1,2-Bis(2-pyridylethynyl)benzene, a Novel Trans-Chelating Bipyridyl Ligand. Structural Characterization of the Complexes with Silver(I) Triflate and Palladium(II) Chloride

Eric Bosch*

Department of Chemistry, Southwest Missouri State University, Springfield, Missouri 65804

Charles L. Barnes

Department of Chemistry, University of Missouri, Columbia, Missouri 65211

Received January 16, 2001

The design, synthesis, and complexation characteristics of the bipyridyl ligand 1,2-bis-(2-pyridylethynyl)benzene are described. The X-ray crystallographic characterization of the 1:1 complexes of 1,2-bis(2-pyridylethynyl)-benzene with silver(I) triflate and palladium(II) chloride are described. In the X-ray crystal structure of the silver-(I) triflate complex the ligand is essentially planar with negligible distortion compatible with a good fit of the cation in the "cavity" between the pyridine N atoms. Indeed the silver center is almost linear with the N(1)−Ag(1)−N(2) angle of 177.02(10)°. The ligand is also essentially planar in the palladium(II) chloride complex with square planar coordination about the palladium with the N(1)−Pd(1)−N(2), Cl(2)−Pd(1)−Cl(2), and N(1)−Pd(1)−Cl(2) angles at 179.53(7), 177.17(2), and 90.52(5)°, respectively.

Introduction

The field of pyridine and polypyridine metal complexes is a historically rich and expanding area in coordination chemistry.[1] Current interest in pyridines is centered on their use as building blocks in macro- and supramolecular chemistry. Indeed a host of supramolecular structures,[2] polymers,[3] and dendrimers[4] have been assembled using in situ pyridine metal complexation as the means of construction.

Among dipyridyl ligands 2,2′-bipyridine and 1,10-phenanthroline are especially common ligands used in the synthesis of wide variety of metal complexes.[5,6] In 1,10-phenanthroline the N atoms are locked in space and the relative position and orientation of the N atoms facilitates cis chelation of metal cations. Free rotation about the pyridyl linkage in 2,2-dipyridyl allows the same conformation and this ligand also forms cis-chelated coordination complexes.

In contrast polymeric complexes are formed from dipyridyl ligands in which the N atoms are oriented in opposite directions as typified by 4,4′-bipyridyl.[7]

As part of our study of monomeric and polymeric metal−pyridinyl complexes,[8] we have designed a bipyridyl ligand in which the pyridyl N atoms easily attain the appropriate separation for trans chelation of metal cations. In this paper we present the synthesis and characterization of the ligand 1,2-bis-(2-pyridylethynyl)benzene and the structural characterization of the 1:1 complex of the ligand with silver(I) triflate and palladium(II) chloride.[9]

We are currently exploring the application of this structural motif to the formation of one- and two-dimensional pyridine−metal coordination polymers on the basis of the reaction of the analogous tetrakis(2-pyridylethynyl)benzene and hexakis(2-pyridylethynyl)benzene with metal ions favoring square planar coordination.

Experimental Section

General Methods. The ^{1}H NMR spectra were recorded at 200 MHz, and the ^{13}C NMR spectra were recorded at 50 MHz. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Materials. Diethylamine (Across), 2-bromopyridine, 1,2-dibromobenzene, copper iodide (Aldrich), (trimethylsilyl)acetylene (GFS), hexanes, ethyl acetate (Fisher), *trans*-dichlorobis(triphenylphosphine)-palladium(II), silver(I) trifluoromethanesulfonate, silver(I) hexafluoroantimonate, palladium(II) dichloride bis(acetonitrile) (Strem), and silica gel (Merck) were used as received.

