

Anal. Calcd for $\text{HfClO}_3\text{C}_{42}\text{H}_{63}$ (2): C, 60.79; H, 7.65; Cl, 4.27. Found: C, 60.97; H, 7.60; Cl, 4.48.

2. **Synthesis of $\text{Ti}(\text{OAr}')_3\text{X}_2$ [X = Cl (3), Br (4)].** The addition of TiX_4 (X = Cl, Br) to a suspension of LiOAr' (4 equiv) in benzene gave an immediate dark red coloration. After stirring for 12 h, the mixture was filtered and solvent removed from the clear red solution to leave a dark red oil. Analysis by ^1H NMR showed the product plus traces of free 2,6-di-*tert*-butylphenol (HOAr') as an impurity. The oil was transferred to a round-bottom flask connected to a straight tube sublimator, and the mixture was heated at 70 °C (10^{-3} mm) to remove the more volatile phenol component. On cooling, a dark red solid mass of either 3 or 4 was given. Due to their extreme solubility in hydrocarbon solvents, recrystallization was not possible. Anal. Calcd for $\text{TiCl}_2\text{O}_2\text{C}_{28}\text{H}_{42}$ (3): C, 63.52; H, 8.00; Cl, 13.39. Found: C, 63.74; H, 7.95; Cl, 13.13. Anal. Calcd for $\text{TiBr}_2\text{O}_2\text{C}_{28}\text{H}_{42}$: C, 54.43; H, 6.86; Br, 25.84. Found: C, 53.26; H, 6.62; Br, 24.94. ^1H NMR (C_6D_6 , 30 °C): (3) δ 1.60 (s, *t*-Bu), 7.74 (m, C_6H_3); (4) δ 1.55 (s, *t*-Bu), 7.74 (m, C_6H_3).

3. **Synthesis of $\text{Ti}(\text{OAr}')_3$ (5).** Addition of LiOAr' (excess) to a blue solution of $\text{TiCl}_3(\text{HNMe}_2)_2$ in benzene initially gave a dark green suspension. On stirring for 24 h, a deep blue mixture was given. Solvent was removed under vacuum and the resulting solid mass extracted with cold hexane. After the blue solution was cooled, dark blue plates of product were given.

4. **Synthesis of $\text{Ti}(\text{OAr}')_3\text{X}$ [X = Cl (6), Br (7), I (8)].** To a solution of $\text{Ti}(\text{OAr}')_3$ (5) in hexane was condensed CX_4 (X = Cl, Br; 4 equiv) from a calibrated gas manifold. Over a period of a few hours the solution became reddish orange. Cooling to -15 °C gave crystals of product: X = Cl (6), Br (7). The blue color of a hexane solution of 5 was immediately discharged upon addition of I_2 crystals. Cooling gave crystals of the iodide (8). Anal. Calcd for $\text{TiClO}_3\text{C}_{42}\text{H}_{63}$ (6): C, 72.13; H, 9.08; Cl, 5.07. Found: 71.82; H, 9.14; Cl, 5.29. Anal. Calcd for $\text{TiBrO}_3\text{C}_{42}\text{H}_{63}$ (7): C, 67.84; H, 8.54; Br, 16.74. Found: C, 67.64; H, 8.62; Br, 10.97. Anal. Calcd for $\text{TiIO}_3\text{C}_{42}\text{H}_{63}$ (8): C, 63.80; H, 8.03; I, 16.05. Found: C, 61.79; H, 8.23; I, 19.05. The unsatisfactory analysis for 8 we believe may be due to some iodination of the aryloxy ligands. However, no evidence of such was seen in the X-ray structure.

X-ray Crystallography. General operating procedures have been reported previously.³¹ For both structures the octants collected were $+h$, $\pm k$, $\pm l$.

(i) $\text{HfCl}(\text{OAr}')_3$ (2). The structure was solved by successive Fourier

syntheses after initially locating the Hf and Cl atoms by a Patterson function. All atoms, including hydrogens, were located and refined. Hydrogen atoms were assigned isotropic thermal parameters and all other atoms anisotropic thermal parameters. A final difference Fourier synthesis was essentially featureless, the largest peak being 0.35 e/Å³. χ scans were essentially flat, and no absorption correction was performed. The transmission factors for this complex were calculated to range from 0.614 to 0.763 while the effect of secondary extinction in the diffraction data was found to be minimal.

(ii) $\text{Ti}(\text{OAr}')_3$ (8). A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no systematic absences or symmetry. Statistical tests and the solution and refinement of the structure indicated the proper choice for space group is $P\bar{1}$.

The structure was solved by direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and refined (anisotropic for Ti, I, O, and C; isotropic for H). A final difference Fourier was featureless, the largest peak being 0.18 e/Å³. χ scans were essentially flat, and no absorption correction was performed.

Electrochemical Measurements. Cyclic voltammograms were obtained on a BioAnalytical Systems, Inc. Model CV-1A instrument. Potential control for coulometric experiments was performed with a potentiostat purchased from Bio Analytical Systems, Inc. A three-compartment H-cell was used with a Pt-disk or gauze working electrode, Pt-wire auxiliary electrode, and a Ag/AgCl pseudoreference electrode to which all potentials refer. Scan rates were 25 mV/s. Under these conditions the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple was measured at +0.47 V, consistent to ± 10 mV, with a separation between the anodic and cathodic waves of 90 mV.

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Supplementary Material Available: Listings of anisotropic thermal parameters, complete bond distances and angles, and observed and calculated structure factors (75 pages). Ordering information is given on any current masthead page.

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“Obstacle Effect” in Palladium(II) Complexes of Tetraamine Ligands with Terminal Pyridyl or Picolyl Residues¹

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Palladium(II) complexes of several tetraamine ligands with terminal pyridyl or picolyl residues were synthesized, and to ascertain the effect of the 6-methyl group in the microenvironment of the core metal (obstacle effect), single-crystal X-ray analyses on some of the complexes have been conducted. 1,6-Bis(6-methyl-2-pyridyl)-2,5-diazahexane formed 1:2 $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}]$ as well as 1:1 $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ complexes. Both crystallize in the triclinic space group $P\bar{1}$. The unit cell dimensions of the former are $a = 10.726$ (1) Å, $b = 12.400$ (2) Å, and $c = 15.380$ (3) Å with $\alpha = 91.36$ (1)°, $\beta = 91.48$ (1)°, and $\gamma = 112.10$ (1)°; $Z = 2$. The latter has $a = 7.243$ (2) Å, $b = 9.979$ (2) Å, and $c = 15.001$ (3) Å with $\alpha = 94.68$ (2)°, $\beta = 96.20$ (2)°, and $\gamma = 103.68$ (2)°; $Z = 2$. 1,7-Bis(6-methyl-2-pyridyl)-2,6-diazheptane formed only the 1:1 complex $[\text{Pd}(\text{C}_{17}\text{H}_{24}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, which forms triclinic crystals with space group $P\bar{1}$. The unit cell dimensions are $a = 7.6906$ (4) Å, $b = 10.732$ (1) Å, and $c = 14.114$ (5) Å with $\alpha = 86.82$ (2)°, $\beta = 80.90$ (2)°, and $\gamma = 70.52$ (1)°; $Z = 2$. In all the complexes there is expected square-planar coordination around the Pd atoms. The salient features in the structure and hydrogen bonding of chloride ions are discussed.

