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Palladium(II) Complexes of N-(2-ThienyImethylidene)aniline Derivatives

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Coordination reactions of *N*-(2-thienylmethylidene)aniline derivatives, L, with PdCl₂ or $[PdCl_4]^2$ in ethanol yield stable complexes of the type *trans*-(L)₂PdCl₂ with the azomethine nitrogen atoms as σ donors. These are not readily convertible to *othor*-palladated complexes. An X-ray crystallographic study of the complex (L₂)₂PdCl₂ reveals a centrosymmetric geometry. The structure is in the triclinic space group P I with a = 8.633(2) Å, b = 12.759(3) Å, c = 8.398(2) Å, $\alpha = 96.65(5)^\circ$, $\beta = 111.47(5)^\circ$, $\gamma = 101.28(6)^\circ$, and Z = 1. The final R factor is 0.043 (Rw = 0.044) for 2396 observed reflections. There is no real bonding between a thiophene sulfur atom and a central palladium ion. However, a long distance interaction between S and Pd does exist.

INTRODUCTION

It is known that the reaction of Pd(OAc)₂ on *N*-(2methylbenzilidene)aniline gives only the five-membered endo derivative with a Pd-C aromatic bond under mild condition.¹ Cyclometalation reaction of *N*-donor ligands, including *N*-benzilidene amines derivatives, by using Pd(OAc)₂, PdCl₄⁼, PdCl₂(RCN)₂, etc. have been extensively studied,² but the factors that control the process are not thoroughly understood. In general, an intramolecular electrophilic attack of the metal at the carbon atom, a strong tendency to form five-membered rings, and preferential activation of aromatic over aliphatic C-H bonds are widely accepted.

Recently we reported the results of the reaction of Fe₂(CO)₉ on *N*-(2-thienylmethylidene)aniline derivatives.³ Cyclometalation occurred at the β -carbon of the thienyl ring upon the coordination of the azomethine nitrogen to one of the iron centers. A similar result had been found in the reaction of Fe₂(CO)₉ on the analogous ligand *N*-bezilidene-anililene.⁴ Isomeric species *N*-(3-thienylmethylidene)aniline was also found to undergo orthopalladation in high yield at α -carbon of the thienyl ring.⁵ However, *N*-methyl-(2-thienylmethylidene)amine did not undergo orthopalladation in a similar way and was proposed to act as a sulfur-donor monodentate ligand.⁶

In connection with our previous work on the metal complexes from thiophene-containing Schiff bases, we have investigated the reaction of palladium(II) on N-(2-thienylmethylidene)aniline derivatives. Reported herein are the results of the investigation. Although orthopalladation does not occur as usual in this system, from the structure determination and spectroscopic data, the coordination mode of Ndonor instead of S-donor monodentate ligands is confirmed.

RESULTS AND DISCUSSION

The reactions of palladium chloride with thiophenecontained Schiff bases, N-(2-thienylmethylidene)aniline derivatives (L), derived by condensing 2-thiophenecarboxaldehyde derivatives with aniline, in anhydrous alcohol at room temperature is represented by the following equation.



The same results were obtained from the reactions of the ligands with K_2PdCl_4 . However, no reaction occurred when the ligands were treated with $Pd(OAc)_2/CH_3CN$, $Pd(acac)_2$, or $Pd(COD)Cl_2$. The ligands, L, yield only complexes of the type *trans*-[PdCl_2L_2] with the azomethine nitrogen atoms as σ donor under all conditions tried. These are not readily convertible to the *ortho*-palladated complexes. Treatment with base failed to eliminate hydrogen chloride from the complexes to yield the desired metallated compounds. The physical properties and analytical data for the complexes are given in Table 1. All complexes are air-

Complex	Color	Mp (°C)	Found/(Calcd) %				Λ_{M}^{*} (Ohm ⁻¹ cm ² mol ⁻¹)	
			C	н	N	S	CH ₃ OH	CH₃CN
$(L_1)_2PdCl_2$	Yellow	168-169	47.85	3.36	5.17	11.52	0.09	0.07
$(L_1)_2$ PdCl ₂	Yellow	170 ^b	(47.51) 49.58	3.84	4.78	10.98	0.09	0.08
$(L_1)_2$ PdCl ₂	Yellow	196-197	(49.74) 47.20 (47.14)	(3.80) 3.74 (3.60)	(4.84) 5.53 (4.58)	(11.05) 10.41 (10.47)	0.11	0.14

Table 1. Physical and Analytical Data for Complexes

^a At 25 °C, 5.00×10^{-4} M.

