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Pd···H−C Interactions. Preparation and Structure of Orthometalated Tetranuclear Complexes of Palladium(II) and Platinum(II)

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The reaction of 2-(1-naphthyl)benzothiazoline with palladium(II) acetate leads to helical mononuclear and orthometalated tetranuclear products. The molecular structures of mononuclear palladium(II) $[Pd(H1\text{-}nabz)_2]$ **(1)** ($H_21\text{-}nabz$ = 2-*N*-(1-naphthylmethylideneamino)benzenethiolate), tetranuclear palladium(II) $[Pd_4(1\text{-}nabz)_4]$ **(2)** and tetranuclear platinum(II) $[Pt_4(1\text{-}nabz)_4]$ **(3)** have been determined by single-crystal X-ray diffraction method. Crystal data for complex **1** are as follows: $a = 14.208(3)$ Å, $b = 18.227(4)$ Å, $c = 14.398(8)$ Å; $\beta = 94.55(3)°$; $V = 3717.0(23)$ Å^3; space group = $P2_1/n$, $Z = 4$. Crystal data for the complex **2** are as follows: $a = b = 15.798(3)$ Å, $c = 23.728(4)$ Å; $V = 5921.7(20)$ Å^3; space group = $I4_1/a$, $Z = 16$ for the Pd(1-nabz) unit. Crystal data for the complex **3** are as follows: $a = b = 15.496(2)$ Å, c = 24.348(3) Å; $V = 5846.3(20)$ Å^3; space group = $I4_1/a$, $Z = 16$ for the Pt(1-nabz) unit. The mononuclear palladium(II) complex reveals short *ortho*-hydrogen···palladium distances of 2.66(7) and 2.48(7) Å. These short distances and ^{1}H NMR studies provide a M···H−C interaction which can be regarded as a three-center four-electron interaction. The molecular structures of **2** and **3** confirm the formation of unusual tetranuclear compounds featuring a rare C,N,S-tridentate ligand derived from orthometalation of pendant side arm. The structural and chemical properties of the mononuclear palladium(II) complex **1** clearly suggest that **1** is a potential intermediate in the formation of the tetranuclear complex **2** by orthometalation reactions.

Introduction

For many years there has been considerable interest in the activation of C−H bonds by transition metal complexes. In this connection, many examples of transition metal complexes showing the agostic M···H−C interaction have been recognized.[1] Recently a few examples of the three-center four-electron M···H−N interaction, in contrast to the three-center two-electron agostic interaction, have been reported.[2] In addition, particular attention has been focused on the M···H−C interaction between *ortho*-hydrogen and transition metal because of the selective activation of the *ortho*-hydrogen−carbon bonds in many important transition-metal-catalyzed reactions.[3] Although many examples of the orthometalation reaction, in which aryl carbon-metal σ bonds are formed by the replacement of *ortho*-hydrogens by metal atoms, are now known,[4] it is rare that both an intermediate complex containing an activated C−H bond interacting with metal atom and the corresponding orthometalated complex resulting from the dissociation of the C−H bond are isolated in crystals.[5]

The present authors show herein a mononuclear palladium(II) complex with a Pd···H−C interaction caused by the ideally positioned *ortho* C−H bond and the corresponding orthometalated tetranuclear complex. The molecular structures of two palladium(II) complexes and a related orthometalated tetranuclear platinum(II) complex are presented. In a previous communication we reported the structure of orthometalated tetranuclear palladium(II) complex.[6]

Experimental Section

General Procedures. Reactions were normally carried out under argon; solvents were thoroughly degassed by argon purge. Ethanol was dried over molecular sieves, type 3A. Chloroform was dried over $CaCl_2$. Unless otherwise states, commercial grade chemicals were used without further purification.

Infrared spectra were obtained on a Perkin-Elmer 983G Infrared Spectrophotometer (4000−180 cm^{-1}) using the Nujol mulls. NMR spectra were measured on a JEOL EX 270 instrument using tetramethylsilane as internal standard ($\delta = 0$). The UV/VIS spectra were recorded on a Hitachi U-3400 spectrophotometer. Elemental analyses of 2-(1-naphthyl)benzothiazoline, **1**, **2**, and **3** were performed at Osaka University.