Introduction

Palladium(II) complexes that possess simple N donors are well documented in the literature,³ and a number of structural studies have been conducted on these complexes.⁴ Recently we reported the structural aspects of pyridine⁵ or 2,2'-bipyridine⁶ Pd(II)

complexes that exhibited an “obstacle effect” as a result of juxtaposed 6-methyl groups. Such an effect has been observed,^{7,8} but no structural studies have been made to measure the influence of a 6-alkyl group(s) in pyridine and bipyridine complexes. To

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ascertain the effect of the 6-methyl group in the microenvironment of the core metal, herein specifically d^8 Pd(II), which favors a square-planar coordination^{9,10} several tetradentate N ligands with terminal pyridyl or picolyl residues were synthesized. From known data on complexes with either linear¹¹⁻¹⁴ or cyclic¹⁵⁻²⁰ tetradentate ligands, this study was limited to ligands capable of forming complexes containing 5-5-5, 5-6-5, and 5-7-5 chelate ring systems, in which the central bridges were either ethano, propano, or biphenyl, respectively. The Pd(II) complexes of these ligands were subsequently synthesized and fully characterized. Selected complexes were subjected to single-crystal X-ray analysis and compared to the previously reported literature assumptions.

Experimental Section

General Comments. All melting points were taken in capillary tubes with a Thomas-Hoover Uni-melt apparatus and are uncorrected. ¹H NMR spectra were determined on an IBM NR/80 spectrometer using CDCl₃ as solvent, with Me₄Si (0.1%), as the internal standard. Mass spectral (MS) data (70 eV) were determined by D. Patterson on a Hewlett-Packard 5985 GC/mass spectrometer and reported herein as (assignment, relative intensity). Elemental analyses were performed in the Centre de Recherche sur les Macromolécules, Strasbourg, France.

2-Pyridinecarboxaldehyde, 6-methyl-2-pyridinecarboxaldehyde, ethylenediamine, 1,3-diaminopropane, and ammonium hexafluorophosphate were purchased from Aldrich. Dowex 1-X8 ion-exchange resin (Cl⁻ form) was purchased from J. T. Baker Co.

Ligand Synthesis. General Procedure. Under a nitrogen atmosphere, to a rapidly stirred solution of purified diamine in absolute EtOH (10 mL), a solution of distilled aldehyde in absolute EtOH (10 mL) was slowly added over a period of 1 h. The mixture was then refluxed for 1 h. After the mixture was cooled to 25 °C, the solvent was removed in vacuo to give an oily residue, which was dissolved in absolute EtOH (150 mL). Excess NaBH₄ was added, and the mixture was refluxed with stirring for 24 h. After the mixture was cooled to 25 °C, concentrated HCl (5 mL) was carefully added and the solvents were evaporated to afford the crude ligand, which was dried in vacuo for 1 h. Aqueous HCl (50 mL) was added, and the solution was washed with CHCl₃ (2 ×, 50 mL). The pH of the aqueous solution was adjusted to 12 with concentrated NaOH, and the polyamine was extracted with CHCl₃ (5 × 50 mL). The organic phase was dried over anhydrous MgSO₄ and then concentrated in vacuo to give an oil that was purified on an Al₂O₃ column eluting with C₆H₅Me/CHCl₃ (2:1) to afford the desired tetraaza ligand.

1,6-Bis(2-pyridyl)-2,5-diazahexane (1) was prepared from 2-pyridinecarboxaldehyde (5.35 g, 50 mmol), 1,2-diaminoethane (1.5 g, 25 mmol), and NaBH₄ (2.9 g, 75 mmol): light yellow oil;^{22,23} 3.1 g (51%); ¹H NMR δ 2.25 (s, NH), 2.79 (s, CH₂N), 3.89 (s, pyCH₂N), 7.15 (2 dd, *J*_{5,6} = 4.8 Hz, *J*_{5,4} = 7.3 Hz, *J*_{5,3} = 1.8 Hz, py 5-H), 7.28 (ddd, *J*_{3,4} = 7.8 Hz, *J*_{3,5} = 1.8 Hz, *J*_{3,6} = 1.0 Hz, py 3-H), 7.62 (2 dd, *J*_{4,5} = 7.3 Hz, *J*_{4,3} = 7.8 Hz, *J*_{4,6} = 1.8 Hz, py 4-H), 8.50 (ddd, *J*_{6,5} = 4.8 Hz, *J*_{6,4} = 1.8 Hz, *J*_{6,3} = 1.0 Hz, py 6-H); MS *m/e* 242 (M⁺, 1), 150 (M⁺ - C₆H₆N, 10), 134 (M⁺ - C₆H₈N₂, 8), 121 (M⁺ - C₇H₉N₂, 100), 107 (M⁺ - C₈H₁₁N₂, 5), 93 (M⁺ - C₉H₁₃N₂, 72), 79 (M⁺ - C₉H₁₃N₃, 4).

1,6-Bis(6-methyl-2-pyridyl)-2,5-diazahexane (2) was prepared from 6-methyl-2-pyridinecarboxaldehyde (6.05 g, 50 mmol), ethylenediamine (1.5 g, 25 mmol), and NaBH₄ (2.9 g, 75 mmol): light yellow oil;⁷ 4.3 g (64%); ¹H NMR δ 2.23 (s, NH), 2.52 (s, pyCH₃), 2.82 (s, CH₂CH₂N),

3.87 (s, pyCH₂N), 7.00 (d, *J* = 7.6 Hz, py 5-H), 7.12 (d, *J* = 7.6 Hz, py 3-H), 7.52 (t, *J* = 7.6 Hz, py 4-H); MS *m/e* 270 (M⁺, 1), 164 (M⁺ - C₇H₈N, 9), 148 (M⁺ - C₇H₁₀N₂, 9), 135 (M⁺ - C₈H₁₁N₂, 100), 121 (M⁺ - C₉H₁₃N₂, 5), 107 (M⁺ - C₉H₁₃N₃, 73), 93 (M⁺ - C₁₀H₁₅N₃, 5).