Synthesis. 1,2-Diethynylbenzene (1).[10] A solution of 1,2-dibromobenzene (2.5 g, 10.6 mmol), (trimethylsilyl)acetylene (3.2 mL, 23.3 mmol), triphenylphosphine (120 mg, 0.74 mmol), copper iodide (8 mg, 0.04 mmol), and bis(triphenylphosphine)palladium(II) chloride (78 mg, 0.11 mmol) in diethylamine (60 mL) was prepared in a pressure flask. Argon was bubbled through the solution for 5 min and the vessel then sealed with a Teflon stopcock and heated at 70 °C for 8 h. The flask was allowed to cool to room temperature, diluted with hexane, and

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 348−354. (b) Tomasik, P.; Ratajewicz, Z. *Chemistry of Heterocyclic Compounds, Pyridine Metal Complexes*; Wiley: New York, 1985; Vol. 14, Part 6. (c) Garnovskii, A. D.; Sadimenko, A. P. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Wiley: New York, 1999; p 1.

(2) (a) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524. (b) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53. (c) Constable, E. C. *Prog. Inorg.Chem.* **1994**, *42*, 67.

(3) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1727.

(4) Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Lasado, J. *Coord. Chem. Rev.* **1999**, *193*−*195*, 395.

(5) (a) Constable, E. C. *Adv. Inorg. Chem.* **1989**, *34*, 1. (b) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135. (c) Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gilllard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1986; Vol. 2, p 73.

(6) (a) Schilt, A. A. *Analytical Applications of 1,10-Phenanthroline and Related Compounds*; Pergamon: Oxford, U.K., 1969. (b) Krohnke, F. *Synthesis* **1976**, 1.

(7) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755. (b) Plater, M. J.; Foreman, M. R. St. J.; Gelbrich, T.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2000**, 3065.

(8) Bosch, E.; Barnes, C. L. *Inorg. Chem.* **2001**, in press.

(9) For a recent report of a trans-chelating ligand based on ferrocene, see: Pilloni, G.; Longato, B.; Bandoli, G. *Inorg. Chim. Acta* **2000**, *298*, 251.

(10) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

10.1021/ic010058u CCC: $20.00
Published on Web 05/16/2001

washed twice with water and then with saturated aqueous sodium chloride. The organic phase was separated and dried with magnesium sulfate, and the solvent was removed in vacuo to yield a light brown oil. The ^{1}H NMR spectrum indicated that this material was essentially pure 1,2-bis((trimethylsilanyl)ethynyl)benzene: ^{1}H NMR δ ($CDCl_3$) 7.39 (dd, $J = 3.3$, 5.6 Hz, 2H), 7.25 (dd, $J = 3.3$, 5.6 Hz, 2H), 0.28 (s, 18H). The crude oil was thus immediately deprotected as follows: The crude oil was dissolved in methanol (100 mL) and sodium carbonate (0.5 g) added, and the heterogeneous mixture was stirred at room temperature for 2 h. The mixture was diluted with water and extracted twice with hexanes (2 × 100 mL). The hexane extracts were washed with water and saturated aqueous sodium chloride and then dried over magnesium sulfate. The hexane was evaporated in vacuo and the crude product purified by flash chromatography with hexanes as eluant. 1,2-Diethynylbenzene was obtained as a pale yellow oil (1.27 g, 95%). ^{1}H NMR ($CDCl_3$): δ 7.61 (m, 2 H), 7.45 (m, 2 H), 3.49 (s, 2H). ^{13}C NMR: δ 132.59, 128.47, 125.00, 81.79, 81.15.

1,2-Bis(2-pyridylethynyl)benzene (2). A diethylamine (20 mL) solution of 1,2-diethynylbenzene (220 mg, 1.74 mmol), 2-bromopyridine (950 mg, 6.1 mmol), triphenylphosphine (30 mg), copper iodide (5 mg), and bis(triphenylphosphine)palladium(II) chloride (36 mg) in a pressure flask was degassed as described above and sealed with a Teflon stopper. The flask was heated at 80 °C for 8 h and then allowed to cool to room temperature. The reaction mixture was diluted with ethyl acetate and washed with dilute aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride. The organic phase was dried with magnesium sulfate and the solvent removed in vacuo. The crude product was subjected to flash chromatography with ether/hexane (3:1) as eluant and the desired compound obtained as an off-white solid (404 mg, 83%). The material was recrystallized from ether/hexane as colorless cubic crystals. Anal. Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.31; N, 9.99. Found: C, 85.66; H, 4.27; N, 9.94. ^{1}H NMR (CD_3CN): δ 8.64 (t d, $J = 1.4$, 5.2 Hz, 2 H), 7.79−7.76 (m, 4 H), 7.68 (dd, $J = 3.4$, 5.4 Hz, 2H), 7.47 (dd, $J = 3.4$, 5.8 Hz, 2 H), 7.38−7.32 (m, 2 H). ^{13}C NMR: δ 151.8, 144.3, 138.1, 133.8, 130.8, 129.3, 126.5, 125.0, 94.6, 88.2.

