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Copper(I) and Silver(I) Complexes of the Crown Thioether Ligand 2,5,8-Trithia[9]-o-benzenophane (TT[9]OB). Structures of [Cu(PPh₂Me)(TT[9]OB)][ClO₄] and [Ag(PPh₃)(TT[9]OB)][ClO₄]

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The crown thioether ligand 2,5,8-trithia[9]-o-benzenophane, TT[9]OB, was prepared in 90–95% yield via the Cs⁺-mediated cyclization of α,α′-dibromo-o-xylene and 3-thiapentane-1,5-dithiol. This thioether ligand reacted with [Cu(CH₃CN)₄][ClO₄] to give the Cu(I) complex [Cu(CH₃CN)(TT[9]OB)][ClO₄]. The coordinated acetonitrile molecule was displaced by ancillary ligands to form complexes of the formula [Cu(L)(TT[9]OB)][ClO₄], where L = benzonitrile, pyridine, PPh₃, or PPh₂Me. The complexes were characterized by infrared spectroscopy, ^{13}C and ^{1}H NMR spectroscopy, and X-ray crystallography. The complex [Cu(PPh₂Me)(TT[9]OB)][ClO₄] crystallized in the space group $P\bar{1}$ with $a = 12.888$ (4) Å, $b = 8.156$ (2) Å, $c = 31.575$ (8) Å, $\alpha = 115.64$ (2)°, $\beta = 104.56$ (2)°, $\gamma = 99.73$ (2)°, $V = 2745$ (1) Å³, and $Z = 4$. The structure refined to $R = 4.65\%$ and $R_w = 5.88\%$ for 5069 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Cu(I) ion is in a tetrahedral geometry with the ligand TT[9]OB coordinated facially and the fourth site occupied by the PPh₂Me ligand. The Ag(I) complex [Ag(PPh₃)(TT[9]OB)][ClO₄] was prepared directly by reacting stoichiometric amounts of AgClO₄, TT[9]OB, and PPh₃ in CH₃CN. The complex [Ag(PPh₃)(TT[9]OB)][ClO₄] crystallized in the space group $P2_1/c$ with $a = 8.1704$ (8) Å, $b = 16.239$ (2) Å, $c = 23.349$ (2) Å, $\beta = 101.364$ (8)°, $V = 3037.1$ (5) Å³, and $Z = 4$. The structure refined to $R = 3.50\%$ and $R_w = 4.59\%$ for 2972 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Ag(I) ion is in a tetrahedral geometry with the ligand TT[9]OB coordinated facially and the fourth site occupied by the PPh₃ ligand.

Introduction

The coordination chemistry of 1,4,7-trithiacyclononane, 9S3, is an intensive area of study, and numerous transition-metal complexes of this crown thioether ligand are known.[1–16] The
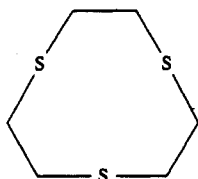
9S3

exceptional stability and unique electronic properties of these 9S3 complexes can be attributed to the endodentate conformation of the free ligand.[5] The sulfur donor atoms are divergent and thus preorganized in advance of coordination. The result is that almost no conformational change is required for coordination to a metal center and this thermodynamic barrier to complex formation is essentially removed.

Our recent investigation into the use of xylyl-linked crown thioethers as ligands showed that the crown thioether 2,5,8-trithia[9]-o-benzenophane, TT[9]OB, might complement the
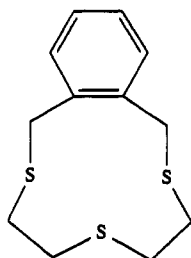
TT[9]OB

coordination chemistry of 9S3.[17] Although the structure of the free ligand was shown by X-ray analysis to have all three sulfur donor atoms oriented exodentate to the ring, the S–C–C–S torsional angles of the –SCH₂CH₂SCH₂CH₂S– linkages showed considerable distortion from an anti conformation. Also, molecular mechanics calculations indicated the possibility of an all endo-

dentate conformation for TT[9]OB suitable for facial coordination. The hypothesis that TT[9]OB might undergo some low-energy conformational change to a stable endodentate conformation and act as a capping ligand was confirmed by the synthesis and X-ray structure of the octahedral complex *fac*-Mo(CO)₃(TT[9]OB).[17] The geometry for TT[9]OB in this complex was essentially that predicted by molecular mechanics calculations.