1,7-Bis(2-pyridyl)-2,6-diazahexane (3) was prepared from 2-pyridinecarboxaldehyde (5.35 g, 50 mmol), 1,3-diaminopropane (1.85 g, 25 mmol), and NaBH₄ (2.9 g, 75 mmol): light yellow oil;^{22,24} 3.2 g (50%); ¹H NMR δ 1.77 (m, CH₂CH₂CH₂), 2.03 (s, NH), 2.75 (t, *J* = 6.8 Hz, CH₂N), 3.90 (s, pyCH₂N), 7.15 (2 dd, *J*_{5,6} = 4.8 Hz, *J*_{5,4} = 7.3 Hz, *J*_{5,3} = 1.8 Hz, py 5-H) 7.28 (ddd, *J*_{3,4} = 7.8 Hz, *J*_{3,5} = 1.8 Hz, *J*_{3,6} = 1.0 Hz, py 3-H), 7.63 (2 dd, *J*_{4,5} = 7.3 Hz, *J*_{4,3} = 7.8 Hz, *J*_{4,6} = 1.8 Hz, py 4-H), 8.53 (ddd, *J*_{6,5} = 4.8 Hz, *J*_{6,4} = 1.8 Hz, *J*_{6,3} = 1.0 Hz, py 6-H); MS *m/e* 256 (M⁺, 1), 165 (M⁺ - C₆H₆N, 15), 148 (M⁺ - C₆H₈N₂, 4), 135 (M⁺ - C₇H₉N₂, 37), 121 (M⁺ - C₈H₁₁N₂, 69), 109 (M⁺ - C₉H₁₁N₂, 25), 93 (M⁺ - C₉H₁₃N₃, 100), 79 (M⁺ - C₁₀H₁₅N₃, 6).

1,7-Bis(6-methyl-2-pyridyl)-2,6-diazahexane (4) was prepared from 6-methyl-2-pyridinecarboxaldehyde (6.05 g, 50 mmol), 1,3-diaminopropane (1.85 g, 25 mmol), and NaBH₄ (2.9 g, 75 mmol): light yellow oil;⁷ 4.6 g (65%); ¹H NMR δ 1.76 (m, CH₂CH₂CH₂), 2.36 (s, NH), 2.51 (s, pyCH₃), 2.74 (t, *J* = 6.8 Hz, CH₂CH₂N), 3.85 (s, pyCH₂N), 6.98 (d, *J* = 7.6 Hz, py 5-H), 7.08 (d, *J* = 7.6 Hz, py 3-H), 7.49 (t, *J* = 7.6 Hz, py 4-H); MS *m/e* 284 (M⁺, 1), 178 (M⁺ - C₇H₈N, 13), 162 (M⁺ - C₇H₁₀N₂, 3), 149 (M⁺ - C₈H₁₁N₂, 17), 135 (M⁺ - C₉H₁₃N₂, 35), 123 (M⁺ - C₁₀H₁₅N₂, 14), 107 (M⁺ - C₁₀H₁₅N₃, 100), 93 (M⁺ - C₁₁H₁₇N₃, 5).

2,2'-Bis((2-pyridylmethyl)amino)biphenyl (5) was prepared from 2-pyridinecarboxaldehyde (4.28 g, 40 mmol), 2,2'-diaminobiphenyl²¹ (3.68 g, 20 mmol), and NaBH₄ (2.0 g, 52 mmol): mp 137-138 °C (yellow crystals, lit.^{7,21} mp 135-137 °C); 4.6 g (63%); ¹H NMR δ 4.48 (s, pyCH₂), 4.75 (s, NH), 7.59 (m, pyH and arH), 8.49 (ddd, *J*_{6,5} = 4.8 Hz, *J*_{6,4} = 1.8 Hz, *J*_{6,3} = 1.0 Hz, py 6-H); MS *m/e* 366 (M⁺, 13), 274 (M⁺ - C₆H₆N, 53), 258 (M⁺ - C₆H₈N₂, 7), 180 (M⁺ - C₁₂H₁₄N₂, 100), 107 (M⁺ - C₁₈H₁₅N₂, 6), 93 (M⁺ - C₁₈H₁₅N₃, 72), 80 (M⁺ - C₁₉H₁₆N₃, 40).

2,2'-Bis((6-methyl-2-pyridylmethyl)amino)biphenyl (6) was prepared from 6-methyl-2-pyridinecarboxaldehyde (4.85 g, 40 mmol), 2,2'-diaminobiphenyl²¹ (3.68 g, 20 mmol), and NaBH₄ (2.0 g, 52 mmol): light yellow oil;^{7,21} 6.2 g (79%); ¹H NMR 2.43 (s, pyCH₃), 4.43 (s, pyCH₂N), 4.86 (s, NH), 7.48 (m, pyH and arH); MS *m/e* 394 (M⁺, 12), 288 (M⁺ - C₇H₈N, 58), 272 (M⁺ - C₇H₁₀N₂, 13), 180 (M⁺ - C₁₄H₁₈N₂, 100), 121 (M⁺ - C₁₉H₁₇N₂, 8), 107 (M⁺ - C₁₉H₁₇N₃, 96), 94 (M⁺ - C₂₀H₁₈H₃, 56).

Complex Formation. Procedure A. To a warm, stirred absolute EtOH solution of ligand, a warm aqueous solution of Na₂PdCl₄ was added slowly. The light brown precipitate, which formed immediately, was redissolved by heating on a steam bath. When the solution became clear, acetone (5 mL) was added. The warm solution was filtered through a Celite pad, and upon slow cooling, the complex crystallized. The complex was filtered, washed with acetone, and recrystallized from absolute EtOH.

Procedure B. The method of Gibson and McKenzie⁸ was utilized; thus, an aqueous solution of Na₂PdCl₄ and the appropriate ligand was heated to dissolve the precipitate, and the mixture was then filtered. To the filtrate was added a saturated solution of NH₄PF₆, whereupon a yellow precipitate formed. This precipitate was washed with water, then mixed with water (10 mL) and Dowex 1-X8 ion-exchange resin (Cl⁻ form, **2g**), and allowed to stand overnight. After removal of the resin, the complex was precipitated with acetone and subsequently recrystallized from EtOH.

