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Thiacyclophanes Containing the $-S(CH_2)_3S(CH_2)_3S-$ Linkage. Synthesis and Structures of 2,6,10-Trithia[11]-*o*-cyclophane (TT[11]OC), 2,6,10-Trithia[11]-*m*-cyclophane (TT[11]MC), and the Palladation Product $[Pd(TT[11]MC)][BF_4]$

Garth R. Giesbrecht, Garry S. Hanan, James E. Kickham, and Stephen J. Loeb*

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

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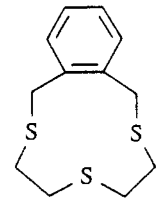
The thiacyclophanes 2,6,10-trithia[11]-*o*-cyclophane, TT[11]OC, and 2,6,10-trithia[11]-*m*-cyclophane, TT[11]-MC, are prepared via the Cs^+-mediated cyclization of (i) α,α'-dibromo-*o*-xylene and α,α'-dibromo-*m*-xylene with 4-thiaheptane-1,7-dithiol or (ii) *o*-xylene-α,α'-dithiol and *m*-xylene-α,α'-dithiol with 4-thiaheptane 1,7-ditosylate. These molecules each contain an 11-atom chain attached to an aromatic ring with sulfur donor atoms at the 2-, 6-, and 10-positions. Both are characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and single-crystal X-ray diffraction. The compound TT[11]OC, chemical formula $C_{14}H_{20}S_3$, crystallized in the space group $P2_1/n$ with $a = 5.285$ (1) Å, $b = 15.673$ (6) Å, $c = 17.384$ (5) Å, $\beta = 90.29$ (3)°, $V = 1439.9$ (13) Å^3, and $Z = 4$. The structure was refined to $R = 2.91\%$ and $R_w = 3.92\%$ for 1527 reflections with $F_o^2 > 3\sigma(F_o^2)$. The compound TT[11]MC, chemical formula $C_{14}H_{20}S_3$, crystallized in the space group $P2_1/c$ with $a = 8.764$ (1) Å, $b = 18.267$ (4) Å, $c = 9.607$ (2) Å, $\beta = 105.09$ (1)°, $V = 1485.2$ (9) Å^3, and $Z = 4$. The structure was refined to $R = 5.69\%$ and $R_w = 6.12\%$ for 1465 reflections with $F_o^2 > 3\sigma(F_o^2)$. Both molecules exhibit an exodentate conformation for the S atoms, but the relative orientations of the benzylic S atoms are anti in TT[11]OC and syn in TT[11]MC with respect to the aromatic ring. Results of molecular mechanics calculations are compared to the experimentally determined solid-state structures. Reactions of TT[11]OC and TT[11]MC with $PdCl_2(PhCN)_2$ produce square planar complexes with a $PdCl_2S_2$ coordination sphere in which the thioether ligand acts as a simple bidentate ligand for Pd(II). Addition of $AgBF_4$ to $PdCl_2$-(TT[11]MC), in refluxing acetonitrile, results in palladation of the TT[11]MC ligand at the 2-position of the aromatic ring. The resulting complex, $[Pd(TT[11]MC)][BF_4]$, is characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray diffraction. $[Pd(TT[11]MC)][BF_4]$, chemical formula $C_{14}H_{19}BF_4PdS_3$, crystallized in the space group $P2_1/c$ with $a = 8.383$ (2) Å, $b = 21.289$ (5) Å, $c = 9.437$ (3) Å, $\beta = 95.89$ (2)°, $V = 1722.5$ (14) Å^3, and $Z = 4$. The structure was refined to $R = 3.88\%$ and $R_w = 4.50\%$ for 2121 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Pd atom is in a square planar S_3C environment within the metalated macrocycle. The reaction of $[Pd(TT[11]MC)][BF_4]$ with PPh_2Me yields the 5-coordinate adduct $[Pd(PPh_2Me)(TT[11]MC)][BF_4]$.

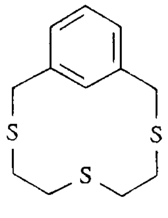
Introduction

We are currently interested in the design and synthesis of thiacyclophanes and their utility as ligands in transition metal chemistry.[1-3] The aromatic ring in these molecules may function as a spacing-unit for the separation of binding sites,[3] a skeleton for studying substituent effects or attachment to a solid support. This fragment may also dramatically affect the conformational properties of the molecule, and one of the major criteria in determining the suitability of a thiacyclophane, or any crown-like thioether molecule, for use as a macrocyclic ligand is the free-ligand conformation.[4-6] It is well established that crown thioether ligands prefer to adopt an exodentate conformation rather than the more favorable preorganized, endodentate conformation commonly found for crown ethers.[7] The introduction of a xylene group into the crown thioether framework[8] may produce one of two results. The inherent rigidity of these fragments may serve to aid in preorganization of the S donor atoms, or it may simply add to the stability of an exodentate conformation.

We have recently prepared and fully characterized the thiacyclophanes 2,5,8-trithia[9]-*o*-cyclophane, TT[9]OC, and 2,5,8-trithia[9]-*m*-cyclophane, TT[9]MC,[9] containing the $-S(CH_2)_2S(CH_2)_2S-$ linkage, and investigated the coordination chemistry of these potentially tridentate ligands.[1] Although both molecules were shown to have exodentate conformations, the ortho and meta substitution patterns were observed to have dramatically different effects on the coordinating ability of each ligand. The *o*-xylyl fragment was found to introduce strain into the free-ligand conformation, which favored an exo- to endodentate conformational change and facial S_3-coordination to a single metal ion.[1,10-13] In contrast, the effect of the *m*-xylyl group was to



TT[9]OC



TT[9]MC

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[9] These ligands were named 2,5,8-trithia[9]-*o*-benzenophane and 2,5,8-trithia[9]-*m*-benzenophane in the original literature (see ref 8) and abbreviated TTOB and TTMB in ref 1. The cyclophane nomenclature used herein is a more correct one, and the abbreviations used are TT[9]OC and TT[9]MC where the numeral in brackets indicates the number of atoms in the aliphatic chain in accordance with cyclophane nomenclature.

