

# Palladium(II) Complexes of Bowls, Pinwheels, Cages, and *N,C,N*-Pincers of Starburst Ligands 1,3,5-Tris(di-2-pyridylamino)benzene and 2,4,6-Tris(di-2-pyridylamino)-1,3,5-triazene

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The reactions of Pd(II) ions with starburst ligands 1,3,5-tris(di-2-pyridylamino)benzene (tdab) and 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazene (tdat) have been investigated. Complexes with the Pd:tdab (or tdat) ratio being 1:1 and 3:1 have been isolated and characterized. The structures of five new Pd(II) complexes containing the starburst ligands have been determined by X-ray diffraction analyses, which include chelate compounds [PdCl<sub>2</sub>(tdab)], **1**, [(PdCl<sub>2</sub>)<sub>3</sub>(tdab)], **2**, [(Pd(OAc)<sub>2</sub>)<sub>3</sub>(tdab)], **4**, and [(Pd(OAc)<sub>2</sub>)<sub>3</sub>(tdat)], **5**, and a cyclometalated compound [Pd(OAc)(*N,C,N*-tdab)], **3**. The Pd(II) ion in the 1:1 compound **1** is chelated by two pyridyl groups. Similarly, each Pd(II) center in the 3:1 compounds **2**, **4**, and **5** is chelated by two pyridyl groups. However, these three compounds display distinct structural features: **2** adopts a "bowl-shaped" structure, **4** has a "pinwheel"-like structure, and **5** has a "up-and-down" structure. Compounds **4** and **5** were examined in solution by variable-temperature <sup>1</sup>H NMR, which revealed that both compounds retain the "pinwheel" and the "up-and-down" structure, respectively. The observed structural preference by **4** and **5** is attributed to both electronic and steric factors.

## Introduction

Our interest in starburst derivatives of di-2-pyridylamine stems from their potential application as emitters and sensors in optoelectronic devices. Star-shaped luminescent molecules have been of particular interest for use in organic light-emitting diodes (OLEDs), largely due to their good film-forming properties.<sup>1</sup> Recently we reported the syntheses and structures of several series of starburst ligands that contain the di-2-pyridylamino (dpa) chelate functional group.<sup>2</sup> Zn(II) and Pt(II) complexes of these starburst molecules have been found to typically display chelate bonding modes; i.e., the ligand coordinates exclusively through chelation by the dpa subunits.<sup>3</sup> Some of the Zn(II) complexes have been found to be effective fluorescent sensors for benzene molecules,

due to their unique molecular structures and molecular interactions in the solid state.<sup>3a</sup> To further explore the chemistry of these ligands, we investigated the coordination chemistry of palladium(II) with the smallest starburst dpa derivatives, 1,3,5-tris(di-2-pyridylamino)benzene, tdab, and 2,4,6-tris-(di-2-pyridylamino)-1,3,5-triazene, tdat (Scheme 1). In contrast to the corresponding Pt(II) complexes, where the ligand coordinates exclusively through chelation by the dpa subunits, the Pd(II) complexes display surprisingly versatile coordination modes of the starburst ligands. For example, a recent report by the Steel group has shown that it is possible to have three Pd(II) centers cyclometalate the central benzene ring of tdab after a 7-day benzene reflux of Pd(OAc)<sub>2</sub> with tdab in the presence LiCl to produce [Pd<sub>3</sub>Cl<sub>3</sub>(*N,C,N*-tdab)].<sup>4</sup> We have observed, though, that the products and structures of the reactions of Pd(II) with tdab are dependent on the stoichiometry and the reaction conditions. For example, combining tdab with 1 equiv of Pd(OAc)<sub>2</sub> at ambient temperature and in a neutral solvent yields a *N,C,N*-pincer complex, in which the Pd(II) center removes a proton from the central benzene ring to form [Pd(OAc)(*N,C,N*-tdab)] (**3**). However, combining 3 equiv of Pd(OAc)<sub>2</sub> with tdab at

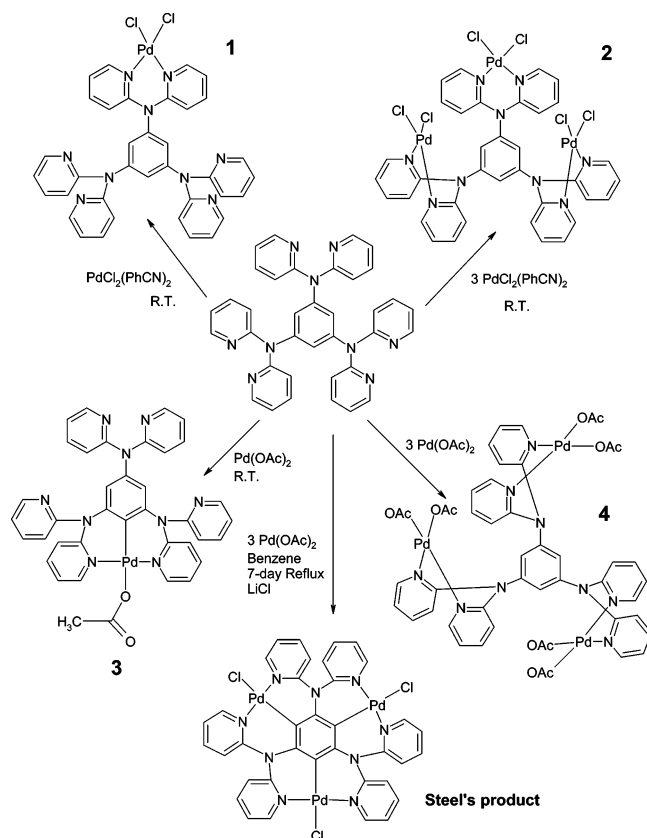
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Scheme 1



ambient temperature produces only the dpa chelate compound  $[\text{Pd}_3(\text{OAc})_6(\text{tdab})]$ , **4**. The reactions that produced compounds **3** and **4** clearly have implications on the formation mechanism of the exciting triple pincer compound  $[\text{Pd}_3\text{Cl}_3(\text{N},\text{C},\text{N}-\text{tdab})]$ , reported by Steel et al.<sup>4</sup> Herein we provided a complete account on the reactions of  $\text{PdCl}_2$  and  $\text{Pd}(\text{OAc})_2$  with the ttab ligand and the related tdat ligand.

### Experimental Section

$\text{PdCl}_2(\text{PhCN})_2$  and  $\text{Pd}(\text{OAc})_2$  were purchased from Aldrich, and solvents were purchased from Fisher and used without further purification. The ttab and tdat ligands were synthesized according to previously published methods.<sup>2</sup> All syntheses and recrystallizations were conducted under air, in a fume hood.  $^1\text{H}$  NMR spectra were recorded on Bruker Avance 300, 400, and 500 MHz spectrometers. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., Delta, BC, Canada. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer.