Complex 1a was prepared (procedure A) from **1** (61 mg, 0.25 mmol) and Na₂PdCl₄ (74 mg, 0.25 mmol): pale cream crystals; mp 183-190 °C dec; 75 mg (42%). Anal. Calcd for C₂₈H₄₂Cl₂N₈O₃Pd: C, 46.97; H, 5.91; N, 15.65; Cl, 9.90. Found: C, 46.84; H, 5.84; N, 15.55; Cl, 10.05.

Complex 1b was prepared (procedure B) from **1** (121 mg, 0.5 mmol) and Na₂PdCl₄ (147 mg, 0.5 mmol): yellow crystals; mp 155-160 °C dec; 96 mg (44%). Anal. Calcd for C₁₄H₂₀Cl₂N₄PdO₃: C, 38.42; H, 4.61; N, 12.80; Cl, 16.20. Found: C, 38.72; H, 5.04; N, 13.01; Cl, 16.56.

Complex 2a was prepared (procedure A) from **2** (68 mg, 0.25 mmol) and Na₂PdCl₄ (74 mg, 0.25 mmol): pale yellow crystals; mp 172-177 °C dec; 75 mg (39%). Anal. Calcd for C₃₂H₅₀Cl₂N₈O₃Pd: C, 49.78; H, 6.53; N, 14.51; Cl, 9.82. Found: C, 49.82; H, 6.60; N, 14.41; Cl, 9.75. Crystals for X-ray analysis were obtained by recrystallization from MeOH.

Complex 2b was prepared (procedure B) from **2** (135 mg, 0.5 mmol) and Na₂PdCl₄ (147 mg, 0.5 mmol): yellow crystals; mp 135-140 °C dec; 103 mg (41%). Anal. Calcd for C₁₆H₂₈Cl₂N₄PdO₃: C, 42.92; H, 4.95; N, 12.51. Found: C, 42.84; H, 5.19; N, 12.42. Crystals for X-ray analysis were obtained from water.

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Table I. Crystal Data and Data Collection Parameters

	2a	2b	4a
formula	[Pd(C ₁₆ H ₂₂ N ₄) ₂]Cl ₂ ·3H ₂ O	[Pd(C ₁₆ H ₂₂ N ₄)]Cl ₂ ·3H ₂ O	[Pd(C ₁₇ H ₂₄ N ₄)]Cl ₂ ·3H ₂ O
fw	772.1	501.7	515.8
cryst syst	triclinic	triclinic	triclinic
space group	P1	P1	P1
a, Å	10.726 (1)	7.243 (2)	7.6906 (4)
b, Å	12.400 (2)	9.979 (2)	10.732 (1)
c, Å	15.380 (3)	15.001 (3)	14.114 (5)
α, deg	91.36 (1)	94.68 (2)	86.82 (2)
β, deg	91.48 (1)	96.20 (2)	80.90 (2)
γ, deg	112.10 (1)	103.68 (2)	70.52 (1)
V, Å ³	1893.4 (9)	1040.9 (9)	1084.4 (4)
d, g cm ⁻³	1.354	1.601	1.579
Z	2	2	2
μ(Mo Kα), cm ⁻¹	6.65	11.60	11.16
min rel transmissn, %	91.92	91.02	83.97
cryst size, mm	0.16 × 0.16 × 0.20	0.36 × 0.36 × 0.48	0.28 × 0.36 × 0.48
θ limits, deg	1–25	1–25	1–25
scan rates, deg min ⁻¹	0.53–20.0	0.49–5.0	0.61–10.0
precision	I ≈ 25σ(I)	I ≈ 50σ(I)	I ≈ 25σ(I)
max scan time, s	120	120	90
no. of unique data	6654	3856	3804
no. of obsd data	3340	3460	3193
variables	418	236	244
R	0.031	0.049	0.029
R _w	0.043	0.065	0.046
max residual, e Å ⁻³	0.32	0.56	0.60
color	colorless	pale yellow	pale yellow
temp, °C	25	26	26
extinction		2.00 (3) × 10 ⁻⁶	

Complex 3a was prepared (procedure A) from **3** (64 mg, 0.25 mmol) and Na₂PdCl₄ (74 mg, 0.25 mmol): yellow crystals; mp 250–255 °C dec; 100 mg (82%). Anal. Calcd for C₁₅H₂₆Cl₂N₄O₃Pd: C, 36.94; H, 5.37; N, 11.49; Cl, 14.54. Found: C, 36.88; H, 5.31; N, 11.58; Cl, 14.74.

Complex 4a was prepared (procedure A) from **4** (142 mg, 0.5 mmol) and Na₂PdCl₄ (147 mg, 0.5 mmol): yellow crystals; mp 170–172 °C dec; 240 mg (93%). Anal. Calcd for C₁₇H₃₀Cl₂N₄O₃Pd: C, 39.59; H, 5.86; N, 10.86; Cl, 13.75. Found: C, 40.00; H, 5.87; N, 10.94; Cl, 13.65. The crystals for X-ray analysis were obtained from EtOH/ether (1:1).

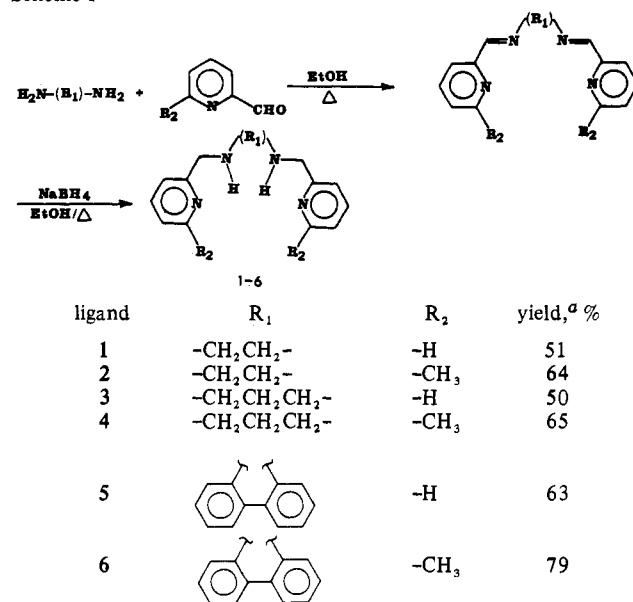
Complex 5a was prepared (procedure A) from **5** (183 mg, 0.5 mmol) and Na₂PdCl₄ (147 mg, 0.5 mmol): yellow crystals; mp 270–272 °C dec; 245 mg (90%). Anal. Calcd for C₂₄H₂₂Cl₂N₄Pd: C, 53.01; H, 4.08; N, 10.30; Cl, 13.04. Found: C, 53.02; H, 4.26; N, 10.21; Cl, 12.86.

