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# Synthesis and characterization of mononuclear and tetranuclear palladium(II) complexes with 2-(phenylmethyleneamino)benzenethiolate

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#### Abstract

Two palladium(II) complexes,  $[Pd(Hphbt-N,S)_2]$  (1; Hphbt = 2-(phenylmethyleneamino)benzenethiolate) and  $[Pd_4(phbt-C,N,S)_4]$  (2), were newly prepared. X-ray and <sup>1</sup>H NMR studies indicated the presence of Pd···H-C interaction in the mononuclear 1, which is assumed to play an important role in the cyclometalation reaction leading to the tetranuclear structure in 2. © 2002 Elsevier Science B.V. All rights reserved.

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# 1. Introduction

The chemistry of the activation of C-H bonds is undoubtedly one of the most advanced areas. In the field of C-H activation, the importance of the threecenter two-electron agostic interaction has been well recognized through many examples [1]. On the other hand, recently, there is an increasing body of evidence which shows interactions between electron-rich metal centers and hydrogen atoms, being hydrogen bonding of the three-center four-electron in character [2]. Previously, we reported that the hydrogen bonding-like  $Pd \cdots H-C$  interaction in the mononuclear palladium(II) complex,  $[Pd(H1-nabz-N,S)_2]$ , which is the precursor of the thiolato-bridged tetranuclear palladium(II) complex,  $[Pd_4(1-nabz-C,N,S)_4]$ , plays an important role in the cyclometalation reaction [3]. However, the recognition for the hydrogen bonding-like M···H-C interaction in cyclometalation reaction is still not enough.

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In this context, it is worthwhile to investigate whether a similar cyclometalation reaction could take place for palladium(II) complexes with a flexible pendant arm, instead of the rigid 1-naphthyl group in [Pd(H1-nabz- $N,S)_2$ ]. In this paper, we report on the synthesis and structural characterization of the mononuclear palladium(II) complex having phenyl groups as a pendant arm, [Pd(Hphbt- $N,S)_2$ ] (1), together with that of its cyclometalation product [Pd<sub>4</sub>(phbt- $C,N,S)_4$ ] (2).

## 2. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Reagents were commercial samples and were not purified further. The compound 2-phenylbenzothiazoline was prepared by literature methods [4].

The UV–Vis spectra were measured on a JASCO V-570 spectrophotometer. The <sup>1</sup>H NMR spectra were measured on a JEOL EX 270 instrument using tetramethylsilane as the internal standard ( $\delta = 0$ ). IR spectra were measured on a JASCO FT/IR-5000 instrument (4000–400 cm<sup>-1</sup>) using the Nujol mulls. Elemental analyses were performed at Osaka University.

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2.1. Synthesis

# 2.1.1. Synthesis of bis[2-

# (phenylmethyleneamino)benzenethiolato]palladium(II) [Pd(Hphbt-N,S)<sub>2</sub>] (1)

To an ethanol solution (20 cm<sup>3</sup>) of 2-phenylbenzothiazoline (0.43 g, 2.0 mmol) was added palladium(II) acetate (0.22 g, 1.0 mmol). The reaction mixture was refluxed for 20 min and cooled in a refrigerator overnight. The red-brown precipitate, which was spectroscopically pure (<sup>1</sup>H NMR), was collected by filtration and dried in vacuo. Yield, 0.34 g (64%). This crude precipitate (0.10 g) was recrystallized from chloroformdiethyl ether (yield, 0.04 g). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a 1,2-dichloroethane solution of 1. Found: C, 55.06; H, 3.68; N, 4.97%. Calc. for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>PdS<sub>2</sub>·1/3CHCl<sub>3</sub>: C, 55.41; H, 3.59; N, 4.91%. IR: v<sub>max</sub> cm<sup>-1</sup> (Nujol): 1599 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  = 7.95 (4H, d, J = 7.3, C<sub>aryl</sub>-H), 7.80 (2H, s, CH=N), 7.50 (2H, t, J =7.4,  $C_{aryl}$ -H), 7.43 (2H, dd, J = 7.9 and 1.3,  $C_{aryl}$ -H), 7.27 (4H, t, J = 7.7,  $C_{aryl}$ -H), 7.05 (2H, dt, J = 7.5 and 1.2,  $C_{aryl}$ -H), 6.83 (2H, dt, J = 7.7 and 1.3,  $C_{aryl}$ -H) and 6.57 (2H, d, J = 8.2 Hz,  $C_{aryl}$ -H). UV-Vis:  $v_{max}$ (CHCl<sub>3</sub>) 10<sup>3</sup> cm<sup>-1</sup> [log( $\varepsilon$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 22.6 (3.61).