(1,2-Bis(2-pyridylethynyl)benzene)silver Trifluoromethanesulfonate (3). Silver trifluoromethanesulfonate (41 mg, 0.16 mmol) and 1,2-bis-(2-pyridylethynyl)benzene (48 mg, 0.17 mmol) were added to a Schlenk flask under an argon atmosphere, and the flask was sealed with a rubber septum. Dichloromethane (0.5 mL) was added with the aid of a syringe and the resultant slurry stirred and heated gently until a clear solution formed. Hexane (2 mL) was added and the clear solution cooled in a freezer. Colorless needles formed and were filtered after 2 days and dried under vacuo (70 mg, 85%). Anal. Calcd for $C_{21}H_{12}AgF_3N_2O_3S$: C, 46.95; H, 2.25; N, 5.21. Found: C, 46.69; H, 2.72; N, 5.13. ^{1}H NMR (CD_3CN): δ 8.34 (md, $J = 5.0$ Hz, 2 H), 7.76 (dt, $J = 1.8$, 7.8 Hz, 2 H), 7.42 (td, $J = 1.0$, 6.0 Hz, 2 H), 7.35 (ddd, $J = 1.4$, 5.0, 7.8 Hz, 2 H), 7.29−7.23 (m, 2 H), 7.21−7.15 (m, 2 H). ^{13}C NMR: δ 152.6, 143.7, 140.4, 133.6, 131.0, 129.5, 126.0, 124.2, 93.0, 91.0.

(1,2-Bis(2-pyridylethynyl)benzene)silver Hexafluoroantimonate (4). The colorless needles were prepared in a way similar to that for **3** and recrystallized from mesitylene/acetonitrile. Anal. Calcd for $C_{20}H_{12}$-$AgF_6N_2Sb\cdot CH_3CN$: C: 39.76; H: 2.27; N: 6.31. Found: C, 39.51; H, 2.20; N, 5.69. ^{1}H NMR (CD_3CN): δ 8.64 (td, $J = 0.8$, 5.6 Hz, 2 H), 7.99 (dt, $J = 1.4$, 8.0 Hz, 2 H), 7.80 (dd, $J = 0.8$, 8.0 Hz, 2H), 7.70 (dd, $J = 3.8$, 5.7 Hz, 2 H), 7.57 (ddd, 1.0, 5.6, 8.0 Hz, 2 H), 7.51 (dd, $J = 3.8$, 5.7 Hz, 2 H). ^{13}C NMR: δ 152.69, 144.15, 140.42, 133.87, 131.39, 129.57, 126.17, 124.85, 93.40, 90.79.

(1,2-Bis(2-pyridylethynyl)benzene)palladium(II) Dichloride (5). The ligand **2** (65 mg, 0.33 mmol) was dissolved in 4 mL of dichloromethane and a separate solution of $Pd(Cl)_2(CH_3CN)_2$ (83 mg, 0.33 mmol) in 10 mL of acetonitrile prepared. The acetonitrile solution was carefully layered over the dichloromethane solution and the vial capped and placed in the dark. After 10 days orange crystals were harvested (86 mg, 57%). Anal. Calcd for $C_{20}H_{12}Cl_2N_2Pd$: C, 52.49; H, 2.64; N, 6.12. Found: C, 52.42; H, 2.70; N, 6.17.