Complex 6a was prepared (procedure A) from **6** (197 mg, 0.5 mmol) and Na₂PdCl₄ (147 mg, 0.5 mmol): yellow crystals; mp 242–245 °C dec; 266 mg (93%). Anal. Calcd for C₂₆H₂₆Cl₂N₄Pd: C, 54.61; H, 4.58; N, 9.80; Cl, 12.40. Found: C, 54.42; H, 4.71; N, 9.72; Cl, 12.26.

X-ray Experiments. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The θ-2θ scans were made at variable rates, designed to yield measurements of equal precision for all significant data in each structure. A maximum was placed on the scan time spent on any reflection. Crystal data and specifics for each data collection are given in Table I. One hemisphere of data was measured for each crystal within the specified angular limits. Data reduction included corrections for background, Lorentz, polarization, and absorption, the latter based upon ψ scans of reflections near χ = 90°, using the program EAC of the Enraf-Nonius SDP.²⁵ Reflections having I > 3σ(I) were considered observed and used in the refinements.

All structures were solved by the heavy-atom method and refined by full-matrix least squares based upon F, with weights w = σ⁻²(F_o), using the Enraf-Nonius SDP programs,²⁵ scattering factors of Cromer and Waber,²⁶ and anomalous dispersion coefficients of Cromer.²⁷ Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in difference maps and included as fixed contributions. For **4a**, hydrogen atoms of one of the water molecules (O3) could not be located, and for **2b** none of the water hydrogen atoms were located. Final R factors and residuals in final difference maps are given in Table I. The coordinates

Scheme I



^a Isolated yields.

of non-hydrogen atoms for **2a**, **2b**, and **4a** are given in Tables II–IV respectively.

Results and Discussion

A. Ligand Formation. The condensation of the appropriate diamine with the heteroaromatic aldehydes in EtOH under reflux gave the anticipated bis(Schiff base) intermediate. Subsequent reduction of this diimine with NaBH₄ in EtOH under reflux gave the corresponding crude diamine **1–6**, as the major product (Scheme I). The overall yields were only moderate (50–79%), since the reduction of diimines generally affords a mixture of diverse diamino, aminoimino, and diimino compounds; however, separation by column chromatography on alumina afforded the pure diamine.

In the ¹H NMR spectra of **1–6**, the characteristic peak of the intermediary formylimino hydrogen (H–C–N) was absent, and the mass spectra did not show the peaks due to the intermediates

(25) Frenz, B. A.; Okaya, Y. "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1982.

(26) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(27) Cromer, D. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table II. Coordinates for Non-Hydrogen Atoms, $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2a**)^a

atom	x	y	z	atom	x	y	z
Pd1	0	0	0	C12	0.0097 (5)	0.0755 (5)	0.2989 (3)
Pd2	0.5	0.5	0.5	C13	-0.0106 (6)	-0.0167 (6)	0.3524 (4)
Cl1	0.7980 (1)	0.3992 (1)	0.4132 (1)	C14	0.0321 (6)	-0.1017 (5)	0.3291 (4)
Cl2	0.1146 (2)	0.3631 (1)	0.9777 (1)	C15	0.0998 (5)	-0.0951 (4)	0.2529 (4)
N1	-0.4315 (4)	-0.1990 (3)	-0.0909 (3)	C16	0.1514 (7)	-0.1869 (5)	0.2250 (5)
N2	-0.2036 (3)	-0.0389 (3)	-0.0085 (2)	C17	0.2390 (6)	0.3663 (6)	0.7514 (4)
N3	0.0040 (3)	0.1371 (3)	0.0807 (2)	C18	0.3878 (5)	0.4141 (4)	0.7669 (3)
N4	0.1197 (4)	-0.0066 (3)	0.1987 (3)	C19	0.4461 (5)	0.4661 (4)	0.8459 (3)
N5	0.4614 (4)	0.4038 (3)	0.7003 (3)	C20	0.5843 (6)	0.5093 (5)	0.8562 (3)
N6	0.6753 (4)	0.5035 (3)	0.5615 (2)	C21	0.6606 (5)	0.5008 (5)	0.7880 (4)
N7	0.6085 (4)	0.6738 (3)	0.4845 (2)	C22	0.5958 (4)	0.4468 (4)	0.7118 (3)
N8	0.5885 (4)	0.8708 (3)	0.4095 (3)	C23	0.6729 (5)	0.4284 (4)	0.6365 (3)
C1	-0.5456 (8)	-0.2531 (6)	-0.2310 (5)	C24	0.7635 (5)	0.6269 (5)	0.5802 (3)
C2	-0.5489 (5)	-0.2529 (4)	-0.1342 (4)	C25	0.7522 (5)	0.6947 (4)	0.5031 (3)
C3	-0.6662 (5)	-0.3062 (5)	-0.0905 (5)	C26	0.5633 (5)	0.7545 (4)	0.5354 (3)
C4	-0.6616 (5)	-0.3027 (5)	-0.0011 (5)	C27	0.6119 (4)	0.8741 (4)	0.4952 (4)
C5	-0.5393 (5)	-0.2476 (4)	0.0439 (4)	C28	0.6676 (6)	0.9755 (4)	0.5441 (4)
C6	-0.4269 (4)	-0.1987 (4)	-0.0049 (3)	C29	0.7050 (6)	1.0790 (5)	0.5003 (5)
C7	-0.2865 (5)	-0.1445 (4)	0.0366 (3)	C30	0.6843 (6)	1.0767 (5)	0.4139 (5)
C8	-0.2249 (4)	0.0676 (4)	0.0223 (3)	C31	0.6246 (5)	0.9709 (5)	0.3689 (4)
C9	-0.1368 (5)	0.1169 (4)	0.1031 (3)	C32	0.5980 (9)	0.9609 (7)	0.2730 (5)
C10	0.0983 (5)	0.1733 (4)	0.1597 (3)	O1	0.9717 (4)	0.5037 (4)	0.8716 (3)
C11	0.0746 (4)	0.0774 (4)	0.2220 (3)	O2	0.9634 (4)	0.3446 (4)	0.2633 (3)
				O3	0.9619 (4)	0.3462 (4)	0.5721 (3)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Coordinates for Non-Hydrogen Atoms, $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2b**)^a