Synthesis of 2-(1-Naphthyl)benzothiazoline ($H_2$1-nabz). 2-(1-Naphthyl)benzothiazoline was prepared by the method given in the literature.[7] 2-Aminobenzenethiol (1.25 g, 9.99 mmol) was added to a solution of 1-naphthylaldehyde (1.56 g, 9.99 mmol) in ethanol (20 mL) and stirred at ca. 70 °C for 1 h. Yield: 2.56 g, 97%. Infrared spectrum: ν(N−H) at 3334 cm^{-1}, ν(aromatic C=C) at 1580 cm^{-1}. NMR ($CDCl_3$, 23 °C): ^{1}H (270 MHz), δ 8.03 (d, H), 7.89 (d, H), 7.88 (dd, H), 7.81 (d, H), 7.56 (dt, H), 7.51 (dt, H), 7.45 (t, H), 7.08 (s, H),

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7.06 (dd, H), 6.98 (dt, H), 6.79 (dt, H), and 6.76 (dd, H); ^{13}C (67.8 MHz), δ 146.51, 136.50, 133.87, 130.03, 128.95, 126.65, 126.56, 125.93, 125.45, 123.72, 122.77, 121.94, 120.70, 110.15, 66.76. Anal. Calcd for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.32. Found: C, 77.69; H, 5.11; N, 5.27.

Synthesis of Bis[2-*N*-(1-naphthylmethylideneamino)benzenethiolato]palladium(II) [Pd(H1-nabz)$_2$] (1). A suspension of 2-(1-naphthyl)benzothiazoline (0.226 g, 0.858 mmol) and palladium acetate (0.096 g, 0.428 mmol) in ethanol (20 mL) was heated to reflux for 30 min. A dark red precipitate was collected by filtration and dissolved in CH_2Cl_2 (20 mL). The solution was again filtered, and the red orange precipitate **1** was recrystallized from chloroform (0.105 g). The filtrate was purified by chromatography on a silica gel (230−400 mesh) column. The following products were separated, in order of elution, with CH_2Cl_2: the tetranuclear complex **2** (<0.001 g) as a red band, the mononuclear complex **1** (0.056 g) as a orange-red band, and a small amount of unidentified material as a dark red band that did not move. Yield: 43%. Crystals suitable for X-ray diffraction were grown by slow evaporation of a chloroform solution. Infrared spectrum: ν(C=N) at 1599 cm^{-1}, ν(aromatic C=C) at 1570 cm^{-1}. NMR ($CDCl_3$, 23 °C): ^{1}H (270 MHz), δ 9.28 (d, 2H), 8.38 (s, 2H), 7.98 (d, 2H), 7.84 (d, 2H), 7.49 (dd, 2H), 7.33 (dt, 2H), 7.24 (t, 2H), 7.10 (dt, 2H), 6.89 (dt, 2H), 6.81 (dt, 2H), 6.65 (dd, 2H), and 6.42 (d, 2H); ^{13}C (67.8 MHz), δ 161.79, 151.23, 146.51, 132.43, 132.06, 131.11, 129.85, 129.63, 129.48, 128.94, 128.61, 127.37, 126.28, 124.98, 122.30, 120.91, 118.58. Anal. Calcd for $C_{34}H_{24}N_2PdS_2 \cdot 2CHCl_3$: C, 49.71; H, 3.02; N, 3.22. Found: C, 49.78; H, 3.09; N, 3.28.

The following is a revised version of the synthesis of complex **1** owing to the poor solubility in chloroform. Palladium acetate (0.177 g, 0.788 mmol) was added to 2-(1-naphthyl)benzothiazoline (0.417 g, 1.58 mmol) in chloroform (20 mL). The resulting solution was heated under reflux for 20 min. After cooling, the mixture was evaporated to *ca.* 10 mL. The red powder precipitate was filtered, washed with ether, and dried under vacuum (0.340 g). Yield: 50%.

Synthesis of Tetrakis[2-*N*-(1-naphthylmethylideneamino)benzenethiolato-*C*^{o},*N*,*S*]tetrapalladium(II) [Pd$_4$(1-nabz)$_4$] (2). A stirred suspension of 2-(1-naphthyl)benzothiazoline (0.212 g, 0.805 mmol) in ethanol (20 mL) was treated with a palladium acetate (0.181 g, 0.806 mmol) and refluxed for 30 min. The dark red precipitate (0.205 g) obtained was collected by filtration. The compound was dissolved in a minimum of CH_2Cl_2 and purified by chromatography on a silica gel (230−400 mesh) column eluting with CH_2Cl_2. A dark red complex **2** (0.019 g) resulted on evaporation of the solvent, and due to the extensive purification procedure, the yield was 1.6%, based on the amount of the starting palladium acetate. Crystals suitable for X-ray diffraction were selected by inspection of the crystal shapes under a microscope in crude crystals (red needlelike **1** and dark red square bipyramidal **2**). The second red band due to complex **1** was dried in vacuo and recrystallized from chloroform (0.014 g). The dark red band remained on the top of the column but was desorbed on stirring that portion of the column material in chloroform, and the dark red square bipyramidal crystals were grown from the chloroform solution. The crystals exhibited nearly the same cell constants ($a = 15.83(2)$, $b = 15.81(6)$, $c = 23.7(2)$ Å, $\alpha = 89.98(5)$, $\beta = 89.8(1)$, $\gamma = 89.92(7)$°) as compound **2** by X-ray diffraction method. Anal. Calcd for $C_{68}H_{44}N_4Pd_4S_4$: C, 55.52; H, 3.02; N, 3.81. Found: C, 55.52; H, 3.15; N, 3.74.