**Synthesis of  $[\text{PdCl}_2(\text{tdab})]$ , **1**.** Toluene (5 mL) and a solution of  $\text{PdCl}_2(\text{PhCN})_2$  (33 mg, 0.0854 mmol) in THF (5 mL) were successively layered upon a solution of ttab (50 mg, 0.0854 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL). The solvents were allowed to diffuse slowly at room temperature over several days, yielding a yellow crystalline solid of  $[\text{PdCl}_2(\text{tdab})]\cdot\text{THF}$  (36 mg, 51%). Anal. Calcd for  $\text{C}_{36}\text{H}_{27}\text{N}_9\text{Cl}_2\text{Pd}\cdot\text{C}_6\text{H}_6\text{O}$  ( $M_r = 835.08$ ): C, 57.53; H, 4.22; N, 15.10. Found: C, 57.36; H, 4.27; N, 14.45.  $^1\text{H}$  NMR data ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 8.26 (ddd,  $J = 5.0$  Hz, 2.0 Hz, 0.8 Hz, 6H, py), 7.57 (ddd,  $J = 8.4$  Hz, 7.2 Hz, 2.0 Hz, 6H, py), 7.09 (dd,  $J = 8.4$ , 0.8 Hz, 6H, py), 6.93 (ddd,  $J = 7.2$ , 5.0, 0.8 Hz, 6H, py), 6.70 (s, 3H,

ph).  $^{13}\text{C}$  NMR ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 157.95, 148.55, 146.91, 137.82, 121.44, 118.84, 117.72. A TGA experiment showed a loss of solvent beginning at 30 °C, with an 8.65% weight loss (corresponding to 1 equiv of THF) by 135 °C, followed by decomposition of the sample. UV-vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm),  $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 298 (53 180), 232 (18 430).

**Synthesis of  $[\text{PdCl}_2(\text{tdab})]$ , **2**.** Toluene (5 mL) and a solution of  $\text{PdCl}_2(\text{PhCN})_2$  (98 mg, 0.256 mmol) in THF (5 mL) were successively layered upon a solution of ttab (50 mg, 0.0854 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL). The solvents were allowed to diffuse slowly at room temperature over several days, yielding a yellow crystalline solid of  $[\text{PdCl}_2(\text{tdab})]\cdot 3\text{tol}$  (tol = toluene) (81 mg, 68%). Anal. Calcd for  $\text{C}_{36}\text{H}_{27}\text{N}_9\text{Cl}_6\text{Pd}_3\cdot\text{C}_7\text{H}_8\cdot\text{H}_2\text{O}$  ( $M_r = 1227.81$ ): C, 42.06; H, 3.04; N, 10.27. Found: C, 42.12; H, 3.08; N, 10.46. It was not possible to obtain NMR data for **2** due to its insolubility in organic solvents.

**Synthesis of  $[\text{Pd}(\text{OAc})(\text{NCN}-\text{tdab})]$ , **3**.** Toluene (6 mL) and a solution of  $\text{Pd}(\text{OAc})_2$  (19 mg, 0.0854 mmol) in THF (6 mL) were successively layered upon a solution of ttab (50 mg, 0.0854 mmol) in  $\text{CH}_2\text{Cl}_2$  (6 mL). The solvents were allowed to diffuse slowly at ambient temperature over several days, yielding a yellow crystalline solid of  $[\text{Pd}(\text{OAc})(\text{NCN}-\text{tdab})]\cdot\text{tol}$  (35 mg, 55%). Anal. Calcd for  $\text{C}_{38}\text{H}_{29}\text{N}_9\text{O}_2\text{Pd}\cdot\text{C}_7\text{H}_8$  ( $M_r = 842.27$ ): C, 64.17; H, 4.43; N, 14.97. Found: C, 63.49; H, 4.32; N, 15.17.  $^1\text{H}$  NMR data ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 8.88 (dt,  $J = 5.7$ , 0.9 Hz, 2H, py), 8.30 (dt,  $J = 4.8$ , 0.9 Hz, 2H, py), 8.23 (dt,  $J = 4.8$ , 0.9 Hz, 2H, py), 7.86 (td,  $J = 8.4$ , 1.8 Hz, 2H, py), 7.80 (dt,  $J = 8.4$ , 0.9 Hz, 2H, py), 7.58 (m, 4H, py), 7.18 (td,  $J = 6.3$ , 1.8 Hz, 2H, py), 7.11 (d,  $J = 8.4$  Hz, 2H, py), 7.02 (d,  $J = 8.4$  Hz, 2H, py), 7.01 (s, 2H, ph), 6.95 (m, 4H, py), 1.95 (s, 3H, OAc).  $^{13}\text{C}$  NMR data ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 177.57, 158.52, 156.81, 153.49, 152.17, 148.92, 148.39, 142.81, 142.08, 138.93, 138.75, 137.94, 130.35, 124.96, 122.41, 121.17, 118.79, 118.33, 117.44, 112.24, 24.44. UV-vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm),  $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 302 (24 710), 278 (27 050), 236 (29 380).

**Synthesis of  $[\text{Pd}(\text{OAc})_2(\text{tdab})]$ , **4**.** Toluene (6 mL) and a solution of  $\text{Pd}(\text{OAc})_2$  (58 mg, 0.256 mmol) in THF (6 mL) were successively layered upon a solution of ttab (50 mg, 0.0854 mmol) in  $\text{CH}_2\text{Cl}_2$  (6 mL). The solvents were allowed to diffuse slowly at ambient temperature over several days, yielding a yellow, microcrystalline solid of  $[\text{Pd}(\text{OAc})_2(\text{tdab})]$  (53 mg, 49%). Recrystallization by slow evaporation of a solution of  $\text{CH}_2\text{Cl}_2$ /toluene/THF afforded small yellow crystals of **4**. Anal. Calcd for  $\text{C}_{48}\text{H}_{45}\text{N}_9\text{O}_{12}\text{Pd}_3\cdot 2\text{H}_2\text{O}$  ( $M_r = 1295.22$ ): C, 44.51; H, 3.81; N, 9.74. Found: C, 44.81; H, 3.83; N, 9.51.  $^1\text{H}$  NMR data ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 9.01 (s, 1H, ph), 8.38 (d,  $J = 5.6$  Hz, 2H, py), 7.95 (d,  $J = 8.4$  Hz, 2H, py), 7.85 (dd,  $J = 8.4$  Hz, 8.0 Hz, 2H, py), 7.19 (dd,  $J = 8.0$ , 5.6, 2H, py), 1.87 (s, 6H, OAc).  $^{13}\text{C}$  NMR ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 177.49, 152.38, 150.46, 146.49, 141.71, 126.70, 122.72, 122.59, 23.29. UV-vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm),  $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 302 (23 960), 278 (14 310), 234 (47 240).

**Synthesis of  $[\text{Pd}(\text{OAc})_2(\text{tdat})]$ , **5**.** Toluene (6 mL) and a solution of  $\text{Pd}(\text{OAc})_2$  (57 mg, 0.255 mmol) in THF (6 mL) were successively layered upon a solution of tdat (50 mg, 0.0849 mmol) in  $\text{CH}_2\text{Cl}_2$  (6 mL). The solvents were allowed to diffuse slowly at ambient temperature over several days, yielding a yellow crystalline solid of  $[\text{Pd}(\text{OAc})_2(\text{tdat})]\cdot\text{toluene}\cdot\text{CH}_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$  (50 mg, 38%). Anal. Calcd for  $\text{C}_{45}\text{H}_{42}\text{N}_{12}\text{O}_{12}\text{Pd}_3\cdot 4\text{H}_2\text{O}$  ( $M_r = 1334.22$ ): C, 40.51; H, 3.78; N, 12.60. Found: C, 39.95; H, 3.51; N, 12.15.  $^1\text{H}$  NMR data ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 8.44 (d, broad, s, 2H, py), 7.99 (broad s, 2H, py), 7.61 (broad, s, 2H, py), 7.27 (broad s, 2H, py), 2.03 (s, 6H, OAc).  $^{13}\text{C}$  NMR data ( $\delta$ , ppm;  $\text{CD}_2\text{Cl}_2$ , 298 K): 178.36, 165.03, 150.22, 148.98, 140.13, 127.66, 124.27. UV-vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm),  $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 292 (36 810), 232 (39 740).