atom	x	y	z	atom	x	y	z
Pd	0.88097 (7)	0.26562 (5)	0.23017 (4)	C4	1.2415 (11)	0.4648 (5)	0.5199 (5)
Cl1	0.2976 (3)	0.1641 (2)	0.1063 (2)	C5	1.1020 (10)	0.3383 (8)	0.5050 (5)
Cl2	0.2142 (3)	-0.0296 (3)	0.3783 (2)	C6	1.0090 (9)	0.2926 (7)	0.4179 (5)
N1	1.0485 (7)	0.3673 (5)	0.3474 (4)	C7	0.8623 (11)	0.1572 (8)	0.3952 (5)
N2	0.8823 (8)	0.1064 (6)	0.3016 (4)	C8	0.7274 (11)	-0.0116 (7)	0.2556 (5)
N3	0.7218 (8)	0.1280 (5)	0.1322 (4)	C9	0.7380 (11)	-0.0126 (7)	0.1550 (5)
N4	0.8276 (7)	0.3952 (5)	0.1337 (4)	C10	0.7891 (10)	0.1723 (7)	0.0475 (5)
O1	0.2053 (12)	0.8681 (7)	0.1754 (5)	C11	0.7893 (9)	0.3221 (7)	0.0492 (5)
O2	0.5352 (10)	0.7320 (8)	0.6852 (6)	C12	0.7496 (10)	0.3837 (8)	-0.0278 (5)
O3	0.4273 (10)	0.1578 (7)	0.5669 (6)	C13	0.7449 (11)	0.5222 (8)	-0.0182 (5)
C1	1.2621 (11)	0.5531 (9)	0.2802 (6)	C14	0.7702 (11)	0.5935 (8)	0.0668 (5)
C2	1.1932 (9)	0.4841 (7)	0.3605 (5)	C15	0.8066 (9)	0.5262 (7)	0.1422 (5)
C3	1.2861 (10)	0.5354 (8)	0.4473 (5)	C16	0.8203 (11)	0.5993 (7)	0.2363 (5)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

or starting material. The purity of these ligands was sufficient for subsequent preparation of the complexes, which then were purified by recrystallization.

B. Complex Formation. Complexes are designated by a number and a letter. The number refers to the corresponding ligand while the letter refers to the method of preparation.

1. Synthesis. A warm EtOH solution of ligand (**1-6**) was treated with 1 equiv of Na_2PdCl_4 in warm water. After stirring, the desired complex was isolated as either a pale cream or yellow crystals and subsequently recrystallized from EtOH. Each complex was characterized by elemental analysis.

The studies show that ligands **1** and **2** with palladium(II) form a mixture of 1:2 and 1:1 complexes (M:L) that could be separated or isolated by different workup procedures; X-ray analyses on single crystals of **2a** and **2b** established the structures. However, under a similar set of experimental conditions, the ligands **3-6** formed exclusively 1:1 complexes having 5-6-5 and 5-7-5 chelate ring systems, respectively. Again, X-ray analysis was conducted on **4a** to confirm the structure. Thus, it appears that the length of the carbon chain between two amine nitrogen atoms is an important factor in deciding the stoichiometry of the complex formed, i.e. 1:2 or 1:1 (M:L). This is true because the bite angle for the metal will be different in 5-5-5, 5-6-5, or 5-7-5 chelate ring systems.

On comparison of the complexes without or with 6-methyl groups (**1a** with **2a**; **1b** with **2b**; **3a** with **4a**; **5a** with **6a**), we found that the terminal methyl groups do not affect the stoichiometry of the complexes⁷ although X-ray analysis showed significant

deviations or distortions in the coordination environment of palladium, which is not unusual.⁶

2. Structure Description. **a. Bis[1,6-bis(6-methyl-2-pyridyl)-2,5-diazahexane]palladium(II) Chloride (**2a**).** Palladium forms a 1:2 (M:L) complex and is coordinated to the four amine nitrogen atoms rather than pyridine nitrogens (Figure 1). There are two half-molecules in the asymmetric unit, and in each, Pd sits on a center of symmetry. In both molecules the Pd atom and the four coordinating nitrogen atoms lie in a perfect plane, as required by symmetry, and there are no significant differences between the two molecules. A comparison of bond lengths and angles in complex **2a** to similar PdN_4 type complexes^{28,29} is shown in Table V. The bidentate ligand appears to chelate Pd in a slightly asymmetric fashion, with the two Pd-N distances averaging 2.052 (3) and 2.068 (3) Å.

b. [1,6-Bis(6-methyl-2-pyridyl)-2,5-diazahexane]palladium(II) Chloride (2b**).** In this (1:1) complex, the palladium atom is surrounded by four nitrogen atoms that are disposed in a trapezoidal form (Figure 2), giving the molecule local C_2 symmetry. The coordination plane around palladium has a slight tetrahedral distortion such that the planes defined by Pd-N1-N2 and Pd-N3-N4 form a dihedral angle of 2.7°. Important bond lengths and angles, which are given in Table VI, resemble those reported for the (triethylenetetramine)palladium(II) complex,¹² $\text{Pd}(\text{trien})^{2+}$,

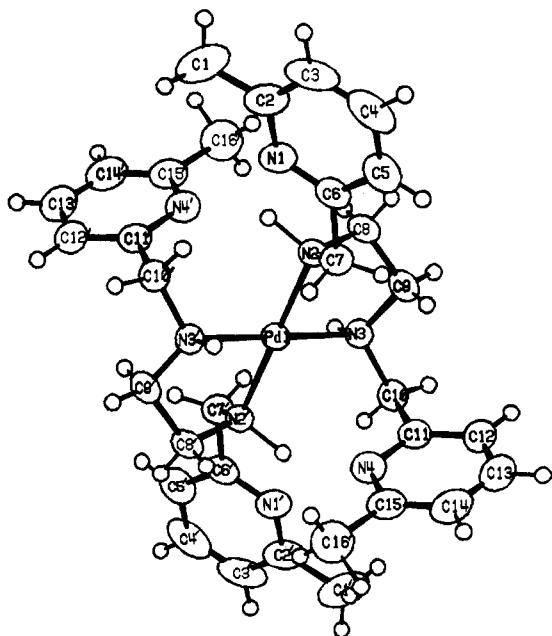
(28) Wiesner, J. R.; Lingafelter, E. C. *Inorg. Chem.* **1966**, *5*, 1770.

(29) Baggio, S.; Amzel, L. M.; Becka, L. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1698.