^b Decomposition point.

stable and slowly hydrolyzed upon contact with water. Electrical conductance measurements in methanol and acetonitrile show that all complexes are non-electrolyte.

An orange prism crystal of $(L_2)_2$ PdCl₂, crystallized from chloroform, with dimensions of $0.33 \times 0.41 \times 0.55$ mm was subjected to a single-crystal x-ray analysis. Crystal and data collection parameters are shown in Table 2. An ORTEP diagram is shown in Fig. 1. Selected bond distances and bond angles are tabulated in Table 3. It is readily seen, from Fig. 1, that the complex $(L_2)_2$ PdCl₂ is in its *trans* form and the coordinated ligand, L₂, behaves as a N-donor monodentate. The isolated $PdCl_2N_2$ rhombohedron is planar and the complex is centrosymmetric about a crystallographic inversion. The coordination environment around the palladium center, which is four-coordinate, involves two nitrogen atoms (of azomethine moiety) from two ligands and two chlorides. The geometric configuration of the coordination sphere may be best described as a distorted square-planar arrangement. Two pairs of bond angles about the central palladium, Cl(1)-Pd-N(1) and Cl(1)-Pd-N(1*), are 88.4(1) and 91.6(1)°, respectively. The bond distance from the central palladium to the azomethine nitrogen is 2.019(4) Å, and that

Table 2. Crystal and Data Collection Parameters for Complex (L₂)₂PdCl₂·CHCl₃

formula	C25H23Cl5N2PdS2
fw	699.29
Cryst syst	triclinic
space group	P 1 (No. 2)
a (Å)	8.633(2)
b (Å)	12.759(3)
c (Å)	8.398(2)
α (deg)	96.65(5)
β (deg)	111.47(5)
$\gamma(deg)$	101.28(6)
$V(\dot{A}^3)$	839.4(7)
Z	1
$D_{calc} (g/cm^3)$	1.383
Cryst. size (mm)	$0.33 \times 0.41 \times 0.55$
Temp (°K)	297.0
20 _{max} (deg)	50.1
scan type	ω-20
no. of refins measd: total, unique	3206, 2989
no. of obsd refins: $(I > 3.00 \sigma(I))$	2396
no. of variables	178
F000	350.00
μ , (MoK α)(cm ⁻¹)	10.90
R	0.043
R.w	0.044



Fig. 1. ORTEP diagram of complex $(L_2)_2$ PdCl₂ at the 50% probability level.

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Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of (L₂)₂PdCl₂

Pd-Cl	2.303(2)	Pd-N	2.019(4)
N(1)-C(6)	1.280(6)	N(1)-C(7)	1.442(6)
C(5)-C(6)	1.425(7)	S(1)-C(5)	1.715(6)
S(1)-C(2)	1.728(6)	C(1)-C(2)	1.490(9)
C(2)-C(3)	1.327(9)	C(3)-C(4)	1.390(9)
C(4)-C(5)	1.391(7)	Pd·····S	3.15
Cl(1)-Pd-Cl(1*)	180.0	N(1)-Pd-N(1)	180.0
Cl(1)-Pd-N(1)	88.4(1)	Cl(1)-Pd-N(1*)	91.6(1)
Pd-N(1)-C(6)	126.3(4)	Pd-N(1)-C(7)	114.4(3)
C(6)-N(1)-C(7)	119.0(5)	N(1)-C(6)-C(5)	128.3(5)
S(1)-C(5)-C(6)	126.5(4)	C(2)-S(1)-C(5)	91.8(3)
S(1)-C(5)-C(4)	109.6(5)	S(1)-C(2)-C(3)	111.7(5)
C(2)-C(3)-C(4)	113.7(6)	C(3)-C(4)-C(5)	113.2(6)
N(1)-C(7)-C(8)	119.5(5)	N(1)-C7)-C(12)	119.2(5)