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**Table 1.** Crystallographic Data

param	1	2	3	4	5
formula	C <sub>36</sub> H <sub>27</sub> Cl <sub>2</sub> N <sub>9</sub> Pd·C <sub>4</sub> H <sub>8</sub> O	C <sub>36</sub> H <sub>27</sub> Cl <sub>6</sub> N <sub>9</sub> Pd <sub>3</sub> ·3C <sub>7</sub> H <sub>8</sub>	C <sub>38</sub> H <sub>29</sub> N <sub>9</sub> O <sub>2</sub> Pd·C <sub>7</sub> H <sub>8</sub>	C <sub>48</sub> H <sub>61</sub> N <sub>9</sub> O <sub>12</sub> Pd <sub>3</sub> ·CH <sub>2</sub> Cl <sub>2</sub> ·1.5C <sub>7</sub> H <sub>8</sub> ·H <sub>2</sub> O	C <sub>90</sub> H <sub>84</sub> N <sub>24</sub> O <sub>24</sub> Pd <sub>6</sub> ·2CH <sub>2</sub> Cl <sub>2</sub> ·3.5C <sub>7</sub> H <sub>8</sub> ·3.5H <sub>2</sub> O
fw	835.07	1393.96	842.24	1093.5	3079.60
space group	<i>P</i> $\bar{1}$	<i>P</i> <sub>2</sub> / <i>m</i>	<i>P</i> <sub>2</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> <sub>2</sub> / <i>c</i>
<i>a</i> , Å	10.477(2)	10.004(2)	16.007(3)	12.611(6)	14.678(4)
<i>b</i> , Å	13.534(3)	24.863(6)	15.583(3)	15.569(7)	28.666(8)
<i>c</i> , Å	14.481(3)	12.034(3)	16.207(3)	17.267(8)	29.930(7)
$\alpha$ , deg	65.439(3)	90	90	69.253(8)	90
$\beta$ , deg	84.935(4)	96.205(5)	97.112(4)	74.993(9)	100.918(7)
$\gamma$ , deg	85.614(4)	90	90	82.484(10)	90
<i>V</i> , Å <sup>3</sup>	1858.6(7)	2616.8(11)	4011.5(14)	3060(2)	12365(5)
<i>Z</i>	2	2	4	2	4
<i>D</i> <sub>calc</sub> , g·cm <sup>-3</sup>	1.492	1.769	1.395	1.629	1.654
<i>T</i> , K	301	294	301	150	180
$\mu$ , cm <sup>-1</sup>	6.89	13.77	5.13	16.29	10.24
$2\theta_{\max}$ , deg	56.68	56.62	56.58	56.42	56.78
reflens measd	13 371	18 664	28 706	22 013	88 054
reflens used ( <i>R</i> <sub>int</sub> )	8561 (0.0485)	6302 (0.0637)	9565 (0.0432)	13 839 (0.0487)	28 649 (0.1418)
params	586	285	502	768	1486
final <i>R</i> values <i>I</i> > 2 $\sigma$ ( <i>I</i> ): <i>R</i> <sub>1</sub> , <sup>a</sup> w <i>R</i> <sub>2</sub> <sup>b</sup>	0.0506, 0.0712	0.0583, 0.1337	0.0462, 0.0991	0.0512, 0.0882	0.0963, 0.2122
<i>R</i> values (all data): <i>R</i> <sub>1</sub> , <sup>a</sup> w <i>R</i> <sub>2</sub> <sup>b</sup>	0.1569, 0.0881	0.1473, 0.1566	0.1090, 0.1173	0.1261, 0.1039	0.3013, 0.2727
GOF on <i>F</i> <sup>2</sup>	0.674	0.835	0.871	0.807	0.860

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]^{1/2}$ .  $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ , where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ .

**X-ray Crystallographic Analysis.** Crystals of **1–3** and **5** were obtained from the original reaction vessel. Crystals of **4** were obtained via the slow evaporation from a solution of **4** in CH<sub>2</sub>Cl<sub>2</sub>, toluene, and THF. All data were collected on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo K $\alpha$  radiation, operating at 50 kV and 30 mA. Data for **1** and **3** were collected at 28 °C, data for **2** were collected at 21 °C, and data for **4** and **5** were collected at 150 and 180 K, respectively, using an Oxford Cryosystem low-temperature device. Data were collected over  $2\theta$  ranges of 3.10–56.68°, 3.88–56.62°, 3.64–56.58°, 2.68–56.40°, and 2.78–56.78° for **1–5**, respectively. No significant decay was observed during the data collection. Data were processed on a Pentium PC using the Bruker AXS Windows NT SHELXTL software package (version 5.10).<sup>6</sup> Neutral atom scattering factors were taken from Cromer and Waber.<sup>7</sup> Crystals of **3** and **5** belong to the monoclinic space group *P*<sub>2</sub>/*c*, crystals of **2** belong to the monoclinic space group *P*<sub>2</sub>/*m*, and crystals of **1** and **4** belong to the triclinic space group *P* $\bar{1}$ , uniquely determined by systematic absences. All structures were solved by direct methods. There are two independent molecules in the asymmetric unit of **5**. One of the acetate ligands in **5** displays some positional disorder, which was refined successfully. Compound **1** has one disordered THF molecule which was partially resolved and refined. Some of the toluene solvent molecules in **2**, **4**, and **5** are disordered and could not be fully resolved. All non-hydrogen atoms were refined anisotropically, with the exceptions of disordered solvent molecules. Positions for all hydrogen atoms except the disordered solvent molecules and water molecules were either located directly or calculated for **1–5**, and their contributions were included in the structure factor calculations. Crystallographic data are given in Table 1, and selected bond lengths and angles are given in Table 2.

