H NMR: δ 7.67–7.12 (m, 72H). ³¹P{¹H} NMR: δ 13.13(s). Anal. Calcd for C₇₂H₅₂Cl₄P₄Pd₂S₆: C, 54.45; H, 3.30. Found: C, 54.36; H, 3.38%.

Results and Discussion

Synthesis. The metallamacrocycles **1–3** were prepared by the reaction of diphenylphosphino oligothiénylene with [Pd(CH₃CN)₂Cl₂] in benzene in 90–94% yields as illustrated



Scheme 1. reagents and condition: (i) [Pd(CH₃CN)₂Cl₂], benzene, r.t. 4 h.

in Scheme 1. They are stable in the air, and soluble in most of polar organic solvents such as CHCl₃, pyridine, NMP, DMSO, and THF. Structural confirmations of our new compounds come from various spectroscopic and analytical techniques. For instance, they exhibit a characteristic IR band at about 357 cm⁻¹ assignable to the Pd–Cl stretch, which is common in a square planar Pd(II)-bis(phosphine) complex.^{27,28} Their ³¹P NMR spectra show a typical low-field resonance at 12.86, 22.30, and 13.30 ppm, respectively, for **1**, **2**, and **3**. As the ³¹P NMR for *cis*-PdCl₂(phosphine)₂ complexes are known to exhibit a chemical shift in the more deshielding area than its *trans* counterparts,¹⁹ the geometry of **1** and **3** can be suggested to be *trans* while that of **2** would be *cis*. More definitive structural confirmation comes from their X-ray crystallographic data (*vide infra*).

Molecular Structures. Crystals of **1** suitable for single-crystal X-ray diffraction studies were grown by the slow diffusion of ethyl acetate into a solution of the compound in dichloromethane. It crystallizes in the $P2_1/n$ space group with C_{2h} symmetry. The X-ray structure is shown in Figure 1 and the selected bond lengths, bond angles, and torsional

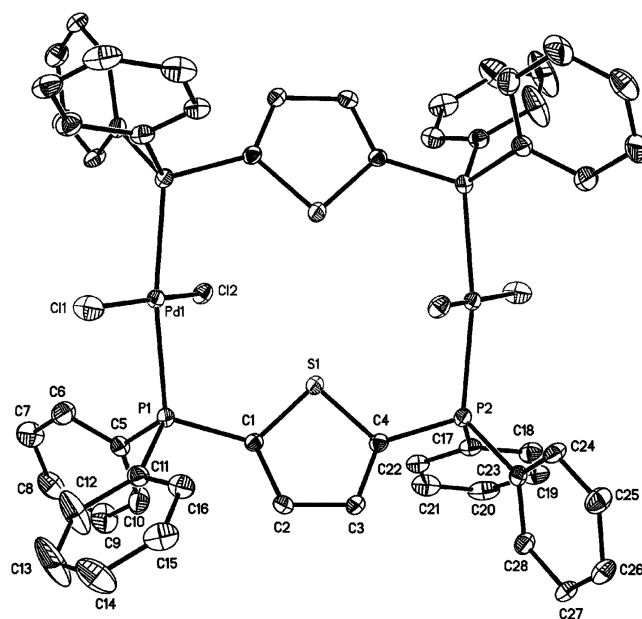


Figure 1. Molecular structure of **1** with atomic labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.

Table 1. Crystal data and structure refinement for **1**

Formula	C ₅₆ H ₄₄ C ₁₄ P ₄ Pd ₂ S ₂
MW	1259.51
T/K	173(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
a / Å	12.0737(13)
b / Å	17.1993(18)
c / Å	13.0951(14)
α / °	90
β / °	101.505(2)
γ / °	90
V / Å ³	2664.7(5)
Z	4
μ (Mo-K α) / mm ⁻¹	1.111
Crystal size / mm ³	0.40 × 0.20 × 0.10 mm ³
Absorption correction	SADABS
T _{min.}	0.3351
T _{max.}	0.2167
Reflections collected	16961
Independent reflections	6173
Data/restraints/parameters	6173/0/307
Goodness-of-fit on F ²	0.991
Final R1, wR2 [I > 2σ(I)]	0.0451, 0.0746
all data	0.1054, 0.0906