# 2.1.2. Synthesis of tetrakis[2-(phenylmethyleneamino)benzenethiolato-C,N,S]tetrapalladium(II) [Pd<sub>4</sub>(phbt-C,N,S)<sub>4</sub>] (2)

To a suspension of crude complex 1 (0.22 g, 0.41 mmol) in ethanol (20 cm<sup>3</sup>) was added an equimolar amount of palladium(II) acetate (0.092 g, 0.41 mmol). The mixture was refluxed for 1 h and cooled to room temperature (r.t.). The fine brown precipitate (0.16 g)was collected by filtration and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>). The solution was purified by chromatography on a silica gel (230-400 mesh) column, eluting with  $CH_2Cl_2$ . The first band, which corresponds to 2, was collected, and removal of CH<sub>2</sub>Cl<sub>2</sub> under reduced pressure yielded a red powdery solid. This product was then washed with diethyl ether. Yield, 0.03 g (22% based on Pd). Crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a chloroform solution of 2. Found: C, 49.64; H, 3.41; N, 4.44%. Calc. for C<sub>52</sub>H<sub>36</sub>N<sub>4</sub>Pd<sub>4</sub>S<sub>4</sub>·C<sub>4</sub>H<sub>10</sub>O: C, 50.01; H, 3.45; N, 4.17%. IR:  $v_{\text{max}} \text{ cm}^{-1}$  (Nujol): 1586 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta = 7.65 - 7.60$  (4H, m, C<sub>arvl</sub>-H), 7.34 (4H, s, CH=N), 7.11 (4H, d, J=6.9 Hz, C<sub>aryl</sub>-H), 7.03-6.97 (16H, m, Carvl-H), and 6.90-6.82 (8H, m, C<sub>aryl</sub>-H). UV-Vis:  $v_{max}$ (CHCl<sub>3</sub>) 10<sup>3</sup> cm<sup>-1</sup> [log( $\varepsilon$  dm<sup>3</sup>  $mol^{-1} cm^{-1}$ ]: 19.8(sh) (3.84), 21.8 (3.97) and 29.4 (4.85).

### 2.2. X-ray structure determination

Intensity data were collected on a Mac Science MXC3 diffractometer with Mo K $\alpha$  radiation at r.t.  $\theta$  –2 $\theta$  scans were employed; no significant decomposition of the crystal occurred during the data collection. The structures of complexes 1 and 2 were solved by direct methods using SIR 92 [5] and refined anisotropically for all non-hydrogen atoms with full-matrix leastsquares calculations. The solution and refinement procedures were made by the use of the CRYSTAN-GM software package [6]. Crystallographic data: for 1.2/ $3C_5H_{12}$ ;  $C_{29,3}H_{28}N_2PdS_2$ , fw = 578.71, monoclinic, space group C2/c, a = 27.82(2), b = 18.269(6), c =16.699(6) Å,  $\beta = 118.70(4)^{\circ}$ , V = 7446(6) Å<sup>3</sup>, Z = 12,  $D_{\text{calc}} = 1.55 \text{ g cm}^{-3}, \ \mu(\text{Mo K}\alpha) = 1.22 \text{ mm}^{-1}, \ \text{crystal}$ size  $0.45 \times 0.40 \times 0.40$  mm, 4380 observed reflections  $[I > 2.0\sigma(I)]$  used in the refinement, R = 0.045,  $R_w =$ goodness-of-fit = 2.76. For 0.051 and  $2 \cdot Et_2O;$  $C_{56}H_{46}N_4OPd_4S_4$ , fw = 1344.95, monoclinic, space group  $P2_1/n$ , a = 19.928(3), b = 17.526(2), c = 14.583(2)Å,  $\beta = 94.68(1)^{\circ}$ , V = 5076(1) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.76$  g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 1.57 mm<sup>-1</sup>, crystal size 0.45 ×  $0.35 \times 0.20$  mm, 7433 observed reflections  $[I > 2.0\sigma(I)]$ used in the refinement, R = 0.050,  $R_w = 0.053$  and goodness-of-fit = 2.46.

# 3. Results and discussion

The reaction of 2-phenylbenzothiazoline with palladium(II) acetate in a molar ratio of 2:1 in ethanol gave a red-brown complex,  $[Pd(Hphbt-N,S)_2]$  (1) (Scheme 1). When 1 was treated with an equimolar amount of palladium(II) acetate in ethanol, a brown powder was precipitated. This powder was purified by a silica gel



Scheme 1. Synthetic scheme of complexes.

column chromatography to isolate a red complex,  $[Pd_4(phbt-C,N,S)_4]$  (2). Complexes 1 and 2 were characterized by <sup>1</sup>H NMR, IR and UV–Vis spectroscopies, besides elemental analyses, and their molecular structures were determined by single-crystal X-ray analyses.

Crystal 1 contains two crystallographically independent, yet nearly identical, complex molecules. One has a palladium atom (Pd(1)) in a general position, while the palladium atom (Pd(2)) of the other molecule locates on a twofold axis; the former molecule is selected in Fig. 1. The coordination geometry at the palladium atom in 1 is a slightly distorted square planar with a *cis* arrangement of the sulfur and nitrogen atoms. The dihedral angles between the two PdNS planes are  $7(6)^{\circ}$  for Pd(1) and 7(5)° for Pd(2). The Pd-S and Pd-N distances, which range from 2.256(4) to 2.267(4) Å and from 2.089(9) to 2.096(8) Å, respectively, compare well with those observed in the related square planar palladium(II) complexes [3,7]. A closer examination of the structure of 1 reveals the interesting intramolecular Pd···H-C interaction between the metal center and the ortho aromatic C-H with the average Pd···H distance of 2.65(6) Å, though it is slightly longer than the corresponding distance (2.57(7) Å) in the closely related  $[Pd(H1-nabz-N,S)_2]$  having 1-naphthyl groups as a pendant arm [3].

