

# Notes

## Palladium(II) Arenethiolates with Chelating Diamines: Formation of N–H···S Hydrogen Bonds with Protonated *N,N,N',N'*-Tetramethylethylenediamine

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### Introduction

Recently, the formation of N–H···S hydrogen bonds has attracted attention in transition metal arenethiolate chemistry.<sup>1</sup> Several model complexes, *e.g.* [Fe<sup>II</sup>(SAR)<sub>4</sub>]<sup>2-</sup>,<sup>2a</sup> [Fe<sup>III</sup>(Cys–S)<sub>4</sub>]<sup>-</sup>,<sup>2b</sup> [Mo<sup>VO</sup>(SAR)<sub>4</sub>]<sup>-</sup>,<sup>3a</sup> and [Ni<sup>II</sup>(SAR)<sub>4</sub>]<sup>2-</sup>,<sup>3b</sup> have been studied in order to establish the influence of such bonds on M–S coordination. Understanding the nature of N–H···S bonds in inorganic complexes is also important for biochemists to gain insights into the function of enzymes on a molecular level.<sup>4</sup> Here, we report the reaction of bidentate N-donor-ligated bis(aryloxo)palladium(II) complexes with an aromatic thiol; depending upon the alkyl substitution in the tetraalkylethylenediamine ligand used, either a neutral bis(arenethiolato)-palladium(II) diamine species or a tetrakis(arenethiolato)-palladium(II) diprotonated diamine species is formed. The latter complex is the first example of a hydrogen-bonded “bridging” [Me<sub>2</sub>(H)NCH<sub>2</sub>CH<sub>2</sub>N(H)Me<sub>2</sub>]<sup>2+</sup> ligand, and this paper describes the influence of N–H···S hydrogen bonding on the square-planar coordination geometry of the Pd(SC<sub>6</sub>F<sub>5</sub>)<sub>4</sub> dianion.

### Experimental Section

**General Considerations.** Pentafluorothiophenol was purchased from Aldrich Chemical Co. and used as received. The complexes [Pd(OC<sub>6</sub>X<sub>5</sub>)<sub>2</sub>(tmeda)] (tmeda = *N,N,N',N'*-tetramethylethylenediamine; X = H, F) and [Pd(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(teeda)] (teeda = *N,N,N',N'*-tetraethylethyl-

Table 1. Crystallographic Data for 2

formula	C <sub>24</sub> F <sub>20</sub> PdS <sub>4</sub> ·C <sub>6</sub> H <sub>18</sub> N <sub>2</sub>
space group	C2/c (No. 15)
cryst system	monoclinic
Z	4
a, Å	9.9905(6)
b, Å	18.8645(11)
c, Å	19.2540(14)
β, deg	90.399(5)
V, Å <sup>3</sup>	3628.6(4)
D <sub>calcd</sub> , g cm <sup>-3</sup>	1.869
μ <sub>calcd</sub> , cm <sup>-1</sup>	8.5
radiation (Mo Kα), Å	0.71073 (graphite monochromator)
T, K	298
R <sub>F</sub> <sup>a</sup>	0.047
R <sub>wF</sub> <sup>b</sup>	0.046

$$^a R_F = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_{wF} = [\sum [w(F_o - F_c)^2] / \sum [w(F_o)^2]]^{1/2}.$$

enediamine) were prepared according to the literature.<sup>5</sup> <sup>1</sup>H NMR (300.13 MHz) spectra were recorded on a Bruker AC 300 spectrometer at ambient temperature in CD<sub>3</sub>CN obtained from ISOTEC Inc. Infrared spectra (KBr disks) were recorded on a Perkin-Elmer 283 spectrometer. Elemental analyses were carried out by Domis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

**[Pd(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NET<sub>2</sub>)] (1).** To a stirred solution of [Pd(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(teeda)] (0.20 g, 0.43 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added pentafluorothiophenol (0.70 g, 3.5 mmol). The pure product was obtained by diffusion of pentane into this solution. The resulting needle-shaped deep-red crystals were washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield: 0.28 g (95%). Mp: 166 °C dec. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.20 (dq, 4H, CH<sub>a</sub>H<sub>b</sub>Me, <sup>2</sup>J<sub>a,b</sub> = 13 Hz, <sup>3</sup>J<sub>a,Me</sub> = 7 Hz), 3.01 (dq, 4H, CH<sub>a</sub>H<sub>b</sub>Me, <sup>2</sup>J<sub>a,b</sub> = 13 Hz, <sup>3</sup>J<sub>b,Me</sub> = 7 Hz), 2.86 (s, 4H, N(CH<sub>2</sub>)<sub>2</sub>N), 1.40 (t, 12H, CH<sub>3</sub>). Anal. Calcd for C<sub>22</sub>H<sub>24</sub>F<sub>10</sub>N<sub>2</sub>S<sub>2</sub>Pd: C, 39.03; H, 3.57; N, 4.14. Found: C, 38.74; H, 3.75; N, 4.08.