to the chlorine is 2.303(2) Å. The bond angles about the coordinated nitrogen, Pd-N(1)-C(6), Pd-N(1)-C(7), and C(6)-N(1)-C(7), are 126.3(4)°, 114.4(3)°, and 119.0(5)°, respectively, indicating that the azomethine nitrogen is well kept in its sp² configuration that makes the Pd, N(1), C(6), and C(7) atoms perfectly coplanar. The C(6)-N bond length is 1.280(6), which keeps the C-N bond in its double bond feature,⁷ and C(7)-N bond length is 1.442(6) Å. With its nitrogen atom, the azomethine plane perpendicularly coordinates to the central palladium (with a dihedral angle of 92.11°). Bond angles and bond distances in the benzene rings and in the thienyl rings are in agreement with the values in the literature.^{3,8} The thienyl plane forms a dihedral angle of 8.40° to the azomethine plane and is almost perpendicular to the PdCl₂N₂ coordination plane (with a dihedral angle of 86.95°). The sulfur atoms in the thienyl rings point directly, from the top and underside of the coordination plane, to the palladium center with a S...Pd distance of 3.15 Å, shorter than the sum of their van der Waals radii 3.4 Å, and form a weak interaction with the palladium atom. The long distance interactions complete the coordination polyhedron to an elongated distorted octahedron.

While no direct structural evidence is available for the other complexes, the physical properties as well as spectroscopic data, as shown in Table 4, suggested that the other two complexes, $(L_1)_2PdCl_2$ and $(L_3)_2PdCl_2$, have similar structures to that of $(L_2)_2PdCl_2$ as described above. The ¹H NMR spectra of complexes show about the same patterns as that of their corresponding free ligands. In each complex, while the imine proton shows an up-field chemical shift, all thienyl protons show a down-field chemical shift relative to the free ligand. This phenomenon is attributed to the coordination of the azomethine nitrogen and the existence of a long-distance interaction between the sulfur of the thienyl ring and the central palladium ion.

Comparison of the IR spectra of complexes with that of free ligands shows no significant change in the v(C=N)

Compound IR^{b} (v, cm⁻¹) ¹H NMR^a (δ, ppm) MS(m/z)imine thiophene (J/Hz) Me/OH O-H C=N Pd-N Pd-O 8.56 187 (M⁺) L_1 7.49 (d, 5.1) 1617 7.26 (d, 3.9) 7.13 (dd, 4.5, 3.3) $(L_1)_2 PdCl_2$ 8.10 1610 441 336 550, 552, 554 (M⁺); 7.76 (d, 3.9) 7.66 (d, 4.8) 515, 517 (M⁺-Cl); 292 (M*-2CI-L-1), 187 (L) 7.16 (dd, 4.5, 4.2) L_2 8.46 7.29 (d, 3.6) 2.55 1614 201 (M⁺) 6.80 (d, 3.6) 577, 579 (M⁺-1); 543, 545 $(L_2)_2 PdCl_2$ 2.55 1611 447 334 7.95 7.46 (d, 3.9) (M⁺-Cl); 507 (M⁺-2Cl-1); 6.83 (d, 3.3) 306 (M*-2Cl-L-1); 201 (L) 217 (M⁺) 8.71 7.47 (d, 3.6) 2.51/8.98 3357 1628 6.91 (d, 3.9) 610, 612 (M⁺); 575, 577 445 336 $(L_3)_2 PdCl_2$ 8.30 2.49/9.18 3257 1621 7.77 (d, 3.6) (M⁺-Cl); 539 (M⁺-2Cl-1); 7.06 (d, 3.9) 218 (L+1)

Table 4. Selected ¹H NMR, IR, and Mass Spectral Data for Ligands and Complexes

^a Except for L₃ and $(L_3)_2$ PdCl₂ (d⁶DMSO), all spectra were recorded in CDCl₃ with TMS as internal standard: d = doublet, dd = doublet of doublet.