Reaction of 1 with Palladium Acetate. A suspension of **1** (0.097 g, 0.112 mmol) in ethanol (10 mL) was treated with a palladium acetate (0.025 g, 0.111 mmol) and refluxed for 30 min. The brown precipitate (0.041 g) was collected by filtration and was dissolved in CH_2Cl_2 (10 mL). The solution was purified by chromatography on a silica gel (230−400 mesh) column. The products eluted (CH_2Cl_2) in the following order: the complex **2** (yield: 0.3%), the starting complex **1**, and the unidentified material as a dark red band that did not move.

Synthesis of Tetrakis[2-*N*-(1-naphthylmethylideneamino)benzenethiolato-*C*^{o},*N*,*S*]tetraplatinum(II) [Pt$_4$(1-nabz)$_4$] (3). To a solution of 2-(1-naphthyl)benzothiazoline (0.088 g, 0.32 mmol) in toluene (20mL) was added an equimolar amount of Pt(hfacac)$_2$[8] (0.200 g, 0.32 mmol), and the mixture was refluxed over 3 h. The solvent was removed from the reaction mixture by using a rotary evaporator. The resulting dark red precipitate was dissolved in a minimum amount of CH_2Cl_2 and purified on a silica gel (230−400 mesh) column with CH_2Cl_2 as the eluent. The first band, which corresponded to compound **3**, was collected, and the yield was 35% based on the amount of the starting Pt(hfacac)$_2$. Single crystals of **3** suitable for X-ray analysis were grown by the slow evaporation of a CH_2Cl_2 solution. The mononuclear platinum(II) complex corresponding to complex **1** could not be detected, even in 2:1 ratio of H$_2$1-nabz and Pt(hfacac)$_2$. Anal. Calcd for $C_{68}H_{44}N_4Pt_4S_4$: C, 44.73; H, 2.43; N, 3.07. Found: C, 44.19; H, 2.62; N, 3.11. We could not get high resolution NMR spectra for tetranuclear complexes (**2** and **3**) even at −50 °C. This fact suggests that the height of the barrier for the exchange process in **2** and **3** is not suitable to be observed by NMR spectroscopy because of slow conformational changes for tetranuclear complex. This conformational equilibrium is consistent with the results of IR spectroscopy, which exhibit five bands (1610, 1583, 1570, 1564, and 1558 cm^{-1}) and four bands (1611, 1583, 1561, and 1553 cm^{-1}) for ν(N=C) and ν(aromatic C=C) of **2** and **3**, respectively.[9,10]

X-ray Crystallography. All crystals were attached to the end of glass fiber and coated with epoxy. X-ray measurements of [Pd(H1-nabz)$_2$] **1** and [Pd$_4$(1-nabz)$_4$] **2** were made on a Rigaku AFC-5 diffractometer with Mo-Kα radiation and X-ray measurement of [Pt$_4$(1-nabz)$_4$] **3** was made on a Rigaku AFC-5R diffractometer with Cu-Kα radiation; ω-2θ scans were used. Crystallographic data are summarized in Table 1. Empirical absorption corrections were applied for **3**. The intensities of three standard reflections were monitored every 100 reflections and showed no greater fluctuations during the data collection than expected from Poisson statistics. The structures were solved by direct methods (MULTAN 80[11] for **1** and **2**, SHELXS-86[12] for **3**). All structures were refined by block-diagonal least-squares methods with anisotropic thermal parameters for non-H atoms and isotropic parameters for H atoms. Atomic scattering factors and anomalous scattering coefficients were taken from ref 13. The calculations for **1** and **2** were carried out using the program system UNICS III[14] on a HITAC M680 Hitachi computer at the Computer Center of the Institute for Molecular Science. On the ethanol in the crystal **2**, the terminal C atom could not be determined due to disorder character. The calculation for **3** was carried out using the program HBLS-V[15] on an ACOS & SX NEC computer at the Computation Center Osaka University. Figures 1 and 2 were drawn by the ORTEP program.[16] Final atomic coordinates for the non-hydrogen atoms of **1**, **2**, and **3** are given in Tables 2−4, respectively.