## Results and Discussion

**Syntheses.** The reactions of 1 or 3 equiv of PdCl<sub>2</sub>(PhCN)<sub>2</sub> with ttab at ambient temperature afforded the chelate

**Table 2.** Bond Lengths (Å) and Angles (deg) for Compounds **1** and **3–5**

Compound 1			
Pd(1)–N(2)	2.007(4)	Pd(1)–N(1)	2.025(4)
Pd(1)–Cl(1)	2.2960(14)	Pd(1)–Cl(2)	2.3002(13)
N(1)–Pd(1)–Cl(2)	177.75(13)	N(2)–Pd(1)–Cl(1)	175.94(11)
Compound 2			
Pd(1)–N(1)	2.023(6)	Pd(1)–N(2)	2.030(5)
Pd(1)–Cl(2)	2.276(2)	Pd(1)–Cl(1)	2.281(2)
Pd(2)–N(3)	2.023(6)	Pd(2)–Cl(3)	2.266(2)
N(2)–Pd(1)–Cl(2)	176.74(17)	N(1)–Pd(1)–Cl(1)	177.19(16)
N(3)–Pd(2)–Cl(3A)	177.72(18)		
Compound 3			
Pd(1)–C(32)	1.937(3)	Pd(1)–N(1)	2.041(3)
Pd(1)–N(3)	2.030(3)	Pd(1)–O(1)	2.126(3)
N(3)–Pd(1)–N(1)	175.53(11)	C(32)–Pd(1)–O(1)	169.89(13)
Compound 4			
Pd(1)–N(3)	1.981(5)	Pd(2)–O(5)	2.000(4)
Pd(1)–N(1)	1.985(4)	Pd(2)–O(7)	2.002(4)
Pd(1)–O(3)	2.002(4)	Pd(3)–O(11)	1.983(4)
Pd(1)–O(1)	2.014(4)	Pd(3)–N(9)	1.982(5)
Pd(2)–N(4)	1.990(4)	Pd(3)–O(9)	2.001(4)
Pd(2)–N(6)	1.996(5)	Pd(3)–N(7)	2.007(5)
N(1)–Pd(1)–O(3)	178.85(18)	N(6)–Pd(2)–O(7)	178.18(17)
N(3)–Pd(1)–O(1)	179.18(18)	N(9)–Pd(3)–O(9)	177.03(17)
N(4)–Pd(2)–O(5)	178.80(18)	O(11)–Pd(3)–N(7)	178.34(18)
Compound 5			
Pd(1)–O(3)	1.945(11)	Pd(4)–N(14)	1.974(13)
Pd(1)–O(1)	1.958(11)	Pd(4)–O(15)	2.002(15)
Pd(1)–N(1)	1.981(12)	Pd(4)–N(13)	2.012(12)
Pd(1)–N(2)	2.009(12)	Pd(4)–O(13)	2.032(11)
Pd(2)–O(7)	1.948(12)	Pd(5)–O(19)	1.902(14)
Pd(2)–N(5)	1.973(11)	Pd(5)–N(16)	1.993(13)
Pd(2)–O(5)	1.983(11)	Pd(5)–N(17)	2.002(12)
Pd(2)–N(4)	1.989(12)	Pd(5)–O(17)	2.020(10)
Pd(3)–N(7)	1.991(12)	Pd(6)–O(23)	1.996(12)
Pd(3)–N(8)	2.015(12)	Pd(6)–O(21)	2.009(10)
Pd(3)–O(9)	2.024(17)	Pd(6)–N(19)	2.019(12)
Pd(3)–O(11)	2.049(18)	Pd(6)–N(20)	2.021(11)
Pd(3)–O(11A)	2.07(4)		
O(1)–Pd(1)–N(1)	175.3(4)	N(14)–Pd(4)–O(15)	172.0(5)
O(3)–Pd(1)–N(2)	174.0(5)	N(13)–Pd(4)–O(13)	174.2(5)
N(5)–Pd(2)–O(5)	173.4(4)	O(19)–Pd(5)–N(17)	177.3(5)
O(7)–Pd(2)–N(4)	174.1(4)	N(16)–Pd(5)–O(17)	178.1(5)
N(7)–Pd(3)–O(9)	172.6(7)	O(23)–Pd(6)–N(19)	174.5(4)
N(8)–Pd(3)–O(11)	170.1(7)	O(21)–Pd(6)–N(20)	176.3(4)
N(8)–Pd(3)–O(11A)	162.8(12)		

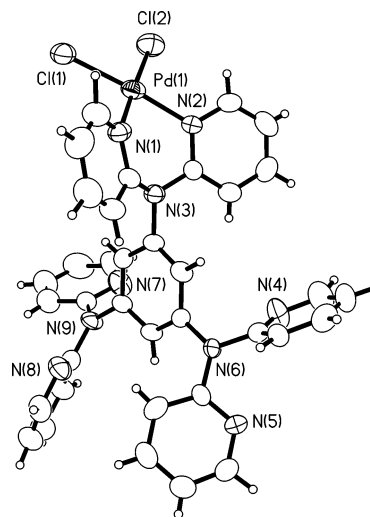
(6) SHELXTL NT Crystal Structure Analysis Package, version 5.10; Bruker AXS Analytical X-ray System; Madison, WI, 1999.

(7) Cromer, D. T., and Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2A.

products,  $[\text{PdCl}_2(\text{tdab})]$ , **1**, and  $[(\text{PdCl}_2)_3(\text{tdab})]$ , **2**, respectively. Due to the poor solubility of these Pd(II) complexes, solvent-layering techniques are used to produce single crystals from the reaction mixture. No cyclometalated products were observed. The reaction of  $\text{tdab}$  with 1 equiv of  $\text{Pd}(\text{OAc})_2$  at ambient temperature in THF and  $\text{CH}_2\text{Cl}_2$ , on the other hand, yields the *N,C,N*-pincer complex<sup>5</sup>  $[\text{Pd}(\text{OAc})(\text{N,C,N-tdab})]$  (**3**), in which the Pd(II) center removes a proton from the central benzene ring. The reaction of 3 equiv of  $\text{Pd}(\text{OAc})_2$  with  $\text{tdab}$  at ambient temperature produces the dpa chelate compound  $[\text{Pd}_3(\text{OAc})_6(\text{tdab})]$  (**4**). We also carried out the same reaction in refluxing acetic acid for 24 h. However, only compound **4** was isolated. The reactivity of the  $\text{tdab}$  ligand with Pd(II) ions clearly is not as straightforward as the corresponding Pt(II) or Zn(II) reactions, where only chelation products via the pyridyl groups were observed.<sup>3</sup> The observed reactivity patterns of  $\text{PdCl}_2$  and  $\text{Pd}(\text{OAc})_2$  with  $\text{tdab}$  are summarized in Scheme 1. When  $\text{tdat}$  is used in place of  $\text{tdab}$  in the 3:1 reaction, with no abstractable protons on the central ring, the chelation product  $[\text{Pd}_3(\text{OAc})_6(\text{tdat})]$ , **5**, was obtained, as expected. Attempts to produce the 1:1 complex of palladium(II) acetate and  $\text{tdat}$  yielded only the 3:1 complex, **5**, and the free  $\text{tdat}$  ligand. In principle, the  $\text{tdat}$  ligand should be able to chelate to a metal ion through both the pyridyl nitrogen donor atoms and the triazene nitrogen atoms to form a tridentate *N,N,N*- $\text{tdat}$  pincer ring in the same manner as the *N,C,N*- $\text{tdab}$  pincer. However, the *N,N,N*- $\text{tdat}$  pincer bonding mode has not been observed in any of the Pt(II), Zn(II), Pd(II), or<sup>3b</sup> Ag(I) complexes we have investigated to date. Although the free ligands  $\text{tdab}$  and  $\text{tdat}$  are brightly blue luminescent, the Pd(II) complexes of **1–5** do not display any luminescence. This is attributed to luminescent quenching by the Pd(II) ions in the complexes, a common phenomenon for Pd(II) compounds.<sup>8</sup> The new Pd(II) complexes were characterized by NMR, elemental analysis, and X-ray diffraction.

