Simultaneous First- and Second-Sphere Coordination. Organopalladium Crown Ether Complexes as Metalloreceptors for *o*-Aminopyridine Derivatives

James E. Kickham and Stephen J. Loeb*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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The complexes $[Pd(L)(CH_3CN)][BF_4]$ (L = 2, 14-dithia[15]-*m*-cyclophane (L^0), 5-oxa-2,8-dithia[9]-*m*-cyclophane (L^1), 5,8,11-trioxa-2,14-dithia[15]-*m*-cyclophane (L^3)) were prepared by palladation of the respective thiacyclophane employing $[Pd(CH_3CN)_4][BF_4]_2$. For studies involving L^1, $[Pd(L^1)(CH_3CN)][CF_3SO_3]$ was also prepared in an analogous manner from $[Pd(CH_3CN)_4][CF_3SO_3]$. $[Pd(L^0)(CH_3CN)][BF_4]\cdot CH_3CN$ crystallized in the space group *C*2/*c* with $a = 13.237(4)$ Å, $b = 19.206(2)$ Å, $c = 20.232(2)$ Å, $V = 5168(3)$ Å^3, and $Z = 8$. The structure refined to $R = 5.62\%$ and $R_w = 4.76\%$ for 3112 reflections with $F_o^2 > 3\sigma(F_o^2)$. $[Pd(L^1)(CH_3CN)][CF_3SO_3]$ crystallized in the space group $P2_1/c$ with $a = 8.639(2)$ Å, $b = 17.165(2)$ Å, $c = 13.099(2)$ Å, $\beta = 91.85(2)°$, $V = 1941.3(5)$ Å^3, and $Z = 4$. The structure refined to $R = 4.07\%$ and $R_w = 4.67\%$ for 1441 reflections with $F_o^2 > 3\sigma(F_o^2)$. $[Pd(L^3)(CH_3CN)][BF_4]$ crystallized in the space group $P\bar{1}$ with $a = 10.838(5)$ Å, $b = 11.295(4)$ Å, $c = 10.219(6)$ Å, $\alpha = 98.31(4)°$, $\beta = 108.86(4)°$, $\gamma = 102.78(4)°$, $V = 1122(2)$ Å^3, and $Z = 2$. The structure refined to $R = 4.38\%$ and $R_w = 4.71\%$ for 2375 reflections with $F_o^2 > 3\sigma(F_o^2)$. The complexes with ether oxygen atoms act as metalloreceptors for *o*-aminopyridine derivatives (*o*-aminopyridine (oap), 2-amino-4-picoline (pic), cytosine (cyt)) *via* simultaneous first- and second-sphere coordination: the formation of a first-sphere Pd—N σ bond and peripheral, second-sphere NH···O hydrogen bonds. NMR and X-ray crystallographic evidence for these interactions is presented and compared to that obtained with pyridine (py) as a substrate and $[Pd(L^0)(CH_3CN)][BF_4]$ as a metalloreceptor, for which no second-sphere hydrogen bonding is possible. $[Pd(L^1)(oap)][BF_4]$ crystallized in the space group $P2_1/c$ with $a = 10.056(2)$ Å, $b = 18.889(2)$ Å, $c = 11.294(7)$ Å, $\beta = 112.32(4)°$, $V = 1976(2)$ Å^3, and $Z = 4$. The structure refined to $R = 6.95\%$ and $R_w = 6.14\%$ for 2326 reflections with $F_o^2 > 3\sigma(F_o^2)$. $[Pd(L^3)(py)][BF_4]\cdot CHCl_3$ crystallized in the space group $P\bar{1}$ with $a = 11.982(3)$ Å, $b = 12.858(3)$ Å, $c = 10.048(2)$ Å, $\alpha = 103.59(2)°$, $\beta = 99.63(2)°$, $\gamma = 77.56(2)°$, $V = 1458.2(6)$ Å^3, and $Z = 2$. The structure refined to $R = 5.14\%$ and $R_w = 4.62\%$ for 2079 reflections with $F_o^2 > 3\sigma(F_o^2)$. $[Pd(L^3)(pic)][BF_4]$ crystallized in the space group $P\bar{1}$ with $a = 12.588(4)$ Å, $b = 14.249(6)$ Å, $c = 8.206(2)$ Å, $\alpha = 95.65(3)°$, $\beta = 104.26(2)°$, $\gamma = 66.07(3)°$, $V = 1304(2)$ Å^3, and $Z = 2$. The structure refined to $R = 4.38\%$ and $R_w = 4.72\%$ for 3084 reflections with $F_o^2 > 3\sigma(F_o^2)$. $[Pd(L^3)(cyt)][BF_4]\cdot CH_3CN$ crystallized in the space group $P2_1/c$ with $a = 12.871(4)$ Å, $b = 16.567(3)$ Å, $c = 13.714(5)$ Å, $\beta = 101.53(3)°$, $V = 2867(2)$ Å^3, and $Z = 4$. The structure refined to $R = 3.99\%$ and $R_w = 4.57\%$ for 2469 reflections with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The concept of second-sphere coordination was originally necessary to explain a number of phenomena, such as the presence of solvent (e.g. H_2O) of crystallization in cobalt(III) complexes and the observation that molar optical rotations of chiral complexes depend strongly on the nature of the solvents and counterion.[1] A wide range of other phenomena are accountable only by second-sphere coordination, and the forces responsible include hydrogen bonding, polar and dipolar attractions, dispersion forces, and charge-transfer interactions.[2] Recently, this non-covalent outer-sphere binding was modeled by the interaction of crown ethers with metal-bound ligands such as NH_3 in which the metal complex approximates the behavior of an ammonium cation.[3] For example, in the presence of 18-crown-6, the NH_3 ligand in *trans*-$[PtCl_2(NH_3)(PEt_3)]$, which is σ-bonded to Pt in the first sphere of coordination of the complex, also interacts with 18-crown-6 using a three-point hydrogen-bonding array with alternating ether oxygen atoms.[4] This type of interaction of crown ethers with metal complexes has been observed for a number of complexes containing NH_3,[5] H_2O,[6] and even CH_3CN.[7]

It is also possible for a substrate molecule or ancillary ligand to interact with a metal-containing receptor such that it occupies sites in *both* the first *and* second coordination spheres of a transition metal complex.[3] Only a limited number of complexes have been characterized which show evidence of this phenom-

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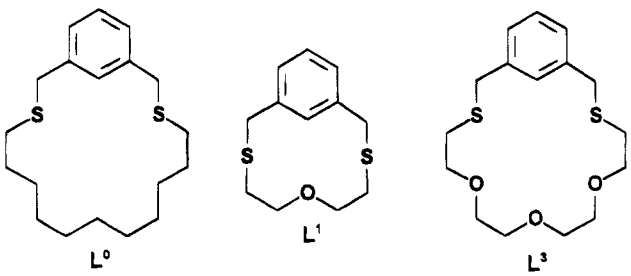
enon known as simultaneous first- and second-sphere coordination. Originally, these complexes were rarely synthesized by design and are usually limited to substrates such as H_2O[8] and NH_3.[9] Only recently was this type of multiple-point binding demonstrated in more sophisticated systems and applied to metal complexes of important substrates such as barbiturates and amino acids.[10] In this paper, we report the synthesis, structural investigation, and binding properties of macrocyclic metal complexes, based on the thiacyclophane ligands L^0, L^1, and L^3 (where 0, 1, and 3 refer to the number of ether oxygen atoms).



These complexes act as metalloreceptors selectively binding substrate molecules such as *o*-aminopyridine derivatives via *simultaneous* first- and second-sphere coordination. This is accomplished by σ donation to a transition metal (Pd) and hydrogen-bonding to peripheral ether oxygen sites on the ligand. Preliminary results describing the application of these receptors to the molecular recognition of nucleobases[11] and the multiple-point binding of the hydrazinium ion[12] by $[Pd(L^3)]^+$ were the subjects of recent communications.

Experimental Section

All starting materials, pyridine (py), 2-amino-4-picoline (pic), *o*-aminopyridine (oap), cytosine (cyt), deuterated solvents, and anhydrous *N,N*-dimethylformamide (DMF), were purchased from Aldrich Chemicals and used without further purification, except acetonitrile, which was distilled from CaH_2 under N_2(g). All reactions were performed under an atmosphere of N_2(g) using standard Schlenk or drybox techniques, and all solvents and liquid starting materials were degassed prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC300 spectrometer locked to the deuterated solvent at 300.1 and 75.5 MHz, respectively, and infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia.

Preparation of 2,14-Dithia[15]-*m*-cyclophane (L^0). To a suspension of Cs_2CO_3 (7.27 g, 22.3 mmol) in DMF (500 mL) at 60 °C was added a solution of 1,11-dibromoundecane (3.50 g, 11.1 mmol) and *m*-xylene-α,α′-dithiol (1.900 g, 11.2 mmol) in DMF (120 mL) over 24 h. Upon completion of the slow addition, the suspension was cooled for 2 h and the DMF removed *in vacuo*, leaving a brown oil and cesium salts. The oil was dissolved in CH_2Cl_2 (200 mL), the solution filtered, and the filtrate washed with 0.1 M NaOH (2 × 50 mL) and distilled water (50 mL). The solution was dried over anhydrous $MgSO_4$ for 3 h and filtered, and the CH_2Cl_2 filtrate was reduced to 25 mL. This solution was then added to boiling anhydrous ethanol (250 mL), the mixture was cooled to −10 °C and filtered, and the resulting solid was dried *in vacuo*. Crude yield: 2.679 g (75%). Further purification was accomplished by concentrating a petroleum ether solution of L^0 and stirring it over silica gel (10 g, 70−230 mesh, 60 Å) for 0.5 h, filtering, and then evaporating the solution to dryness. Yield: 2.179 g (61%). Mp: 27 °C. NMR (δ, ppm): ^1H ($CDCl_3$, 295 K) 7.25−7.19 (m, 4H, aromatic), 3.68 (s, 4H, benzylic), 2.39 (t, 4H, SCH_2), 1.45 (q, 4H, β-CH_2), 1.32 (q, 4H, γ-CH_2), 1.25 (s, br, 10H, CH_2); $^{13}C\{^1H\}$ ($CDCl_3$, 295 K) 138.77, 129.23, 128.78, 127.38 (aromatic), 36.16 (benzylic), 30.98 (SCH_2), 28.50, 27.52, 27.12, 26.84 (CH_2). Anal. Calcd for $C_{19}H_{30}S_2$: C, 70.37; H, 9.39. Found: C, 71.68; H, 9.39.