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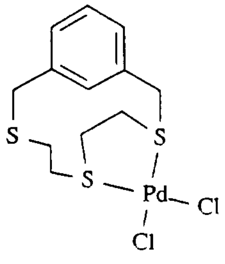
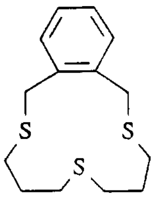
prevent this type of S_3-coordination by reinforcing a rigid exodentate conformation.[1,12]

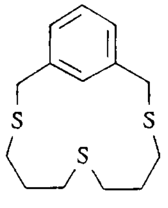
The only mononuclear complex of TT[9]MC characterized, to date, is the simple $PdCl_2$ adduct $PdCl_2$(TT[9]MC).[12] In this complex, the thiacyclophane acts as a bidentate ligand employing two adjacent S donors to form a five-membered chelate ring. This results in a square planar $PdCl_2S_2$ complex with the third S atom remaining exodentate to the macrocyclic ring. The geometry of this complex, in particular the orientation of the C–H bond at the 2-position of the aromatic ring toward the Pd center, prompted us to investigate the possibility of metalation inside the macrocyclic cavity of a thiacyclophane ligand. This article describes the synthesis, structure, and complexation to palladium(II) of the thiacyclophanes 2,6,10-trithia[11]-*o*-cyclophane, TT[11]OC, and 2,6,10-trithia[11]-*m*-cyclophane, TT[11]MC, which contain the $-S(CH_2)_3S(CH_2)_3S-$ linkage. In particular, palladation of TT[11]MC is demonstrated and the physical properties and basic reaction chemistry of the resulting product, [Pd(TT[11]MC)][BF_4], are described.



$PdCl_2$(TT[9]MC)



TT[11]OC



TT[11]MC

Experimental Section

4-Thiaheptane-1,7-diol,[14] 4-thiaheptane-1,7-dithiol,[14] 4-thiaheptane 1,7-ditosylate,[15] and $PdCl_2(PhCN)_2$[16] were prepared by literature methods. α,α′-Dibromo-*o*-xylene, α,α′-dibromo-*m*-xylene, *o*-xylene-α,α′-dithiol, *m*-xylene-α,α′-dithiol, and all deuterated solvents were purchased from Aldrich and used as received. All reactions were conducted under an atmosphere of N_2 using standard Schlenk techniques, and all solvents were degassed prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra (300 K) were recorded at 300.1 and 75.4 MHz, respectively, on a Bruker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Microanalytical Services, New Westminister, British Columbia, Canada. Molecular mechanics calculations were performed on an IBM 386 compatible computer using Serena Software's program PCMODEL 4.0 employing MMX and MMP force fields and parameters provided with the program.

Preparation of 2,6,10-Trithia[11]-*m*-cyclophane, TT[11]MC. Method A. Cesium carbonate (9.19 g, 28.2 mmol) was suspended in DMF (400 mL) under an atmosphere of N_2(g). To this mixture was added a solution of α,α′-dibromo-*m*-xylene (3.72 g, 14.1 mmol) and 4-thiaheptane-1,7-dithiol (2.57 g, 14.1 mmol) in DMF (200 mL). The addition was performed over a period of 27 h with the reaction temperature maintained at 50–55 °C. After addition, the mixture was cooled to room temperature and stirred for a further 24 h. The DMF was removed under vacuum and the resulting solid residue extracted wth CH_2Cl_2 (150 mL). The CH_2Cl_2 fraction was extracted with 0.05 M NaOH (2 × 50 mL), and the organic fractions were dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was recrystallized from acetone/absolute ethanol; yield 3.28 g (82%).

Method B. Cesium carbonate (7.69 g, 23.6 mmol) was suspended in DMF (300 mL) under an atmosphere of N_2(g). To this mixture was added a solution of 4-thiaheptane 1,7-ditosylate (5.40 g, 11.8 mmol) and *m*-xylene-α,α′-dithiol (2.00 g, 1.74 mL, 11.8 mmol) in DMF (200 mL). The addition was performed over a period of 17 h with the reaction temperture maintained at 60 °C. After addition, the mixture was cooled to room temperature and stirred for a further 12 h and the product isolated as in method A: yield 2.69 g (80%); mp 57–58 °C. NMR (δ ppm): ^1H ($CDCl_3$) 7.43 (s, 1 H, aromatic), 7.17–7.25 (m, 3 H, aromatic), 3.70 (s, 4 H, benzylic), 2.48 (t, 4 H, ^2J = 7.1, SCH_2), 2.38 (t, 4 H, ^2J = 7.1, SCH_2), 1.58 (m, 4 H, CH_2); $^{13}C\{^1H\}$ 139.49, 129.35, 128.75, 127.74 (aromatic), 36.88 (benzylic), 31.24 (CH_2S), 30.25, (CH_2S), 29.88 (CH_2). Anal. Calcd for $C_{14}H_{20}S_3$: C, 59.09; H, 7.10; S, 33.81. Found: C, 58.88; H, 7.00; S, 33.54.

Preparation of 2,6,10-Trithia[11]-*o*-cyclophane, TT[11]OC. Cesium carbonate (4.95 g, 15.2 mmol) was suspended in DMF (300 mL) under an atmosphere of N_2(g). To this mixture was added a solution of α,α′-dibromo-*o*-xylene (2.01, 7.6 mmol) and 4-thiaheptane-1,7-dithiol (1.39 g, 7.6 mmol) in DMF (100 mL). The addition was performed over a period of 18 h with the reaction temperature maintained at 50–55 °C. After addition, the mixture was cooled to room temperature and stirred for a further 12 h. The DMF was removed under vacuum and the resulting solid residue extracted with CH_2Cl_2 (100 mL). The CH_2Cl_2 fraction was extracted with 0.05 M NaOH (2 × 50 mL), and the organic fractions were dried over $MgSO_4$. After filtration and removal of the solvent, the residue was isolated and recrystallized from acetone: yield 2.63 g (90%); mp 146–148 °C. NMR (δ, ppm): ^1H ($CDCl_3$) 7.29 (m, 4 H, aromatic), 3.99 (s, 4 H, benzylic) 2.69 (t, 4 H, ^2J = 6.6, SCH_2), 2.67 (t, 4 H, ^2J = 6.6, SCH_2), 2.02 (m, 4 H, CH_2); $^{13}C\{^1H\}$ 135.69, 130.68, 127.81 (aromatic), 32.88 (benzylic), 31.54 (CH_2S), 27.81 (CH_2S), 27.72 (CH_2). Anal. Calcd for $C_{14}H_{20}S_3$: C, 59.09; H, 7.10; S, 33.81. Found: C, 58.91; H, 7.02; S, 33.67.