**Structures.** The environments around the palladium atoms in all 5 compounds are square planar, with some minor deviations. This is consistent with the  $d^8$ -electronic configuration of a typical palladium(II) center. The dpa amino nitrogens in each complex have a trigonal planar geometry with only small deviations in the plane, whether the attached pyridyl nitrogens are coordinated or not and whether the coordination is through dpa chelation or the *N,C,N*-pincer mode (see Table 2).

As shown by Figure 1, there is some steric strain in the dpa chelate of **1**, with an  $\text{N}(1)\text{—Pd}(1)\text{—N}(2)$  angle of  $84.3^\circ$ . This appears to be due to a combination of the small bite angle of dpa in relation to the palladium center and the orientation forced by steric interactions in the crystal lattice. The coordinated pyridyl unit in **1** adopts an almost perpendicular orientation with respect to the central benzene ring.



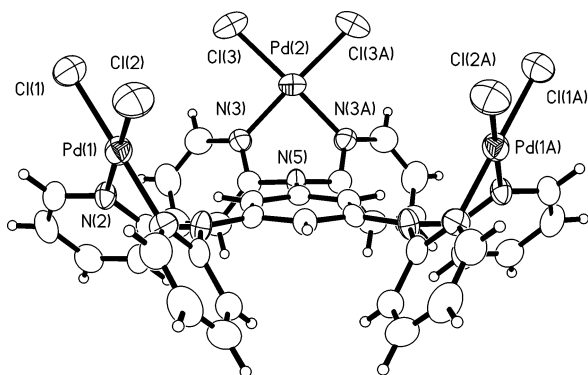
**Figure 1.** Molecular structure of **1**. The THF solvent molecule has been removed for clarity.

The dihedral angle between the amino  $\text{NC}_2$  plane (C is the carbon atom on the Py ring) and the central benzene ring is  $84.4^\circ$  (Figure 1). This likely occurs because of a combination of steric packing effects in the bulk crystal and the greater conjugation achieved by the dpa amine nitrogen with the pyridyl groups, as opposed to the central benzene ring. In compound **1**, the THF solvent molecule is found in channels that parallel the crystallographic *a*-axis but are not involved in any strong interactions with the  $[\text{PdCl}_2(\text{tdab})]$  molecules (see Supporting Information). Interestingly, despite being present in the crystal lattice and having no significant interactions with the host framework, hardly any solvent loss was observed during the X-ray data collection of **1** at  $28^\circ\text{C}$ . A thermogravimetric analysis experiment was therefore performed for **1**, which showed that the crystals begin to lose their lattice solvent at  $30^\circ\text{C}$ , with a mass loss of 8.65% (corresponding to 1 equiv of THF) by  $135^\circ\text{C}$ , and followed shortly by the total decomposition of the solid. The most likely explanation for this behavior is that the solvent channels in **1** are not completely passable by the THF molecules until the temperature is elevated.

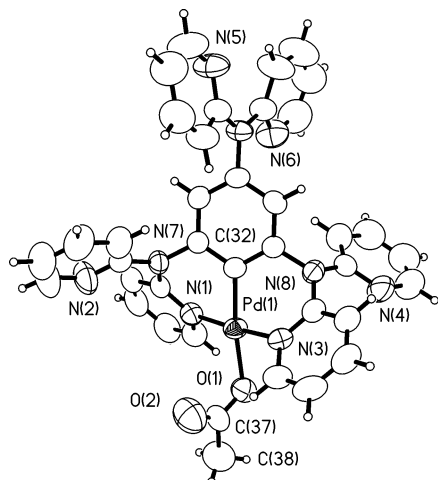
Compound **2** is isostructural to its platinum(II) analogue, which has been previously reported.<sup>3b</sup> One notable feature, however, is that all three of the chelated dpa units are oriented in the same direction, forming a bowl-shaped complex, shown in Figure 2. While the  $\text{PdN}_2\text{C}_2$  planes are at a  $78$  or  $79^\circ$  angle from the plane of the central ring, the amino  $\text{NC}_2$  planes of the dpa units form dihedral angles of  $3\text{--}7^\circ$  with the central benzene ring. Therefore, substantial conjugation between the amino nitrogen atoms and the central benzene ring is present. In the solid state, the “bowls” of compound **2** stack on top of each other to form one-dimensional polar columns, although the bulk crystal is not polar as adjacent columns are oriented in opposite directions (see Supporting Information).

Compound **3** is a cyclometalated *N,C,N*-pincer complex, in which one of the protons of the central benzene ring has been abstracted in favor of coordination to the palladium(II) center. To accommodate this arrangement, the pyridyl

(8) (a) Lai, S. W.; Cheung, T. C.; Chan, M. C. W.; Cheung, K. K.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **2000**, *39*, 255. (b) Tzeng, B. C.; Chan, S. C.; Chan, M. C. W.; Che, C. M.; Cheung, K. K.; Peng, S. M. *Inorg. Chem.* **2001**, *40*, 6699. (c) Tzeng, B. C.; Fu, W. F.; Che, C. M.; Chao, H. Y.; Cheung, K. K.; Peng, S. M., *J. Chem. Soc., Dalton Trans.* **1999**, 1017. (d) Che, C. M.; He, L. Y.; Poon, C. K.; Mak, T. C. W. *Inorg. Chem.* **1989**, *28*, 3081.



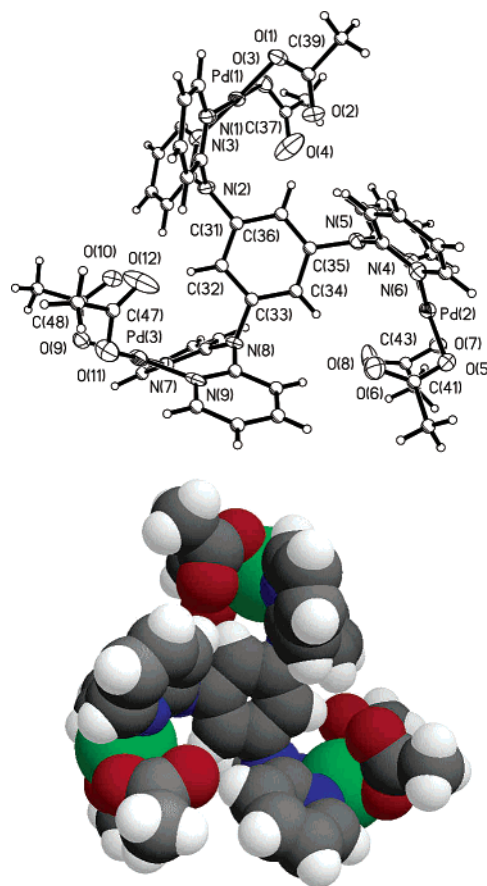
**Figure 2.** Molecular structure of the bowl-shaped molecule of **2**.



**Figure 3.** Molecular structure of **3**.

groups of the coordinated dpa moieties are twisted out of the plane in such a fashion as to make the Pd(OAc)(*N,C,N*-tdab) molecular structure chiral (see Figure 3). The bulk crystals of **3**, however, are racemic, and the crystallographic unit cell incorporates a center of inversion. The palladium center in **3** exhibits the largest deviation from an optimal square planar complex of any of the five complexes reported herein. The acetate ligand is forced to bend out of the square plane because of steric interactions with the pyridyl groups of the tdab ligand. There is one toluene molecule/molecule of **3** in the crystal lattice. The toluene solvent molecules occupy the pocket void space within the crystal structure and does not have any interactions with the organopalladium molecule beyond van der Waals contacts (see Supporting Information.).