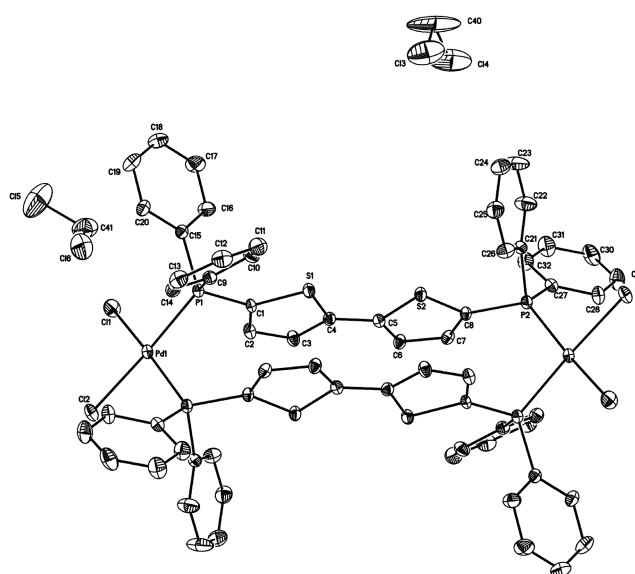
Table 2. Selected bond lengths (Å) and angles (°) for **1**

Pd(1)-Cl(1)	2.268(1)	P(1)-C(1)	1.812(4)
Pd(1)-Cl(2)	2.313(1)	P(2)-C(4)	1.803(4)
Pd(1)-P(1)	2.317(1)		
Cl(1)-Pd(1)-Cl(2)	171.28(5)	P(1)-Pd(1)-P(2)#1	171.00(4)
Cl(2)-Pd(1)-P(1)	87.28(4)	C(1)-P(1)-Pd(1)	111.22(14)
Cl(1)-Pd(1)-P(1)	91.39(4)	S(1)-C(1)-P(1)	122.4(2)
C(2)-C(1)-P(1)	126.5(3)	S(1)-C(4)-P(2)	118.8(2)
C(3)-C(4)-P(2)	129.6(3)		
Pd(1)-P(1)-C(1)-S(1)	-18.3(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+2

angles outlined in Table 2. The palladium atom is coordinated in a distorted square planar geometry with a *trans* arrangement of two P-donors and two Cl atoms. The average Pd-Cl and Pd-P bond lengths are comparable with those observed in other phosphinopalladium(II) chloride complexes.²⁹⁻³¹ Both thienyl sulfur atoms point inwards the molecular cavity. A pseudo-rectangular geometry where the four corners are occupied P atoms are revealed with a dimension of *ca.* 5.95 × 4.64 Å. The Pd...Pd distance and the distance between the centroids of the thienyl rings are 6.296(9) Å and 6.10 Å, respectively. The thienyl ring is tilted by 26.16(8)^o with respect to the P-P-P-P plane.

Crystals of **2** suitable for single-crystal X-ray diffraction studies were also grown by the slow diffusion ethyl acetate

**Figure 2.** Molecular structure of **2** with atomic labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.**Table 3.** Crystal data for **2**

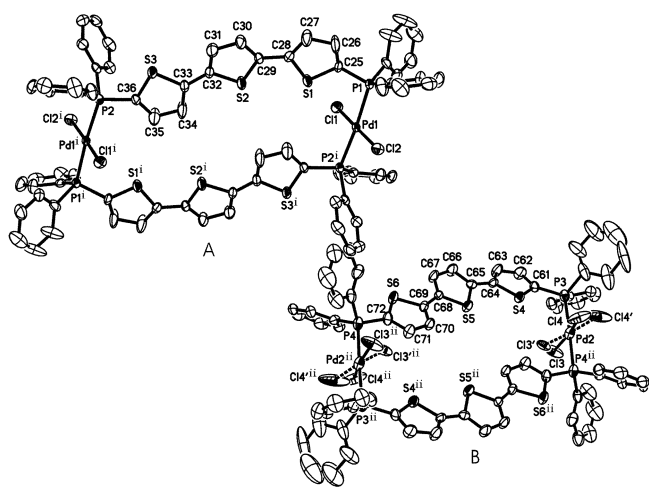
Formula	C ₆₄ H ₄₈ Cl ₄ P ₄ Pd ₂ S ₄
MW	1763.53
T/K	298(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a / Å	10.4353(19)
b / Å	13.482(3)
c / Å	13.816(3)
α / °	108.027(4)
β / °	90.461(4)
γ / °	93.261(4)
V / Å ³	1844.7(6)
Z	2
μ (Mo-K α) / mm ⁻¹	1.162
Crystal size / mm ³	0.03 × 0.15 × 0.4 mm ³
Absorption correction	SADABS
T _{min.}	0.2986
T _{max.}	0.3773
Reflections collected	11925
Independent reflections	8291
Data/restraints/parameters	8291/0/406
Goodness-of-fit on F ²	0.726
Final R1, wR2 [I > 2σ(I)]	0.0554, 0.1241
all data	0.1538, 0.1711

into a solution of the compound in dichloromethane. It crystallizes in the *P*-1 space group with an inversion center of symmetry. The crystal structure is shown in Figure 2 and the crystallographic data summarized in Table 3. The selected bond lengths, bond angles, and torsional angle are outlined in Table 4. It is worth noting that the compound **2** adopts a *cis* geometry around the Pd center in contrast to **1** and **3** where a *trans* geometry is preferred. As noted above,