^b Spectra were recorded in KBr film.

stretching band. They all exhibit a v(C=N) stretching in the range of 1611-1625 cm⁻¹, indicating a C=N double bond character both in ligands and complexes. Saleem and Hadali⁶ ruled out the coordination of palladium to the azomethine nitrogen in an analogous complex, trans-(2thiophene-CH=N-CH₃)₂PdCl₂, based on the fact that there is no significant change in v(C=N) stretching upon coordination of the ligand. They proposed a thienyl sulfur-palladium coordination mode for the complex because the low Lewis basicity of the azomethine nitrogen that makes the ligand act as an unidentate through the thienyl sulfur. However, since the absorption associated with the stretching vibration of the long (thienyl)-CH=N- conjugate chain, only a slight shift of the v(C=N) stretching band upon the coordination of the azomethine nitrogen of the ligand to the metal is possible and reasonable.^{8c,9} The electron distribution in thiophene or 2-thiophenecarboxaldehyde is considerably affected by π electron delocalization associated with the contribution of highly polar resonance structures. The compound might be expected to act as a bidentate ligand in forming a metal chelate complex, but the low electron density on the thiophene sulfur atom resulting from resonance weakens the donor property of the sulfur atom, and as a result, attempts to form a metal chelate containing sulfur from the compound is very difficult. However, metal chelates with thiophene-contained Schiff bases are possible due to the presence of an azomethine group, although spectral studies indicated that the formation of sulfur-to-metal bond in the complex does not effectively block the resonance in the thiophene ring due to the second pair of sulfur pz electrons, and the delocalization of these electrons is not appreciably decreased by chelation.¹⁰ Obviously, the Lewis basicity of the azomethine nitrogen is stronger than that of thiophene sulfur. Therefore, this type of ligand may coordinate with 1:1, 1:2, or 2:2 metal to ligand ratios with or without sulfur-to-metal bonding.¹¹ The feature of the N-donor coordination mode is further supported by the appearance of a v(Pd-N) band at 441-447 cm^{-1} . All three complexes also show v(Pd-Cl) stretching bands at 334-336 cm⁻¹. The appearance of an O-H stretching at 3257 cm⁻¹ in complex (L₃)₂PdCl₂ (relative to a 3345 cm^{-1} band in the free ligand L₃) indicates that the hydrogen is not dissociated from the hydroxyl group during the course of ligand coordination.

EXPERIMENTAL SECTION

All chemicals were reagent grade and used without purification. Solvents were dried and distilled under nitrogen prior to use by standard methods. All the reactions were carried out under an atmosphere of purified nitrogen. The NMR spectra were recorded on a Varian-300 NMR spectrometer (¹H, 299.95 MHz; ¹³C, 75.43 MHz). Chemical shifts were referenced to TMS, and deuterated chloroform or DMSO was used as a solvent and as a secondary reference. Mass spectra were obtained on a VG-Biotech Quattro 5022 spectrometer. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer. Elemental analyses were performed using a Heraeus CHN-O-rapid analyzer. Electric conductance was measured by a Basic DCM-3 digital conductivity meter, with a dip type conductivity cell of 0.1 cell constant. Crystal for X-ray diffraction was obtained by recrystallization of the species from a chloroform solution at 25 °C. A single crystal was mounted on a glass fiber, and the X-ray diffraction intensity data were measured on a Rigaku AFC7S diffractometer at room temperature.

Synthesis of Ligands (L)

N-(2-Thienylmethylidene)aniline (L₁) and N-(5methyl-2-thienylmethylidene)aniline (L_2) were prepared as previously described.³ N-(5-methyl-2-thienylmethylidene)o-aminophenol (L3) was prepared in a similar way by refluxing equimolar quantities (20 mmol) of 5-methyl-2-thiophenecarboxaldehyde and o-aminophenol in 100 mL of absolute ethanol for 12 h. After the solvent was removed from the reaction mixture under vacuum, the residue was recrystallized from a 60 mL of ethanol/n-hexane (1:5) solution to give 3.58 g (80% yield) of brown crystalline product L₃. Mp 75 °C. ¹H NMR (d⁶-DMSO): δ 8.98 (s, 1H), 8.71 (s, 1H), 7.47 (d, J = 3.6 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 7.02 (d, J= 7.8 Hz, 1H), 6.90 (d, J = 3.9 Hz, 1H), 6.88 (d, J = 7.2 Hz), 6.80 (t, J = 7.5 Hz, 1H), 2.51 (s, 3H). ¹³C NMR (d⁶-DMSO): δ 153.5, 150.8, 145.4, 141.0, 138.3, 133.7, 127.0, 126.9, 120.6, 119.8, 116.2, 15.7. IR (KBr film) v_{C=N}: 1628 cm⁻¹, v_{O-H} : 3357 cm⁻¹, MS (EI): m/z 217 (M⁺).