Results and Discussion

Synthesis of 1−3. Treatment of H$_2$1-nabz with 0.5 molar equiv of palladium acetate in ethanol gave the mononuclear complex **1** together with a small amount of the tetranuclear complex **2** (Scheme 1). In the case of the 1:1 stoichiometry for the reaction of H$_2$1-nabz with palladium acetate, the tetranuclear complex **2** was obtained together with the mononuclear complex **1** and an unidentified red compound. The unidentified compound is regarded as degradation products of the complex **2** by column chromatograpy (see Experimental Section). When mononuclear complex **1** instead of H$_2$1-nabz

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Table 1. Crystallographic Data for **1**−**3**

	1	**2**	**3**
formula	$C_{34}H_{24}N_2PdS_2\cdot 2CHCl_3$	$C_{17}H_{11}NPdS\cdot 0.5C_2H_5OH$	$C_{17}H_{11}NPtS$
M	869.83	390.77	456.44
cryst syst	monoclinic	tetragonal	tetragonal
space group	$P2_1/n$	$I4_1/a$	$I4_1/a$
a/Å	14.208(3)	15.798(3)	15.496(2)
b/Å	18.227(4)	15.798(3)	15.496(2)
c/Å	14.398(8)	23.728(4)	24.348(3)
β/deg	94.55(3)		
V/Å^3	3717.0(23)	5921.7(20)	5846.3(20)
Z	4	16	16
cryst size/mm	0.35 × 0.20 × 0.20	0.25 × 0.25 × 0.25	0.15 × 0.15 × 0.15
T/°C	23	23	23
λ/Å	0.71073	0.71073	1.54184
D_c/g cm^{-3}	1.56	1.75	2.08
μ/cm^{-1}	10.6 (Mo Kα)	13.7 (Mo Kα)	193.6 (Cu Kα)
$2\theta_{max}$/°	50	60	110
no. of measd reflcns	8188	4703	2558
no. of reflcns used in refinement	2970 [$\lvert F_o\rvert > 3\sigma(F_o)$]	2284 [$\lvert F_o\rvert > 3\sigma(F_o)$]	1275 [$\lvert F_o\rvert > 3\sigma(F_o)$]
R^a	0.063	0.061	0.083
$R_w{}^b$	0.053	0.064	0.085

[a] $R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$. [b] $Rw = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w(F_o)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(F_o)]$.

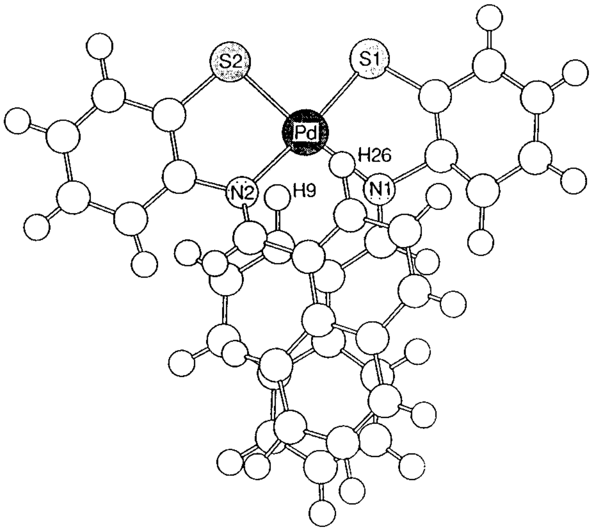

Figure 1. Molecular structure of [Pd(H1-nabz)$_2$] (**1**).

is reacted with Pd(CH$_3$COO)$_2$, a mixture of **1** and **2** is formed. This synthetic result indicates that **1** is an intermediate in the orthometalation reaction leading to the formation of **2**. Treatment of H$_2$1-nabz with 1 molar equiv of [Pt(hfacac)$_2$] gave the tetranuclear complex **3** together with an unidentified red compound.

Molecular Structure of [Pd(H1-nabz)$_2$] (1). The molecular structure of **1** together with the adopted numbering scheme is shown in Figure 1. The gross structure of **1** shows a mono-helical geometry similar to those of the nickel(II) and palladium(II) complexes containing ferrocenyl groups in place of 1-naphthyl groups.[17] Complex **1** possesses approximate C_2 symmetry (noncrystallographic) with pseudo-2-fold axes passing through the palladium atom and the midpoint between the two sulfur atoms. Palladium atom is in a slightly distorted square-planar coordination environment. The dihedral angle between the S−Pd−N planes is 4.4(2)°. The arrangement of the sulfur and nitrogen atoms around the palladium atom is *cis*-type though very strong interligand steric interactions occur. Geometrical parameters are given in Table 5. The average Pd−S distance of 2.273(3) Å and the average Pd−N distance of 2.092(7) Å are normal.[17,18] However, the N−Pd−N bond angle, 102.5(3)°, is relatively wide and we attribute this distortion to repulsion between the pendant side arms. The most interesting features of this structure are the short hydrogen contacts, Pd···H(9)−C 2.66(7) Å and Pd···H(26)−C 2.48(7) Å. In addition, the C−H groups are positioned above and below the N$_2$S$_2$Pd plane and they are fixed toward the palladium atom owing to the limitation of the degree of freedom of the pendant side arms. Albinati et al. have shown that similar intramolecular Pt···H−C contacts