Preparation of 5-Oxa-2,8-dithia[9]-*m*-cyclophane (L^1). To a suspension of Cs_2CO_3 (4.756 g, 14.59 mmol) in DMF (350 mL) at 56 °C was added a solution of 3-oxapentane-1,5-dithiol (0.965 g, 6.98 mmol) and α,α′-dibromo-*m*-xylene (1.839 g, 6.97 mmol) in DMF (140 mL) over 36 h. The solution was stirred for an additional 8 h at 56 °C, after which the DMF was removed *in vacuo*, leaving a brown oil and cesium salts. The residue was dissolved in CH_2Cl_2 (200 mL), the solution filtered, and the filtrate washed with 0.1 M NaOH (2 × 50 mL) and distilled water (50 mL). The solution was stirred over anhydrous $MgSO_4$/charcoal for 12 h and filtered twice, the solvent was evaporated, and the white solid was dried *in vacuo*. Yield: 1.114 g (66%). Mp: 46 °C. NMR (δ, ppm): ^1H ($CDCl_3$, 295 K) 7.61 (s, 1H, aromatic), 7.31−7.17 (m, 3H, aromatic), 3.76 (s, 4H, benzylic), 2.98 (t, 4H, CH_2O), 2.55 (t, 4H, SCH_2); $^{13}C\{^1H\}$ ($CDCl_3$, 295 K) 138.61, 130.26, 129.20, 127.87 (aromatic), 67.63 (CH_2O), 37.04 (benzylic), 29.82 (SCH_2). Anal. Calcd for $C_{12}H_{16}OS_2$: C, 59.95; H, 6.72. Found: C, 59.84; H, 6.72.

Preparation of 5,8,11-Trioxa-2,14-dithia[15]-*m*-cyclophane (L^3). To a suspension of Cs_2CO_3 (3.790 g, 11.6 mmol) in DMF (250 mL), at 62 °C, was added a solution of *m*-xylene-α,α′-dithiol (0.960 g, 5.64 mmol) and tetraethylene glycol di-*p*-tosylate (2.833 g, 5.64 mmol) in DMF (125 mL) over 48 h. After the slow addition was complete, the DMF was removed *in vacuo*, leaving a brown oil and cesium salts. The residue was dissolved in CH_2Cl_2 (200 mL), the solution filtered, and the filtrate washed with 0.1 M NaOH (2 × 50 mL) and distilled water (50 mL) and then dried over anhydrous $MgSO_4$/charcoal for 3 h. The solution was then filtered and the CH_2Cl_2 evaporated to dryness *in vacuo*. Column chromatography using 50/50 petroleum ether/diethyl ether as eluent (R_f = 0.30) and 40 g of silica gel (70−230 mesh, 60 Å) gave a white solid upon evaporation of the solvent. Yield: 1.110 g (60%). Mp: 53 °C. NMR (δ, ppm): ^1H ($CDCl_3$, 295 K) 7.33 (s, 1H, aromatic), 7.29−7.21 (m, 3H, aromatic), 3.81 (s, 4H, benzylic), 3.67−3.58 (m, 12H, CH_2O), 2.51 (t, 4H, SCH_2); $^{13}C\{^1H\}$ ($CDCl_3$, 295 K) 138.41, 130.82, 129.23, 127.51 (aromatic), 72.13, 70.92, 70.37 (CH_2O), 36.22 (benzylic), 29.59 (SCH_2). Anal. Calcd for $C_{16}H_{24}O_3S_2$: C, 58.49; H, 7.38. Found: C, 58.46; H, 7.34.

Preparation of Metalloreceptor Complexes. In a typical palladation reaction, 1-equiv samples each of $[Pd(CH_3CN)_4][BF_4]_2$ and L^0, L^1, or L^3 were added to a Schlenk flask (100 mL) and dissolved in *ca.* 40 mL of dry CH_3CN with stirring. Within 5−10 min, the solution changed color from orange to pale yellow. The solution was then refluxed for 2−12 h. Upon cooling, the solution was concentrated to 3−5 mL and the complex crystallized by vapor diffusion of diethyl ether into the CH_3CN solution of the complex.

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Preparation of [Pd(L^0)(CH_3CN)][BF_4]. The reactants were [Pd(CH_3CN)$_4$][BF_4]$_2$ (0.162 g, 0.366 mmol) and L^0 (0.117 g, 0.363 mmol). Yield of pale yellow crystals: 0.180 g (89%). NMR (δ, ppm): ^{1}H ($CDCl_3$, 295 K) 7.04−6.93 (m, 3H, aromatic), 4.35 (d, 2H, benzylic, J = 16.0 Hz), 4.06 (d, 2H, benzylic), 3.05 (m, 4H, SCH_2), 2.38 (s, br, 3H, CH_3CN), 1.96 (m, 4H, β-CH_2), 1.62−1.18 (m, 14H, CH_2). Anal. Calcd for $C_{21}H_{32}BF_4NPdS_2$: C, 45.37; H, 5.81. Found: C, 45.01; H, 5.75.

Preparation of [Pd(L^1)(CH_3CN)][BF_4]. The reactants were [Pd(CH_3CN)$_4$][BF_4]$_2$ (0.185 g, 0.416 mmol) and L^1 (0.103 g, 0.429 mmol). Yield of deep orange crystals: 0.117 g (60%). NMR (δ, ppm): ^{1}H (CD_3CN, 295 K) 7.01−6.92 (m, 3H, aromatic), 4.49 (d, 2H, benzylic, J = 17.0 Hz), 4.11 (d, 2H, benzylic), 3.95 (dt, 2H, CH_2O), 3.54−3.40 (m, 4H, SCH_2CH_2O), 2.89 (td, 2H, SCH_2); ^{13}C{^{1}H} (CD_3CN, 295 K) 157.04 (Pd−C, aromatic), 154.60, 125.72, 122.88 (aromatic), 67.39 (CH_2O), 45.06 (benzylic), 24.96 (SCH_2).

Preparation of [Pd(L^1)(CH_3CN)][CF_3SO_3]. $PdCl_2$ (0.091 g, 0.513 mmol) and [$AgCF_3SO_3$] (0.127 g, 1.05 mmol) were dissolved in dry CH_3CN (30 mL), and the solution was protected from light. The mixture was refluxed for 1 h, and the solution was then filtered from the AgCl precipitate onto L^1 (0.127 g, 0.528 mmol). The resulting solution was then refluxed for 2 h. A flocculent white precipitate was filtered from a yellow solution and the solvent reduced to 5 mL. The product was crystallized by vapor diffusion of diethyl ether into a CH_3CN solution of the complex. Yield of deep orange crystals: 0.168 g (61%). ^{1}H NMR and ^{13}C{^{1}H} NMR (CD_3CN, 295 K) were identical to those found for [Pd(L^1)(CH_3CN)][BF_4]. Anal. Calcd for $C_{15}H_{18}F_3NO_4PdS_3$: C, 33.62; H, 3.39. Found: C, 33.84; H, 3.49.

Preparation of [Pd(L^3)(CH_3CN)][BF_4]. The reactants were [Pd(CH_3CN)$_4$][BF_4]$_2$ (0.272 g, 0.612 mmol) and L^3 (0.201 g, 0.612 mmol). Yield of yellow crystals: 0.295 g (86%). NMR (δ, ppm): ^{1}H ($CDCl_3$, 295 K) 7.00−6.91 (m, 3H, aromatic), 4.37 (s, 4H, benzylic), 4.09 (s, br, 4H, CH_2O), 3.73 (s, 4H, CH_2O), 3.61 (s, 4H, CH_2O), 3.39 (s, br, 4H, SCH_2), 2.20 (s, 3H, CH_3CN). Anal. Calcd for $C_{18}H_{26}BF_4NO_3PdS_2$: C, 38.48; H, 4.67. Found: C, 38.25; H, 4.66.

Preparation of Metalloreceptor−Substrate Complexes. In a typical reaction, 5 mL of an acetonitrile solution of [Pd(L^0)(CH_3CN)][BF_4], [Pd(L^1)(CH_3CN)][CF_3SO_3], [Pd(L^1)(CH_3CN)][BF_4], or [Pd(L^3)(CH_3CN)][BF_4] was combined with the appropriate amount of substrate solution (pyridine (py), *o*-aminopyridine (oap), or 2-amino-4-picoline (pic) in CH_3CN) and shaken for 5 min. The solvent was removed *in vacuo* and the pasty solid triturated with 5 mL of diethyl ether for 1 h to remove excess substrate and solvent. The solid was then dried *in vacuo* for 1 h, providing essentially quantitative yields of receptor−substrate complex.