Preparation of [$PdCl_2$(TT[11]MC)]. $PdCl_2(PhCN)_2$ (0.092 g, 0.24 mmol) and TT[11]MC (0.066 g, 0.23 mmol) were combined in acetonitrile (10 mL), and the mixture was stirred for 12 h. The resulting yellow precipitate was filtered off and washed with acetonitrile (5 mL) and diethyl ether (10 mL); yield 0.084 g (78%). NMR (δ, ppm): ^1H (DMSO-d_6) 8.29 (s, 1 H, aromatic), 7.41 (br m, 2 H, aromatic), 7.30 (br s, 1 H, aromatic), 4.73 (br d, 1 H, benzylic), 4.30 (br m, 1 H, benzylic), 3.92 (br d, 1 H, benzylic), 3.72 (br m, 1 H, benzylic), 2.94 (br m, 2 H), 2.57 (m, 5 H), 2.16 (br m, 2 H), 1.88 (m, 2 H), 1.30 (m, 1 H). Anal. Calcd for $C_{14}H_{20}Cl_2PdS_3$: C, 36.40; H, 4.37; S, 20.83. Found: C, 36.12; H, 4.22; S, 20.67.

Preparation of [$PdCl_2$(TT[11]OC)]. $PdCl_2(CH_3CN)_2$ (0.094 g, 0.362 mmol) and TT[11]OC (0.103 g, 0.362 mmol) were combined in acetonitrile (20 mL), and the mixture was stirred for 12 h. The resulting yellow precipitate was filtered off and washed with acetonitrile (5 mL) and diethyl ether (10 mL); yield 0.150 g (90%). NMR (δ, ppm): ^1H (DMSO-d_6) 7.37 (m, 4 H, aromatic), 4.44 (br m, 4 H, benzylic), 3.04 (br m, 4 H, SCH_2), 2.78 (br m, 4 H, SCH_2), 2.17 (br m, 4 H, CH_2).

Preparation of [Pd(TT[11]MC)][BF_4]. $PdCl_2(PhCN)_2$ (0.404 g, 1.00 mmol), TT[11]MC (0.297 g, 1.00 mmol), and $AgBF_4$ (0.234 g, 1.20 mmol) were combined in acetonitrile (10 mL), and the mixture was refluxed for 48 h. The resulting mixture was filtered to remove AgCl and the solvent removed to yield an orange solid, which was recrystallized from acetonitrile, yield 0.348 (75%). NMR (δ, ppm): ^1H (CD_3CN) 7.06 (br s, 3 H, aromatic), 4.71 (d, 2 H, ^2J = 16.0 Hz, benzylic), 4.31 (d, 2 H, ^2J = 16.0 Hz, benzylic), 3.44 (ddd, 2 H, ^2J = 1.8, 7.59, 11.9 Hz), 3.21 (dt, 2 H, ^2J = 1.9, 11.1 Hz), 3.10 (t, 2 H, ^2J = 5.0 Hz), 2.86 (t, 2 H, ^2J = 11.4 Hz), 2.58 (q, 2 H, ^2J = 7.3 Hz), 2.00 (t, 2 H, ^2J = 10.6 Hz); $^{13}C\{^1H\}$ (CD_3CN) 165.85 (Pd–C1), 149.80, 126.61, 123.02 (aromatic), 49.99 (benzylic), 38.29 (CH_2S), 35.07, (CH_2S), 27.68 (CH_2). Anal. Calcd for $C_{14}H_{19}BF_4PdS$: C, 35.27; H, 4.03; S, 20.18. Found: C, 35.11; H, 3.92; S, 20.29.

Preparation of [Pd(PPh_2Me)(TT[11]MC)][BF_4]. [Pd(TT[11]MC)][BF_4] (0.100 g, 0.21 mmol) was dissolved in acetonitrile (10 mL), and PPh_2Me (0.043 g, 0.21 mmol) was added with stirring. The solvent was removed, yielding a yellow solid, which was recrystallized from acetonitrile; yield 0.125 g (86%). NMR (δ, ppm): ^1H (CD_3CN) 7.70 (m, 4

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for TT[11]OC, TT[11]MC, and [Pd(TT[11]MC)][BF$_4$]

chem formula	$C_{14}H_{20}S_3$(*o*)	$C_{14}H_{20}S_3$(*m*)	$C_{14}H_{19}BF_4PdS_3$
fw	284.54	284.54	476.77
a, Å	5.285 (1)	8.764 (1)	8.383 (2)
b, Å	15.673 (6)	18.267 (4)	21.889 (5)
c, Å	17.384 (6)	9.607 (2)	9.437 (3)
β, deg	90.29 (3)	105.09 (1)	95.89 (2)
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
V, Å^3	1439.9 (13)	1485.2 (9)	1722.5 (14)
ρ(calcd), g cm^{-3}	1.312	1.272	1.838
Z	4	4	4
μ, cm^{-1}	4.719	4.567	14.441
λ, Å	0.710 69	0.710 69	0.710 69
T, °C	24	24	24
$R(F_o)$,[a] %	2.91	5.69	3.88
$R_w(F_o)$,[a] %	3.92	6.12	4.50

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

H, PPh$_2$Me), 7.54 (m, 6 H, PPh$_2$Me), 7.06 (br s, 3 H, TT[11]MC aromatic), 4.75 (d, 2 H, ^2J = 16.7 Hz, benzylic), 4.25 (d, 2 H, ^2J = 16.7 Hz, benzylic), 3.11 (m, 2 H), 2.70 (m, 6 H), 2.14 (br s, 4 H), 1.87 (d, 3 H, $^2J_{PH}$ = 3.6 Hz); $^{13}C\{^1H\}$ (CD$_3$CN) 151.39, 126.61, 123.37 (TT[11]MC, aromatic, Pd–Cl not observed), 133.01, 131.09, 129.87 (PPh$_2$Me, aromatic), 49.72 (benzylic), 38.24 (CH$_2$S), 32.17 (CH$_2$S), 28.49 (CH$_2$), 12.87 (d, $^1J_{PC}$ = 9.8 Hz); $^{13}P\{^1H\}$ −11.23. Anal. Calcd for $C_{27}H_{32}BF_4PPdS_3$: C, 50.16; H, 5.00; S, 14.89. Found: C, 49.89; H, 4.83; S, 14.99.