Table 1. Crystal Data and Structure Refinement for **3** and **5**

	3	**5**
empirical formula	$C_{22}H_{14}AgCl_2F_3N_2O_3S$	$C_{20}H_{12}Cl_2N_2Pd$
fw	622.18	457.62
cryst system, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, Å	8.3926(17)	7.4297(9)
b, Å	13.788(3)	8.4100(10)
c, Å	20.091(4)	15.1003(18)
α, deg	90	80.269(2)
β, deg	90.438(4)	87.255(2)
γ, deg	90	70.697(2)
V, A^3	2324.7(8)	877.64(18)
Z	4	2
D_{calc}, Mg/m^3	1.778	1.732
temp, K	173(2)	173(2)
λ(Mo Kα), Å	0.710 73	0.710 73
μ(Mo Kα), mm^{-1}	1.239	1.366
F(000)	1232	452
R1 [$I > 2\sigma(I)$]	0.0366	0.0259
wR2 [$I > 2\sigma(I)$]	0.0817	0.0687
R1 (all data)	0.0586	0.0285
wR2 (all data)	0.0890	0.0702
largest diff peak and hole, e Å^{-3}	0.904 and −0.702	0.635 and −0.459

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

Bond Lengths			
Ag(1)−N(1)	2.152 (2)	Ag(1)−N(2)	2.155(3)
C(6)−C(7)	1.192(4)	C(14)−C(15)	1.194(4)
C(8)−C(13)	1.416(4)	C(10)−C(11)	1.391(5)
Bond Angles			
N(1)−Ag(1)−N(2)	177.02(10)	Ag(1)−N(2)−C(16)	121.48(19)
Ag(1)−N(1)−C(5)	120.61(19)	C(5)−C(6)−C(7)	177.8(3)
C(6)−C(7)−C(8)	176.5(3)	C(13)−C(14)−C(15)	178.4(3)
C(14)−C(15)−C(16)	179.2(4)		

Crystallography. Rod-shaped crystals of **3** suitable for X-ray crystal structure analysis were formed on cooling a concentrated dichloromethane solution in the freezer overnight. These crystals rapidly became opaque when removed from the mother liquor. Consequently the crystals and mother liquor were kept at −15 °C and were transferred with a Pasteur pipet onto a watch glass resting directly on a slurry of ethylene glycol/CO_2 (−15 °C) under a microscope. A rod-shaped crystal was selected and cut to size (0.35 × 0.15 × 0.15 mm) in the mother liquor at −15 °C. The crystal was picked out of the cold mother liquor with the glass fiber attached to the goniometer head and the goniometer head rapidly replaced on the diffractometer in a flow of cold nitrogen gas (173 K). Table 1 lists the crystallographic data. A total of 5103 unique reflections were collected with $1.79° < \theta < 27.11°$. The structure was solved using SHELXS-97[11] and refined using SHELXL-97.[12] Hydrogen atoms were included in the calculated positions. Selected interatomic distances and angles for **3** are given in Table 2.

Crystals of **5** suitable for X-ray analysis were obtained as described in the synthesis section. These crystals are indefinitely stable in the atmosphere and were thus handled without special precautions. A crystal with dimensions 0.25 × 0.15 × 0.15 mm was selected. Table 1 lists the crystallographic data. A total of 3766 unique reflections were collected with $2.60° < \theta < 27.12°$. The structure was solved using SHELXS-97[11] and refined using SHELXL-97.[12] Hydrogen atoms were included in the calculated positions. Selected interatomic distances, angles, and torsional angles for **5** are given in Table 3.

Results and Discussion

Ligand Design and Synthesis. We used Spartan Plus[13] to model a variety of dipyridyl ligands and analyze their potential as trans-chelating ligands. The ligand L was found to have a favorable spacing between the two pyridyl nitrogen atoms of

(11) Sheldrick, G. M. *SHELXS-97, Crystal Structure Solution*; University of Gottingen: Gottingen, Germany, 1997.
(12) Sheldrick, G. M. *SHELXL-97, Crystal Structure Refinement*; University of: Germany, Gottingen, 1997.
(13) Wavefunction, Inc., Irvine, CA 92612.