Preparation of [Pd(L^0)(py)][BF_4]. The reactants were [Pd(L^0)(CH_3CN)][BF_4] (5.0 mL, 7.4 × 10^{-3} M, 37 μmol) and pyridine (0.25 mL, 0.16 M, 40 μmol). Yield of white solid: 0.021 g (95%). NMR (δ, ppm): ^{1}H ($CDCl_3$, 295 K) 8.56 (d, 2H, py), 8.02 (t, 1H, py), 7.70 (t, 2H, py), 7.09−6.91 (m, 3H, aromatic), 4.52 (d, 2H, benzylic, J = 16.4 Hz), 4.17 (d, 2H, benzylic), 2.95−2.79 (m, 4H, SCH_2), 1.95 (m, 4H, β-CH_2), 1.49−1.34 (m, 14H, CH_2). Anal. Calcd for $C_{24}H_{34}BF_4NPdS_2$: C, 48.53; H, 5.78. Found: C, 48.60; H, 5.71.

Preparation of [Pd(L^0)(oap)][BF_4]. The reactants were [Pd(L^0)(CH_3CN)][BF_4] (5.0 mL, 7.4 × 10^{-3} M, 37 μmol) and *o*-aminopyridine (0.23 mL, 0.16 M, 37 μmol). Yield of white powder: 0.022 g (100%). NMR (δ, ppm): ^{1}H ($CDCl_3$, 295 K) 7.67 (d, 1H, oap), 7.51 (t, 1H, oap), 7.06−6.96 (m, 3H + 1H, aromatic + oap), 6.66 (t, 1H, oap), 5.92 (s, 2H, NH_2), 4.53 (d, 2H, benzylic, J = 16.2 Hz), 4.17 (d, 2H, benzylic), 2.80 (dm, 4H, SCH_2), 2.01−1.84 (m, 4H, β-CH_2), 1.50 (s, br, 6H, CH_2), 1.35 (s, br, 8H, CH_2). Anal. Calcd for $C_{34}H_{35}BF_4N_2PdS_2$: C, 47.33; H, 5.81. Found: C, 47.05; H, 5.77.

Preparation of [Pd(L^1)(py)][CF_3SO_3]. The reactants were [Pd(L^1)(CH_3CN)][CF_3SO_3] (5.0 mL, 7.5 × 10^{-3} M, 37 μmol) and pyridine (0.25 mL, 0.16 M, 40 μmol). Yield of orange-yellow powder: 0.019 g (89%). NMR (δ, ppm): ^{1}H (CD_3CN, 295 K) 8.66 (d, 2H, py), 7.99 (t, 1H, py), 7.58 (t, 2H, py), 7.02−6.95 (m, 3H, aromatic), 4.62 (d, 2H, benzylic, J = 17.5 Hz), 4.54 (d, 2H, benzylic), 4.10 (dt, 2H, SCH_2), 3.43 (dt, 4H, SCH_2), 3.01 (dt, 2H, SCH_2). Anal. Calcd for $C_{18}H_{20}F_3NO_4PdS_3$: C, 37.66; H, 3.52. Found: C, 37.34; H, 3.57. [Pd(L^1)(py)][BF_4] was prepared in exactly the same manner from [Pd(L^1)(CH_3CN)][BF_4] and was identical to the triflate salt by spectroscopic analysis.

Preparation of [Pd(L^1)(oap)][CF_3SO_3]. The reactants were [Pd(L^1)(CH_3CN)][CF_3SO_3] (5.0 mL, 7.5 × 10^{-3} M, 37 μmol) and *o*-aminopyridine (0.24 mL, 0.16 M, 37 μmol). Yield of orange powder: 0.023 g (100%). NMR (δ, ppm): ^{1}H (CD_3CN, 295 K) 8.16 (dd, 1H, oap), 7.56 (dt, 1H, oap), 6.98 (m, 3H, aromatic), 6.73 (t, 1H, oap), 6.68 (d, 1H, oap), 6.03 (s, 2H, NH_2), 4.61 (d, 2H, benzylic, J = 17.5 Hz), 4.20 (d, 2H, benzylic), 4.05 (dt, 2H, SCH_2), 3.44 (dt, 4H, SCH_2), 2.99 (dt, 2H, SCH_2). Anal. Calcd for $C_{18}H_{21}F_3N_2O_4PdS_3$: C, 36.70; H, 3.60. Found: C, 36.76; H, 3.65. [Pd(L^1)(oap)][BF_4] was prepared in exactly the same manner from [Pd(L^1)(CH_3CN)][BF_4] and was identical to the triflate salt by spectroscopic analysis.

Preparation of [Pd(L^3)(py)][BF_4]. The reactants were [Pd(L^3)(CH_3CN)][BF_4] (5.0 mL, 7.1 × 10^{-3} M, 36 μmol) and pyridine (0.25 mL, 0.16 M, 40 μmol). Yield of pale yellow powder: 0.021 g (100%). NMR (δ, ppm): ^{1}H ($CDCl_3$, 295 K) 8.77 (d, 2H, py), 7.93 (t, 1H, py), 7.60 (t, 2H, py), 6.99 (s, br, 3H, aromatic), 4.55−4.43 (q, br, 4H, benzylic), 4.00 (br, s, 4H, SCH_2CH_2O), 3.60 (s, br, 4H, CH_2O), 3.60 (s, br, 4H, CH_2O), 3.05 (dm, 4H, SCH_2). Anal. Calcd for $C_{21}H_{28}BF_4NO_3PdS_2$: C, 42.05; H, 4.71. Found: C, 42.15; H, 4.66.

Preparation of [Pd(L^3)(oap)][BF_4]. The reactants were [Pd(L^3)(CH_3CN)][BF_4] (5.0 mL, 7.1 × 10^{-3} M, 36 μmol) and *o*-aminopyridine (0.23 mL, 0.16 M, 36 μmol). Yield of a white powder: 0.022 g (100%). NMR (δ, ppm): ^{1}H ($CDCl_3$, 295 K) 7.88 (d, 1H, oap), 7.45 (t, 1H, oap), 7.01−6.99 (m, 3H, aromatic), 6.94 (d, 1H, oap), 6.56 (t, 1H, oap), 6.40 (s, br, 2H, NH_2), 4.67 (d, 2H, benzylic, J = 15.3 Hz), 4.41 (d, 2H, benzylic), 3.88−3.37 (m, 12H, CH_2O), 3.20−3.02 (m, 4H, SCH_2). Anal. Calcd for $C_{21}H_{29}BF_4N_2O_3PdS_2$: C, 41.02; H, 4.76. Found: C, 40.76; H, 4.77.

Preparation of [Pd(L^3)(pic)][BF_4]. A 0.5-mL portion of a 2.25 × 10^{-2} M solution of [Pd(L^3)(CH_3CN)][BF_4] in $CDCl_3$ and 14.9 μL of a 0.753 M solution of 2-amino-4-picoline in $CDCl_3$ were mixed and the NMR recorded. The product was crystallized by vapor diffusion of diethyl ether into this $CDCl_3$ solution of the complex. Yield of yellow crystals: 0.005 g (71%). NMR (δ, ppm): ^{1}H ($CDCl_3$, 295 K) 7.75 (d, 1H, pic), 6.98 (m, 3H, aromatic), 6.70 (s, 1H, pic), 6.40 (d, 1H, pic), 6.20 (s, br, 2H, NH_2), 4.65 (d, 2H, benzylic, J = 15.4 Hz), 4.47 (d, 2H, benzylic), 3.87−3.37 (m, 12H, CH_2O), 3.15−3.01 (m, 4H, SCH_2), 2.22 (s, 3H, CH_3). Anal. Calcd for $C_{22}H_{31}BF_4N_2O_3PdS_2$: C, 42.01; H, 4.98. Found: C, 41.94; H, 4.95.

Preparation of [Pd(L^3)(cyt)][BF_4]. A 0.75-mL portion of a 9.6 × 10^{-3} M $CDCl_3$ solution of [Pd(L^3)(CH_3CN)][BF_4] was added to *ca.* 10-fold excess of cytosine, and the mixture was sonicated for 15 min. The $CDCl_3$ solution was filtered, and the filtrate was washed with CH_3CN (1 mL). Diethyl ether (3 mL) was added and the solution cooled to −10 °C to yield colorless crystals. NMR (δ, ppm): ^{1}H (CD_3CN, 295 K) 9.20 (s, br, 1H, NH, cyt), 7.39 (d, 1H, aromatic, cyt), 7.29 (s, br, 1H, aromatic, cyt), 7.00−6.95 (m, 3H, aromatic), 6.49 (s, br, 1H, NH_2), 5.81 (d, 1H, NH_2, cyt), 4.57 (d, 2H, benzylic, J = 15.9 Hz), 4.45 (d, 2H, benzylic), 4.21−3.85 (m, 4H, CH_2O), 3.58−3.33 (m, 8H, CH_2O), 3.20−2.99 (m, 4H, SCH_2). Anal. Calcd for $C_{20}H_{28}BF_4N_3O_4PdS_2$: C, 38.02; H, 4.48. Found: C, 37.99; H, 4.44.