General X-ray Diffraction Data Collection, Solution, and Refinement. Diffraction experiments were performed on a four-circle Rigaku AFC6 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 I and supplementary Table S-I. 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, and 50°). Absorption coefficients were small, and thus no absorption corrections were applied to the data. The data were processed using the TEXSAN software[17] package running on a VAX 3520 computer. Refinements were carried out by using full-matrix least-squares techniques on *F* by 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[18] and anomalous dispersion terms[19,20] were taken from the usual sources. Fixed H atom contributions were included with C–H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameter of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued.

Structure Determination of TT[11]OC. Colorless crystals of TT[11]OC were grown by slow evaporation of a benzene solution of the compound. A statistical analysis of intensity distributions and a determination of observed extinctions were consistent with space group $P2_1/n$, and this was confirmed by a successful solution and refinement. A total of 1986 reflections were collected, and 1527 unique reflections with $F_o^2 < 3\sigma(F_o^2)$ were used in the refinement. The positions of the sulfur atoms were determined by direct methods from the *E* map with highest figure of merit. The remaining carbon atoms were located from a difference Fourier map calculation. In the final cycles of refinement, the sulfur and carbon atoms were assigned anisotropic thermal parameters. This resulted in $R = \sum||F_o|-|F_c|/\sum|F_o|| = 0.0291$ and $R_w = (\sum w(|F_o|-|F_c|)^2/\sum wF_o^2)^{1/2} = 0.0392$ at final convergence. The Δ/σ value for any parameter in the final cycle was less than 0.001. A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.244 electron/Å^3 and was associated with the S2 sulfur atom. Selected atomic positional parameters are summarized in Table II, and selected bond distances and angles are summarized in Table III. Listings of atomic positional parameters (Table S-II), nonessential bonding parameters (Table S-III), thermal parameters (Table S-IV), hydrogen atom parameters (Table S-V), and values of $10|F_o|$ and $10|F_c|$ (Table S-XIV) are deposited as supplementary material.

Table II. Selected Positional Parameters and *B*(eq)[a] Values for TT[11]OC

atom	*x*	*y*	*z*	*B*(eq), Å^2
S1	0.50845 (12)	0.11905 (4)	0.04146 (3)	3.49 (3)
S2	0.19103 (13)	0.41246 (4)	0.06637 (4)	4.47 (4)
S3	0.49308 (12)	0.29351 (4)	−0.18158 (4)	3.51 (3)
C7	0.7407 (5)	0.1603 (2)	−0.02592 (14)	3.6 (1)
C8	0.5672 (5)	0.1873 (2)	0.1235 (1)	4.0 (1)
C9	0.5206 (5)	0.2821 (2)	0.1120 (1)	4.0 (1)
C10	0.2482 (5)	0.3033 (2)	0.0951 (1)	3.9 (1)
C11	0.2978 (5)	0.4103 (2)	−0.0320 (1)	3.8 (1)
C12	0.1188 (5)	0.3668 (2)	−0.0870 (1)	3.5 (1)
C13	0.2156 (5)	0.3597 (2)	−0.1684 (1)	3.7 (1)
C14	0.3681 (4)	0.1903 (2)	−0.1531 (1)	3.5 (1)

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

Table III. Selected Bond Distances and Angles for TT[11]OC

	Distances (Å)		
S1–C7	1.820 (3)	S1–C8	1.809 (3)
S2–C10	1.808 (3)	S2–C11	1.804 (3)
S3–C13	1.812 (3)	S3–C14	1.818 (3)
C6–C7	1.499 (3)	C8–C9	1.519 (4)
C9–C10	1.505 (4)	C11–C12	1.505 (4)
C12–C13	1.512 (4)	C1–C14	1.497 (3)
	Angles (deg)		
C7–S1–C8	100.6 (1)	C10–S2–C11	101.0 (1)
C13–S3–C14	100.4 (1)	C2–C1–C14	119.1 (2)
C6–C1–C14	122.0 (2)	C1–C6–C7	122.2 (2)
C5–C6–C7	118.8 (2)	C6–C7–S1	110.6 (2)
S1–C8–C9	116.6 (2)	C8–C9–C10	113.3 (2)
C9–C10–S2	114.9 (2)	S2–C11–C12	114.3 (2)
C11–C12–C13	114.4 (2)	C12–C13–S3	116.0 (2)
S3–C14–C1	110.7 (2)		

Table IV. Selected Positional Parameters and *B*(eq)[a] Values for TT[11]MC

atom	*x*	*y*	*z*	*B*(eq), Å^2
S1	−0.6435 (2)	0.10295 (9)	0.1898 (1)	5.01 (7)
S2	−0.3412 (2)	0.33790 (9)	0.2393 (2)	6.30 (8)
S3	0.0512 (2)	0.18735 (8)	0.5691 (1)	4.91 (7)
C7	−0.5031 (6)	0.0547 (3)	0.3310 (5)	4.5 (2)
C8	−0.5531 (7)	0.1919 (3)	0.1930 (5)	4.5 (3)
C9	−0.5401 (7)	0.2359 (3)	0.3272 (6)	5.2 (3)
C10	−0.5126 (7)	0.3164 (3)	0.3049 (6)	5.5 (3)
C11	−0.1916 (10)	0.3611 (6)	0.3927 (11)	12.9 (6)
C12	−0.1057 (13)	0.3148 (4)	0.4838 (8)	12.0 (5)
C13	−0.0824 (6)	0.2520 (3)	0.4268 (6)	6.8 (3)
C14	0.0824 (6)	0.1086 (3)	0.4682 (5)	4.5 (2)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{i4}ja^*{}_4ia^*{}_j\vec{a}_i\cdot\vec{a}_j$.