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsional Angles (deg) for **5**

Bond Lengths			
Pd(1)−N(2)	2.0113(19)	Pd(1)−N(1)	2.0143(18)
Pd(1)−Cl(2)	2.3119(6)	Pd(1)−Cl(3)	2.3185(6)
C(6)−C(7)	1.189(3)	C(14)−C(15)	1.198(3)
C(8)−C(13)	1.410(3)	C(10)−C(11)	1.378(4)
Bond Angles			
N(2)−Pd(1)−N(1)	179.53(7)	N(2)−Pd(1)−Cl(2)	89.85(5)
N(1)−Pd(1)−Cl(2)	90.52(5)	N(2)−Pd(1)−Cl(3)	89.96(6)
N(1)−Pd(1)−l(3)	89.66(5)	Cl(2)−Pd(1)−Cl(3)	177.17(2)
C(1)−N(1)−Pd(1)	120.73(15)	N(1)−C(1)−C(2)	122.4(2)
C(20)−N(2)−Pd(1)	119.20(16)	N(1)−C(5)−C(6)	117.9(2)
C(7)−C(6)−C(5)	175.2(2)	C(6)−C(7)−C(8)	175.9(2)
C(15)−C(14)−C(13)	177.6(2)	C(14)−C(15)−C(16)	177.7(2)
C(20)−C(19)−C(18)	119.0(2)		
Torsional Angles			
Cl(2)−Pd(1)−N(1)−C(1)	−102.68(17)	Cl(3)−Pd(1)−N(1)−C(1)	74.49(17)
Cl(2)−Pd(1)−N(1)−C(5)	78.34(16)	Cl(3)−Pd(1)−N(1)−C(5)	−104.49(16)
Cl(2)−Pd(1)−N(2)−C(20)	94.06(17)	Cl(3)−Pd(1)−N(2)−C(20)	−83.11(17)
Cl(2)−Pd(1)−N(2)−C(16)	−86.72(16)	Cl(3)−Pd(1)−N(2)−C(16)	96.11(16)

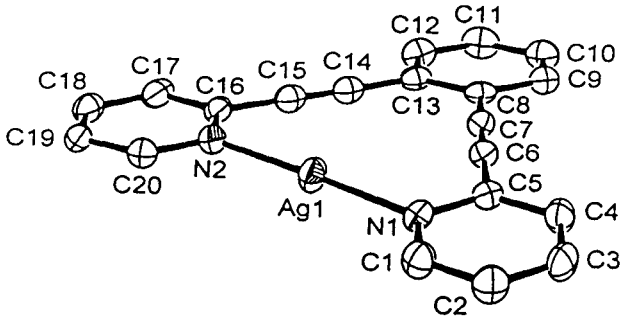

Figure 1. Perspective Ortep[19] view of **3** ($C_{22}H_{12}AgF_3N_2O_3S$) with ellipsoids drawn at 50% probability and H atoms, the triflate anion, and the solvent molecule, CH_2Cl_2, omitted for clarity.

3.86 Å. We reasoned that the alkynyl groups would be able to flex sufficiently to accommodate a range of transition metal cations including silver(I) and palladium(II).

Accordingly we synthesized the ligand to verify this prediction. 1,2-Diethynylbenzene, **1**, was first synthesized from 1,2-dibromobenzene using Sonogashira's palladium-catalyzed coupling procedure.[10] Thus the palladium-catalyzed coupling of 1,2-dibromobenzene with 2 equiv of (trimethylsilyl)acetylene was followed by base-promoted deprotection. The resultant 1,2-diethynylbenzene was coupled with a moderate excess of 2-bromopyridine to yield the ligand, **2**, 1,2-bis(2-pyridylethynyl)benzene, in 83% yield.