X-ray Diffraction Data Collection, Solution, and Refinement. Pale yellow, yellow, or orange-yellow crystals were grown by diffusion of diethyl ether into an acetonitrile solution of the complex, except for [Pd(L^1)(CH_3CN)][CF_3SO_3] and [Pd(L^3)(py)][BF_4], for which acetone and chloroform solutions, respectively, were employed. Diffraction experiments were performed on a four-circle Rigaku AFC6S diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell constants and orientation matrices for data collection were obtained from 25 centered reflections (15° < 2θ < 35°). Machine parameters, crystal data, and data collection parameters are summarized in Table 1 and in the supplementary material. The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collections. The intensity data were collected using the ω−2θ scan technique, in four shells (2θ < 30, 40, 45, 50°). Absorption coefficients were calculated and corrections applied to the data. The data were processed using the TEXSAN software[13] package running on a VAX 3520 or SGI computer. For each solution, the position of the palladium atom

(13) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

Table 1. Summary of X-ray Crystallographic Data Collection, Solution, and Refinement Details

	$[Pd(L^0)(CH_3CN)][BF_4]\cdot CH_3CN$	$[Pd(L^1)(CH_3CN)][CF_3SO_3]$	$[Pd(L^3)(CH_3CN)][BF_4]$	$[Pd(L^1)(oap)][BF_4]$	$[Pd(L^3)(py)][BF_4]\cdot CHCl_3$	$Pd(L^3)(pic)][BF_4]$	$[Pd(L^3)(cyt)][BF_4]\cdot CH_3CN$
formula	$C_{23}H_{35}N_2BF_4S_2Pd$	$C_{15}H_{18}O_4NF_3S_3Pd$	$C_{18}H_{26}O_3NBF_4S_2Pd$	$C_{17}H_{21}ON_2BF_4S_2Pd$	$C_{22}H_{29}O_3NBF_4S_2PdCl_3$	$C_{22}H_{31}O_3N_2BF_4S_2Pd$	$C_{20}H_{28}O_4N_3BF_4S_2Pd$
fw	596.87	535.89	561.73	526.69	719.16	628.82	631.79
a, Å	13.273(4)	8.639(2)	10.838(5)	10.056(2)	11.982(3)	12.588(4)	12.871(4)
b, Å	19.206(2)	17.165(2)	11.295(4)	18.889(2)	12.858(3)	14.249(6)	16.567(3)
c, Å	20.323(2)	13.099(2)	10.219(6)	11.294(7)	10.048(2)	8.206(2)	13.714(5)
α, deg			98.31(4)		103.59(2)	95.65(3)	
β, deg	93.98(2)	91.85(2)	108.86(4)	112.32(4)	99.63(2)	104.26(2)	101.53(3)
γ, deg			102.78(4)		77.56(2)	66.07(3)	
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
V, Å^3	5168(3)	1941.3(5)	1122(2)	1976(2)	1458.2(6)	1304(2)	2867(2)
ϱ, g/cm^3	1.48	1.83	1.66	1.77	1.64	1.60	1.56
Z	8	4	2	4	2	2	4
μ, cm^{-1}	9.02	13.28	10.45	11.75	11.05	9.09	8.37
λ, Å	0.701 69	0.701 69	0.701 69	0.701 69	0.701 69	0.701 69	0.701 69
T, °C	23	23	23	23	23	23	23
goodness of fit	2.49	1.36	1.25	2.54	1.87	1.24	1.49
$R(F_o)$,[a] %	5.62	4.07	4.38	6.95	5.14	4.38	3.99
$R_w(F_o)$,[a] %	4.78	4.67	4.71	6.14	4.62	4.72	4.57

[a] $R = \sum||F_o| - |F_c||/\sum|F_o||$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$, and $w = 1/\sigma^2(F)$.

Table 2. Selected Positional Parameters and B(eq)[a] Values for $[Pd(L^0)(CH_3CN)][BF_4]\cdot CH_3CN$

atom	x	y	z	B(eq), Å^2
Pd	0.77425(4)	0.16126(3)	0.50639(3)	3.32(3)
S(1)	0.8932(2)	0.1938(1)	0.5882(1)	4.4(1)
S(2)	0.6780(2)	0.1259(1)	0.4122(1)	4.4(1)
N(1)	0.6649(5)	0.1392(3)	0.5751(3)	4.2(3)
C(1)	0.8810(6)	0.1816(3)	0.4452(4)	3.3(4)
C(7)	1.0050(6)	0.2035(5)	0.5427(5)	6.3(6)
C(8)	0.9213(6)	0.1166(5)	0.6376(4)	5.3(5)
C(9)	0.9308(7)	0.0507(5)	0.5993(5)	6.1(5)
C(10)	0.9549(8)	−0.0125(6)	0.6431(6)	8.2(7)
C(11)	0.880(1)	−0.0296(6)	0.6926(6)	8.7(8)
C(12)	0.770(1)	−0.0368(6)	0.6668(6)	8.4(8)
C(13)	0.746(1)	−0.0912(6)	0.6181(6)	8.3(8)
C(14)	0.6398(8)	−0.0905(6)	0.5867(6)	7.4(7)
C(15)	0.6307(9)	−0.1190(6)	0.5181(6)	8.5(7)
C(16)	0.685(1)	−0.0799(6)	0.4669(6)	8.6(8)
C(17)	0.6553(9)	−0.0063(6)	0.4606(5)	7.4(7)
C(18)	0.7091(8)	0.0330(5)	0.4065(5)	6.8(6)
C(19)	0.7544(6)	0.1621(5)	0.3500(4)	5.0(4)
C(20)	0.6152(6)	0.1270(4)	0.6162(4)	4.0(4)
C(21)	0.5525(6)	0.1101(5)	0.6701(4)	5.6(5)

[a] $B(\text{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\cdot\vec{a}_i\vec{a}_j$.

was determined by conventional Patterson methods and the remaining non-hydrogen atoms were located from a series of difference fourier map calculations. Refinements were carried out by using full-matrix least-squares techniques on F and minimizing the function $\sum w(F_o - F_c)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[14] and anomalous dispersion terms[15,16] were taken from the usual sources. In the final cycles of refinement, all non H atoms were assigned anisotropic thermal parameters, except for the carbon atoms in $[Pd(L^1)(CH_3CN)][CF_3SO_3]$, $[Pd(L^3)(py)][BF_4]$, and $[Pd(L^3)(cyt)][BF_4]$. With one minor exception, fixed H atom contributions were included with C—H distances of 0.95 Å and thermal parameters 1.2 times the isotopic thermal parameter of the bonded C atoms. These H atoms were not refined, but all values were updated as refinement continued. The H atoms of the NH_2 group on cytosine in $[Pd(L^3)(cyt)][BF_4]\cdot CH_3CN$ were located and refined. Selected atomic positional parameters and selected bonding parameters are given in Tables 2−15. Full listings of atomic positional parameters,

(14) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.
(15) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1974**, *17*, 781.
(16) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974, Vol. IV, Table 2.3.1.

Table 3. Selected Bonding Parameters for $[Pd(L^0)(CH_3CN)][BF_4]\cdot CH_3CN$

	Distances (Å)		
Pd—S(1)	2.299(2)	Pd—S(2)	2.327(2)
Pd—N(1)	2.125(6)	Pd—C(1)	1.987(7)
S(1)—C(7)	1.811(9)	S(1)—C(8)	1.814(9)
S(2)—C(18)	1.84(1)	S(2)—C(19)	1.814(8)
N(1)—C(20)	1.124(8)	N(2)—C(22)	1.09(2)
C(2)—C(19)	1.49(1)	C(6)—C(7)	1.49(1)
C(8)—C(9)	1.50(1)	C(9)—C(10)	1.53(1)
C(10)—C(11)	1.50(1)	C(11)—C(12)	1.52(1)
C(12)—C(13)	1.46(1)	C(13)—C(14)	1.50(1)
C(14)—C(15)	1.49(1)	C(15)—C(16)	1.51(1)
C(16)—C(17)	1.47(1)	C(17)—C(18)	1.55(1)
C(20)—C(21)	1.46(1)	C(22)—C(23)	1.43(2)
	Angles (deg)		
S(1)—Pd—S(2)	169.86(8)	S(1)—Pd—N(1)	92.6(2)
S(1)—Pd—C(1)	85.1(2)	S(2)—Pd—N(1)	97.0(2)
S(2)—Pd—C(1)	85.3(2)	N(1)—Pd—C(1)	177.6(3)
C(7)—S(1)—C(8)	102.9(4)	C(18)—S(2)—C(19)	100.9(4)

Table 4. Selected Positional Parameters and B(eq)[a] Values for $[Pd(L^1)(CH_3CN)][CF_3SO_3]$

atom	x	y	z	B(eq), Å^2
Pd	0.4927(1)	0.03704(6)	0.11411(8)	2.47(4)
S(1)	0.7545(4)	0.0204(2)	0.1511(3)	3.5(2)
S(2)	0.2272(4)	0.0396(3)	0.1336(3)	3.7(2)
O(1)	0.492(1)	0.0658(5)	0.3178(6)	3.4(5)
N(1)	0.507(1)	0.1597(6)	0.0915(8)	3.3(6)
C(1)	0.476(2)	−0.0761(7)	0.1406(8)	2.3(6)
C(7)	0.765(2)	−0.0850(9)	0.153(1)	3.8(3)
C(8)	0.762(1)	0.046(1)	0.288(1)	4.1(3)
C(9)	0.624(1)	0.0233(8)	0.348(1)	3.6(3)
C(10)	0.343(1)	0.0315(9)	0.339(1)	3.7(3)
C(11)	0.221(2)	0.0658(9)	0.270(1)	4.3(3)
C(12)	0.183(2)	−0.0636(8)	0.133(1)	4.0(3)
C(13)	0.513(2)	0.2251(8)	0.081(1)	3.3(3)
C(14)	0.520(2)	0.3091(8)	0.067(1)	3.9(3)

[a] $B(\text{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\cdot\vec{a}_i\vec{a}_j$.

nonessential bonding parameters, thermal parameters, and hydrogen atom parameters are deposited as supplementary material.