Structure Determination of TT[11]MC. Colorless crystals of TT[11]MC were grown by slow evaporation of an acetone solution of the compound. A statistical analysis of intensity distributions and a determination of observed extinctions were consistent with space group $P2_1/c$, and this was confirmed by a successful solution refinement. A total of 2720 reflections were collected, and 1465 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The positions of the sulfur atoms were determined by direct methods from the *E* map with highest figure of merit. The remaining carbon atoms were located from a difference Fourier map calculation. In the final cycles of refinement, the sulfur and carbon atoms were assigned anisotropic thermal parameters. This resulted in *R* = 0.0569 and R_w = 0.0612 at final convergence. The Δ/σ value for any parameter in the final cycle was less than 0.001. A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.446 electron/Å^3 and was associated with the C12 carbon atom. Selected atomic positional parameters are summarized in Table IV, and selected bond distances and angles are summarized in Table V. Listings of atomic positional parameters (Table S-VI), nonessential bonding parameters (Table S-VII), thermal parameters (Table S-VIII), hydrogen atom parameters (Table S-IX), and values of $10|F_o|$ and $10|F_c|$ (Table S-XV) are deposited as supplementary material.

Structure Determination of [Pd(TT[11]MC)][BF$_4$]. Orange crystals of [Pd(TT[11]MC)][BF$_4$] were grown by slow evaporation of an ace-

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(17) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp. 1985.

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

(19) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr., Sect. A* **1974**, *17*, 781.

(20) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

Table V. Selected Bond Distances and Angles for TT[11]MC

	Distances (Å)		
S1–C7	1.806 (5)	S1–C8	1.805 (6)
S2–C10	1.817 (6)	S2–C11	1.750 (8)
S3–C13	1.792 (6)	S3–C14	1.795 (5)
C6–C7	1.514 (6)	C8–C9	1.499 (7)
C9–C10	1.514 (7)	C11–C12	1.31 (1)
C2–C14	1.507 (7)	C12–C13	1.54 (1)
	Angles (deg)		
C7–S1–C8	102.5 (2)	C10–S2–C11	105.4 (4)
C13–S3–C14	100.9 (3)	C2–C1–C14	119.1 (2)
C3–C2–C14	119.0 (5)	C1–C6–C7	120.6 (4)
C5–C6–C7	120.8 (5)	C6–C7–S1	114.2 (3)
S1–C8–C9	115.6 (4)	C8–C9–C10	112.3 (4)
C9–C10–S2	115.8 (4)	S2–C11–C12	125.6 (8)
C11–C12–C13	119.4 (7)	C12–C13–S3	108.9 (5)
S3–C14–C2	117.1 (4)		

Table VI. Selected Positional Parameters and *B*(eq)[a] Values for [Pd(TT[11]MB)][BF$_4$]

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pd	0.61503 (6)	0.10951 (2)	0.61143 (5)	2.46 (2)
S1	0.4612 (2)	0.03685 (9)	0.7015 (2)	3.60 (8)
S2	0.8288 (2)	0.04592 (8)	0.5564 (2)	2.96 (7)
S3	0.6933 (2)	0.19120 (8)	0.4865 (2)	3.10 (7)
C1	0.4589 (7)	0.1664 (3)	0.6854 (6)	3.1 (3)
C2	0.4608 (8)	0.2290 (3)	0.6505 (7)	3.5 (3)
C3	0.3489 (9)	0.2677 (4)	0.6997 (8)	4.4 (4)
C4	0.2398 (9)	0.2463 (5)	0.7870 (9)	5.2 (4)
C5	0.2437 (9)	0.1861 (5)	0.8322 (8)	4.8 (4)
C6	0.3556 (7)	0.1460 (3)	0.7823 (7)	3.2 (3)
C7	0.3749 (8)	0.0814 (4)	0.8368 (7)	4.3 (4)
C8	0.5827 (9)	−0.0195 (4)	0.8025 (8)	4.6 (4)
C9	0.7085 (10)	−0.0472 (4)	0.7197 (8)	4.9 (4)
C10	0.8546 (9)	−0.0083 (3)	0.7054 (7)	3.8 (3)
C11	0.9984 (7)	0.0951 (3)	0.6095 (7)	3.0 (3)
C12	1.0050 (7)	0.1518 (3)	0.5165 (7)	3.4 (3)
C13	0.9004 (8)	0.2045 (3)	0.5531 (8)	3.7 (3)
C14	0.5882 (8)	0.2529 (3)	0.5658 (8)	4.1 (1)

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

Table VII. Selected Bond Distances and Angles for [Pd(TT[11]MB)][BF$_4$]

	Distances (Å)		
Pd–S1	2.267 (2)	C1–C6	1.396 (9)
Pd–S2	2.369 (2)	C2–C3	1.379 (9)
Pd–S3	2.275 (2)	C2–C14	1.493 (9)
Pd–C1	1.984 (7)	C3–C4	1.375 (11)
S1–C7	1.815 (8)	C4–C5	1.385 (12)
S1–C8	1.808 (8)	C5–C6	1.401 (10)
S2–C10	1.836 (7)	C6–C7	1.508 (10)
S2–C11	1.813 (7)	C8–C9	1.503 (11)
S3–C13	1.808 (7)	C9–C10	1.509 (10)
S3–C14	1.815 (7)	C11–C12	1.525 (9)
C1–C2	1.409 (10)	C12–C13	1.510 (9)
	Angles (deg)		
S1–Pd–S2	98.17 (7)	C2–C3–C4	120.7 (8)
S1–Pd–S3	162.00 (7)	C3–C4–C5	120.8 (7)
S2–Pd–S3	94.77 (6)	C3–C5–C6	119.2 (7)
S1–Pd–C1	83.5 (2)	C5–C6–C1	120.1 (7)
S2–Pd–C1	170.8 (2)	C5–C6–C7	121.7 (6)
S3–Pd–C1	85.7 (2)	C6–C7–S1	107.5 (5)
C7–S1–C8	103.8 (4)	S1–C8–C9	112.8 (5)
C10–S2–C11	98.3 (3)	C8–C9–C10	116.0 (7)
C13–S3–C14	103.1 (3)	C9–C10–S2	113.6 (5)
C2–C1–C6	119.1 (6)	S2–C11–C12	113.5 (4)
C1–C2–C3	119.6 (7)	C12–C13–S3	110.9 (5)
C1–C2–C14	119.4 (6)	S3–C14–C2	111.4 (5)

tonitrile solution of the compound. A statistical analysis of intensity distributions and a determination of observed extinctions were consistent with space group $P2_1/c$, and this was confirmed by a successful solution refinement. A total of 3124 reflections were collected, and 2121 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The position of the palladium atom was determined by the Patterson method. The remaining sulfur, fluorine, boron, and carbon atoms were located from difference Fourier map calculations. In the final cycles of refinement, the palladium, sulfur, fluorine, boron, and carbon atoms were all assigned anisotropic thermal parameters. This resulted in $R = 0.0388$ and $R_w = 0.0450$ at final convergence. The Δ/σ value for any parameter in the final cycle was less than 0.001. A final difference Fourier map calculation showed no peaks at chemical significance; the largest was 0.573 electron/Å^3 and was associated with the F4 fluorine atom. Selected atomic positional parameters are summarized in Table VI, and selected bond distances and angles are summarized in Table VII. Listings of atomic positional parameters (Table S-X), nonessential bonding parameters (Table S-XI), thermal parameters (Table S-XII), hydrogen atom parameters (Table S-XIII), and values of $10|F_o|$ and $10|F_c|$ (Table S-XVI) are deposited as supplementary material.