Synthesis of Complexes (L)₂PdCl₂

In a typical reaction, 4.60 mmol of ligand L and 2.30 mmol of $PdCl_2$ in 50 mL of anhydrous ethanol (for ligands L_1 and L_2) or methanol (for ligand L_3) was stirred under nitrogen atmosphere at room temperature for 3 days. The yellow solid thus precipitated was filtered and washed with méthanol and chloroform to give a pure complex product.

$(L_1)_2PdCl_2$

76% yield. Mp 168-169 °C. ¹H NMR (CDCI₃): δ 8.10 (s, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.75 (d, J = 3.9 Hz, 1H), 7.66 (d, J = 4.8 Hz, 1H), 7.48 (m, 3H), 7.16 (dd, J = 4.5, 4.2 Hz, 1H). ¹³C NMR (CDCI₃): δ 162.4, 153.0, 151.2, 140.6, 134.1, 129.0, 127.5, 126.3, 124.6. IR (KBr film) $v_{C=N}$: 1610

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cm⁻¹, v_{M-N} : 441 cm⁻¹, v_{M-Cl} : 336 cm⁻¹. MS (FAB): *m*/z 550, 552, 554 (M⁺), 515, 517 (M⁺ - Cl), 292 (M⁺ - L - 2Cl - 1), 187 (L⁺).

$(L_2)_2 PdCl_2$

78% yield. Mp 170-171 °C (decomp.). ¹H NMR (CDCl₃): δ 7.95 (s, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.48 (m, 3H), 7.46 (d, J = 3.3 Hz, 1H), 6.83 (d, J = 3.6 Hz, 1H), 2.47 (s, 3H). ¹³C NMR (CDCl₃): δ 163.0, 151.1, 139.7, 136.2, 136.0, 129.1, 127.9, 127.4, 124.4, 16.2. IR (KBr film) v_{C=N}: 1611 cm⁻¹, v_{M-N}: 447 cm⁻¹, v_{M-Cl}: 334 cm⁻¹. MS (FAB): m/z577, 579 (M⁺ - 1), 543, 545 (M⁺ - Cl), 507 (M⁺ - 2Cl - 1), 343, 341 (M⁺ - L - Cl - 1), 306 (M⁺ - L - 2Cl - 1), 201 (L⁺).

(L₃)₂PdCl₂

81% yield. Mp 196-191 °C. ¹H NMR (d⁶-DMSO): δ 8.30 (s, 1H), 7.95 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 3.6 Hz, 1H), 7.28 (t, J = 8.1 Hz, 1H), 7.06 (d, J = 3.9 Hz, 1H), 7.02 (m, 2H), 2.49 (s, 3H). ¹³C NMR (CDCl₃): δ 153.5, 150.8, 145.4, 141.0, 138.3, 133.7, 127.0, 126.9, 120.6, 119.8, 116.2, 15.8. IR (KBr film) v_{O-H}: 3257 cm⁻¹, v_{C=N}: 1621 cm⁻¹, v_{M-N}: 445 cm⁻¹, v_{M-C}: 336 cm⁻¹. MS (FAB): m/z 610, 612 (M⁺), 575, 577 (M⁺ - Cl), 539 (M⁺ - 2Cl - 1), 218 (L⁺ + 1).

Reactions of thiophene-contained Schiff bases, L_t , L_2 , and L_3 , with PdCL², under the same conditions gave exactly the same results as described above. No coordination reaction occurred when the ligands were treated with Pd(OAc)₂ in acetonitrile, Pd(acac)₂, or Pd(COD)Cl₂ in alcohol or in THF under the same conditions. Vigorous conditions or prolonged reaction time caused the hydrolysis of the ligands.

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Supplemental Material Available Upon Request

Text of atomic parameters, anisotropic displacement parameters, bond distances and bond angles, and structure diagram (13 pages).

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Key Words

Bis(N-(2-thienylmethylidene)aniline)dichloropalladate(II); Thiophene-contained Schiff base; N-(2thienylmethylidene)aniline; Palladium(II) complex; Crystal structure.

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