**[Pd(SC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>][Me<sub>2</sub>(H)NCH<sub>2</sub>CH<sub>2</sub>N(H)Me<sub>2</sub>] (2).** To a stirred solution of [Pd(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(tmeda)] (0.20 g, 0.49 mmol) or a solution of [Pd(OC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tmeda)] (0.29 g, 0.49 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added pentafluorothiophenol (0.80 g, 4.0 mmol). After 1 min the dark red solution was filtered. The pure product was obtained by diffusion of pentane into this solution. The resulting block-shaped red crystals (suitable for X-ray diffraction) were washed with pentane (3 × 10 mL) and dried *in vacuo*. Yield: 0.49 g (97%). Mp: 185 °C dec. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.84 (s, 4H, NCH<sub>2</sub>), 2.72 (s, 12H, NCH<sub>3</sub>), 2.69 (br s, 2H, NH). IR(KBr): ν<sub>N–H</sub> 3250 cm<sup>-1</sup>. UV–vis (CD<sub>3</sub>CN): abs. (ε (L mol<sup>-1</sup> cm<sup>-1</sup>)): 24 300 (4100, d–d), 37 500 (49 200, MLCT), 49 500 (34 200, MLCT) cm<sup>-1</sup>. Anal. Calcd for C<sub>30</sub>H<sub>18</sub>F<sub>20</sub>N<sub>2</sub>S<sub>4</sub>Pd: C, 35.29; H, 1.78; N, 2.74. Found: C, 35.02; H, 2.07; N, 3.19.

**Crystal Structure Determination of 2.** A dark red block-shaped crystal was glued to the tip of a glass fiber and transferred to an Enraf-Nonius CAD4-Turbo diffractometer with rotating anode. Lattice parameters were determined by least-squares treatment, using the setting angles (SET4) of 25 reflections in the range 10.0° < θ < 13.7°. The unit cell parameters were checked for the presence of higher lattice symmetry.<sup>6</sup> Crystal data and details on data collection and refinement are given in Table 1. Data were collected at ambient temperature in ω/2θ mode with scan angle Δω = 0.63 + 0.35 tan θ. Intensity data of 4667 reflections were collected in the range 1.06° < θ < 27.50°, of which 4159 are independent. A total of 2222 reflections with intensities above 2.5σ(I) were used in the structure analysis. Data were corrected for Lorentz–polarization effects and for a linear decay of 3% of the three periodically measured reference reflections (225, 225, 442) during 11 h of X-ray exposure time. The structure was solved by automated

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**Table 2.** Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for **2**

atom	x	y	z	$U_{eq}, \text{\AA}^2$
Pd(1)	1/2	0.37648(4)	1/4	0.0367(2)
S(1)	0.28190(14)	0.36327(8)	0.29010(8)	0.0449(5)
S(2)	0.56562(15)	0.38069(11)	0.36665(8)	0.0574(6)
F(1)	0.1689(5)	0.2472(2)	0.1997(3)	0.101(2)
F(2)	-0.0003(5)	0.2602(3)	0.0923(3)	0.124(2)
F(3)	-0.0870(4)	0.3884(3)	0.0516(2)	0.100(2)
F(4)	-0.0093(5)	0.5060(2)	0.1232(2)	0.0924(19)
F(5)	0.1580(4)	0.49347(19)	0.2308(2)	0.0758(16)
F(6)	0.4990(5)	0.5292(2)	0.31977(19)	0.0922(19)
F(7)	0.3219(6)	0.6191(2)	0.3756(2)	0.118(2)
F(8)	0.1947(5)	0.5865(3)	0.4925(3)	0.103(2)
F(9)	0.2424(4)	0.4601(2)	0.5544(2)	0.0865(17)
F(10)	0.4043(4)	0.3660(2)	0.49667(19)	0.0726(16)
C(1)	0.1714(5)	0.3695(3)	0.2187(3)	0.0430(19)
C(2)	0.1259(7)	0.3121(4)	0.1818(4)	0.060(3)
C(3)	0.0397(7)	0.3176(4)	0.1260(4)	0.072(3)
C(4)	-0.0043(6)	0.3829(5)	0.1064(3)	0.065(3)
C(5)	0.0354(7)	0.4410(4)	0.1413(4)	0.063(3)
C(6)	0.1226(6)	0.4336(3)	0.1969(3)	0.046(2)
C(7)	0.4573(6)	0.4428(3)	0.4045(3)	0.0440(19)
C(8)	0.4357(7)	0.5093(4)	0.3772(3)	0.055(3)
C(9)	0.3470(8)	0.5569(4)	0.4058(4)	0.062(3)
C(10)	0.2820(7)	0.5402(4)	0.4650(4)	0.061(3)
C(11)	0.3052(7)	0.4772(4)	0.4948(3)	0.055(3)
C(12)	0.3896(6)	0.4290(3)	0.4653(3)	0.048(2)
N(1)	0.6221(7)	0.2018(3)	0.1766(3)	0.067(2)
C(13)	0.6014(9)	0.2093(4)	0.0999(4)	0.086(3)
C(14)	0.7295(8)	0.1481(4)	0.1910(4)	0.079(3)
C(15)	0.4921(8)	0.1861(3)	0.2108(3)	0.064(3)