Results

Thiacyclophane Synthesis and Characterization. The thiacyclophanes TT[11]OC and TT[11]MC can be prepared in high yields by employing the Cs$^+$-mediated cyclization method of Buter and Kellogg.[21] The complete synthesis is a one-pot reaction from easily prepared or commercially available materials and can be achieved by two similar routes, depending on the choice of reactants. Either the appropriate α,α'-dibromoxylene is reacted with 4-thiaheptane-1,7-dithiol (eq 1), or the appropriate xylene-α,α'-dithiol is combined with 4-thiaheptane 1,7-ditosylate (eq 2). No effort was made to optimize the yields, since the scale of the reactions was sufficient to produce good quantities of pure material for future complexation studies. Both ligands are air-stable, colorless, crystalline solids that have good solubility in a

$$\mathrm{HS(CH_2)_3S(CH_2)_3SH + BrCH_2(C_6H_4)CH_2Br} \xrightarrow[\mathrm{DMF}]{\mathrm{Cs_2CO_3}} \mathrm{TT[11]OC\ or\ TT[11]MC} \quad (1)$$

$$\mathrm{TsO(CH_2)_3S(CH_2)_3OTs + HSCH_2(C_6H_4)CH_2SH} \xrightarrow[\mathrm{DMF}]{\mathrm{Cs_2CO_3}} \mathrm{TT[11]OC\ or\ TT[11]MC} \quad (2)$$

variety of organic solvents: acetone, CH$_2$Cl$_2$, CHCl$_3$, benzene, CH$_3$CN.

The ^{1}H NMR spectra of TT[11]OC and TT[11]MC show the expected patterns for ortho and meta aromatic substitution and single resonances for the benzylic CH$_2$ groups, 3.70 and 3.99 ppm, respectively. The methylene units of the aliphatic chains appear as separate multiplets, with those in TT[11]MC resonating slightly upfield of the corresponding protons in TT[11]OC. Those adjacent to sulfur appear as triplets at 2.69, 2.67 and at 2.48, 2.38 ppm, respectively, while the central CH$_2$ groups are less deshielded and appear at 2.02 and 1.58 ppm.

X-ray Structures and Conformations of Thiacyclophanes. The unit cell contains four molecules of TT[11]OC. A perspective view of the molecule, indicating the atom-numbering scheme, is shown in Figure 1. Complete listings of interatomic distances and angles are found in Tables III and S-III. Sulfur–carbon distances range from 1.804 (3) to 1.820 (3) Å, and carbon C(sp^2)–C(sp^2) bonds range from 1.373 (4) to 1.399 (4) Å. The C(sp^3)–C(sp^3) bonds range from 1.505 (4) to 1.519 (4) Å, and the two C(sp^2)–C(sp^3) bonds are 1.497 (3) and 1.499 (4) Å. These distances compare well to those found previously for other thiacyclophanes and macrocyclic thioethers.[1,7]

The unit cell contains four molecules of TT[11]MC. A perspective view of the molecule, indicating the atom-numbering scheme, is shown in Figure 2. Complete listings of interatomic distances and angles are found in Tables V and S-VII. Sulfur–carbon distances range from 1.792 (6) to 1.806 (5) Å, and carbon C(sp^2)–C(sp^2) bonds range from 1.373 (6) to 1.384 (6) Å. The two C(sp^2)–C(sp^3) bonds are 1.514 (6) and 1.507 (7) Å, and the C(sp^3)–C(sp^3) bonds average 1.47 (9) Å, with a relatively large range from 1.31 (1) to 1.54 (1) Å resulting from a slight disorder

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[21] Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481–4485.

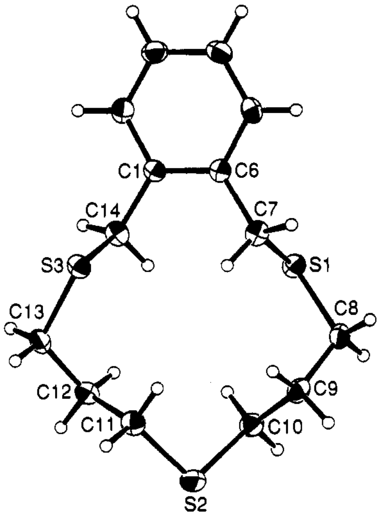


Figure 1. Perspective ORTEP drawing of TT[11]OC, showing the atom-numbering scheme.

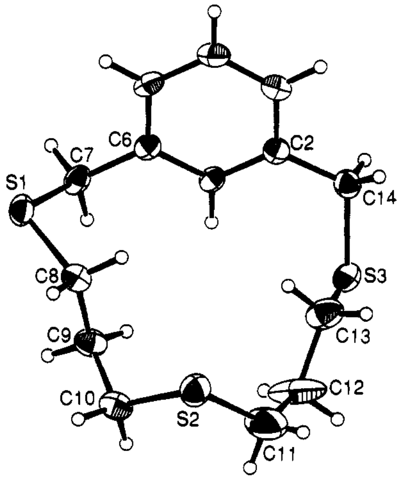


Figure 2. Perspective ORTEP drawing of TT[11]MC, showing the atom-numbering scheme.

about the C11–C12 linkage. These distances also compare well to those found previously for other thiacyclophanes and macrocyclic thioethers.[1,7]

Thiacyclophanes containing only three sulfur atoms are relatively rigid, macrocyclic molecules comprising a xylyl fragment and a $-S(CH_2)_nS(CH_2)_nS-$ linkage fused at the benzylic carbon–sulfur bonds. In general, the overall structures of thiacyclo phane molecules are best described in terms of the torsional angles (Table VIII) associated with the $-S(CH_2)_nS(CH_2)_nS-$ linkage and the orientation of the xylyl fragment with respect to the aliphatic chain. Indeed, the major structural difference between TT[11]OC and TT[11]MC is the way the aliphatic chain is positioned with respect to the aromatic ring. In TT[11]MC, as in TT[9]OC and TT[9]MC,[1] the C(benzylic)–S bonds are positioned on the same side of the aromatic ring (syn conformation) and the aliphatic portion of the molecule is oriented approximately perpendicular to one face of the ring. In contrast, for TT[11]OC, the C(benzylic)–S bonds are positioned on opposite sides of the aromatic ring (anti conformation) and the aliphatic chain "loops" around from one face of the aromatic ring to the other.

