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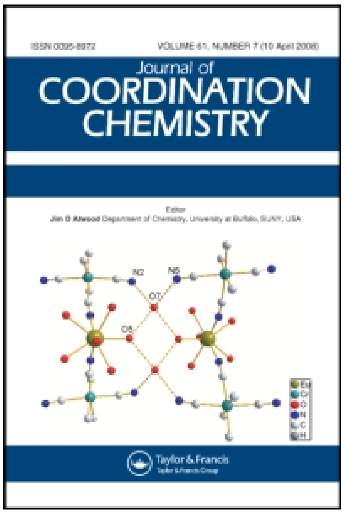

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Synthesis of 1,2-<i>bis</i>(2'-ethynylpyrimidyl) benzene and characterization of the coordination complexes with palladium(II) chloride and silver(I) trifluoromethanesulfonate

Nate Schultheiss[a]; Joseph M. Ellsworth[a]; Eric Bosch[a]; Charles L. Barnes[b]
[a] Department of Chemistry, Missouri State University, Springfield, MO, 65897 [b] Department of Chemistry, University of Missouri, Columbia, MO, 65211

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Synthesis of 1,2-*bis*(2′-ethynylpyrimidyl) benzene and characterization of the coordination complexes with palladium(II) chloride and silver(I) trifluoromethanesulfonate

NATE SCHULTHEISS†, JOSEPH M. ELLSWORTH†, ERIC BOSCH*† and CHARLES L. BARNES‡

†Department of Chemistry, Missouri State University, Springfield, MO, 65897
‡Department of Chemistry, University of Missouri, Columbia, MO, 65211

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Design, synthesis and coordination chemistry of a new trans-coordinating dipyrimidyl ligand are reported. Sonogashira coupling of 2-iodopyrimidine with 1,2-diethynylbenzene yielded the ligand 1,2-*bis*(2′-ethynylpyrimidyl)benzene (**3**), in good yield. Coordination complexes were formed with silver(I) and palladium(II) salts. The X-ray crystallographic characterization of the 1 : 1 complex formed between palladium(II) dichloride and **3**, and the 4 : 2 complex formed between silver(I) trifluoromethanesulfonate and **3** are reported.

Keywords: N-ligands; Pyrimidine; Ligand design; Silver; Palladium

1. Introduction

We have been interested in N-based ligands for several years and in 2001 reported the design of the first *trans*-coordinating bipyridyl ligand, 1,2-*bis*(2′-pyridylethynyl) benzene, shown as **1** in scheme 1 [1]. We modeled the planar conformation of the ligand as shown in scheme 1 and noted that this conformation would position the N-atoms in the ideal position to coordinate certain transition metal cations. Indeed, we reported the formation and the X-ray structural characterization of the essentially planar coordination complexes of **1** with silver(I) and palladium(II) cations. Thummel [2] independently reported the synthesis of **1** while Bunz [3] reported the synthesis and coordination chemistry of the 4,5-dimethoxybenzene analogue of **1** in the same year. We subsequently reported the size-selective coordination chemistry of the related dipyrazyl ligand (**2**) (scheme 1) [4]. We are interested in exploring the coordination chemistry of the related dipyrimidyl ligand (**3**) in particular whether all four nitrogen

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*Corresponding author. Email: ericbosch@missouristate.edu

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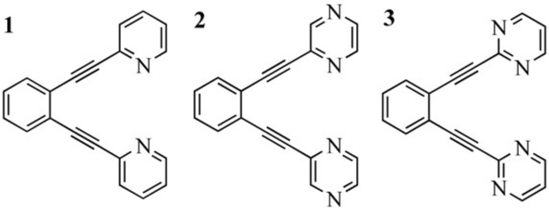

Scheme 1. Related trans-coordinating ligands.

atoms will be involved in coordinating to metal cations. In this note we report our preliminary results of the coordination chemistry of the dipyrimidyl ligand (**3**).

2. Results

The dipyrimidyl ligand (**3**) was synthesized by Sonogashira coupling of 2-iodopyrimidine and 1,2-diethynyl benzene [5]. The ligand was then reacted with palladium(II) salts and silver(I) salts. When mixtures of the ligand with palladium dichloride in acetonitrile were allowed to evaporate, microcrystalline solids and powders were formed. In order to prepare crystals suitable for X-ray analysis a solution of the palladium salt in acetonitrile was layered over a dichloromethane solution of the ligand **3**. Slow diffusion resulted in formation an orange crystalline solid. Elemental analysis confirmed that a 1 : 1 complex was formed. A suitable crystal was chosen for single-crystal X-ray analysis and this revealed an essentially planar coordination complex with the palladium(II) dichloride nestled between the two N atoms as shown in figure 1. One acetonitrile molecule was included in the crystal. The crystallographic data are shown in table 1.