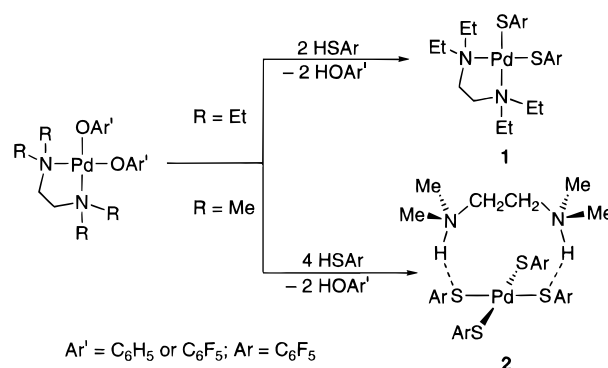
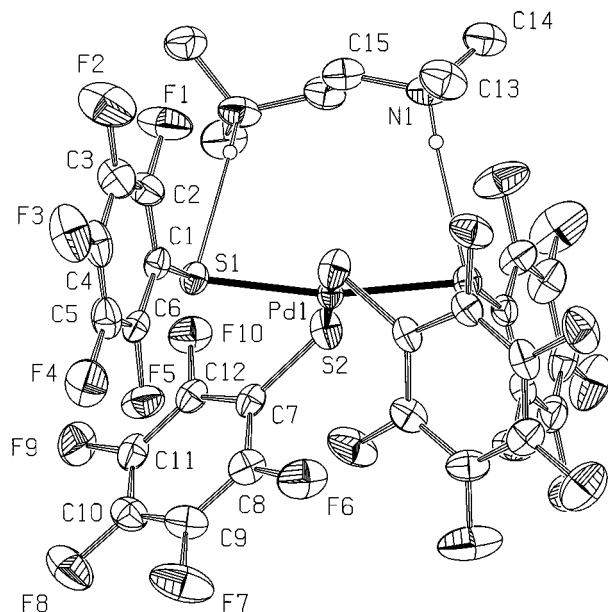
$^a U_{eq} = 1/3$  of the trace of the orthogonalized  $U$  tensor.

Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).<sup>7</sup> Refinement on  $F$  was carried out by full-matrix least-squares techniques (SHELX76).<sup>8</sup> Hydrogen atoms were included in the refinement on calculated positions ( $C-H = 0.98 \text{ \AA}$ ) riding on their carrier atoms, except for the amine hydrogen which was located on a difference Fourier map and subsequently included in the refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with isotropic thermal parameters of  $0.076(7) \text{ \AA}^2$ . Weights were introduced in the final refinement cycles. Convergence was reached at  $R = 0.047$ ,  $R_w = 0.046$ ,  $w = 1/[\sigma^2(F) + 0.000337F^2]$ ,  $S = 3.28$ , for 262 parameters. A final difference Fourier map showed no residual density outside  $-0.43$  and  $0.48 \text{ e \AA}^3$ . Positional parameters are listed in Table 2.