We previously used molecular mechanics calculations to provide some insight into the conformational preferences of thiacyclophanes TT[9]OC and TT[9]MC. For these ligands, the lowest energy conformations were essentially the same as determined by X-ray crystallography.[1] The minimization energies of these two isomeric thiacyclophanes (ortho, 70.3 kJ mol^{-1}; meta, 49.4 kJ mol^{-1}) showed that the *o*-xylyl fragment introduced strain into the ring system relative to the *m*-xylyl unit. Similar calculations for TT[11]OC and TT[11]MC showed the conformations determined by X-ray diffraction are also the minimum-energy conformations for these ligands, with values of 62.8 and 69.9 kJ mol^{-1}, respectively; see Figure 3. Although these values do not allow a direct comparison between the [9]- and [11]-cyclophanes, some general observations can be made regarding the effect of different xylyl substitution patterns on the relative energies of each type. Whereas, in the case of TT[9]OC and TT[9]MC, the *o*-xylyl fragment created strain in the ring system relative to the *m*-xylyl unit, the opposite was found for TT[11]OC and TT[11]MC. The calculated energy difference is small and is presumably due to the presence of a longer, more flexible aliphatic chain which is less strained in the anti conformation, resulting in a slightly lower energy for TT[11]OC.

Table VIII. Comparison of Torsional Angles[a] in TT[11]OC and TT[11]MC

angle	TT[11]OC	TT[11]MC
C1–C6–C7–S1	83.4 (2)	114.9 (4)
C6–C7–S1–C8	175.9 (2)	–62.0 (4)
C7–S1–C8–C9	62.5 (2)	–65.7 (4)
S1–C8–C9–C10	63.9 (3)	–161.9 (4)
C8–C9–C10–S2	–170.9 (2)	–56.3 (6)
C9–C10–S2–C11	76.8 (2)	–97.4 (5)
C10–S2–C11–C12	75.5 (2)	79 (1)
S2–C11–C12–C13	–176.1 (2)	52 (2)
C11–C12–C13–S3	64.8 (3)	–167.8 (9)
C12–C13–S3–C14	63.6 (2)	161.5 (5)
C13–S3–C14–C1[b]	–179.3 (2)	
C13–S3–C14–C2[c]		–66.5 (4)
S3–C14–C1–C6[b]	–95.9 (2)	
S3–C14–C2–C1[c]		–24.4 (6)
C14–C1–C6–C7[b]	–1.2 (3)	
C14–C2–C1–C6[c]		–178.8 (4)
C2–C1–C6–C7[c]		–179.3 (4)

[a] Sign is positive for a clockwise rotation of 1 to 4 viewed down the 2–3 bond. [b] A torsional angle associated with ortho substitution of the aromatic ring. [c] A torsional angle associated with meta substitution of the aromatic ring.

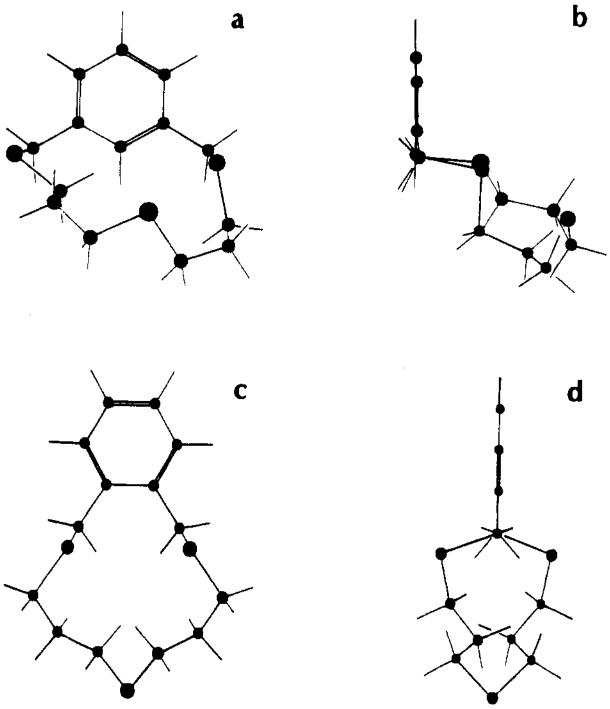


Figure 3. Ball and stick drawings of the molecular mechanics derived conformations, showing the orientation of the aliphatic chain with respect to the aromatic ring: (a, b) TT[11]MC; (c, d) TT[11]OC.

Complexation and Palladation Studies. The reaction of TT[11]MC or TT[11]OC with 1 equiv of $PdCl_2(PhCN)_2$ in acetonitrile yields the simple $PdCl_2$ adducts $PdCl_2(TT[11]MC)$ and $PdCl_2(TT[11]OC)$. Both complexes are bright yellow crystalline solids with only limited solubility in polar organic solvents (DMF, DMSO). Their ^{1}H NMR spectra are very similar to that observed

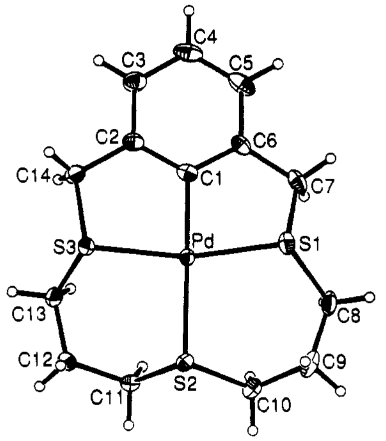
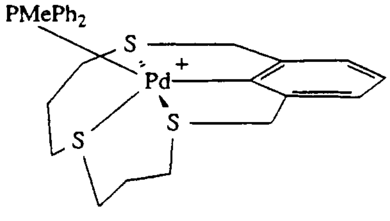


Figure 4. Perspective ORTEP drawing of the $[Pd(TT[11]MC)]^+$ cation, showing the atom-numbering scheme.

for $PdCl_2(TT[9]MC)$ in which the coordination of TT[9]MC as a bidentate ligand results in nonequivalent halves for the macrocycle and separate resonances for each of the 12 H atoms of this ligand.[12] Similar patterns are observed for these new complexes of TT[11]MC and TT[11]OC, consistent with the suggested $PdCl_2S_2$ formulation.