The good fit of the palladium(II) cation between the two nitrogen atoms in this complex is clear. For example, the coordination about the palladium atom is also almost perfectly square planar with angles N(1)–Pd(1)–N(3) and Cl(1)–Pd(1)–Cl(1) of 178.75(6) and 176.669(19)°, respectively, and N–Pd–Cl angles ranging from 87.86(4) to 91.42°. Furthermore, the ligand is also essentially planar with a torsional angle of approximately 11° between the phenyl ring and pyrimidine ring N(1)–C(4) and a torsional angle of about 1.5° between the phenyl ring and pyrimidine N(3)–C(18). The palladium–nitrogen bond distances, Pd(1)–N(1) and Pd(1)–N(3), are 2.0150(14) and 2.0164(15) Å respectively. The almost orthogonal packing of adjacent complexes is shown in figure 2. There are no exceptional inter-complex interactions in the crystal although the mutually orthogonal complexes allow for the formation of a weak pyrimidine–pyrimidine C–H···N interaction between adjacent complexes. This is shown as "a" in figure 2. The N···C and N···H distances are 3.612 and 2.692 Å respectively with a C–H···N angle of 163.16°. The second pyrimidine has a weak N···H–C interaction with the acetonitrile molecule – this is shown as "b" in figure 2. The N···C and N···H distances are 3.435 and 2.471 Å respectively with a C–H···N angle of 167.59°.

We expected that a similar planar complex would be formed between **3** and silver(I) salts. We again had to use the method of slow-diffusion to form crystals. We were able to form suitable crystals for X-ray crystallographic analysis by dissolving silver(I)

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Table 1. Crystal data and structure refinement for **4** and **5**.

Compound	**4**	**5**
CCDC identification code	602686	602687
Empirical formula	$C_{20}H_{13}Cl_2N_5Pd$	$C_{10}H_5AgF_3N_2O_3S$
Formula weight	500.65	796.20
Crystal system, Space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a (Å)	8.9035(3)	9.1631(3)
b (Å)	21.2442(8)	18.5536(6)
c (Å)	10.5014(4)	15.1681(5)
β (°)	99.6380(10)	105.5750
Volume (Å^3)	1958.28(12)	2484.02(14)
Z, Calculated density (g cm^{-3})	4, 1.698	4, 2.129
Absorption coefficient (mm^{-1})	1.236	1.836
Reflections collected/unique	13928/4330 [R(int) = 0.0189]	17606/5484 [R(int) = 0.0233]
Goodness-of-fit on F^2	1.031	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0212$, $wR_2 = 0.0539$	$R_1 = 0.0252$, $wR_2 = 0.0578$
R indices (all data)	$R_1 = 0.0244$, $Wr_2 = 0.0556$	$R_1 = 0.0313$, $wR_2 = 0.0607$
Largest diff. peak and hole (e Å^{-3})	0.444 and −0.299	0.629 and −0.520

Absorption correction, Semi-empirical from equivalents; Refinement method, Full-matrix least-squares on F^2.

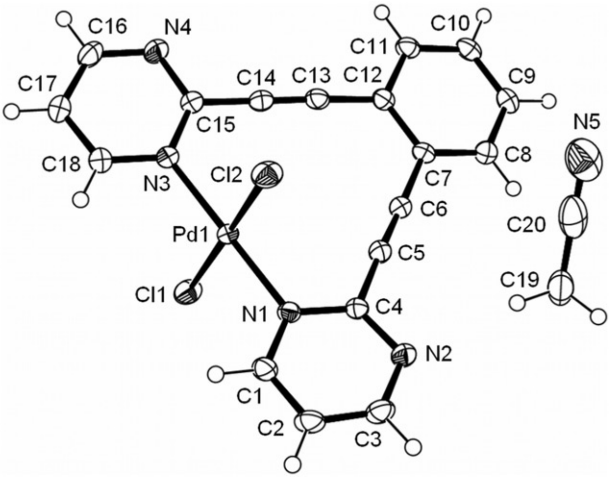

Figure 1. View of complex **4** formed between **3** and palladium(II) dichloride.