## Results and Discussion

Reaction of the bis(aryloxy)palladium complex  $[\text{Pd}(\text{OC}_6\text{H}_5)_2(\text{teeda})]$  (teeda is the tetraethyl-substituted diamine ligand  $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$ ) with an excess of pentafluorothiophenol affords the neutral bis(arenethiolate) complex  $[\text{Pd}(\text{SC}_6\text{F}_5)_2(\text{teeda})]$  (**1**).  $^1\text{H}$  NMR spectra of **1** show the  $\text{NCH}_2\text{CH}_3$  protons of the diamine ligand to be diastereotopic; *i.e.* the nitrogen atom has a stable prochiral ligand array, and this means that the diamine N-donor atoms are chelate *cis*-coordinated to the palladium center. Formation of **1** is not unexpected since in previous studies we have shown that reaction of  $\text{HOC}_6\text{F}_5$  with  $[\text{Pd}(\text{OC}_6\text{H}_5)_2(\text{teeda})]$  leads to replacement of phenoxide ligands by  $\text{OC}_6\text{F}_5$  groups to form the corresponding neutral complex  $[\text{Pd}(\text{OC}_6\text{F}_5)_2(\text{teeda})]$ .<sup>5</sup>

However, when the bis(aryloxy)palladium complexes  $[\text{Pd}(\text{OC}_6\text{X}_5)_2(\text{teeda})]$  ( $X = \text{H}$  or  $\text{F}$ ) containing a tetramethyl substituted diamine ligand are reacted with  $\text{HSC}_6\text{F}_5$ , an unexpected tetrakis(arenethiolate) complex  $[\text{Pd}(\text{SC}_6\text{F}_5)_4][\text{Me}_2(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}_2]$  (**2**) is obtained (see Figure 1). Complex **2** has been isolated in high yield as a red, thermally stable, crystalline solid. A solid state IR spectrum of **2** shows a broad band at *ca.*  $3250 \text{ cm}^{-1}$ , which is characteristic of the presence of  $\text{N-H}\cdots\text{S}$  hydrogen bonding,<sup>1,2a</sup> and  $^1\text{H}$  NMR solution data ( $\text{CD}_3\text{CN}$ ) are consistent with the proposed stoichiometry. To further characterize the  $\text{N-H}\cdots\text{S}$  interaction, the molecular structure of **2** was determined by a single crystal X-ray diffraction study (see Figure 2). This complex is found to have a square-planar-coordinated palladium(II) center that is S-bonded to four anionic  $\text{SC}_6\text{F}_5$  groups to form a  $[\text{Pd}(\text{SC}_6\text{F}_5)_4]^{2-}$  dianion. This dianion binds in a unique way to a dicationic doubly protonated tmeda ligand, which bridges over the metal atom by forming two  $\text{N-H}\cdots\text{S}$  hydrogen bonds with *trans*-positioned sulfur atoms.

**Figure 1.** Formation of arenethiolate palladium complexes **1** and **2**.**Figure 2.** Thermal motion ellipsoid plot (ORTEP, 50% probability) of the molecular structure of  $[\text{Pd}(\text{SC}_6\text{F}_5)_4][\text{Me}_2(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}_2]$  (**2**) together with the adopted numbering scheme. Hydrogen atoms except those of the  $\text{N-H}\cdots\text{S}$  units are omitted for clarity.

The most intriguing aspects of the structure of **2** lie in the geometry and positioning of the two  $\text{N-H}\cdots\text{SC}_6\text{F}_5$  units. In each unit the amine hydrogen atom, which was located on a difference Fourier map, is clearly involved in an interaction with S ( $\text{N}\cdots\text{S} = 3.256(6) \text{ \AA}$ ), but its distances from both Pd ( $\text{H}\cdots\text{Pd} = 3.11 \text{ \AA}$ ) and the closest F atom of the  $\text{C}_6\text{F}_5$  ring ( $\text{H}\cdots\text{F}(1) = 2.72(3) \text{ \AA}$ ) are not considered significant for inclusion in the bonding description of this complex. In **2** the  $\text{Pd-S}_\text{H}-\text{C}$  angle ( $\text{S}_\text{H} = \text{hydrogen-bonded sulfur atom}$ ) of  $108.5(2)^\circ$  compares well with the angle of  $109.0(3)^\circ$  for  $\text{Pt-S-C}$  in  $[\text{Pt}(\text{SC}_6\text{F}_5)_2\text{-}$

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(PBu<sub>3</sub>)<sub>2</sub>],<sup>9</sup> whereas the Pd–S–C angle of the C<sub>6</sub>F<sub>5</sub> ligand in **2** that is not involved in hydrogen bonding is slightly smaller at 104.6(2)°. The arenethiolate ligands participating in hydrogen bonding have the C<sub>6</sub>F<sub>5</sub> ring almost orthogonal (93.2(2)°) to the Pd–S<sub>H</sub>–C plane, representing an out-of-plane conformation for this ring. This preference of the S<sub>H</sub>–C<sub>6</sub>F<sub>5</sub> ring in **2** for the out-of-plane conformation is unexpected, since the in-plane conformation is usually found in transition metal arenethiolate chemistry.<sup>10</sup> In contrast, the Pd–S–C plane and the C<sub>6</sub>F<sub>5</sub> ring in the non-hydrogen-bonded SC<sub>6</sub>F<sub>5</sub> anion make an angle of 50.6°, creating a situation in-between the in- and out-of-plane conformations. The latter orientation of the C<sub>6</sub>F<sub>5</sub> ring could be a result of steric interactions with the methyl groups of the protonated tmeda ligand.