Complex Preparation. Silver(I) complexes were prepared by stirring a slurry containing a 1:1 mixture of the appropriate silver salt and the ligand **2** in dichloromethane until a clear homogeneous solution formed. With silver(I) triflate the slurry was heated gently for several minutes. Crystals formed when the solution was cooled in the refrigerator. The palladium salt was formed by layering a dichloromethane solution of the ligand with an acetonitrile solution of palladium dichloride and allowing the slow diffusion of the two layers over 1 week.

X-ray Crystallographic Characterization. Complex 3. The dipyridyl ligand is essentially planar as shown in Figure 1. Indeed the interplanar dihedral angles formed between the benzene ring and the two pyridyl rings are 2.06 and 8.56°, respectively. The coordination about the silver atom is practically linear with the N(1)−Ag(1)−N(2) angle of 177.02(10)° with normal silver−nitrogen bond lengths of 2.152(2) and 2.155(3) Å.[14] The minimal strain in the dipyridyl ligand is confirmed by the near linearity of the two pendant alkynes with distortions from linearity of only 2.2, 3.5, 1.6, and 0.8° for angles C(5)−C(6)−C(7), C(6)−C(7)−C(8), C(13)−C(14)−C(15), and C(14)−C(15)−C(16), respectively. This slight bending of the alkynes is required to accommodate the silver(I) cation. Indeed the measured N(1)−N(2) distance of 4.305 Å is significantly larger than the calculated optimal distance with all three rings coplanar of 3.861 Å. The bending of the alkynes and opening of the ligand is accompanied by slight elongation of the inner bond of the benzene ring, C(8)−C(13), to 1.416 Å to accommodate the silver cation. The triangular shaped molecules of **3** form staggered slip-stacked columns shown in Figure 2. The interplanar distance is approximately 3.3 Å, and the extent of the overlap between the staggered adjacent molecules is shown in Figure 3 . Complex **3** has approximately the same size and shape as tribenzocyclotriyne,[15] and interestingly there are similarities in the crystal packing of these molecules. Most notably tribenzocyclotriyne forms staggered slip-stacked columns with an interplanar distance of 3.3 Å although the extent of overlap between adjacent molecules within a stack is less than that reported here (Figure 3).[16] By contrast the crystalline nickel(0) complex with tribenzocyclotriyne forms eclipsed slip-stacked columns with an interplanar distance of 3.37 Å.[17] We are currently exploring the potential of the π-stacking of cyclic coordination complexes as a motif for the synthesis of nanochannels.[18]

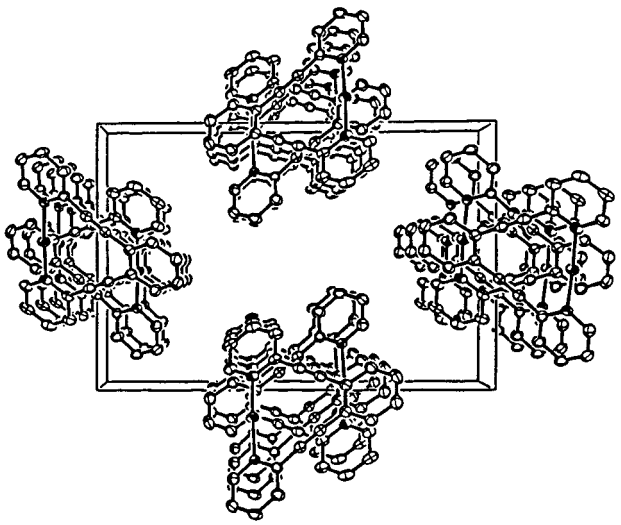

Figure 2. View of the π-stacked columns of coordination complexes **3** with the triflate anions and the solvent of crystalization, CH_2Cl_2, omitted for clarity.

(14) See for example the parent silver(I) dipyridine complex in the following: Menchetti, S.; Rossi, G.; Tazzoli, V. *Rend. Ist. Lomb. Aci. Sci. Lett. A* **1970**, *104*, 309.