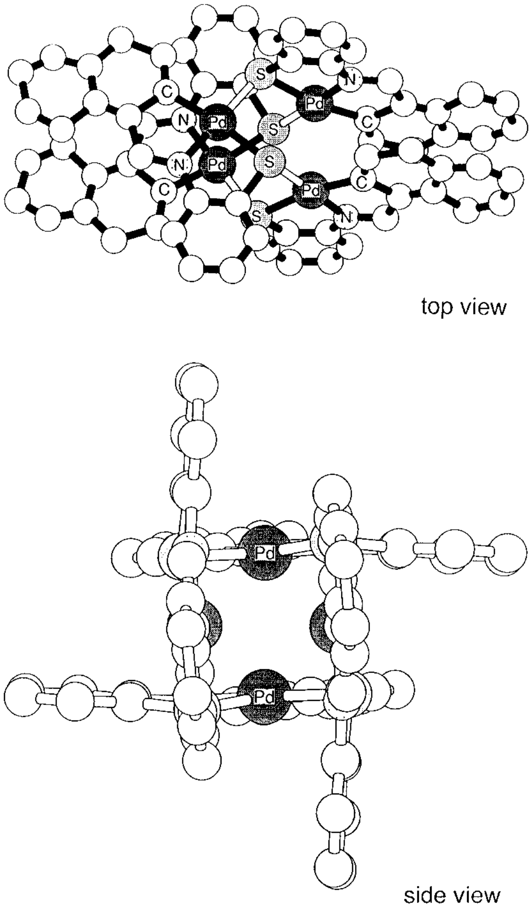

Figure 2. Molecular structure of [Pd$_4$(1-nabz)$_4$] (**2**). Hydrogen atoms are omitted for clarity.

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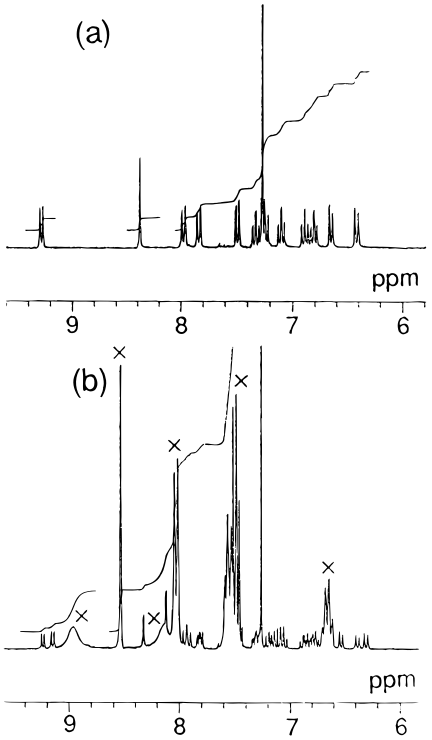

Figure 3. ^{1}H NMR spectra (270 MHz, $CDCl_3$) for azomethine and aromatic protons of (a) **1** and (b) **1** in the presence of 10 equiv of Pirkle's reagent (Pirkle's reagent indicated by ×).

(2.4−2.6 Å) exist in platinum(II) compounds.[19] In the latter case the complexes have distorted-square-planar structures with the appropriate C−H vector directed toward the platinum atom.