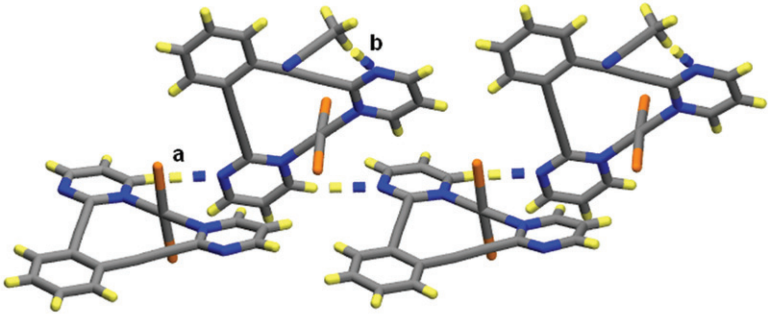

Figure 2. View of the packing of adjacent complexes **4** with the acetonitrile solvent.

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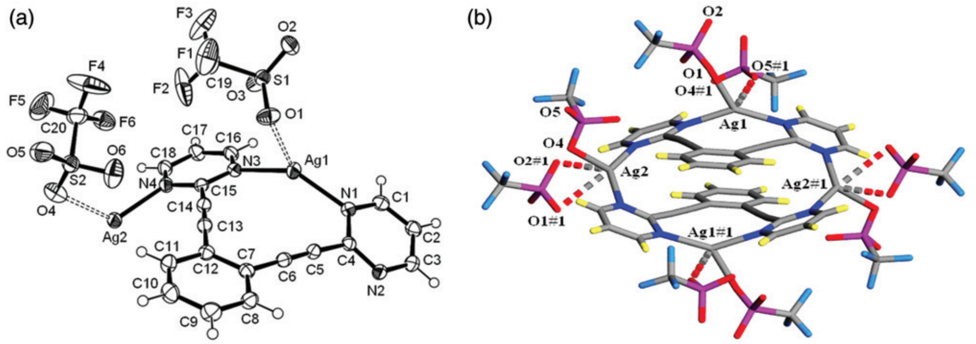

Figure 3. (a) View of the asymmetric unit of **5** formed between ligand **3** and silver(I) trifluoromethanesulfonate. (b) Perspective view of the 2 : 4 complex of **3** with silver(I) trifluoromethansulfonate showing the coordination about each silver atom with all anions shown.

trifluoromethanesulfonate in nitromethane and layering this over a dichloromethane solution of **3**. Elemental analysis indicated that a complex with a 2 : 1 ratio of silver(I) : bipyrimidyl ligand was formed. The asymmetric unit of the structure is shown in figure 3(a).

It is clear from figure 3 that the structure is far more complex than that obtained with palladium(II). There are two distinct silver cations, one coordinated between the two arms of the ligand and the second silver(I) cation coordinated by the outer nitrogen atom. The ligand is not planar and the pyrimidine–silver–pyrimidine bond for the internally coordinated silver is bent with a bond angle N(1)–Ag(1)–N(3) of 141.86(7)°. Furthermore the second silver is coordinated to N(2) of a second ligand and has angle N(4)–Ag(2)–N(2)#1 of 137.76(7)°; this bend allows the formation of a discrete 2 : 4 complex between **3** and silver(I) triflate. Each silver is coordinated to the triflate counterion with silver–oxygen distances of 2.468(2) and 2.552(2) Å for Ag(1)–O(1) and Ag(2)–O(4), respectively. The 2 : 4 complex is shown in figure 3(b). The coordination sphere about each silver atom is completed by coordination to neighboring triflate oxygen atoms. Thus, silver Ag(1) has a weak interaction to O(5)#1 with silver oxygen distance of 2.619 Å while the other triflate anion has a weak bidentate interaction to Ag(2) with silver–oxygen distances of 2.605 Å (O2#2) and 2.892 Å (O1#1).

3. Discussion

We previously reported X-ray structures of the palladium(II) dichloride complexes formed with **1** [1] and **2** [6] and note that the planar complex reported here is very similar. In contrast, the silver(I) trifluoromethansulfonate complex is very different from the silver(I) complexes isolated from **1** and **2**. In both those examples the ligands remainded essentially planar. For example, the silver(I) trifluoromethanesulfonate complex of dipyridyl ligand (**1**) was essentially planar and the discrete complexes stacked on top of each other to form columns of triangular complexes [1]. With dipyrazyl ligand **2** we reported the X-ray structure of the silver(I) nitrate complex and noted that it was also an essentially-coplanar discrete coordination complex [4]. The silver(I) nitrate complexes also stacked on top of each other to form columns of triangular complexes. The complex reported here exhibits rather complex "dimer-like" nature with silver coordinated to both the internal and external nitrogen atoms of the pyrimidines.