This paper describes our investigations into the use of TT[9]OB as a capping ligand for tetrahedral geometry. In particular the synthesis, spectroscopic characterization, and X-ray structures of some copper(I) and silver(I) complexes of the type [M(L)-(TT[9]OB)]⁺ are described.

Experimental Section

[Cu(CH₃CN)₄][ClO₄] was prepared by the literature method.[18] AgClO₄, PPh₃, PPh₂Me, C₅H₅N (pyridine), C₆H₅CN (benzonitrile), CH₃CN, and all deuterated solvents were purchased from Aldrich and used as received. All reactions were conducted under an atmosphere of N₂ by using standard Schlenk techniques, and all solvents were degassed

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prior to use. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.1, 75.4 and 121.5 MHz, respectively, on a Bruker AM300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrometer. Elemental analysis were performed by Microanalytical Services, New Westminister, British Columbia, Canada.

Preparation of 2,5,8-Trithia[9]-*o*-benzenophane, TT[9]OB. Cesium carbonate (10.43 g, 32.0 mmol) was suspended in DMF (600 mL) under an atmosphere of $N_2(g)$. To this mixture was added a solution of α,α'-dibromo-*o*-xylene (7.68 g, 29.1 mmol) and 3-thiapentane-1,5-dithiol (4.49 g, 29.1 mmol) in DMF (150 mL). The addition was over a period of 20 h with the reaction temperature maintained at 70 °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 (200 mL). The CH_2Cl_2 fraction was extracted with 0.05 M NaOH (2 × 125 mL), and the organic fractions were dried over Na_2SO_4. After filtration and removal of the solvent, the solid residue was recrystallized from hot anhydrous ethanol. Yield: 6.8 g (91%). All spectroscopic data and physical properties were consistent with those found previously.[17]

Preparation of [Cu(CH₃CN)(TT[9]OB)][ClO₄]. *Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.* TT[9]OB (1.12 g, 4.36 mmol) was dissolved in CH_3CN (5 mL) under N_2 and this solution warmed to 45 °C. A solution of [Cu(CH₃CN)₄][ClO₄] (1.43 g, 4.36 mmol) in CH_3CN (30 mL) was added dropwise. The resulting solution immediately turned a pale yellow-brown color, but this color faded as the reaction progressed. The mixture was stirred for 2 h and then cooled to room temperature, during which time a white crystalline solid precipitated. The CH_3CN was removed in vacuo and the product recrystallized from CH_3CN. Yield: 1.85 g (94%). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 134.85, 132.57, 129.84 (aromatic), 37.92 (benzylic), 35.67, 35.22 (SCH₂CH₂S). ^1H NMR (acetone-d_6, 180 K): δ 7.41–7.52 (m, 4 H, aromatic), 4.22 (d, 2 H, $^2J_{HH}$ = 11.0 Hz, benzylic), 4.10 (d, 2 H, $^2J_{HH}$ = 11.0 Hz, benzylic), 3.66 (m, SCH₂CH₂S), 3.17 (m, SCH₂CH₂S). IR: ν(CN) 2280 (w), ν(ClO) 1088 cm^{-1} (vs, br). Anal. Calcd for $C_{14}H_{19}ClCuNO_4S_3$: C, 36.51; H, 4.16; S, 20.89. Found: C, 36.57; H, 4.24; S, 21.27.