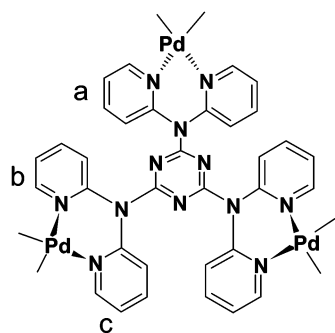
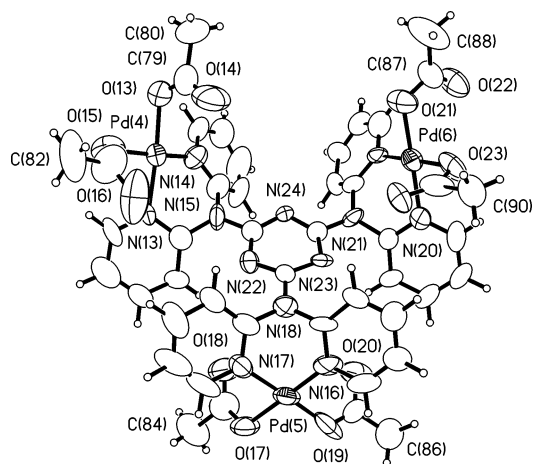
As shown in Figure 4, each Pd(II) ion in **4** is chelated by two pyridyl groups of the dpa unit and terminally coordinated by two acetate ligands with a square planar geometry. The most interesting feature about the structure of **4** is that all of the palladium atoms are nearly coplanar with the central benzene ring, which is in sharp contrast to the structure of **2** where the three Pd(II) ions are all above the central benzene ring. This arrangement is achieved by the sideways twist of the pyridyl groups on each dpa unit so that they are almost perpendicular to the central benzene plane. The amino NC<sub>2</sub> planes have dihedral angles with the central benzene ring ranging from 66.8 to 92.1°. As a consequence of this sideways twist, none of the amino nitrogen atoms are



**Figure 4.** Top: Molecular structure of **4**. For clarity, only Pd, O, and N atoms are shown anisotropically. Bottom: Space-filling diagram showing the close contact between the acetate ligands and the central benzene ring. Key: green, Pd; red, O; blue, N.

conjugated with the central benzene ring. This arrangement leads to close contacts between the carbon atoms of the central benzene ring and the adjacent Pd centers with the Pd–C distance ranging from 3.83 to 4.08 Å. All six noncoordinated acetate oxygen atoms are oriented in the same direction, toward the central benzene ring, as shown in Figure 4. The structure of **4** can be described as an approximate “pinwheel”. There are C–H···O interactions<sup>9</sup> between the central ring protons and the noncoordinating oxygen atoms on the inward-facing acetate ligands, with each pair of acetate oxygen atoms forming one strong and one weak interaction (average short C–O distance 3.47 Å (3.34–3.59 Å), average long C–O distance 3.65 Å (3.49–3.79 Å)). These weak hydrogen-bonding interactions, as well as steric interactions, are likely responsible for the “pinwheel” arrangement of the Pd(OAc)<sub>2</sub> units. The close contacts between the benzene protons and the noncoordinating acetate oxygen atoms are the most likely cause of the large shift of the central ring proton’s NMR signal, from 6.78 ppm in the free ligand to 9.20 ppm in **4**, indicating that the “pinwheel” arrangement persists in solution. A similar perpendicular arrangement by the pyridyl rings of the dpa unit, relative to

(9) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (c) Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891. (d) Steiner, T. *Chem. Commun.* **1997**, 727.

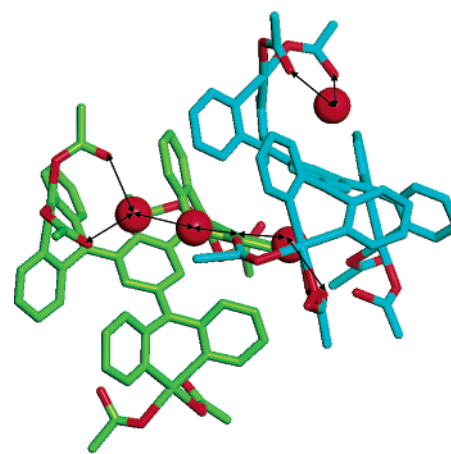


"Up-and-down" structure of **5**

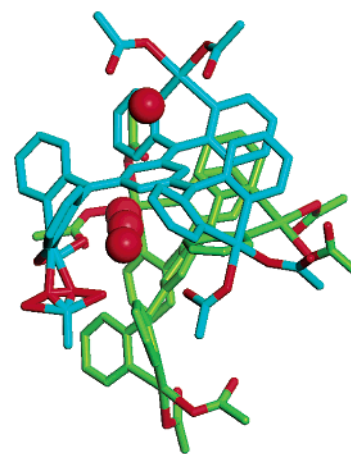
**Figure 5.** Top: Molecular structure of one of the crystallographically independent Pd<sub>3</sub>tdat units of **5**. Thermal ellipsoid plots of the other independent unit can be found in the Supporting Information. Bottom: Sketch showing the structure of **5** and the three distinct sets of pyridyl groups.

the central aromatic ring, was also observed in [(PtPh<sub>2</sub>)<sub>3</sub>-(tdab)], where steric interactions are primarily responsible for the perpendicular twist, but the NMR signal from the central ring proton remains in the same region as the free tdab.<sup>10</sup> This "pinwheel" orientation of the dpa subunits sheds some light on the possible mechanism of the cyclometalation observed in **3**, as discussed below.

In compound **5**, there are two independent [(Pd(OAc)<sub>2</sub>)<sub>3</sub>-(tdat)] molecules in the asymmetric unit of the unit cell. On the basis of the formula, compound **5** appears to be an analogue of compound **4**. However, a close examination on its structure revealed that the structure of **5** is drastically different from that of **4**. The coordination environment around each Pd(II) ion in **5** is similar to that of **4**; i.e., two nitrogen and two oxygen atoms bound to each Pd(II) center (one of the acetate ligands in one of the independent molecules of **5** is disordered as illustrated by Figure 6). As shown in Figure 5, the major difference between **4** and **5** lies in the orientation of Pd(OAc)<sub>2</sub>(Py)<sub>2</sub> units. In **4**, these units are oriented sideways relative to the central ring so that all Pd(II) ions are coplanar with the central ring. In **5**, in contrast, the Pd(OAc)<sub>2</sub>(Py)<sub>2</sub> units are all oriented in an *up* and *down* fashion relative the central ring, resulting in two of the Pd(II) ions being above the triazine ring and the

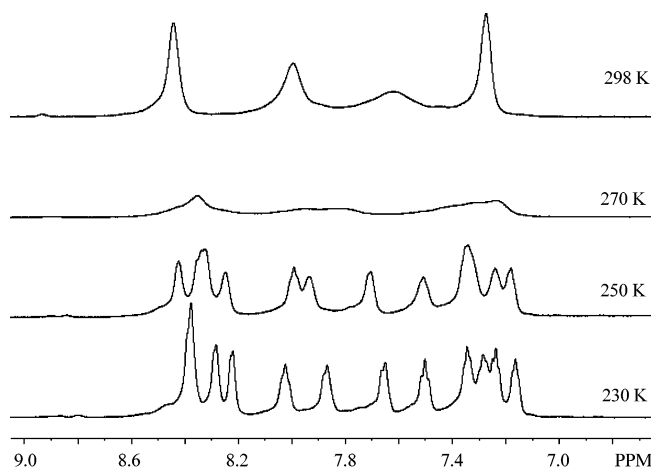


(a)



(b)

**Figure 6.** (a) Side view and (b) end view of the hydrogen-bonded chain of water molecules trapped in a "cage" between two Pd<sub>3</sub>tdat units in **5**. The two different independent Pd<sub>3</sub>tdat units are colored differently, and all hydrogen atoms are removed for clarity. The solvent oxygen molecules are shown at 50% space-filling spheres for visibility. Hydrogen bond connectivity is indicated by arrows.