Table 2. Fractional atomic coordinates ($\times 10^4$) for **1**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Pd	3946(1)	8931(0)	6879(1)
Cl(1)	687(3)	8419(3)	7969(4)
Cl(2)	1339(3)	9860(2)	7703(3)
Cl(3)	242(3)	9142(3)	6259(3)
Cl(4)	3594(5)	7363(3)	4251(4)
Cl(5)	5221(3)	7172(3)	5365(4)
Cl(6)	3843(6)	6110(3)	5274(4)
S(1)	3278(2)	7853(2)	7266(2)
S(2)	2923(2)	9016(2)	5585(2)
N(1)	4761(5)	8798(4)	8140(5)
N(2)	4487(5)	9903(4)	6356(5)
C(1)	4239(7)	7546(5)	8021(7)
C(2)	4936(6)	8034(5)	8375(6)
C(3)	5733(7)	7776(5)	8930(7)
C(4)	5776(8)	7051(5)	9147(7)
C(5)	5081(9)	6574(6)	8817(8)
C(6)	4337(8)	6801(6)	8261(8)
C(7)	5074(7)	9274(5)	8728(6)
C(8)	4885(7)	10061(5)	8671(6)
C(9)	4020(7)	10324(5)	8356(7)
C(10)	3777(8)	11071(6)	8348(7)
C(11)	4447(10)	11548(6)	8708(8)
C(12)	6056(10)	11835(7)	9435(10)
C(13)	6910(10)	11578(7)	9775(9)
C(14)	7133(9)	10862(7)	9789(10)
C(15)	6507(7)	10308(6)	9383(7)
C(16)	5603(7)	10552(5)	9032(6)
C(17)	5383(8)	11312(5)	9063(7)
C(18)	2952(6)	9976(6)	5538(6)
C(19)	3738(6)	10353(5)	5942(6)
C(20)	3778(7)	11099(6)	5979(7)
C(21)	3001(8)	11501(6)	5583(9)
C(22)	2260(8)	11147(7)	5156(8)
C(23)	2200(6)	10408(6)	5137(7)
C(24)	5344(6)	10104(5)	6290(6)
C(25)	6172(6)	9690(5)	6671(6)
C(26)	6184(6)	8934(6)	6620(7)
C(27)	6969(8)	8527(6)	6968(8)
C(28)	7735(8)	8871(7)	7379(8)
C(29)	8582(8)	9993(9)	7824(8)
C(30)	8610(9)	10723(9)	7845(9)
C(31)	7870(9)	11195(8)	7520(8)
C(32)	7050(8)	10851(6)	7126(7)
C(33)	6976(6)	10078(6)	7061(6)
C(34)	7770(7)	9640(7)	7425(7)
C(35)	1095(7)	9031(7)	7176(8)
C(36)	4061(9)	6980(8)	5276(8)

Molecular Structure of [Pd_4(1-nabz)$_4$] (2). This molecular structure has a crystallographically imposed symmetry $\bar{4}$ and consists of four square planes with a Pd4S4 eight-membered ring bridged by the sulfur atoms (Figure 2). Each palladium atom is coordinated by two sulfurs, one nitrogen, and one *ortho* carbon of the 1-naphthyl group in square-planar geometry with the two sulfurs mutually *cis*. Thus this complex is an unusual tetranuclear complex having a rare C,N,S-tridentate ligand derived from orthometalation of the pendant side arm. The Pd−S−Pd angles are fairly close to the ideal tetrahedral value of 109.5 °. The Pd−N and Pd−C bond distances are normal.[20,21] The Pd−terminal S and Pd−bridging S distances are 2.365(2) and 2.317(2) Å, respectively, and are relatively longer than that of complex **1** (Pd−S = 2.273(3) Å) and other reported Pd−S bond lengths of 2.25−2.31 Å.[17,18] In addition, it is noteworthy that the Pd-terminal S distances are longer than the bridging ones. This result is a reflection of the strong *trans* influence of the coordinated carbon of the orthometalated ligand.[22] The Pd−Pd distance of 3.180(1) Å demonstrates the lack of Pd−Pd direct bond.[23] For reference, the interatomic spacing in palladium metal is 2.75 Å.[24] Recently a similar tetranuclear complex has been described by Nicholas et al.[20] However, each of the four monomeric units of their palladium(II) complex consists of six-membered N,O-bonded chelate and five-membered N,C-bonded chelate rings and the C=N bond is not included in the N,C-bonded chelate ring. On the contrary, those of the complex **2** consists of five-membered N,S-bonded chelate and five-membered N,C-bonded chelate rings and the C=N bond is included in the N,C-bonded chelate ring. Thus both tetranuclear complexes are virtually distinct from each other.

Molecular Structure of [Pt_4(1-nabz)$_4$] (3). Complex **3** is isostructural with **2** ; these almost identical cell parameters reflect the equivalence in size of the Pd and Pt atoms (Table 1). This platinum(II) complex with a heteroatomic C,N,S-tridentate ligand is a new type. The core of **3** consists of an eight-membered ring of alternating Pt and S atoms similar to the skeletal structure of braggite.[25] The Pt−N, and Pt−C bond lengths compare well with the relatively few structural data

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Table 3. Fractional Atomic Coordinates ($\times 10^4$) for **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Pd	9497(0)	6628(0)	9416(0)
S	10237(1)	5996(1)	8659(1)
N	10369(4)	6042(3)	9910(3)
C(1)	11100(4)	5611(4)	9073(3)
C(2)	11086(4)	5650(4)	9649(3)
C(3)	11765(6)	5339(6)	9952(4)
C(4)	12437(6)	4976(7)	9681(5)
C(5)	12442(6)	4911(6)	9114(4)
C(6)	11776(5)	5230(5)	8799(4)
C(7)	10227(5)	6060(5)	10455(4)
C(8)	9445(8)	6572(6)	10646(5)
C(9)	8925(5)	6958(5)	10142(3)
C(10)	8207(5)	7454(6)	10202(4)
C(11)	7923(7)	7644(7)	10805(6)
C(12)	8468(7)	7249(6)	11223(4)
C(13)	8308(12)	7323(12)	11742(7)
C(14)	8636(12)	7054(9)	12184(8)
C(15)	9399(9)	6507(7)	12058(6)
C(16)	9734(9)	6311(8)	11576(5)
C(17)	9185(9)	6729(7)	11116(6)
O(E1)	9120(6)	8106(6)	3723(6)
C(E2)	9394(17)	7455(35)	3676(16)