Preparation of [Cu(PPh₂Me)(TT[9]OB)][ClO₄]. To a solution of [Cu(CH₃CN)(TT[9]OB)][ClO₄] (382 mg, 0.83 mmol) in CH_3CN (10 mL) was added, dropwise, PPh₂Me (166 mg, 0.83 mmol) dissolved in CH_3CN (5 mL). No visible change occured as the two colorless solutions were mixed. The mixture was stirred for 3 h at room temperature. Pure crystalline material was produced by diffusion of diethyl ether into the reaction mixture. Yield: 329 mg (64%). $^{13}C\{^1H\}$ NMR (CD₃CN, 230 K): δ 134.48 (d, $^1J_{CP}$ = 34.3 Hz, PPh₂Me), 134.47 (TT[9]OB), 132.13 (d, $^3J_{CP}$ = 14.7 Hz, PPh₂Me), 131.96 (TT[9]OB), 130.70 (PPh₂Me), 129.63 (TT[9]OB), 129.44 (d, $^2J_{CP}$ = 9.4 Hz, PPh₂Me), 36.58 (benzylic), 35.39, 34.34 (SCH₂CH₂S), 11.89 (d, $^1J_{CP}$ = 11.0 Hz, PPh₂Me). ^1H NMR (CD₃CN, 235 K): δ 7.0–7.5 (m, 14 H, aromatic), 4.21 (d, 2 H, $^2J_{HH}$ = 11.3 Hz, $^4J_{HH}$ = 2.2 Hz, benzylic), 3.91 (d, 2 H, $^2J_{HH}$ = 11.3 Hz, benzylic), 3.34 (m, 4 H, SCH₂CH₂S), 3.00 (m, 4 H, SCH₂CH₂S), 1.57 (d, 3 H, $^1J_{PH}$ = 5.3 Hz, PCH₃). $^{31}P\{^1H\}$ NMR (CH₃CN, 300 K): δ -12.80 (s, br). IR: ν(ClO) 1090 cm^{-1} (vs, br). Anal. Calcd for $C_{25}H_{29}ClCuO_4PS_3$: C, 48.46; H, 4.72; S, 15.52. Found: C, 48.38; H, 4.74; S, 15.52.

Preparation of [Cu(PPh₃)(TT[9]OB)][ClO₄]. To a solution of TT[9]OB (0.70 g, 2.7 mmol) in 20 mL of CH_2Cl_2 was added [Cu(CH₃CN)₄][ClO₄] (0.89 g, 2.7 mmol) in CH_3CN (20 mL). The mixture was stirred for 2 h at a temperature of 48 °C and then cooled to room temperature. A further 10 mL of CH_3CN was added to dissolve the white solid that precipitated. While being stirred vigorously, a solution of PPh₃ (0.71 g, 2.7 mmoL) in CH_3CN (15 mL) was added dropwise. Approximately 1 min after the addition, a white precipitate formed. Stirring was continued for 5 min, the solvent removed via syringe, and the crude white solid dried in vacuo. Crystals were obtained by slow diffusion of either acetone or diethyl ether into a CH_3CN solution of the compound. Yield: 1.15 g (65%). $^{13}C\{^1H\}$ NMR (CD₃CN, 230 K): δ 134.27 (TT[9]OB), 133.51 (d, $^3J_{CP}$ = 15.2 Hz, PPh₃), 132.13 (TT[9]OB), 132.08 (d, $^1J_{CP}$ = 35.6 Hz, PPh₃), 131.15 (PPh₃), 129.81 (TT[9]OB), 129.79 (d, $^2J_{CP}$ = 9.4 Hz, PPh₃), 37.19 (benzylic), 35.44, 34.92 (SCH₂CH₂S). ^1H NMR (CD₃CN, 235 K): δ 7.5–6.9 (m, 19 H, aromatic), 4.19 (dd, 2 H, $^2J_{HH}$ = 11.3 Hz, $^4J_{HH}$ = 2.2 Hz, benzylic), 3.98 (d, 2 H, $^2J_{HH}$ = 11.3 Hz, benzylic) 3.46 (m, 4 H, SCH₂CH₂S), 3.00 (m, 4 H, SCH₂CH₂S). $^{31}P\{^1H\}$ NMR (CD₃CN, 300 K): δ 5.55 (s br). IR: ν(ClO) 1094 cm^{-1} (vs, br). Anal. Calcd for $C_{30}H_{31}ClCuO_4PS_3$: C, 52.86; H, 4.58; S, 14.11. Found: C, 53.07; H, 4.46; S, 13.54.