**Figure 7.** Variable-temperature <sup>1</sup>H NMR spectra of the aromatic region for compound **5** in CD<sub>2</sub>Cl<sub>2</sub>.

remaining one below. From the variable-temperature <sup>1</sup>H NMR spectra of **5** (Figure 7), this structure appears to be retained in solution at low temperature. The presence of broad singlets at ambient temperature indicates that there is

(10) Liu, Q.; Jia, W.; Wu, G.; Wang, S. *Organometallics* **2003**, *22*, 3781.

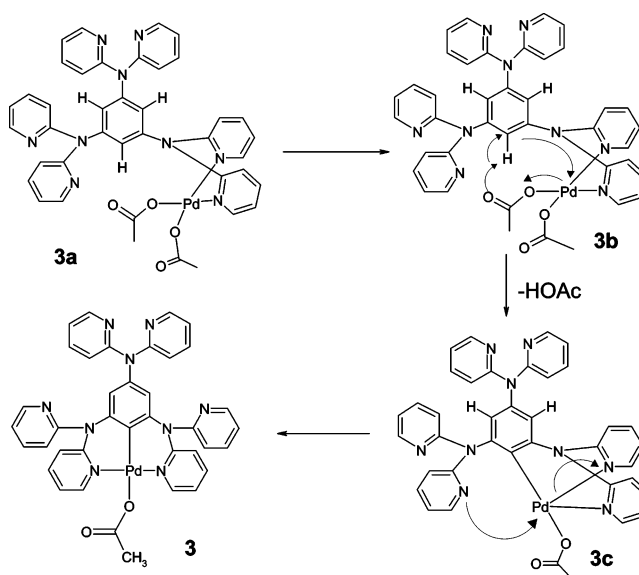
some flipping of the orientation of the  $\text{Pd}(\text{OAc})_2(\text{Py})_2$  units, but it is occurring slowly. At 230 K, 11 well-resolved peaks that correspond to three distinct sets of Py rings (see the sketch in Figure 5) were observed, consistent with the observed crystal structure of **5**. In addition, the amino  $\text{NC}_2$  planes of the dpa units are almost coplanar with the triazene ring, as indicated by the dihedral angles of  $\sim 2\text{--}4^\circ$ . As a consequence, compound **5** does not show the same “pin-wheel” structure as compound **4** does. This can be attributed to two factors: (1) The electronegative nitrogen atoms on the triazene ring favor the conjugation of the amino nitrogen atoms with itself instead of the pyridyl rings. (2) The lack of protons on the triazene ring reduces steric interactions, thus making the conjugation of the amino nitrogen atoms with the triazene ring possible. A similar preference for the “up-and-down” structure in solution and the solid state was observed for  $[\text{Pt}(\text{Ph})_2]_3(\text{tdat})$ .<sup>10</sup> The molecules of **5** are held together in the crystal lattice by a multitude of intermolecular aromatic  $\text{C}\text{--}\text{H}\cdots\text{O}$  interactions between acetate oxygens and hydrogens bonded to carbon atoms of adjacent pyridyl groups. The disordered toluene solvent molecules are not involved in any supramolecular interactions and are only present in the crystal lattice to fill void space.

#### Encapsulation of Water Molecules by Compound **5**.

The most unusual feature of **5** is the encapsulation of water molecules within the cavity of the complexes. As shown by Figure 6, there are four water molecules trapped inside the cavity of the two independent molecules of **5**. Three of the water molecules have an approximately linear arrangement. The water molecule that is not among the linear triad forms hydrogen bonds with two noncoordinating acetate oxygen atoms (shown at the upper right corner of Figure 6a), as indicated by the  $\text{O}\cdots\text{O}$  distances of 2.74 and 2.81 Å. While it is not possible to measure  $\text{O}\text{--}\text{H}\cdots\text{O}$  angles because the hydrogen atoms were not located, the  $\text{O}(\text{acetate})\text{--}\text{O}(\text{water})\text{--}\text{O}(\text{acetate})$  angle of  $105.0^\circ$  is very close to the optimal  $\text{H}\text{--}\text{O}\text{--}\text{H}$  angle in water itself. Among the linear triad, the water molecule at the far left forms hydrogen bonds with two noncoordinating acetate oxygen atoms as evident by the  $\text{O}\cdots\text{O}$  separation distances of 2.75 and 2.77 Å. The same water molecule is also hydrogen bonded to the central water molecule with a short separation distance (2.56 Å). The central water molecule is further hydrogen bonded to a noncoordinating acetate oxygen atom from a neighboring molecule with an  $\text{O}\cdots\text{O}$  separation distance of 2.52 Å. The same noncoordinating oxygen atom also forms a hydrogen bond with the water molecule at the far right of the linear triad with an  $\text{O}\cdots\text{O}$  separation distance of 2.73 Å, which is further hydrogen bonded to a second noncoordinating acetate oxygen atom of the neighboring molecule with an  $\text{O}\cdots\text{O}$  separation distance of 2.635 Å. The two independent molecules of **5** can therefore be described as a hydrogen bond linked dimer via water molecules. The linear water molecule triad is clearly encapsulated in the molecular cage by hydrogen bond interactions.

**Cyclometalation.** Cyclopallated compounds are an important class of compounds because many of them with a pincer structure similar to that of **3** have been shown to play