Results

Synthesis of L^0, L^1, L^3 and Metalloreceptors $[Pd(L)(CH_3CN)][BF_4]$. The thiacyclophanes employed in this study were prepared from the reaction of *m*-xylene-α,α'-dithiol with the appropriate dichloride or ditosylate or from the reaction of α,α'-

Table 5. Selected Bonding Parameters for $[Pd(L^1)(CH_3CN)][CF_3SO_3]$

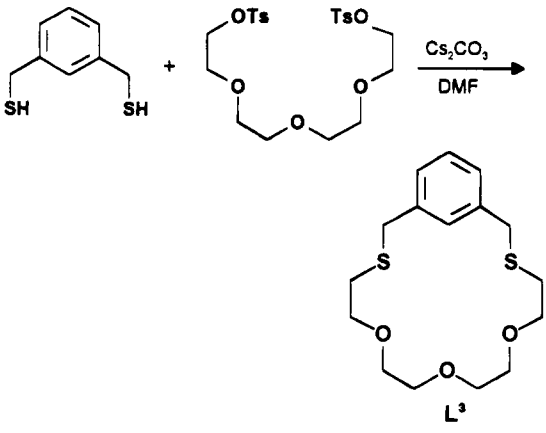
	Distances (Å)		
Pd—(1)	2.316(4)	Pd—S(2)	2.316(4)
Pd—N(1)	2.13(1)	Pd—C(1)	1.98(1)
S(1)—C(7)	1.81(1)	S(1)—C(8)	1.85(1)
S(2)—C(11)	1.84(1)	S(2)—C(12)	1.81(1)
O(1)—C(9)	1.40(1)	O(1)—C(10)	1.45(1)
N(1)—C(13)	1.13(1)	C(2)—C(12)	1.50(2)
C(6)—C(7)	1.50(2)	C(8)—C(9)	1.50(2)
C(10)—C(11)	1.49(2)	C(13)—C(14)	1.46(2)
	Angles (deg)		
S(1)—Pd—S(2)	160.6(1)	S(1)—Pd—N(1)	95.3(3)
S(1)—Pd—C(1)	85.4(4)	S(2)—Pd—N(1)	93.3(3)
S(2)—Pd—C(1)	85.4(4)	N(1)—Pd—C(1)	177.6(5)
C(7)—S(1)—C(8)	103.0(7)	C(11)—S(2)—C(12)	103.3(7)
C(9)—O(1)—C(10)	117(1)		

Table 6. Selected Positional Parameters and $B(eq)^a$ Values for $[Pd(L^3)(CH_3CN)][BF_4]$

atom	*x*	*y*	*z*	$B(eq)$, Å^2
Pd	0.54145(6)	0.87465(6)	0.42239(7)	3.85(2)
S(1)	0.5122(2)	0.9565(2)	0.2240(2)	4.54(7)
S(2)	0.6004(2)	0.8180(2)	0.6364(2)	4.36(8)
O(1)	0.6113(6)	0.7006(5)	−0.0045(6)	5.9(2)
O(2)	0.7389(6)	0.5627(5)	0.2162(6)	5.4(2)
O(3)	0.7065(6)	0.5201(5)	0.4976(6)	5.1(2)
N(1)	0.3467(6)	0.7420(6)	0.3344(7)	4.9(3)
C(1)	0.7272(7)	0.9927(6)	0.5005(8)	3.6(2)
C(7)	0.6747(8)	1.0733(7)	0.2795(9)	5.0(3)
C(8)	0.5147(9)	0.8420(8)	0.081(1)	5.8(3)
C(9)	0.6207(9)	0.7777(8)	0.123(1)	5.8(4)
C(10)	0.722(1)	0.648(1)	0.014(1)	6.2(4)
C(11)	0.708(1)	0.533(1)	0.068(1)	5.9(4)
C(12)	0.734(1)	0.4534(8)	0.271(1)	6.1(4)
C(13)	0.7938(9)	0.4886(8)	0.430(1)	5.5(4)
C(14)	0.6974(8)	0.6444(7)	0.5037(8)	4.4(3)
C(15)	0.6255(8)	0.6655(7)	0.6033(8)	4.5(3)
C(16)	0.7720(8)	0.9212(7)	0.7304(8)	4.8(3)
C(17)	0.2432(8)	0.6762(7)	0.2855(8)	4.5(3)
C(18)	0.1055(8)	0.5886(8)	0.224(1)	6.2(4)

$^a B(eq) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

dibromo-*m*-xylene with the appropriate dithiol employing Kellogg's Cs^+-mediated method in DMF solution[17] as outlined in eq 1 for L^3. This synthetic route produced these compounds



(1)

L^3

as colorless, crystalline materials in yields of 60−66%. The ^1H NMR spectra of L^1 and L^3 contain four sets of well-separated resonances atrributable to OCH_2, SCH_2, benzylic, and aromatic protons, with the aromatic proton at the 2-position easily assigned to a singlet slightly downfield of the other three aromatic protons. For L^0, the ^1H NMR spectrum has the same basic features except there are, of course, no OCH_2 resonances and the aromatic protons appear as a single multiplet. The $^{13}C\{^1H\}$ NMR spectra for these ligands show well-resolved peaks for all carbon atoms, and full spectral interpretation was relatively straightforward. The X-ray structures of L^1 and L^3 were determined and will be reported elsewhere.

The palladium center and an ancillary acetonitrile group were incorporated into the macrocycles *via* direct metalation of the aromatic ring employing $[Pd(CH_3CN)_4][BF_4]_2$ in acetonitrile solution.[18] The resulting complexes $[Pd(L)(CH_3CN)][BF_4]$ (L = L^0, L^1, L^3) are yellow, air-stable crystalline solids that are

Table 7. Selected Bonding Parameters for $[Pd(L^3)(CH_3CN)][BF_4]$

	Distances (Å)		
Pd—S(1)	2.307(3)	Pd—S(2)	2.299(3)
Pd—N(1)	2.120(6)	Pd—C(1)	1.984(6)
S(1)—C(7)	1.810(8)	S(1)—C(8)	1.82(1)
S(2)—C(15)	1.804(9)	S(2)—C(16)	1.818(7)
O(1)—C(9)	1.42(1)	O(1)—C(10)	1.43(1)
O(2)—C(11)	1.41(1)	O(2)—C(12)	1.42(1)
O(3)—C(13)	1.42(1)	O(3)—C(14)	1.42(1)
N(1)—C(17)	1.106(9)	C(2)—C(16)	1.50(1)
C(6)—C(7)	1.50(1)	C(8)—C(9)	1.47(1)
C(10)—C(11)	1.47(2)	C(12)—C(13)	1.49(1)
C(14)—C(15)	1.49(1)	C(17)—C(18)	1.47(1)
	Angles (deg)		
S(1)—Pd—S(2)	171.27(7)	S(1)—Pd—N(1)	94.2(2)
S(1)—Pd—C(1)	85.7(2)	S(2)—Pd—N(1)	94.4(2)
N(1)—Pd—C(1)	177.2(3)	C(7)—S(1)—C(8)	103.7(4)
C(15)—S(2)—C(16)	103.6(4)	C(9)—O(1)—C(10)	113.2(6)
C(11)—O(2)—C(12)	111.2(7)	C(13)—O(3)—C(14)	114.5(7)

Table 8. Selected Positional Parameters and $B(eq)^a$ Values for $[Pd(L^1)(oap)][BF_4]$

atom	*x*	*y*	*z*	$B(eq)$, Å^2
Pd	0.2441(1)	0.09334(5)	0.2570(1)	2.00(3)
S(1)	0.3920(3)	0.0933(2)	0.4700(3)	3.2(1)
S(2)	0.0392(3)	0.1003(2)	0.0726(3)	2.7(1)
O(1)	0.047(1)	0.0502(5)	0.3566(7)	3.0(4)
N(1)	0.311(1)	−0.0077(6)	0.213(1)	2.7(4)
N(2)	0.177(1)	−0.0765(6)	0.291(1)	4.5(6)
C(1)	0.199(1)	0.1933(6)	0.287(1)	2.1(5)
C(7)	0.393(1)	0.1872(8)	0.508(1)	3.0(5)
C(8)	0.268(2)	0.0573(8)	0.540(1)	4.0(6)
C(9)	0.111(1)	0.0798(8)	0.480(1)	3.5(6)
C(10)	−0.077(1)	0.0845(8)	0.266(1)	3.4(6)
C(11)	−0.093(1)	0.0650(7)	0.132(1)	3.3(5)
C(12)	0.005(2)	0.1945(7)	0.067(1)	3.4(6)

$^a B(eq) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

Table 9. Selected Bonding Parameters for $[Pd(L^1)(oap)][BF_4]$

	Distances (Å)		
Pd—S(1)	2.298(4)	Pd—S(2)	2.312(4)
Pd—N(1)	2.14(1)	Pd—C(1)	1.99(1)
N(2)—C(13)	1.29(2)	S(1)—C(7)	1.82(1)
S(1)—C(8)	1.84(1)	S(2)—C(11)	1.83(1)
S(2)—C(12)	1.80(1)	O(1)—C(9)	1.41(1)
O(1)—C(10)	1.43(1)	N(1)—C(13)	1.35(1)
N(1)—C(17)	1.36(2)	C(2)—C(12)	1.51(2)
C(6)—C(7)	1.50(2)	C(8)—C(9)	1.53(2)
C(10)—C(11)	1.50(2)		
	Angles (deg)		
S(1)—Pd—S(2)	160.8(1)	S(1)—Pd—N(1)	96.1(3)
S(1)—Pd—C(1)	85.5(4)	S(2)—Pd—N(1)	95.4(3)
S(2)—Pd—C(1)	85.3(4)	N(1)—Pd—C(1)	172.0(4)
C(7)—S(1)—C(8)	101.7(7)	C(11)—S(2)—C(12)	102.4(7)
C(9)—O(1)—C(10)	118(1)	C(13)—N(1)—C(17)	117(1)

(17) (a) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, 4481−4486. (b) Buter, J.; Kellogg, R. M. *Org. Synth.* **1987**, *65*, 150−152.

(18) Geisbrecht, G. R.; Hanan, G. S.; Kickham, J. E.; Loeb, S. J. *Inorg. Chem.* **1992**, *31*, 3286.