Preparation of [Cu(C₅H₅N)(TT[9]OB)][ClO₄]. To a solution of TT[9]OB (238 mg, 0.9 mmol) in CH_3CN (10 mL) at a temperature of 45 °C, under N_2, was added, dropwise by syringe, [Cu(CH₃CN)₄][ClO₄] (304 mg, 0.9 mmol) dissolved in CH_3CN (5 mL). The colorless mixture

Table I. Crystallographic Data for [Cu(PPh₂Me)(TT[9]OB)][ClO₄] and [Ag(PPh₃)(TT[9]OB)][ClO₄]

	$C_{25}H_{29}ClCuO_4PS_3$	$C_{30}H_{31}AgClO_4PS_3$
chem formula		
fw	619.64	726.10
a, Å	12.888 (4)	8.1704 (8)
b, Å	8.156 (2)	16.239 (2)
c, Å	31.575 (8)	23.349 (2)
α, deg	115.64 (2)	
β, deg	104.56 (2)	101.364 (8)
γ, deg	99.73 (2)	
space group	$P\bar{1}$	$P2_1/c$
V, Å^3	2745 (1)	3037.1 (5)
ρ(calcd), g/cm^{-3}	1.50	1.59
Z	4	4
μ, cm^{-1}	12.00	10.29
λ, Å	0.710 69	0.710 69
T, °C	24	24
$R(F_o)$, %	4.65	3.50
$R_w(F_o)$, %	5.88	4.59

was stirred for 2 h. C_5H_5N, pyridine (237 mg, 3 mmol), was then added via syringe. The mixture was stirred for a further 1 h. The solvent was removed in vacuo and the off-white solid recrystallized from CH_3CN. Yield: 390 mg (87%). $^{13}C\{^1H\}$ NMR (CD₃CN, 300 K): δ 150.51, 137.98, 134.90, 132.57, 129.94 (aromatic), 37.48 (benzylic), 35.59, 35.39 (SCH₂CH₂S). ^1H NMR (CD₃CN, 235 K): δ 8.29 (br, 2 H), 7.82 (m, 1 H), 7.40–7.32 (m, 6 H), 4.07 (d, 2 H, ^2J = 11.3 Hz, benzylic), 3.85 (d, 2 H, ^2J = 11.3 Hz, benzylic), 3.49 (m, 4 H, SCH₂CH₂S) 2.89 (m, 2 H, SCH₂CH₂S). IR: ν(ClO) 1090 cm^{-1} (vs, br). Anal. Calcd for $C_{17}H_{21}ClCuNO_4S_3$: C, 40.96; H, 4.25; S, 19.29. Found: C, 40.31; H, 3.78; S, 19.91.

Preparation of [Cu(C₆H₅CN)(TT[9]OB)][ClO₄]. This compound was obtained by recrystallization of [Cu(CH₃CN)(TT[9]OB)][ClO₄] from C_6H_5CN (benzonitrile). ^1H NMR (CD₃CN): δ 7.8–7.3 (m, 9 H, aromatic), 3.95 (s, 4 H, br, benzylic), 3.6–2.7 (s, 8 H, br, SCH₂CH₂S). Due to persistent contamination of samples by [Cu(CH₃CN)(TT[9]OB)]-[ClO₄] and the limited range of solvents for recrystallization, a suitable elemental analysis could not be obtained.