Table IV. Coordinates for Non-Hydrogen Atoms, $[\text{Pd}(\text{C}_{17}\text{H}_{24}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**4a**)^a

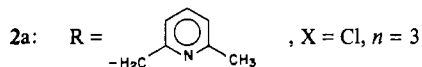
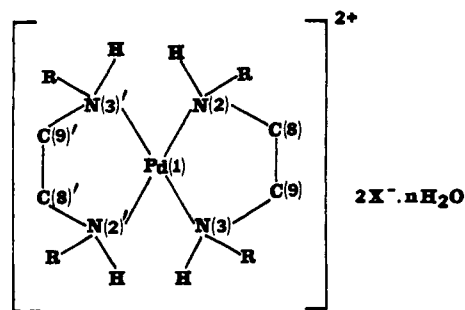
atom	x	y	z
Pd	0.14325 (3)	0.23664 (2)	0.24323 (1)
Cl1	0.2552 (1)	0.6175 (1)	0.91549 (7)
Cl2	0.3787 (1)	0.3636 (1)	0.44065 (7)
O1	0.4003 (5)	0.6422 (3)	0.3755 (2)
O2	0.4929 (6)	0.3299 (4)	0.8238 (2)
O3	0.3357 (5)	0.7956 (3)	0.7394 (2)
N1	0.2073 (4)	0.1115 (3)	0.1258 (2)
N2	0.1331 (4)	0.3714 (3)	0.1364 (2)
N3	0.0316 (4)	0.3783 (2)	0.3449 (2)
N4	0.1820 (4)	0.1224 (2)	0.3667 (2)
C1	0.0880 (5)	-0.0576 (3)	0.2059 (3)
C2	0.1759 (5)	-0.0039 (3)	0.1187 (2)
C3	0.2170 (5)	-0.0676 (3)	0.0327 (2)
C4	0.2820 (5)	-0.0105 (4)	-0.0506 (2)
C5	0.3017 (5)	0.1116 (4)	-0.0440 (2)
C6	0.2648 (5)	0.1688 (3)	0.0442 (2)
C7	0.2831 (6)	0.3022 (3)	0.0581 (2)
C8	0.1665 (6)	0.4918 (3)	0.1665 (3)
C9	0.0071 (7)	0.5750 (4)	0.2374 (3)
C10	-0.0956 (6)	0.5038 (3)	0.3083 (3)
C11	-0.0708 (5)	0.3177 (3)	0.4208 (2)
C12	0.0606 (5)	0.1865 (3)	0.4438 (2)
C13	0.0665 (5)	0.1343 (3)	0.5362 (2)
C14	0.1986 (5)	0.0169 (4)	0.5496 (2)
C15	0.3295 (5)	-0.0454 (3)	0.4728 (2)
C16	0.3208 (5)	0.0100 (3)	0.3807 (2)
C17	0.4706 (5)	-0.0487 (3)	0.2993 (2)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

**Figure 1.** Perspective drawing of $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2a**), molecule 1.

which is also a 5-5-5 chelate. As expected, the Pd-N(terminal) bond lengths (average 2.073 Å) are longer than Pd-N(middle) bond lengths (average 1.986 Å) and are analogous to those of Pd(trien)²⁺.¹² The N1-Pd-N4 bond angle of 114.5° in **2b** is considerably larger than 104° reported for Pd(trien)²⁺, showing that there is considerable strain in complex **2b**. Involvement of sp²-hybridized nitrogens and carbons instead of sp³ as in Pd(trien)²⁺ appears to be the main reason for this enlargement of N1-Pd-N4 angle; the terminal methyl groups might have a slight influence. Both pyridine rings are planar within 0.042 (5) Å and make a dihedral angle of 47.7° with each other.

c. [1,7-Bis(6-methyl-2-pyridyl)-2,6-diazaheptane]palladium(II) Chloride (4a). In complex **4a**, palladium is bonded to four nitrogen atoms and severe deviations from the square-planar geometry are

Table V. Important Bond Lengths (Å) and Angles (deg) in Complex **2a** and Related Compounds

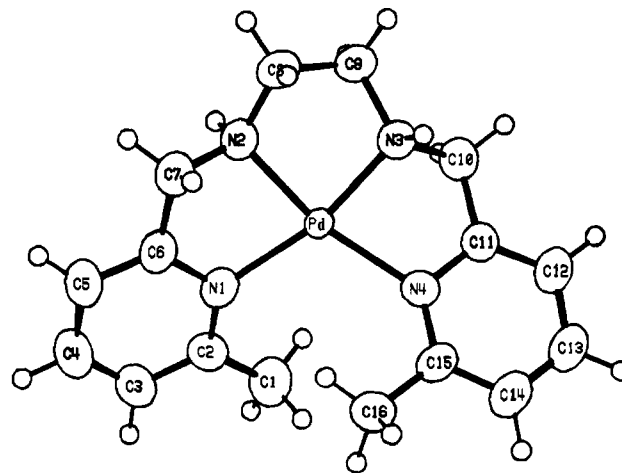
7:²⁸ R = H, X = Cl, n = 0

8:²⁹ R = H, X = (H₂NCH₂CH₂NH₂)Pd(S₂O₃)₂, n = 0

	2a	7	8
Pd-N2	2.052 (3)	2.030 (6)	2.059 (14)
Pd-N3	2.068 (3)	2.043 (7)	2.048 (14)
N2-Pd-N3	84.34 (14)	83.6 (3)	83.1 (10)
Pd-N3-C9	107.9 (3)	108.2 (5)	109.3 (11)
C8-N2-Pd	106.7 (3)	109.6 (5)	109.6 (11)

Table VI. Important Bond Lengths (Å) and Angles (deg) in Complexes **2b** and **4a**

	2b	4a	2b	4a
Pd-N1	2.063 (4)	2.083 (2)	N1-Pd-N2	79.67 (17)
Pd-N2	1.989 (4)	2.023 (2)	N2-Pd-N3	86.68 (17)
Pd-N3	1.983 (4)	2.023 (2)	N3-Pd-N4	79.17 (16)
Pd-N4	2.082 (4)	2.077 (2)	N4-Pd-N1	114.52 (15)
			N1-Pd-N3	166.31 (16)
			N2-Pd-N4	165.61 (16)
				167.83 (10)
				167.34 (10)

**Figure 2.** Perspective drawing of $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2b**).

noted. The molecule acquires a twisted conformation overall, and there is an approximate C₂ axis passing through the Pd and C9 atoms (Figure 3). Thus, the coordination plane around palladium is tetrahedrally distorted such that the plane defined by Pd-N1-N2 and Pd-N3-N4 forms a dihedral angle of 14.5°, which is much larger than in **2b** and **3a**.¹⁴ Important bond lengths and angles are given in Table VI and are comparable to those of **3a**.¹⁴ The Pd-N(middle) bond length (average 2.023 (2) Å) in **4a** is significantly larger than in **2b** because of the 5-6-5 system in **4a** instead of 5-5-5 in **2b**. The Pd-N(terminal) bond length of 2.080 (2) Å (average) in **4a** does not differ significantly from that of **2b**. The six-membered chelate ring has a twist-boat conformation.