In **2** the N–H···S hydrogen bonds of 3.256(6) Å are much shorter than those in neutral organic compounds (~3.40 Å) but do fall in the range encountered in inorganic model complexes with amides (3.24–3.50 Å).<sup>1</sup> The angle of approach of the N–H···S hydrogen bonds to the normal of the plane containing the Pd–S–C atoms (*i.e.* angle of electrophilic approach) is 12.7°. This angle is similar to those reported for electrophiles in close proximity to divalent organic sulfur; the most prevalent angle (relative to the normal of the M–S–C plane) on S has been found to be 21 (±9)°.<sup>11</sup> The relatively small angle in **2** is due to the fact that the two N–H···S hydrogen bonds in this complex originate from the same ligand, which is positioned as a [Me<sub>2</sub>(H)NCH<sub>2</sub>CH<sub>2</sub>N(H)Me<sub>2</sub>]<sup>2+</sup> bridge over the [Pd(SAr)<sub>4</sub>]<sup>2-</sup> dianion. Larger angles of approach would elongate the N–H···S hydrogen bonds and destabilize the structure. The two N–H vectors (N–H = 0.89(6) Å) point toward the S atoms (∠N–H···S = 163(5)°) and force the tmeda unit into a specific orientation (NCCN dihedral angle ω = 155.5(3)°) over the metal center. Bridging units over metal centers and N–H···S interactions like those in **2** have also been reported for the Cys–X–Y–Cys unit (X, Y = amino acids) in rubredoxin, and they have been shown to be an important factor in the shift of the redox potential of metalloproteins.<sup>4</sup> According to the “frontier orbital” model,<sup>12</sup> the HOMO in the N–H···S unit is essentially a sulfur lone pair which has substantial p-orbital character and which extends nearly perpendicular to the Pd–S–C plane. The other sulfur lone pair can be considered to belong to an orbital with predominantly sp<sup>2</sup> character that lies in the Pd–S–C plane. This

description indicates a sulfur valence orbital hybridization intermediate between {sp<sup>3</sup>} and {sp<sup>2</sup> + p}.<sup>1a,2b</sup> In **2** the non-hydrogen-bonded sulfur atom, S(2), affords a Pd–S bond length of 2.3367(16) Å, which is slightly longer than the hydrogen-bonded Pd–S(1) bond length of 2.3301(14) Å. This small difference in bond length is consistent with the N–H···S hydrogen bond utilizing a sulfur orbital which has nearly pure p character and which is orthogonal to, and therefore has little influence on, the Pd–S σ-orbital.

In **2** one can expect some weakening of the Pd–S bond through the interaction of the sulfur π-orbitals (occupied by lone pair electrons) with occupied orbitals on the palladium center that results in the formation of molecular orbitals with anti-bonding character. However, this is more than counterbalanced by the stabilizing factors mentioned above. Namely, stabilization of the Pd–S<sub>H</sub> interaction is provided by involvement of S<sub>H</sub> p-orbitals in N–H···S hydrogen bonding with conjugation with the aryl ring π-electrons (out-of-plane), whereas stabilization of the Pd–S interaction is afforded by conjugation of S p-electrons with those of the aryl ring (partly in-plane).

In conclusion, a subtle variation in the nature of the N-donor dialkyl substituents (Me or Et) in tetraalkylethylenediamines leads to a different reactivity of the corresponding palladium bis(aryloxide) complex with HSC<sub>6</sub>F<sub>5</sub> to afford either di- or tetra-substituted products. The unexpected situation in **2** where a diprotonated tmeda functions as a bridging ligand, through formation of N–H···S hydrogen bonds, reveals a new aspect of tmeda chemistry in the field of N–H···X interactions in metal amine species. In particular, N–H···X interactions are believed to be important in a number of metal-complex-catalyzed processes,<sup>13</sup> and in a related context we have investigated the occurrence of N–H···Pt and N–H···Br interactions in organometallic species.<sup>14</sup>

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**Supporting Information Available:** For **2**, further details of the structure determination, including listings of data collection parameters, atomic coordinates, bond lengths and angles, and thermal parameters (9 pages). Ordering information is given on any current masthead page.

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