Preparation of [Ag(PPh₃)(TT[9]OB)][ClO₄]. To a solution of TT-[9]OB (0.70 g, 2.7 mmol) and PPh₃ in 20 mL of CH_3CN was added AgClO₄ (0.89 g, 2.7 mmol) in CH_3CN (20 mL). The mixture was stirred for 2 h at room temperature resulting in a clear, colorless solution. Crystals were obtained by slow diffusion of diethyl ether into the CH_3CN reaction mixture. Yield: 1.15 g (65%). $^{13}C\{^1H\}$ NMR (CD₃CN, 300 K): $^{13}C\{^1H\}$ δ 134.68 (TT[9]OB), 133.37 (d, $^3J_{CP}$ = 16.5 Hz, PPh₃), 132.13 (TT[9]OB), 131.15 (PPh₃), 129.05 (d, $^2J_{CP}$ = 10.0 Hz, PPh₃), 128.55 (TT[9]OB), 35.23 (benzylic), 33.59, 30.91 (SCH₂CH₂S). ^1H NMR (CD₃CN, 250 K): 7.5–7.0 (m, 19 H, aromatic), 4.23 (d, 2 H, $^2J_{HH}$ = 11.0 Hz, benzylic), 3.77 (d, 2 H, $^2J_{HH}$ = 11.0 Hz, benzylic), 3.26 (m, 4 H, SCH₂CH₂S), 3.07 (m, 4 H, SCH₂CH₂S). $^{31}P\{^1H\}$ NMR (CD₃CN, 300 K): δ 14.48 (dd, $^1J_{AgP}$ = 589.9 and 511.4 Hz). IR: ν(ClO) 1094 cm^{-1} (vs, br). Anal. Calcd for $C_{30}H_{31}AgClO_4PS_3$: C, 52.86; H, 4.58; S, 14.11. Found: C. 53.07; H, 4.46; S, 13.54.

General X-ray Diffraction Data Collection, Solution, and Refinement. Diffraction experiments were performed on a four-circle Syntex P2₁ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 15 machine-centered reflections selected from rotation photographs. Partial rotation photographs around each axis were used to determine the crystal systems. Ultimately, 30 high-angle reflections were used to obtain the final lattice parameters and orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I and detailed in Table S-I (deposited as supplementary material). The intensities of standard reflections were recorded every 197 reflections and showed no statistically significant changes over the duration of the data collections. The data were processed by using the TEXSAN program package (Molecular Structure Corp.) running on a VAX 3520 Workstation. The absorption coefficients were small and ψ scans recorded showed no significant absorption effects. Thus, no absorption corrections were applied to the data. Refinement was carried out by using full-matrix least-squares techniques on F 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[19] and anomalous dispersion terms[20]

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Table II. Selected Positional Parameters[a] for [Cu(PPh$_2$Me)(TT[9]OB)][ClO$_4$]

atom	x	y	z
		Molecule 1	
Cu1	7066.0 (6)	4959 (1)	3551.5 (3)
S1	5746 (1)	6542 (2)	3592.8 (6)
S2	5923 (1)	2441 (2)	2721.1 (6)
S3	6915 (1)	2961 (2)	3882.8 (7)
P1	8718 (1)	6645 (2)	3620.4 (6)
C1	5818 (6)	4850 (11)	4469 (3)
C2	6396 (7)	538 (1)	4971 (4)
C3	6576 (7)	714 (2)	5360 (4)
C4	6218 (8)	846 (1)	5259 (3)
C5	5634 (6)	797 (1)	4772 (3)
C6	5427 (5)	6156 (10)	4370 (3)
C7	4779 (5)	5734 (10)	3847 (3)
C8	4920 (5)	5335 (9)	2927 (2)
C9	4659 (5)	3181 (9)	2644 (2)
C10	5520 (6)	0524 (9)	2856 (3)
C11	6426 (6)	0694 (9)	3297 (3)
C12	5669 (6)	2903 (12)	4064 (3)
C13	9395 (5)	9067 (8)	4166 (2)
C19	9824 (5)	5518 (8)	3611 (2)
C25	8561 (6)	7150 (9)	3101 (2)
		Molecule 2	
Cu2	0554.0 (6)	0437.1 (11)	8482.7 (3)
S4	1799 (1)	−1268 (2)	8336.9 (7)
S5	0398 (2)	0822 (3)	7774.0 (7)
S6	1359 (2)	3648 (2)	9040.6 (7)
P2	−0957 (1)	−1142 (2)	8529.9 (6)
C26	3276 (6)	3142 (11)	9478 (3)
C27	3451 (8)	401 (1)	9988 (4)
C28	3745 (9)	307 (2)	10241 (4)
C29	3915 (8)	139 (2)	10023 (5)
C30	3760 (7)	052 (1)	9516 (4)
C31	3430 (5)	1372 (11)	9238 (3)
C32	3254 (5)	0335 (10)	8687 (3)
C33	1595 (6)	−1721 (11)	7704 (3)
C34	1536 (6)	−0058 (12)	7624 (3)
C35	1065 (8)	341 (1)	8096 (3)
C36	0951 (8)	4483 (11)	8595 (4)
C37	2888 (7)	4184 (10)	9208 (3)
C38	−2020 (5)	0052 (8)	8622 (2)
C44	−0612 (5)	−1811 (8)	9011 (2)
C50	−1803 (6)	−3377 (10)	7953 (3)