Table 4. Selected bond lengths (Å) and angles (°) for **2**

Pd(1)-P(1)	2.259(1)	Pd(1)-Cl(2)	2.345(1)
Pd(1)-P(2)#1	2.295(2)	P(1)-C(1)	1.787(6)
Pd(1)-Cl(1)	2.322(2)	P(2)-C(8)	1.811(7)
P(1)-Pd(1)-P(2)#1	96.34(7)	P(1)-Pd(1)-Cl(2)	176.84(8)
P(1)-Pd(1)-Cl(1)	88.77(7)	C(1)-P(1)-Pd(1)	106.3(2)
P(2)#1-Pd(1)-Cl(1)	168.55(8)	Cl(1)-Pd(1)-Cl(2)	90.26(8)
C(8)-P(2)-Pd(1)#1	120.1(2)	S(1)-C(1)-P(1)	128.7(4)
C(7)-C(8)-P(2)	128.9(5)	S(2)-C(8)-P(2)	121.0(4)
Pd(1)-P(1)-C(1)-S(1)	-149.15(36)	S(1)-C(4)-C(5)-S(2)	-1.42(73)
S(2)-C(8)-P(2)-Pd(1)#1	89.48(38)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+2, -z+2$

**Figure 3.** Molecular structure of **3A** and **3B** with atomic labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.

the geometrical aspects of **1-3** are consistent with the corresponding ³¹P NMR data. The average Pd-Cl and Pd-P bond lengths in **2** are comparable to those found in **1**. The pseudo-rectangular shape in which four corners are occupied by P atoms has a dimension of *ca.* 9.47 × 3.39 Å. All thienyl sulfur atoms point outwards from the molecular cavity. The bithiophene ligand unit adopts a *syn* arrangement in the thienyl/thienyl orientation, which is in contrast to the *anti* conformation observed for the 2,2'-bithiophene and free 2,5'-bis(diphenylphino)-2,2'-bithiophene ligand in the solid state.²³ The torsion angles about C(4)-C(5) is -1.42(73)°. The Pd...Pd distance is found to be 11.881(1) Å. The average distance between the centroids of the cofacial thienyl rings is found to be 3.91 Å. Due to the *cis*-arrangement of the two P-donors at the palladium atom, the thienyl rings in **2** are p-stacked more tightly than they are in **1** and **3**.

Compound **3** crystallizes in the *P*-1 space group with a inversion center of symmetry. The crystal structure is shown in Figure 3 and the crystallographic data summarized in Table 5. The selected bond lengths, bond angles, and torsion angles are listed in Table 6. The unit cell is found to contain

Table 5. Crystal data for **3**

Formula	C ₇₂ H ₅₂ Cl ₄ P ₄ Pd ₂ S ₆
MW	1587.98
T/K	100(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	10.2634(4)
<i>b</i> / Å	19.7855(9)
<i>c</i> / Å	21.0851(9)
α / °	63.1010(10)
β / °	86.5880(10)
γ / °	81.2280(10)
<i>V</i> / Å ³	3773.5(3)
<i>Z</i>	2
μ (Mo-K α) / mm ⁻¹	0.908
Crystal size / mm ³	0.40 × 0.30 × 0.05
Absorption correction	SADABS
<i>T</i> _{min.}	0.559888
<i>T</i> _{max.}	0.862111
Reflections collected	45326
Independent reflections	17654
Data/restraints/parameters	17654 / 0 / 812
Goodness-of-fit on <i>F</i> ²	1.065
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0717, 0.1441
all data	0.1060, 0.1596