Table 4. Fractional Atomic Coordinates ($\times 10^4$) for **3**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt	516(2)	3398(2)	616(2)
S	−267(3)	4054(3)	1328(2)
N	−339(3)	3965(3)	119(2)
C(1)	−1111(3)	4435(3)	929(2)
C(2)	−1141(3)	4353(3)	345(2)
C(3)	−1749(3)	4696(3)	38(2)
C(4)	−2503(3)	5012(3)	293(2)
C(5)	−2455(3)	5170(3)	822(2)
C(6)	−1877(3)	4793(3)	1142(2)
C(7)	−198(3)	3916(3)	−428(2)
C(8)	614(4)	3355(4)	−559(2)
C(9)	1029(3)	3090(3)	−89(2)
C(10)	1824(4)	2584(4)	−189(3)
C(11)	2078(3)	2346(3)	−768(2)
C(12)	1593(3)	2734(3)	−1208(2)
C(13)	1895(3)	2497(4)	−1711(2)
C(14)	1389(3)	2838(4)	−2152(2)
C(15)	646(4)	3437(4)	−2057(2)
C(16)	311(4)	3595(4)	−1554(3)
C(17)	901(4)	3221(4)	−1085(3)

already established for similar complexes.[26] The Pt−bridging S distances (2.316(8) Å) are in the range of distances found in other platinum thiolate complexes.[27] The Pt−terminal S distances (2.350(8) Å) are longer than the bridging ones and also are relatively longer than the reported Pt−S bond lengths. This disparity results from the considerable *trans* influence of the Pt−C sp^2 bond as well as that in the palladium complex **2**. Bond lengths involving Pd and Pt atoms are very similar as a consequence of the essential equality of the covalent radii of the two metals (Table 6). The Pt−Pt distance of 3.210(3) Å is regarded as nonbonding.[28]

Spectroscopic Characterization of the Compounds. The ^{1}H NMR spectrum of **1** showed the azomethine proton as a singlet at 8.38 ppm and indicated the symmetrical structure with equivalent ligand side arms. In addition, a surprisingly large splitting of peaks was observed upon addition of excess chiral reagent 9-(1-hydroxy-2,2,2-trifluoroethyl)anthracene[29] to a solution of **1** in $CDCl_3$ (Figure 3). This is indeed a clear