Table 10. Selected Positional Parameters and $B(eq)^a$ Values for $[Pd(L^3)(py)][BF_4]\cdot CHCl_3$

atom	x	y	z	$B(eq)$, Å^2
Pd	0.13430(8)	−0.09833(8)	−0.1230(1)	2.90(5)
S(1)	0.1873(3)	0.0690(3)	−0.0500(3)	3.8(2)
S(2)	0.0321(3)	−0.2368(3)	−0.1791(3)	3.8(2)
O(1)	0.4853(6)	−0.0214(7)	−0.2095(8)	5.1(5)
O(2)	0.4297(7)	−0.2225(7)	−0.4171(8)	4.9(5)
O(3)	0.2540(7)	−0.3280(6)	−0.3764(8)	4.9(5)
N(1)	0.2768(7)	−0.1768(7)	0.000(1)	3.3(5)
C(1)	0.0115(9)	−0.247(9)	−0.246(1)	2.9(2)
C(7)	0.102(1)	0.141(1)	−0.181(1)	4.3(3)
C(8)	0.333(1)	0.0600(9)	−0.078(1)	3.9(3)
C(9)	0.365(1)	−0.008(1)	−0.215(1)	4.1(3)
C(10)	0.529(1)	−0.073(1)	−0.335(1)	6.2(4)
C(11)	0.538(1)	−0.192(1)	−0.371(1)	6.6(4)
C(12)	0.434(1)	−0.335(1)	−0.449(1)	5.6(3)
C(13)	0.316(1)	−0.361(1)	−0.490(1)	5.5(3)
C(14)	0.147(1)	−0.363(1)	−0.408(1)	4.9(3)
C(15)	0.102(1)	−0.364(1)	−0.279(1)	4.4(3)
C(16)	−0.085(1)	−0.188(1)	−0.304(1)	4.4(3)

^{a} $B(eq) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$.

Table 11. Selected Bonding Parameters for $[Pd(L^3)(py)][BF_4]\cdot CHCl_3$

Distances (Å)			
Pd−S(1)	2.294(3)	Pd−S(2)	2.285(3)
Pd−N(1)	2.144(8)	Pd−C(1)	1.98(1)
S(1)−C(7)	1.83(1)	S(1)−C(8)	1.79(1)
S(2)−C(15)	1.82(1)	S(2)−C(16)	1.83(1)
O(1)−C(9)	1.40(1)	O(1)−C(10)	1.41(1)
O(2)−C(11)	1.41(1)	O(2)−C(12)	1.39(1)
O(3)−C(13)	1.40(1)	O(3)−C(14)	1.41(1)
N(1)−C(17)	1.34(1)	N(1)−C(21)	1.33(1)
C(2)−C(16)	1.50(1)	C(6)−C(7)	1.47(1)
C(8)−C(9)	1.51(1)	C(10)−C(11)	1.47(2)
C(12)−C(13)	1.50(2)	C(14)−C(15)	1.49(2)
Angles (deg)			
S(1)−Pd−S(2)	163.7(1)	S(1)−Pd−N(1)	93.7(3)
S(1)−Pd−C(1)	84.7(3)	S(2)−Pd−N(1)	96.8(3)
S(2)−Pd−C(1)	85.6(3)	N(1)−Pd−C(1)	175.4(4)
C(7)−S(1)−C(8)	104.1(5)	C(15)−S(2)−C(16)	102.7(5)
C(9)−O(1)−C(10)	114.8(9)	C(11)−O(2)−C(12)	114(1)
C(13)−O(3)−C(14)	111.3(9)	C(17)−N(1)−C(21)	119(1)

Table 12. Selected Positional Parameters and $B(eq)^a$ Values for $[Pd(L^3)(pic)][BF_4]$

atom	x	y	z	$B(eq)$, Å^2
Pd	0.16963(5)	0.35027(4)	0.49493(7)	2.49(3)
S(1)	0.2733(2)	0.3829(2)	0.7511(2)	3.6(1)
S(2)	0.0426(1)	0.3789(1)	0.2325(2)	3.1(1)
O(1)	0.4560(4)	0.2169(4)	0.5422(6)	3.8(3)
O(2)	0.4694(4)	0.0676(4)	0.2722(7)	4.6(3)
O(3)	0.2022(4)	0.1506(4)	0.1436(7)	4.6(3)
N(1)	0.1195(5)	0.2446(4)	0.5930(7)	2.9(3)
N(2)	0.3078(5)	0.1164(4)	0.6204(9)	4.4(4)
C(1)	0.2234(6)	0.4427(5)	0.4030(8)	2.7(4)
C(7)	0.2958(7)	0.4926(6)	0.697(1)	4.2(5)
C(8)	0.4248(7)	0.2887(6)	0.810(1)	4.9(5)
C(9)	0.4996(7)	0.2663(6)	0.682(1)	4.5(5)
C(10)	0.5110(7)	0.2088(6)	0.407(1)	4.3(5)
C(11)	0.4453(7)	0.1725(6)	0.254(1)	4.4(5)
C(12)	0.3981(8)	0.0302(6)	0.140(1)	5.5(6)
C(13)	0.2809(8)	0.0456(6)	0.172(1)	4.8(5)
C(14)	0.0897(7)	0.1690(6)	0.170(1)	4.3(5)
C(15)	0.0050(7)	0.2758(6)	0.123(1)	4.2(5)
C(16)	0.1399(6)	0.3938(5)	0.1168(8)	3.3(4)

^{a} $B(eq) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$.

air-stable in solution, although $[Pd(L^0)(CH_3CN)][BF_4]$ shows a slight sensitivity to moisture. $[Pd(L^0)(CH_3CN)][BF_4]$ and $[Pd(L^3)(CH_3CN)][BF_4]$ are quite soluble in most polar organic solvents; however, $[Pd(L^1)(CH_3CN)][BF_4]$ was considerably less

Table 13. Selected Bonding Parameters for $[Pd(L^3)(pic)][BF_4]$

Distances (Å)			
Pd−S(1)	2.299(2)	Pd−S(2)	2.304(2)
Pd−N(1)	2.139(5)	Pd−C(1)	1.983(6)
S(1)−C(7)	1.812(8)	S(1)−C(8)	1.809(8)
S(2)−C(15)	1.814(8)	S(2)−C(16)	1.809(7)
O(1)−C(9)	1.400(9)	O(1)−C(10)	1.421(9)
O(2)−C(11)	1.415(9)	O(2)−C(12)	1.434(9)
O(3)−C(13)	1.423(9)	O(3)−C(14)	1.400(9)
N(1)−C(21)	1.353(8)	N(1)−C(17)	1.344(8)
N(2)−C(17)	1.361(9)	C(2)−C(16)	1.496(9)
C(6)−C(7)	1.49(1)	C(8)−C(9)	1.50(1)
C(10)−C(11)	1.49(1)	C(12)−C(13)	1.49(1)
C(14)−C(15)	1.48(1)		
Angles (deg)			
S(1)−Pd−S(2)	159.93(7)	S(1)−Pd−N(1)	94.7(2)
S(1)−Pd−C(1)	85.1(2)	S(2)−Pd−N(1)	99.7(2)
S(2)−Pd−C(1)	81.1(2)	N(1)−Pd−C(1)	177.2(2)
C(7)−S(1)−C(8)	101.9(4)	C(15)−S(2)−C(16)	103.5(3)
C(9)−O(1)−C(10)	112.6(6)	C(11)−O(2)−C(12)	113.4(6)
C(13)−O(3)−C(14)	111.4(6)	C(17)−N(1)−C(21)	116.9(6)

Table 14. Selected Positional Parameters and $B(eq)^a$ Values for $[Pd(L^3)(cyt)][BF_4]\cdot CH_3CN$

atom	x	y	z	$B(eq)$, Å^2
Pd	0.14167(5)	0.06127(5)	0.34342(5)	2.82(3)
S(1)	0.0887(2)	−0.0708(2)	0.3109(1)	3.3(1)
S(2)	0.1696(2)	0.1858(2)	0.4183(2)	4.3(1)
O(1)	−0.0102(4)	0.0466(4)	0.1228(4)	3.7(3)
O(2)	−0.0099(5)	0.2042(4)	0.0288(4)	5.1(3)
O(3)	0.1484(5)	0.2734(4)	0.1995(5)	5.8(4)
C(1)	−0.0031(6)	0.0786(5)	0.3706(5)	2.4(2)
C(7)	−0.0343(6)	−0.0707(6)	0.3576(6)	3.8(2)
C(8)	0.0427(7)	−0.0873(5)	0.1783(6)	3.9(2)
C(9)	−0.0449(7)	−0.0345(6)	0.1245(7)	4.3(2)
C(10)	−0.0976(7)	0.1000(6)	0.1005(6)	4.0(2)
C(11)	−0.0570(8)	0.1845(7)	0.1110(7)	5.0(2)
C(12)	0.0385(9)	0.2803(7)	0.0363(8)	6.2(3)
C(13)	0.149(1)	0.2799(7)	0.0965(8)	6.7(3)
C(14)	0.2487(9)	0.2520(7)	0.2560(8)	5.5(2)
C(15)	0.2471(8)	0.2580(7)	0.3648(8)	5.8(3)
C(16)	0.0348(7)	0.2256(6)	0.3849(7)	4.5(2)
N(1)C	0.4620(5)	−0.0015(5)	0.3648(5)	4.4(4)
O(2)C	0.3658(4)	0.0306(4)	0.4713(4)	4.8(3)
C(2)C	0.3771(7)	0.0232(6)	0.3853(7)	3.6(2)
N(3)C	0.2953(5)	0.0381(4)	0.3067(5)	3.3(3)
N(4)C	0.2304(7)	0.0500(7)	0.1377(6)	5.2(5)
C(4)C	0.3111(7)	0.0320(5)	0.2123(6)	3.5(2)
C(5)C	0.4098(8)	0.0045(6)	0.1923(7)	4.7(2)
C(6)C	0.4880(7)	−0.0117(6)	0.2707(7)	4.4(2)