4. Experimental

All chemicals were purchased from Aldrich and used as received. 1,2-Diethynyl benzene [2] and 2-iodopyrimidine [7] were prepared as described previously.

4.1. *Synthesis*

4.1.1. 1,2-*bis*(2′-Pyrimidylethynyl)benzene. 1,2-Diethynylbenzene (0.544 g, 4.3 mmol), 2-iodopyrimidine (1.904 g, 9.3 mmol), copper iodide (8 mg, 0.04 mmol), triphenylphosphine (60 mg, 0.23 mmol), *bis*(triphenylphosphine)palladium(II) dichloride (60 mg, 0.09 mmol, 0.7 mol%) were added to a reaction tube. Dichloromethane (15 mL) and piperidine (5 mL) were added, and nitrogen bubbled through the resultant mixture for 15 min at room temperature. The tube was sealed with a Teflon stopper and heated at 45°C. The reaction was periodically monitored by TLC and on completion the reaction mixture was diluted with ethyl acetate (200 mL) and washed with water (3 × 100 mL). The organic layer was dried over sodium sulfate and the solvent removed on a rotary evaporator. The residue was chromatographed on silica with hexane/ethyl acetate (3 : 1) as eluant and **3** obtained as a light-brown powder (0.94 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) $\delta = 7.26$ (t, $^3J_{H,H} = 4.8$ Hz, 2H, 4″-H), 7.43 (dd, $^3J_{H,H} = 3.6$, 6.0 Hz, 2H, 4-H and 5-H), 7.74 (dd, $^3J_{H,H} = 3.6$, 6.0 Hz, 2H, 3-H and 6-H), 8.76 (d, $^3J_{H,H} = 4.8$ Hz, 4H, 3″-H and 5″-H); ^{13}C NMR δ 85.86, 92.20, 120.03, 124.92, 129.62, 133.54, 153.42, 157.49; $C_{18}H_{10}N_4$ (282.30): Calcd C, 76.58; H, 3.57; N, 19.85; found: C, 76.79; H, 3.65; N, 19.34.

4.1.2. Complexation of palladium(II) chloride with 3. A solution of palladium(II) chloride (2.6 mg, 0.01 mmol) in acetonitrile (1 mL) was carefully layered over a solution of **3** (2.8 mg, 0.01 mmol) in dichloromethane (1 mL). After 4 days yellow/orange crystals of **4** had formed. $C_{18}H_{10}Cl_2N_4Pd$ (459.62): Calcd C, 47.04; H, 2.19; N, 12.19. found: C, 46.99; H, 2.17; N, 12.15.

4.1.3. Complexation of silver(I) trifluoromethanesulfonate with 3. A solution of silver(I) trifluoromethane sulfonate (10.3 mg, 0.04 mmol) and **3** (11.2 mg, 0.04 mmol) was prepared in warm nitromethane (2 mL). This was cooled to room temperature and carefully layered over dichloromethane (3 mL) in a screw-cap vial. The vial was sealed and allowed to stand in the dark. Clear block-shaped crystals of **5** formed after 24 h. The solution was removed and the crystals dried in the atmosphere. $C_{20}H_{10}Ag_2F_6N_4O_6S_2$ (796.18): Calcd C, 30.17; H, 1.27; N, 7.04. found: C, 30.38; H, 1.15; N, 7.41.

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4.2. *X-ray data collection, structure solution, and refinement*

An orange crystal of coordination complex **4** with dimensions $0.50 \times 0.25 \times 0.20\,\mathrm{mm}^3$ and a colorless needle of complex **5** of dimensions $0.50 \times 0.15 \times 0.10\,\mathrm{mm}^3$ were selected for X-ray analysis. The X-ray data for **4** and **5** were collected at 173(2) K on a Siemens CCD area detector-equipped diffractometer with Mo-Kα radiation. The structures were solved using SHELXS-97 and refined with SHELXL-97 [8]. Hydrogen atoms were included in the calculated positions. Ortep 3 [9] and X-Seed [10] were used to prepare the figures.

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