Scheme 1. Synthetic Routes

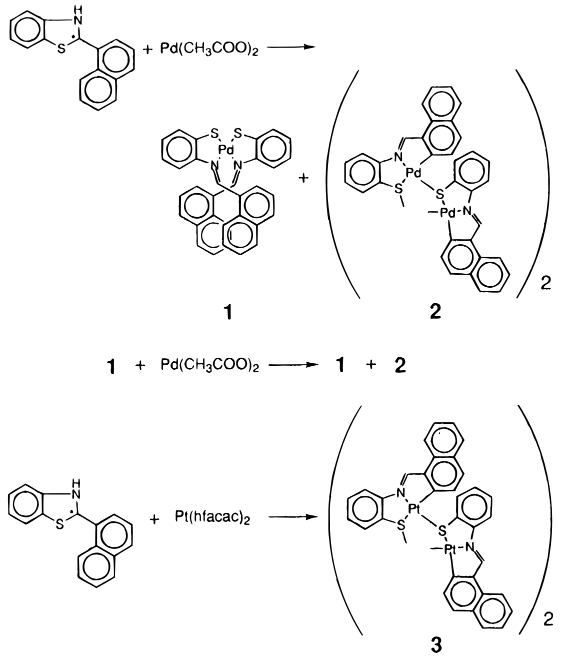

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pd−S(1)	2.270(3)	N(2)−C(24)	1.282(11)
Pd−S(2)	2.275(3)	C(1)−C(2)	1.398(13)
Pd−N(1)	2.089(7)	C(7)−C(8)	1.460(13)
Pd−N(2)	2.096(7)	C(18)−C(19)	1.398(12)
S(1)−C(1)	1.767(10)	C(24)−C(25)	1.468(13)
S(2)−C(18)	1.753(11)	Pd···C(9)	3.309(10)
N(1)−C(2)	1.450(11)	Pd···H(9)	2.66(7)
N(1)−C(7)	1.268(11)	Pd···C(26)	3.232(9)
N(2)−C(19)	1.434(11)	Pd···H(26)	2.48(7)
S(1)−Pd−S(2)	90.5(1)	Pd−N(1)−C(7)	130.0(6)
S(1)−Pd−N(1)	84.3(2)	Pd−N(2)−C(19)	110.6(5)
S(1)−Pd−N(2)	173.0(2)	Pd−N(2)−C(24)	130.2(6)
N(1)−Pd−N(2)	102.5(3)	N(1)−C(7)−C(8)	125.6(8)
Pd−S(1)−C(1)	96.2(3)	N(2)−C(24)−C(25)	124.3(8)
Pd−S(2)−C(18)	94.8(3)	Pd···H(9)−C(9)	115(5)
Pd−N(1)−C(2)	112.8(5)	Pd···H(26)−C(26)	125(5)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **2** and **3**

	M = Pd (**2**)	M = Pt (**3**)
$M-S_{terminal}$	2.365(2)	2.350(8)
$M-S_{bridging}$	2.317(2)	2.316(8)
M−N	2.032(6)	2.01(2)
M−C(9)	2.014(8)	2.00(3)
$S_{terminal}-C(1)$	1.788(7)	1.75(3)
N−C(2)	1.431(9)	1.48(4)
N−C(7)	1.313(10)	1.31(4)
C(1)−C(2)	1.367(10)	1.45(4)
C(7)−C(8)	1.544(14)	1.58(5)
C(8)−C(9)	1.573(14)	1.37(5)
M···M	3.180(1)	3.210(3)
$S_{terminal}-M-S_{bridging}$	94.2(2)	96.3(3)
$S_{terminal}-M-N$	84.9(2)	85.5(7)
$S_{bridging}-M-C(9)$	94.9(3)	96(1)
N−M−C(9)	85.9(3)	82(1)
$M-S_{bridging}-M$	111.9(2)	110.4(3)
$M-S_{terminal}-C(1)$	95.9(3)	97(1)
M−N−C(2)	118.9(5)	121(2)
M−N−C(7)	116.2(5)	118(2)
M−C(9)−C(8)	108.4(6)	115(3)
N−C(7)−C(8)	115.9(8)	112(3)
C(7)−C(8)−C(9)	113.5(8)	114(3)

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demonstration that the molecular system is chiral even in $CDCl_3$. The significant downfield shifts are observed for the aromatic *ortho*-proton (9.28 ppm).[30] Similar downfield shifts for hydrogen atoms involved in Pt···H−C interactions have been shown by Albinati et al.[19] In addition, van Koten et al. have reported that ^{1}H NMR studies show downfield shifts for the resonance of the interacting proton (Pt···H−N).[2] Thus the present low-field resonance can be attributed to an intramolecular three-center four-electron Pd···H−C interaction in contrast to the known three-center two-electron agostic interaction showing a high-field resonance.

Electronic absorption spectra of **1**−**3** in $CHCl_3$ are adequately summarized by the following $\nu_{max}/10^3$ cm^{-1} (log ϵ/cm^3 mol^{-1} cm^{-1}) data: 19.60 (3.42) br, 22.20 (3.64), 26.70 (3.89) br, and 29.50 (4.18) for **1**, 17.60 (3.78) br, 19.60 (4.02) br, 23.00 (4.31) br, 25.80 (4.56) br, and 28.00 (4.70) for **2**, and 15.70 (3.36) sh, 18.40 (3.78) br, and 25.20 (4.33) for **3**. The transitions in the tetranuclear complex **2** have higher intensities than those in the mononuclear complex **1**.

Conclusions

A series of new tetranuclear complexes containing a rare C,N,S-tridentate ligand derived from orthometalation of the pendant side arm has been synthesized and characterized. This Pd(II) complex results from a dissociation of the *ortho*-hydrogen−carbon bond in a helical Pd(II) intermediate containing an unique Pd···H−C moiety. The presence of the Pd···H−C interaction caused by the ideally positioned *ortho* C−H bond can be deduced by the X-ray crystal structure and ^{1}H NMR spectroscopy. The Pd···H−C moiety can be described as a three-center four-electron interaction rather than an agostic interaction. The majority of examples of orthometalated complexes which have been described are with d^8 or d^6 transition metals and, in particular, Pd(II) and Pt(II) compounds readily orthometalate a variety of organic ligands. This study suggests that the orthometalation reactions in Pd(II) and Pt(II) compounds involve the intermediacy of species containing the three-center four-electron M···H−C interactions.

Supporting Information Available: Full tables listing anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for hydrogens, and bond lengths and angles for **1**, **2**, and **3** and a structural figure of **3** showing the labeling scheme (15 pages). Ordering information is given on any current masthead page.

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