^{a} $B(eq) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$.

soluble in the same solvents and was converted to the $[CF_3SO_3]^-$ salt for most manipulations, including X-ray diffraction and substrate competition experiments in $CDCl_3$. NMR spectroscopy indicates that metalation of the aromatic ring has occurred with three features indicative of a metalated structure: the absence of a downfield resonance in the aromatic region of the ^1H NMR spectra, the presence of a large downfield shift for one of the aromatic carbons in the $^{13}C\{^1H\}$ NMR spectra, and the splitting of the benzylic protons into a pair of doublets. This is consistent with other metalated thiacyclophanes.[11,12,18,19]

X-ray Structures of the Metalloreceptors $[Pd(L^0)(CH_3CN)]\cdot CH_3CN$, $[Pd(L^1)(CH_3CN)][CF_3SO_3]$, and $[Pd(L^3)(CH_3CN)][BF_4]$. Perspective ORTEP drawings of the complex cations $[Pd(L^0)(CH_3CN)]^+$, $[Pd(L^1)(CH_3CN)]^+$, and $[Pd(L^3)(CH_3CN)]^+$ are shown in Figures 1−3. All three complexes exhibit

(19) (a) Hanan, G. S.; Kickham, J. E.; Loeb, S. J. *J. Chem. Soc., Chem. Commun.* **1991**, 893. (b) Hanan, G. S.; Kickham, J. E.; Loeb, S. J. *Organometallics* **1992**, *11*, 3063. (c) Loeb, S. J.; Shimizu, G. K. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1395.

Table 15. Selected Bonding Parameters for $[Pd(L^3)(cyt)][BF_4]\cdot CH_3CN$

	Distances (Å)		
Pd—S(1)	2.308(3)	Pd—S(2)	2.300(3)
Pd—N(3)C	2.171(6)	Pd—C(1)	1.993(7)
S(1)—C(7)	1.824(8)	S(1)—C(8)	1.818(8)
S(2)—C(15)	1.80(1)	S(2)—C(16)	1.827(9)
N(3)C—C(4)C	1.354(9)	N(3)C—C(2)C	1.37(1)
N(4)C—C(4)C	1.34(1)	N(1)C—C(6)C	1.36(1)
N(1)C—C(2)C	1.37(1)	N(1)—C(17)	1.10(2)
O(1)—C(9)	1.42(1)	O(1)—C(10)	1.42(1)
O(2)—C(11)	1.42(1)	O(2)—C(12)	1.40(1)
O(3)—C(13)	1.42(1)	O(3)—C(14)	1.41(1)
O(2)C—C(2)C	1.223(9)	C(2)—C(16)	1.48(1)
C(6)—C(7)	1.49(1)	C(8)—C(9)	1.50(1)
C(10)—C(11)	1.49(1)	C(12)—C(13)	1.50(1)
C(14)—C(15)	1.50(1)	C(4)C—C(5)C	1.43(1)
C(5)C—C(6)C	1.34(1)		

	Angles (deg)		
S(1)—Pd—S(2)	161.80(8)	S(1)—Pd—N(3)C	92.0(2)
S(2)—Pd—N(3)C	101.2(2)	S(1)—Pd—C(1)	85.5(2)
S(2)—Pd—C(1)	81.7(2)	N(3)C—Pd—C(1)	176.7(3)
C(7)—S(1)—C(8)	102.7(4)	C(15)—S(2)—C(16)	103.5(5)
C(9)—O(1)—C(10)	110.9(7)	C(11)—O(2)—C(12)	113.8(8)
C(13)—O(3)—C(14)	112.3(8)	C(4)C—N(3)C—C(2)C	120.0(7)
C(6)C—N(1)C—C(2)C	122.9(8)		
N(3)C—C(4)C—N(4)C	118.2(8)	N(3)C—C(4)C—C(5)C	121.2(8)
N(4)C—C(4)C—C(5)C	120.6(9)	C(4)C—C(5)C—C(6)C	117.6(9)
N(1)C—C(6)C—C(5)C	120.2(9)	O(2)C—C(2)C—N(3)C	121.3(8)
O(2)C—C(2)C—N(1)C	120.7(8)	N(3)C—C(2)C—N(1)C	118.0(8)

square planar geometry at Pd with three donor atoms provided by the rigid S_2C chelate and Pd—S distances in the range 2.299(2)—2.327(2) Å. Distortions from ideal, square planar geometry vary depending on the length of the aliphatic chain between the sulfur atoms such that $[Pd(L^1)(CH_3CN)]^+$ containing a short, five-atom chain shows the largest distortion: S(1)—Pd—S(2) = 160.6(1)°. The Pd—C bond distances are equal within experimental error and very similar to those observed previously for related compounds.[18,19] The fourth site *trans* to the Pd—C bond is occupied by an ancillary acetonitrile group with Pd—N(1) distances in the range 2.120(6)—2.13(1) Å and N(1)—Pd—C(1) angles close to linear.

The major structural differences between these complexes are the composition and spatial orientation of the aliphatic chain between the sulfur atoms. The angles at sulfur average just over 100°, resulting in this linkage being oriented away from and approximately perpendicular to the metal coordination plane. For $[Pd(L^0)(CH_3CN)]^+$, the observed conformation of the purely hydrocarbon chain is presumably a result of minimizing repulsive contacts and optimizing packing forces in the solid state. For $[Pd(L^1)(CH_3CN)]^+$ the short, chelating backbone contains a single ether oxygen atom which is positioned above the Pd atom at a distance of 2.714(8) Å. This results in a potential hydrogen-bonding site directly above the metal coordination plane and oriented parallel to the Pd—N(1) bond. Therefore, both the first- and second-sphere coordination sites are directed toward any incoming substrate. The longer chelating backbone for $[Pd(L^3)(CH_3CN)]^+$, which contains three ether oxygen atoms, is also oriented perpendicular to the coordination plane and contains three potential hydrogen-bonding sites available for second-sphere coordination. Similar to the case of $[Pd(L^1)(CH_3CN)]^+$, this results in a second-sphere binding site which has the appropriate orientation to allow hydrogen bonding with a substrate to accompany any first-sphere metal coordination.

Formation of Metalloreceptor—Substrate Complexes. $[Pd(L^0)(CH_3CN)]^+$, $[Pd(L^1)(CH_3CN)]^+$, and $[Pd(L^3)(CH_3CN)]^+$ were reacted with pyridine and *o*-aminopyridine in a 1:1 ratio to produce the aromatic amine adducts in essentially quantitative yield. Coordination of the pyridine derivatives to Pd was evidenced by significant shifts in the aromatic protons of these ligands. For the adducts $[Pd(L^1)(oap)]^+$ and $[Pd(L^3)(oap)]^+$, in which hydrogen bonding of the amino group to ether oxygen atoms on the receptor could occur, significant downfield shifts were also observed for the NH_2 protons in the ^1H NMR spectra. This is indicative of H-bonding and is quite comparable to similar shifts observed for purely organic H-bonding receptors.[20]

One of the goals of this research was to investigate whether the presence of second-sphere hydrogen-bonding interactions accompanying the normal coordination of a substrate would in any way allow for selectivity or molecular recognition by the metalloreceptor. As a simple test of this phenomenon, competition reactions were run between pyridine and *o*-aminopyridine for each of the three receptors and the extent of complexation was determined by ^1H NMR spectroscopy. Thus, a 1:1 mixture of pyridine and *o*-aminopyridine in $CDCl_3$ was mixed with 1 equiv of metalloreceptor in $CDCl_3$ and the ^1H NMR recorded.

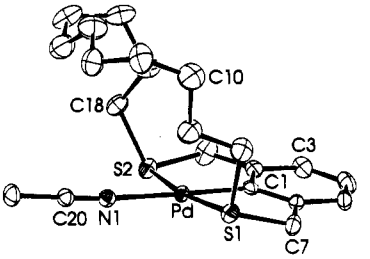


Figure 1. Perspective ORTEP drawing of the $[Pd(L^0)(CH_3CN)]^+$ cation, showing the atom-numbering scheme. Carbon atoms are numbered sequentially beginning with the palladated aromatic ring carbon. Thermal ellipsoids of 30% are shown.

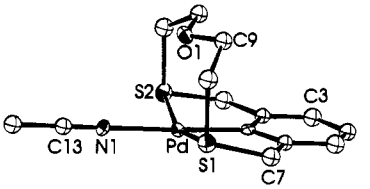


Figure 2. Perspective ORTEP drawing of the $[Pd(L^1)(CH_3CN)]^+$ cation, showing the atom-numbering scheme. Carbon atoms are numbered sequentially beginning with the palladated aromatic ring carbon. Thermal ellipsoids of 30% are shown.

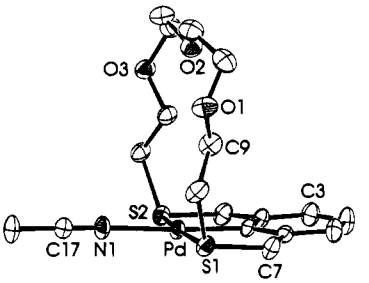


Figure 3. Perspective ORTEP drawing of the $[Pd(L^3)(CH_3CN)]^+$ cation, showing the atom-numbering scheme. Carbon atoms are numbered sequentially beginning with the palladated aromatic ring carbon. Thermal ellipsoids of 30% are shown.

(20) For example: (a) Hamilton, A. D. In *Advances in Supramolecular Chemistry*; Gokel, G., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 1, p 1. (b) Kelly-Rowley, A. M.; Cabell, L. A.; Anslyn, E. V. *J. Am. Chem. Soc.* **1991**, *113*, 9687. (c) Deslongchamps, G.; Galan, A.; de Mendoza, J.; Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 61. (d) Cochran, J. E.; Parrot, T. J.; Whitlock, B. J.; Whitlock, H. W. *J. Am. Chem. Soc.* **1992**, *114*, 2269. (e) Wilcox, C. S.; Adrain, J. C., Jr.; Webb, T. H.; Zawacki, F. J. *J. Am. Chem. Soc.* **1992**, *114*, 10189 and references therein.