Because of the formation of a middle six-membered chelate ring, there is less strain in **4a** as compared to **2b**, as shown by the N1-Pd-N4 bond angle of 108.74 (9)° in **4a**. However, this angle is more than 103° in **3a**¹⁴ obviously due to the presence of terminal

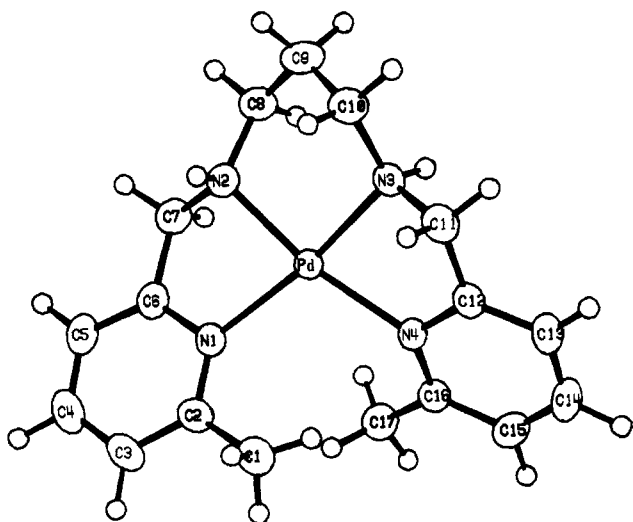


Figure 3. Perspective drawing of $[\text{Pd}(\text{C}_{17}\text{H}_{24}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**4a**).

methyl groups. Both pyridine rings are planar within 0.031 (3) Å and form an angle of 58.0° with each other that is significantly larger than 47.7° in **2b** and 39.6° (average) in **3a**¹⁴ again because of the above reasons.

3. Hydrogen Bonding. In all three structures, the chloride ions and water molecules participate in extensive hydrogen-bonding networks. Typical separations are 3.1–3.3 Å for O...Cl and 2.7–2.9

Å for O...O. In addition, in most cases, the coordinated amine nitrogen atoms serve as hydrogen-bond donors to chloride ions. In **4b**, each amine nitrogen atom donates a near-linear hydrogen bond to a separate Cl ion: N2...Cl1 = 3.149 (3) Å, N–H...Cl = 167°; N3...Cl2 = 3.133 (3) Å, angle 167°. The same situation exists in **2b**, where the hydrogen-bond parameters are as follows: N2...Cl2 = 3.185 (6) Å, N–H...Cl = 152°; N3...Cl1 = 3.163 (6) Å, angle 166°. In the 2:1 complex **2a**, the stoichiometry does not allow for each amine nitrogen atom to form a hydrogen bond with chloride, and only one nitrogen atom of each ligand does this. Geometries: N3...Cl2 = 3.094 (4) Å, N–H...Cl = 152°; N6...Cl1 = 3.147 (4) Å, angle 174°. It is also of interest that for both independent molecules the N–H...Cl hydrogen bond is formed by the nitrogen atoms making the longer coordinate bond with Pd. The asymmetric hydrogen bonding probably causes the asymmetric chelation.

Conclusion. The terminal methyl groups cause slight distortions in the coordination environment around the central Pd(II) atom but do not cause any obstacle effect⁷ so as to change the overall geometry or stoichiometry of the complexes.

Acknowledgment. We thank the National Science Foundation and Center for Energy Studies, Louisiana State University, for partial support of this work.

Supplementary Material Available: Tables of bond distances, bond angles, coordinates for H atoms, anisotropic thermal parameters, and structure factor amplitudes for complexes $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2a**) (Tables S1–S5), $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2b**) (Tables S6–S10), and $[\text{Pd}(\text{C}_{17}\text{H}_{24}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**4a**) (Tables S11–S15) (62 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of California, Irvine, California 92717

Preparation and Crystal Structure of a Diamagnetic Copper(II) Trichloroacetate Complex Containing a Nitroxyl Radical Ligand

LEIGH C. PORTER and ROBERT J. DOEDENS*

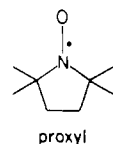
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From copper(II) trichloroacetate and the stable nitroxyl radical 2,2,4,4-tetramethylpyrrolinyl-1-oxy (proxyl) in the presence of water was isolated a stable adduct of stoichiometry $[\text{Cu}(\text{O}_2\text{CCCl}_3)_2(\text{proxyl})]_2 \cdot \text{H}_2\text{O}$. A crystal structure analysis has shown this adduct to have a novel binuclear structure. The two copper atoms are bridged by a pair of *syn,syn*-carboxylate groups and by the oxygen atom of a water molecule. The other two trichloroacetate ligands are monodentate, with the free oxygen participating in a hydrogen bond to the bridging water molecule. The nitroxyl ligands are bound via oxygen with short Cu–O distances of 1.928 (8) and 1.950 (9) Å. Magnetic susceptibility measurements show that this material is diamagnetic from 6 to 300 K. Crystal data: triclinic, $P\bar{1}$, $a = 11.804$ (3) Å, $b = 12.262$ (3) Å, $c = 15.675$ (3) Å, $\alpha = 84.39$ (16)°, $\beta = 83.65$ (16)°, $\gamma = 77.75$ (17)°. $Z = 2$.

Introduction

Recently, we reported the preparation and crystal structure of a novel dimeric copper(II) trichloroacetate adduct of the stable nitroxyl radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo).¹ This adduct, although its stoichiometry was of the well-known $[\text{Cu}(\text{O}_2\text{CR})_2\text{L}]_2$ type, possessed a number of unusual structural features. These included trigonal-bipyramidal copper atoms, short copper–nitroxyl bonds, and a long Cu–Cu distance. In an effort to prepare additional examples of this structure type, and as part of our continuing series of studies of metal complexes of nitroxyl radical ligands,^{2–6} we investigated the reaction of copper(II)

trichloroacetate with the five-membered ring nitroxyl 2,2,4,4-tetramethylpyrrolinyl-1-oxy (proxyl). We now report the prep-



proxyl

aration and structure of a novel adduct obtained from this system. Like the previously reported trichloroacetate adduct, this material is binuclear and contains metal-coordinated nitroxyl groups; however, it proves to be an aqua complex and to have a new type of structure.

Experimental Section

Synthesis. Anhydrous copper(II) trichloroacetate was prepared by the method of Bateman and Conrad.⁷ The ligand proxyl was synthesized

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