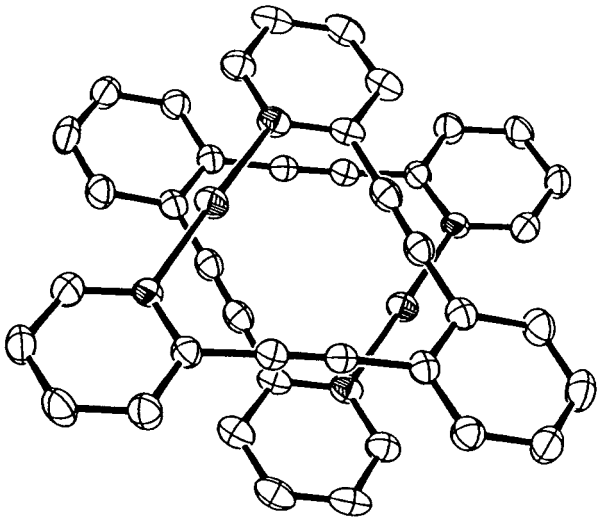

Figure 3. View showing the staggered orientation, and overlap between, adjacent complexes.

Complex 5. The conformation of the ligand in the complex with palladium dichloride is very similar to that of complex **3** (see Figure 4). Thus the ligand is essentially planar with interplanar dihedral angles of 8.9 and 6.6°. The distortion of the alkynes from linearity is 4.8, 4.1, 2.4, and 2.3° for angles C(5)−C(6)−C(7), C(6)−C(7)−C(8), C(13)−C(14)−C(15), and C(14)−C(15)−C(16), respectively, with the corresponding elongation of the inner benzene bond C(8)−C(13) to 1.410(3)°

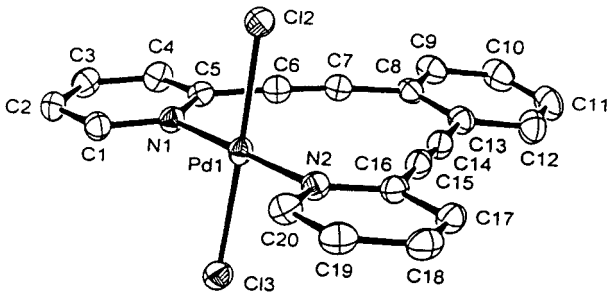

Figure 4. Perspective view of **5** with the hydrogen atoms omitted for clarity.

as noted for 3. The coordination about the palladium is square planar with essentially linear N(1)−Pd(1)−N(2) and Cl(2)−Pd(1)−Cl(3) bonds with angles of 179.53(7) and 177.17(2)°, respectively. The N−Pd−Cl angles are all virtually orthogonal at 89.85(5), 90.52(5), 89.96(6), and 89.66(5)° for each of N(2)−Pd(1)−Cl(2), N(1)−Pd(1)−Cl(2), N(2)−Pd(1)−Cl(3), and N(1)−Pd(1)−Cl(3), respectively. The chlorides are tilted at approximately 80° to the planar organic ligand and clearly preclude any π-stacking as observed with the silver(I) complex.

Acknowledgment. E.B. acknowledges receipt of a Faculty Research Grant and a Summer Faculty Fellowship from the Graduate College of Southwest Missouri State University.

Supporting Information Available: Tables of crystal data and structure refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and CIF files for **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010058U

(15) 1,2:5,6:9,10-Tribenzocyclododeca-1,5,9-triene-3,7,11-triyne. For the synthesis of this molecule, see: Campbell, I. D.; Eglington, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87.

(16) Irngartinger, H.; Leiserowitz, L.; Schmidt, G. M. J. *Chem. Ber.* **1970**, *103*, 1119.

(17) (a) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6719. (b) Ferrara, J. D.; Tanaka, A. A.; Fierro, C.; Tessier-Youngs, C.; Youngs, W. J. *Organometallics* **1989**, *8*, 2089.

(18) (a) Konig, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1833. (b) Venkataraman, D.; Lee, S.; Zhang, J.; Moore, J. S. *Nature* **1994**, *311*, 591.

(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.