[a] Multiplied by 10^4.

were taken from the usual sources. Fixed H 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 [Cu(PPh$_2$Me)(TT[9]OB)][ClO$_4$]. Colorless crystals of [Cu(PPh$_2$Me)(TT[9]OB)][ClO$_4$] were grown by slow diffusion of diethyl ether into an acetonitrile solution of the complex. Preliminary photography was consistent with a triclinic crystal system. Space group $P\bar{1}$ was confirmed by a successful solution refinement. Intensity data ($\pm h, \pm k, +l$) were collected in one shell (4.5° < 2θ < 45°). A total of 7193 reflections were collected, and 5069 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The positions of the Cu atoms were determined by direct methods from the E map with highest figure of merit. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of refinement, the copper, chlorine, sulfur, phosphorus, oxygen, and carbon atoms were assigned anisotropic thermal parameters. This resulted in $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.0465$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.0588$ at final convergence.

The Δ/σ value for any parameter in the final cycle was less than 0.02. A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.87 e/Å^3 and was associated with the Cl1 atom of one of the perchlorate anions. Selected atomic positional parameters are summarized in Table II, and selected bond distances and angles are summarized in Table III. Full listings of positional parameters (Table S-II), nonessential bond distances and angles (Table S-III), thermal parameters (Table S-IV), hydrogen atom parameters (Tables S-V), and values of 10|F_o| and 10|F_c| (Table S-X) are deposited as supplementary material.

Structure Determination of [Ag(PPh$_3$)(TT[9]OB)][ClO$_4$]. Colorless crystals of [Ag(PPh$_3$)(TT[9]OB)][ClO$_4$] were grown by slow evaporation

Table III. Selected Bond Distances and Angles for [Cu(PPh$_2$Me)(TT[9]OB)][ClO$_4$]

Distances (Å) for Molecule 1			
Cu1–S1	2.299 (2)	Cu1–S2	2.374 (2)
Cu1–S3	2.293 (2)	Cu1–P1	2.234 (2)
S1–C7	1.820 (6)	S1–C8	1.802 (6)
S2–C9	1.827 (6)	S2–C10	1.820 (7)
S3–C11	1.816 (8)	S3–C12	1.834 (7)
P1–C25	1.828 (7)	P1–C13	1.830 (6)
P1–C19	1.822 (6)	C6–C7	1.503 (9)
C8–C9	1.513 (8)	C10–C11	1.51 (1)
C12–C1	1.49 (1)	C1–C2	1.40 (1)
C2–C3	1.36 (1)	C3–C4	1.36 (1)
C4–C5	1.37 (1)	C5–C6	1.40 (1)
C6–C1	1.37 (1)		