Table 6. Selected bond lengths (Å) and angles (°) for **3**

Pd(1)-Cl(1)	2.312(1)	Pd(2)-Cl(3)	2.369(4)
Pd(2)-Cl(3')	2.164(8)	Pd(1)-Cl(2)	2.276(1)
Pd(2)-Cl(4)	2.194(4)	Pd(2)-Cl(4')	2.384(7)
Pd(1)-P(1)	2.330(1)	Pd(2)-P(3)	2.320(1)
Pd(1)-P(2) ⁱ	2.328(1)	Pd(2)-P(4) ⁱⁱ	2.331(1)
P(1)-C(25)	1.799(5)	P(2)-C(36)	1.791(5)
P(3)-C(61)	1.796(6)	P(4)-C(72)	1.801(5)
Cl(1)-Pd(1)-Cl(2)	176.81(6)	Cl(3)-Pd(2)-Cl(4)	169.79(19)
Cl(3')-Pd(2)-Cl(4')	75.7(4)	Cl(1)-Pd(1)-P(1)	89.78(5)
Cl(3)-Pd(2)-P(3)	91.83(15)	Cl(3')-Pd(2)-P(3)	87.34(17)
Cl(1)-Pd(1)-P(2) ⁱ	86.71(5)	Cl(3)-Pd(2)-P(4) ⁱⁱ	89.40(14)
Cl(3')-Pd(2)-P(4) ⁱⁱ	92.87(18)	Cl(2)-Pd(1)-P(1)	91.45(5)
Cl(4)-Pd(2)-P(3)	91.50(12)	Cl(4')-Pd(2)-P(3)	88.9(2)
Cl(2)-Pd(1)-P(2) ⁱ	92.22(5)	Cl(4)-Pd(2)-P(4) ⁱⁱ	86.83(12)
Cl(4')-Pd(2)-P(4) ⁱⁱ	90.8(2)	P(1)-Pd(1)-P(2) ⁱ	175.26(5)
P(3)-Pd(2)-P(4) ⁱⁱ	176.99(6)	Pd(1)-P(1)-C(25)	106.60(18)
Pd(2)-P(3)-C(61)	107.6(2)	Pd(1) ⁱ -P(2)-C(36)	111.54(17)
Pd(2) ⁱⁱ -P(4)-C(72)	107.7(2)		
S(1)-C(28)-C(29)-S(2)	-6.7(7)	S(4)-C(64)-C(65)-S(5)	-15.7(7)
S(2)-C(32)-C(33)-S(3)	-167.8(4)	S(5)-C(68)-C(69)-S(6)	-170.6(3)
S(3)-C(36)-P2-Pd(1) ⁱ	15.7(4)	S(6)-C(72)-P(4)-Pd(2) ⁱⁱ	160.9(4)
Pd(2)-P(3)-C(61)-S(4)	27.9(4)		

Symmetry transformations used to generate equivalent atoms: i) $-x+1, -y, -z+1$; ii) $-x+2, -y+1, -z+2$. Since the large positive (1.46 eÅ⁻³) and negative (-1.56 eÅ⁻³) difference Fourier peaks are located at short distances from Pd2 (0.83 and 0.75 Å, respectively), these peaks can be attributed to ghosts of the heavy Pd atom.

Table 7. Absorption data of the ligands and **1-3** in THF

Compounds	Absorption λ_{\max} ($\epsilon M^{-1} \text{ cm}^{-1}$)
diphenylphosphinothienylene	295 (1.3×10^4)
diphenylphosphinobithienylene	348 (2.0×10^4)
diphenylphosphinoterthienylene	389 (3.0×10^4)
1	273 (1.5×10^4)
2	333 (1.7×10^4)
3	376 (1.7×10^4)

two crystallographically independent metallamacrocycles (A and B) incorporating a similar Pd coordination environment. Each palladium atom adopts a distorted square planar geometry with a *trans* arrangement of two P-donors and two Cl atoms. The average Pd-Cl and Pd-P bond lengths are comparable with those in **1** and **2**. In the structure **3B**, two chloride atoms (Cl3 and Cl4) are disordered over two sites with occupancies of 0.65 and 0.35, respectively. Each metallamacrocycle may be considered to be a pseudo-rectangle in which four corners are occupied by P atoms with a dimension of *ca.* $13.2 \times 4.7 \text{ \AA}$. The Pd...Pd distances found in **3A** and **3B** are 13.3144(9) and 13.436(1) \AA , respectively. The average distances between the centroids of the cofacial thienyl rings of **3A** and **3B** are measured to be 6.64 \AA and 6.98 \AA , respectively. The terthienyl ligands adopt a planar *syn/anti* arrangement in the thienyl/thienyl/thienyl orientation in sequence with the torsion angles between the sulfur atoms (S-C-C-S): 6.7(7) $^\circ$ and 167.8(4) $^\circ$ for A, 15.7(7) $^\circ$ and 170.6(3) $^\circ$ for B. The conventional terthiophene systems show commonly an *anti-anti*-parallel conformation.^{32,33}

Absorption Properties. Table 7 exhibits the UV-vis spectral data for diphenylphosphinooligothienylene ligands and **1-3** in THF. As expected, a red shift is observed for both ligands and metallamacrocycles as the number of thienyl groups increases.^{34,35}

Conclusion

Dimeric metallamacrocycles **1-3** were synthesized from the reaction of $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$ with α,ω -bis-(diphenylphosphino)oligothienylene in high yields. They were fully characterized by analytical and various spectroscopic techniques including X-ray crystallography.