The <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub> shows a halfset of protons corresponding to its  $C_2$  symmetrical structure. The resonances for the *ortho* protons of phenyl groups of **1** are observed at relatively lower-field ( $\delta$  7.95) in the aromatic region [8]. This means the presence of a weak Pd···H–C interaction (three-center four-electron), rather than an agostic interaction (threecenter two-electron), which may influence the reactivity of mononuclear complexes leading to tetranuclear com-



Fig. 1. Molecular structure of one of the independent molecules of  $[Pd(Hphbt-N,S)_2]$  (1) (30% probability ellipsoids). Selected bond distances (Å) and angles (°): Pd(1)-S(1) 2.267(4), Pd(1)-S(2) 2.256(4), Pd(1)-N(1) 2.089(9), Pd(1)-N(2) 2.095(8); S(1)-Pd(1)-S(2) 90.3(2), S(1)-Pd(1)-N(1) 84.0(3), S(1)-Pd(1)-N(2) 172.4(3), S(2)-Pd(1)-N(2) 172.4(3), S(2)-Pd(1)-N(2) 83.8(3), N(1)-Pd(1)-N(2) 102.3(4).

plexes. However, the lower-field shift for 1 is not so large as the shift ( $\delta$  9.28) observed for [Pd(H1-nabz- $N,S)_2$ ] [3]. Thus, it is considered that 1 has a weaker Pd···H-C interaction compared with [Pd(H1-nabz- $N,S)_2$ ], owing to the increase of freedom of the pendant arm, which is compatible with the X-ray analytical result.

The asymmetric unit of 2 consists of one formula unit, and all palladium atoms are crystallographically inequivalent. As shown in Fig. 2, the core of 2 consists of an eight-membered ring of alternating Pd and S atoms. This structure is the same as that of [Pd<sub>4</sub>(1-nabz- $(C,N,S)_4$ , but both complexes are not isomorphous [3]. The coordination environment about each palladium atom can be described as a square planar having two sulfur, one imine nitrogen, and one aryl carbon donor atoms. Consequently, the Schiff base ligand acts as a rare C, N, S-chelate. The Pd–C distances being from 2.003(12) to 2.027(13) Å and the Pd–N distances being from 2.032(10) to 2.036(10) Å are quite normal [3,9]. The Pd-S<sub>chelating</sub> distances trans to carbon are longer than the Pd-S<sub>bridging</sub> distances trans to nitrogen (av.  $Pd-S_{chelating} = 2.371(4)$  Å and av.  $Pd-S_{bridging} =$ 2.303(4) Å), which is attributed to trans influence of the coordinated carbon of the cyclometalated ligand. The Pd(1)-Pd(2) and Pd(3)-Pd(4) distances are 3.299(2) and 3.334(2) Å, respectively, showing the absence of any Pd-Pd bonding. These distances are longer than the corresponding distances (3.180(1) Å) found in  $[Pd_4(1$ nabz-C,N,S<sub>4</sub>] [3]. In the <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub>, only one set of well-resolved resonances is observed for the four phbt ligands in the complex. This result suggests that the  $D_2$  symmetrical tetranuclear found in crystal is retained in solution.



Fig. 2. Molecular structure of  $[Pd_4(phbt-C,N,S)_4]$  (2) (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) (average): Pd-S<sub>chelating</sub> 2.371(4), Pd-S<sub>bridging</sub> 2.303(4), Pd-N 2.034(11), Pd-C 2.011(13); S<sub>chelating</sub>-Pd-S<sub>bridging</sub> 99.8(2), S<sub>chelating</sub>-Pd-N 84.6(4), S<sub>chelating</sub>-Pd-C 165.4(4), S<sub>bridging</sub>-Pd-N 175.6(4), S<sub>bridging</sub>-Pd-C 93.7(4), N-Pd-C 82.0(5).

In summary, it was found based on X-ray and <sup>1</sup>H NMR studies that there exists the hydrogen bondinglike interaction between palladium atom and *ortho* aromatic C-H in the mononuclear **1**. Since **1** was converted to the tetranuclear structure in **2** having Pd-C bonds, it is reasonable to assume that the Pd···H-C interaction plays an important role in the cyclometalation reaction even in the present flexible system. The results presented here may be deeply correlated to the studies on understanding the C-H activation during the cyclometalation reaction in palla-dium(II) complexes [10].

# 4. Supplementary material

Tables of all final coordinates and thermal parameters, bond lengths, bond angles, hydrogen atom coordinates and tables of observed and calculated structure factors are available from the authors.

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