Scheme 2

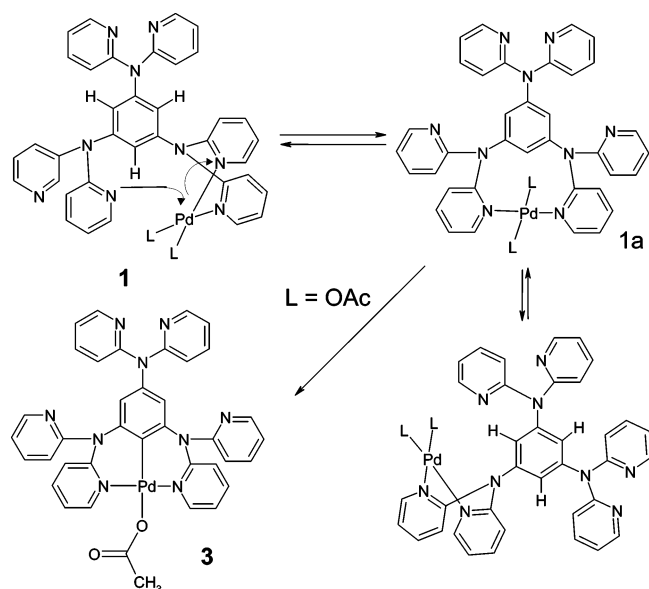


important catalytic functions in organic synthesis.<sup>5,11</sup> Cyclopalladation of an aromatic ring system is believed to occur through an electrophilic aromatic substitution pathway.<sup>12</sup> In the previously proposed mechanism of cyclometalation involving  $\text{Pd}(\text{OAc})_2$  and amines, the most likely precursor prior to  $\text{C}\text{--}\text{H}$  bond breaking was considered to be a 3-coordinate intermediate  $\text{Pd}(\text{OAc})_2(\text{amine})$  with the two acetate ligands cis to each other.<sup>12</sup> The  $\text{C}\text{--}\text{H}$  bond approaches the  $\text{Pd}(\text{II})$  center via the vacant coordination site. For the formation of the compound **3**, a similar mechanism may be operative. As shown in Scheme 2, assuming the reaction of  $\text{Pd}(\text{OAc})_2$  with tda $\text{b}$  produces initially the chelate compound **3a** where the  $\text{Pd}(\text{OAc})_2$  is chelated by two Py groups from the same dpa unit in the same manner as observed in **1**, **2**, **4**, and **5**, to form the 3-coordinate intermediate **3c**, one of the pyridyl groups must dissociate. Because the reaction of  $\text{PdCl}_2(\text{PhCN})_2$  with tda $\text{b}$  under the same condition does not produce any cyclometalated products, we believe that the acetate ligand plays a key role in the formation of **3**. Hydrogen-bonding interactions between the noncoordinating acetate oxygen atoms and the benzene  $\text{C}\text{--}\text{H}$  bond in the same manner as observed in the structure of **4** would facilitate bringing in the  $\text{Pd}(\text{II})$  center close to the  $\text{C}\text{--}\text{H}$  bond and the removal of the H atom as depicted in **3c**. The subsequent coordination by a Py group from a neighboring dpa unit completes the coordination sphere and leads to the formation of **3** as shown in Scheme 2.

There is however an alternative mechanism on the basis of the behavior of compound **1**. An NMR study revealed that compound **1** is highly fluxional in solution. On the basis of the crystal structure, there are 3 different pyridyl groups in compound **1**. At ambient temperature, only one set of

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- (12) (a) Ryabov, A. D. *Chem. Rev.* **1990**, 90, 403. (b) Gómez, N.; Granell, J.; Martínez, M. *Eur. J. Inorg. Chem.* **2000**, 217.

Scheme 3



chemical shifts due to the pyridyl groups was observed. Dynamic exchange of the PdCl<sub>2</sub> unit on different binding sites must be occurring in solution. A similar exchange behavior was previously observed in the 1:1 compound [(ZnCl<sub>2</sub>)(tdat)].<sup>3b</sup> We have proposed that an intermediate involving the chelation of two Py groups from two neighboring dpa units is likely involved in the exchange process of the [(ZnCl<sub>2</sub>)(tdat)] compound. We believe that a similar process could also be responsible for the fluxional behavior of **1**. Although the six-membered chelating ring formed by two Py rings from the same dpa unit (**1** in Scheme 3) is thermodynamically favorable, it is likely in equilibrium in solution with the 10-membered chelating ring formed by two Py rings from two different dpa units (**1a** in Scheme 3) due to the conformational nonrigidity and the proximity of the pyridyl groups in the tdab ligand. The 10-membered ring intermediate **1a** would allow the exchange of the Pd(II) ion among all of the dpa sites, leading to the appearance of one set of chemical shifts due to the Py rings in the NMR spectrum. The coordination site exchange of the Pd(II) ion is probably facilitated by the sideways twist of the dpa unit, which brings the metal center close to the neighboring noncoordinating Py rings as shown in Scheme 3. In the case of [Pd(OAc)<sub>2</sub>(tdab)], the formation of **1a** would bring the Pd(II) center into a favorable position for breaking the C–H bond of the central benzene ring and ultimately leading to the formation of the cyclometalated product **3** as depicted in Scheme 3. In fact, several bidentate ligands that adopt a similar arrangement as in **1a** have been shown<sup>13</sup> to undergo facile internal C–H bond activation in a manner similar to that as in **3**. The formation of Steel's product is likely by the same mechanism. We have followed the reaction of Pd(OAc)<sub>2</sub> with tdab in 1:1 ratio in CD<sub>2</sub>Cl<sub>2</sub> by <sup>1</sup>H NMR. A singlet peak at 9.1 ppm, attributed to the central benzene ring of the chelate compound **1a**, based on the NMR

spectrum of **4**, and several singlet peaks at ~7.0 PPM, that are attributable to the central benzene ring of **3** and other unidentified products appeared in the spectrum immediately after the addition of Pd(OAc)<sub>2</sub> to the tdab solution. We monitored the reaction mixture for a 5-day period, and the single at 9.1 ppm completely disappeared after 2 days. Compound **3** did show up as a major product (~40%). However, other species are also present in the reaction mixture. The fact that we could not isolate the simple chelate product of [Pd(OAc)<sub>2</sub>(tdab)] (**1a**) may be explained by the rapid occurrence of cyclometalation as indicated by NMR results. Interestingly, however, from the reaction of Pd(OAc)<sub>2</sub> with tdab in a 3:1 ratio at ambient temperature or refluxing in acetic acid, we did not isolate any cyclometalated products; instead, compound **4** was the only product isolated and identified by NMR. We believe that the explanation is that once the chelation of all pyridyl groups to the Pd(II) centers is complete, the pyridyl groups are no longer free to move around and the Pd(II) ions are locked in place. As a consequence, the transformation similar to that of **1** to **1a** becomes either very difficult or impossible; thus, no cyclometalation occurs. It is however still conceivable that Steel's product could be formed via the process depicted in Scheme 3. On the basis of our experimental data, we cannot establish conclusively which mechanism is responsible for the formation of **3**, although we favor the mechanism depicted in Scheme 3 since it is consistent with the fluxional behavior illustrated by compound **1** and other related compounds.

## Conclusions

We have synthesized and characterized a series of palladium(II) complexes of the organic starburst ligands tdab and tdat. While palladium(II) chloride complexes of tdab produce only the dpa-chelated product, a 1:1 ratio of palladium(II) acetate with tdab yields an organometallic *N,C,N*-pincer complex. A 3:1 ratio of palladium(II) acetate with either tdab or tdat produces only the dpa-chelated products but with distinct structures. The tdab ligand favors the formation of a pinwheel-like structure, while the tdat ligand favors a “up-and-down” structure, due to both steric and electronic effects. The solution and solid-state structures of **4** give insight into the possible mechanism of the cyclometalation reaction to form the *N,C,N*-pincer complex, **3**, and, by extension, the mechanism for the formation of the triply cyclometalated product reported by Steel et al.

**Acknowledgment.** We thank Queen's University and the Natural Sciences and Engineering and Research Council of Canada for financial support.

**Supporting Information Available:** Listings of X-ray experimental details, atomic coordinates, thermal parameters, and bond distances and angles (in PDF format), crystallographic information files (in CIF format), pictures of the extended packing in **2**, and a diagram for the other independent molecule in the crystal lattice of **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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