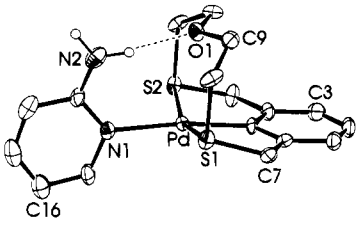


Figure 4. Perspective ORTEP drawing of the $[Pd(L^1)(oap)]^+$ cation, showing the atom-numbering scheme. Carbon atoms are numbered sequentially beginning with the palladated aromatic ring carbon. Thermal ellipsoids of 30% are shown.

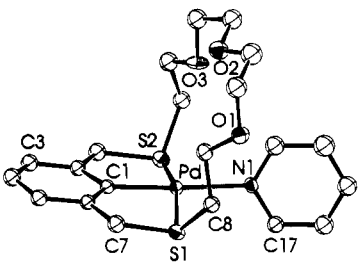


Figure 5. Perspective ORTEP drawing of the $[Pd(L^3)(py)]^+$ cation, showing the atom-numbering scheme. Carbon atoms are numbered sequentially beginning with the palladated aromatic ring carbon. Thermal ellipsoids of 30% are shown.

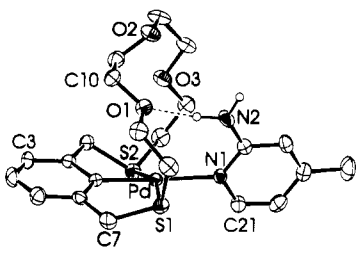


Figure 6. Perspective ORTEP drawing of the $[Pd(L^3)(pic)]^+$ cation, showing the atom-numbering scheme. Carbon atoms are numbered sequentially beginning with the palladated aromatic ring carbon. Thermal ellipsoids of 30% are shown.

Ratios of 2.23:1, 3.46:1, and 6.33:1 for oap:py were observed for $[Pd(L^0(CH_3CN)]^+$, $[Pd(L^1)(CH_3CN)]^+$, and $[Pd(L^3)(CH_3CN)]^+$ at 253 K by integrating the lowest field resonances for coordinated and uncoordinated pyridine. In order to better determine the exact nature of the metalloreceptor/substrate interactions and gain insight into the observed selectivity, X-ray structures were determined for $[Pd(L^1)(oap)][BF_4]$, $[Pd(L^3)(py)][BF_4]\cdot CHCl_3$, and $[Pd(L^3)(pic)][BF_4]$.

X-ray Structures of the Metalloreceptor–Substrate Complexes $[Pd(L^1)(oap)][BF_4]$, $[Pd(L^3)(py)][BF_4]\cdot CHCl_3$, $[Pd(L^3)(pic)][BF_4]$, and $[Pd(L^3)(cyt)][BF_4]\cdot CH_3CN$. Perspective ORTEP drawings of the complex cations $[Pd(L^1)(oap)]^+$, $[Pd(L^3)(py)]^+$, $[Pd(L^3)(pic)]^+$, and $[Pd(L^3)(cyt)]^+$ are shown in Figures 4–7. These adducts show square planar geometry at Pd with three sites occupied by the S_2C chelate and bonding parameters around the metal center similar to those observed for the parent, metalloreceptors. In $[Pd(L^1)(oap)]^+$, $[Pd(L^3)(py)]^+$, and $[Pd(L^3)(pic)]^+$, the plane of the pyridine ring is oriented approximately perpendicular to the square plane of the complex. For $[Pd(L^1)(oap)]^+$, the NH_2 group is oriented on the same side of the coordination plane as the chelating chain and the ether oxygen atom which is positioned above the Pd atom (Pd–O(1) = 2.75(1) Å, essentially unchanged from that of $[Pd(L^1)(CH_3CN)]^+$) is involved in N–H···O hydrogen bonding to the amino group with a N(2)···O(1) distance of 2.95(2) Å. For $[Pd(L^3)(py)]^+$, the polyether chain maintains the open configuration observed in the initial metalloreceptor complex $[Pd(L^3)(CH_3CN)]^+$. However, in the adduct $[Pd(L^3)(pic)]^+$ the polyether chain has reoriented in order to form a hydrogen bond in the second-sphere of coordination. The amino group is positioned on the same side of the coordination plane as the ether oxygens, and there is a N–H···O hydrogen-bonding interaction between N(2) and O(1) at a distance of 2.980(8) Å. Very similar to the picoline ring in $[Pd(L^3)(pic)]^+$, the pyrimidine ring in $[Pd(L^3)(cyt)]^+$ is oriented perpendicular to the coordination plane with the polyether chain containing three ether oxygen atoms reoriented to allow for hydrogen bonding in the second sphere of coordination. The amino group is positioned on the same side of the coordination plane as the ether oxygens, and there is a N–H···O hydrogen-bonding interaction between N(4)C and O(1) at a distance of 3.06(1) Å.

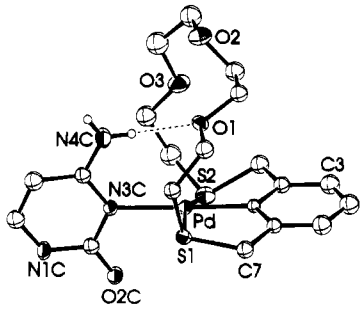


Figure 7. Perspective ORTEP drawing of the $[Pd(L^3)(cyt)]^+$ cation, showing the atom-numbering scheme. Carbon atoms are numbered sequentially beginning with the palladated aromatic ring carbon. Thermal ellipsoids of 30% are shown.

Discussion

The complexes $[Pd(L^1)(CH_3CN)]^+$ and $[Pd(L^3)(CH_3CN)]^+$ were designed as so-called metalloreceptors to coordinate a substrate molecule by σ donation to the Pd center while simultaneously interacting with the peripheral ether oxygen atoms via hydrogen bonding. The solid state structures of these metalloreceptors demonstrate how the two binding sites are oriented with respect to each other and provide a structural basis for selecting appropriate classes of substrate molecules. CPK models indicated that *o*-aminopyridine derivatives were ideally suited to bind to Pd employing the aromatic amine N atom and hydrogen-bond via the NH_2 substituent. The complex $[Pd(L^0)(CH_3CN)]^+$, which contains no H-bonding sites, was chosen as a model receptor while pyridine was employed as a non-H-bonding model substrate.

In addition, the structures of $[Pd(L^1)(CH_3CN)]^+$ and $[Pd(L^3)(CH_3CN)]^+$ demonstrate two different approaches to the design of second-sphere coordination sites in these complexes. For $[Pd(L^1)(CH_3CN)]^+$, the short polyether chain is locked in position and the hydrogen-bonding acceptor site is preorganized in advance of substrate coordination. On the other hand, $[Pd(L^3)(CH_3CN)]^+$ has a much more flexible polyether chain and some reorientation of the hydrogen-bonding sites occurs upon substrate coordination. The structure of $[Pd(L^0)(CH_3CN)]^+$ simply demonstrates that there is no substantial difference in the palladium coordination site in this model compound and that the methylene chain has sufficient flexibility to minimize steric interactions with an aromatic substrate.

In the structure of $[Pd(L^3)(py)]^+$, it is quite important to note that there is essentially no change in the receptor configuration in the absence of a hydrogen-bond donor. This is in contrast to the conformation adopted by the metalloreceptor in the complexes $[Pd(L^3)(pic)]^+$ and $[Pd(L^3)(cyt)]^+$, in which a rearrangement of the polyether chain occurs in order to act as a hydrogen-bond acceptor. The structure of $[Pd(L^1)(oap)]^+$ and

a comparison to $[Pd(L^1)(CH_3CN)]^+$ further demonstrate that this single hydrogen-bond acceptor site can be incorporated into the metalloreceptor in a preorganized fashion. The ether oxygen atom seems perfectly disposed for H bonding to the amino group on an *o*-aminopyridine substrate.

The application of these multiple-interaction modes to molecular recognition and selectivity was demonstrated very simply by observing the ratio of pyridine to *o*-aminopyridine under competitive conditions. Although *o*-aminopyridine might be expected to be a stronger donor than the unsubstituted pyridine, and this is borne out by the oap:py ratio of 2.23 employing $[Pd(L^0)(CH_3CN)]^+$, the increase in this ratio to 3.46 and 6.33 when $[Pd(L^1)(CH_3CN)]^+$ and $[Pd(L^3)(CH_3CN)]^+$ were used demonstrates that the observed second-sphere interactions have a significant effect on the interaction between complex and substrate. Since only one hydrogen bond is formed employing metalloreceptors $[Pd(L^1)(CH_3CN)]^+$ and $[Pd(L^3)(CH_3CN)]^+$, it is difficult to rationalize why the oap:py ratio should be greater for $[Pd(L^3)(CH_3CN)]^+$. It may be that in solution multiple hydrogen bonding contributes signficantly to second-sphere coordination. In particular, intermolecular hydrogen bonding between an ether oxygen and the remaining amino H atom is a distinct possibility. The application of this concept is demonstrated by the structure of $[Pd(L^3)(cyt)]^+$ and our previously communicated extraction results showing $[Pd(L^3)(CH_3CN)]^+$ to be selective for cytosine over the three other DNA nucleobases in polar organic solution (acetonitrile, acetone).[11]

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Supplementary Material Available: Listings of crystallographic data collection parameters, positional parameters, thermal parameters, nonessential bonding parameters, and hydrogen atom parameters (29 pages). Ordering information is given on any current masthead page.