Supplementary Material. Crystallographic data of the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 245978-245980 for **1-3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

References

1. Nguyen, P.; Gómez-Elipé, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.

2. Lehn, J.-M. *Supramolecular Chemistry*; VCH Publishers: New York, 1995.
3. Vogtle, F. *Supramolecular Chemistry*; Wiley: Chichester, 1991.
4. Swagers, G. F.; Malefsete, T. J. *Chem. Rev.* **2000**, *100*, 3483.
5. Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972.
6. Holliday, B. J.; Mirkin, C. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 2022.
7. Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
8. Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759.
9. *Comprehensive Supramolecular Chemistry*; Fujita, M.; Lehn, J.-M., Eds.; Pergamon: New York, 1996; Vol. 9, p 253.
10. *Comprehensive Supramolecular Chemistry*; Sauvage, J.-P.; Hosseini, M. W., Eds.; Pergamon: Oxford, 1996; Vol. 9.
11. Liu, X.; Stern, C. L.; Mirkin, C. A. *Organometallics* **2002**, *21*, 1017.
12. Stang, P. J.; Cao, D. H.; Chen, K.; Garay, G. M.; Muddiman, D. C.; Smith, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5163.
13. Rauter, H.; Mutikainen, I.; Blomberg, M.; Lock, C. J. L.; Omar-Ochoa, P.; Freisinger, E.; Randaccio, L.; Chiarparin, E.; Lippert, B. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1296.
14. Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.
15. Saalfrank, R. W.; Trummer, S.; Krautscheid, H.; Schunemann, V.; Trautwein, A. X.; Hien, S.; Stadler, C.; Daub, J. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2206.
16. Schnebeck, R.-D.; Randaccio, L.; Zangrando, E.; Lippert, B. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 119.
17. Baxter, P. N. W.; Lehn, J.-M.; DeCian, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69.
18. Kramer, R.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 990.
19. Myrex, R. D.; Colbert, C. S.; Gray, G. M. *Organometallics* **2004**, *23*, 409.
20. Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.
21. Roncali, J. *J. Mater. Chem.* **1999**, *9*, 1875.
22. Xu, W.; Wang, Q.; Wurz, R. P. US 6,239,237 BI.
23. Field, J. S.; Haines, R. J.; Lakoba, E. I.; Sosabowski, M. H. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3352.
24. Bruker: *Area Detector Control and Integration Software*. Version 5.0, in SMART and SAINT; Bruker Analytical X-ray Instruments Inc.: Wisconsin, Madison, 1997.
25. Sheldrick, G. M. *SADABS: Empirical Absorption and Correction Software*; University of Göttingen: Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1999.
26. Sheldrick, G. M. *SHEXTL: Programs for Crystal Structure Analysis*; University of Göttingen: Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
27. *Comprehensive Organometallic Chemistry: the Synthesis, Reactions and Structures of Organometallic Compounds*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 6.
28. *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, G. A.; Wilkinson, G., Eds.; A Review of the Literature 1982-1994: Pergamon: Oxford, 1995; Vol. 9.
29. Clot, O.; Akahori, Y.; Moorlag, C.; Leznoff, D. B.; Wolf, M. O.; Batchelor, R. J.; Patrick, B. O.; Ishii, M. *Inorg. Chem.* **2003**, *42*, 2704.
30. Clot, O.; Wolf, M. O.; Patrick, B. O. *J. Am. Chem. Soc.* **2001**, *123*, 9963.
31. Clot, O.; Wolf, M. O.; Patrick, B. O. *J. Am. Chem. Soc.* **2000**, *122*, 10456.
32. Weinberger, D. A.; Higgins, T. B.; Mirkin, C. A.; Stern, C. L.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 2503.
33. Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1597.
34. Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 10217.
35. Kang, B. S.; Seo, M.-L.; Jun, Y. S.; Lee, C. K.; Shin, S. C. *Chem. Commun.* **1996**, 167.