The addition of 1 equiv of Ag^+ to a suspension of $PdCl_2(TT[11]MC)$ in acetonitrile followed by refluxing for 48 h resulted in an orange complex, initially identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy as the palladation product $[Pd(TT[11]MC)][BF_4]$. In particular, the absence of a proton signal at 7.43 ppm originally assigned to the proton attached to the carbon at the 2-position of the aromatic ring and the presence of a large downfield shift, 165.85 ppm, for the $^{13}C\{^1H\}$ resonance of this same C atom were consistent with the formation of a Pd–C bond. This was verified by a single-crystal X-ray diffraction study described below. A number of reactions of $[Pd(TT[11]MC)][BF_4]$ were attempted with simple two-electron donors such as CO, C_2H_4, RC≡CR (R = Ph, COOMe), and PPh_2Me; however, only the strongest donor PPh_2Me resulted in an isolable adduct, $[Pd(PPh_2Me)(TT[11]MC)][BF_4]$. From a comparison of the ^1H and $^{13}C\{^1H\}$ NMR spectra of $[Pd(PPh_2Me)(TT[11]MC)][BF_4]$ with those of $[Pd(TT[11]MC)][BF_4]$, it was concluded that this complex is a five-coordinate Pd(II) adduct with a $PdCS_3P$ coordination sphere. The positions of individual NMR resonances due to the $-S(CH_2)_3S(CH_2)_3S-$ linkage in these two complexes do not differ very much. This is contrary to what might be expected if the central S2 atom had become exodentate and the complex retained a square planar geometry with a $PdCS_2P$ coordination sphere and is more consistent with a five-coordinate geometry, probably distorted TBP with C1, S2, and PPh_2Me in the equatorial plane.



$[Pd(PPh_2Me)(TT[11]MC)]^+$

X-ray Structure of $[Pd(TT[11]MC)][BF_4]$. The unit cell contains four $[Pd(TT[11]MC)]^+$ cations and four $[BF_4]^-$ anions. A perspective view of the cation $[Pd(TT[11]MC)]^+$ indicating the atom-numbering scheme is shown in Figure 4. Complete listings of interatomic distances and angles are found in Tables VII and S-XI.

The Pd atom is in a square planar environment defined by the three sulfur atoms and the carbon atom at the 2-position on the aromatic ring. The Pd–S distances to the mutually trans S atoms are 2.267 (2) and 2.275 (2) Å for S1 and S3, but the Pd–S2 distance trans to the Pd–C1 bond is significantly longer, 2.369 (2) Å, owing to the strong trans influence of the aromatic group. The Pd–C1 distance is 1.984 (7) Å. The S–Pd–S angles for the two six-membered chelate rings are 98.17 (7) and 94.77 (6)° for S1–Pd–S2 and S2–Pd–S3, and the C1–Pd–S angles, which involve the xylyl fragment, are 83.5 (1) and 85.7 (1)° for S1 and S3, respectively. There is a slight tetrahedral distortion at Pd, as evidenced by S1–Pd–S3 and C1–Pd–S3 angles of 162.00 (7) and 170.8 (2)°.

Discussion

The initial coordination of TT[11]MC and TT[11]OC to Pd(II) results in the formation of simple square planar complexes of the form $PdCl_2(L)$. The same result was obtained for Pd(II) complexes of the thiacyclophanes TT[9]OC and TT[9]MC, except that for $PdCl_2(TT[9]OC)$ a third Pd···S interaction was found due to this ligand's preference for a facial coordination mode. For $PdCl_2(TT[9]MC)$, the X-ray structure showed that the H atom of the C–H bond at the 2-position in the aromatic ring was actually over 2 Å closer to the Pd(II) center than the third S atom, which was in an exodentate position. Examination of molecular models indicated that if one of the chloride ligands was removed from the Pd coordination sphere and this vacant site filled intramolecularly with the third S donor, the H atom at the 2-position on the aromatic ring would be directly "on top of" the Pd center. We therefore reasoned that the addition of 1 equiv of Ag^+ to this complex would induce coordination of the third S donor and promote concomitant palladation at the 2-position of the thiacyclophane. This reaction proceeded smoothly, forming the palladation product $[Pd(TT[11]MC)][BF_4]$ in good yield. Since the aromatic group exerts a strong trans influence, we also investigated the possibility of displacing the potentially labile central S2 atom and replacing it with some simple 2-electron donor. This proved to be impossible, and only a five-coordinate adduct with PPh_2Me could be isolated. This does demonstrate, however, that the $-S(CH_2)_3S(CH_2)_3S-$ portion of the macrocyclic complex has some flexibility, and this may still be important in the substitution chemistry of these complexes with other metals. Also, if S2 could be replaced by a poorer donor such as an ether oxygen, substitution trans to the Pd–C bond might be more likely. We are currently investigating these possibilities.

Attempts to palladate the smaller thiacyclophane TT[9]MC containing the $-S(CH_2)_2S(CH_2)_2S-$ linkage failed. This was presumably due to the restricted size of the macrocyclic cavity and the requirement of having four fused five-membered chelate rings in the final product. It should be possible to incorporate the rigid $-SCH_2(C_6H_4)CH_2S-$ fragment into other macrocyclic ligands and, with the correct attention to steric and geometric requirements, prepare other palladated macrocyclic thioether complexes. This possibility is also currently under investigation.

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Supplementary Material Available: Listings of crystallographic data collection parameters, positional parameters, thermal parameters, nonessential bond distances and angles, and hydrogen atom parameters (Table S-I–S-XIII) (6 pages); listings of observed and calculated structure factors (Table S-XIV–S-XVI) (36 pages). Ordering information is given on any current masthead page.