Angles (deg) for Molecule 1			
S1–Cu1–S2	92.61 (6)	S1–Cu1–S3	113.49 (6)
S2–Cu1–S3	92.57 (7)	S1–Cu1–P1	113.68 (6)
S2–Cu1–P1	114.65 (7)	S3–Cu1–P1	123.33 (6)
C7–S1–C8	103.0 (3)	C9–S2–C10	102.3 (3)
C11–S3–C12	102.2 (4)	S1–C8–C9	116.1 (4)
C8–C9–S2	113.0 (4)	S2–C10–C11	112.8 (5)
C10–C11–S3	115.9 (4)	S3–C12–C1	109.4 (5)
C12–C1–C6	122.5 (7)	C1–C6–C7	123.4 (6)
C6–C7–S1	109.7 (4)		

Distances (Å) for Molecule 2			
Cu2–S4	2.300 (2)	Cu2–S5	2.356 (2)
Cu2–S6	2.282 (2)	Cu2–P2	2.222 (2)
S4–C32	1.824 (7)	S4–C33	1.806 (8)
S5–C34	1.817 (8)	S5–C35	1.822 (9)
S6–C36	1.817 (9)	S6–C37	1.827 (8)
P2–C50	1.813 (7)	P2–C44	1.806 (7)
P2–C38	1.821 (6)	C31–C32	1.50 (1)
C33–C34	1.49 (1)	C35–C36	1.49 (1)
C26–C37	1.50 (1)	C26–C27	1.39 (1)
C27–C28	1.36 (2)	C28–C29	1.33 (2)
C29–C30	1.39 (1)	C30–C31	1.37 (1)
C26–C31	1.39 (1)		

Angles (deg) for Molecule 2			
S4–Cu2–S5	92.82 (7)	S4–Cu2–S6	115.53 (7)
S5–Cu2–S6	93.46 (8)	S4–Cu2–P2	112.59 (7)
S5–Cu2–P2	120.31 (7)	S6–Cu2–P2	118.33 (7)
C32–S4–C33	102.1 (3)	C34–S5–C353	101.8 (4)
C36–S6–C37	103.8 (4)	S4–C33–C34	115.3 (5)
C33–C34–S5	112.2 (5)	S5–C35–C36	114.3 (6)
C35–C36–S6	116.8 (5)	S6–C37–C26	108.1 (5)
C37–C26–C31	123.0 (7)	C26–C31–C32	123.4 (7)
C31–C32–S4	108.4 (4)		

of an acetonitrile solution of the complex. Preliminary photography was consistent with a monoclinic crystal system. Observed extinctions were consistent with the space group $P2_1/c$. Intensity data ($\pm h, +k, +l$) were collected in one shell (4.5 < 2θ < 45°). A total of 4328 reflections were collected, and 2972 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The position of the Ag atom was determined by the conventional heavy-atom method. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of refinement, the silver, chlorine, sulfur, phosphorus, oxygen, and carbon atoms were assigned anisotropic thermal parameters. This resulted in $R = 0.0350$ and $R_w = 0.0459$ 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 0.46 e/Å^3 and was associated with the perchlorate anion. Selected atomic positional parameters are summarized in Table IV, and selected bond distances and angles are summarized in Table V. Complete listings of positional parameters (Table S-VI), non-essential bond distances and angles (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-XI) are deposited as supplementary material.

Results

Synthesis. The crown thioether 2,5,8-trithia[9]-o-benzenophane, TT[9]OB, can be prepared by two different synthetic routes. Both routes are one-step synthesis from commercially available starting materials and require minimal manipulation in workup. We previously reported[17] a yield of 21% from the reaction of the

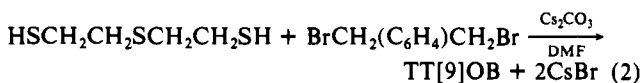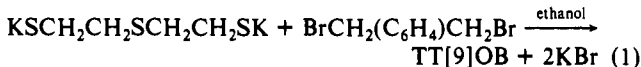**Table IV.** Selected Positional Parameters[a] for [Ag(PPh₃)(TT[9]OB)][ClO₄]

atom	x	y	z
Ag	9913.9 (5)	1903.6 (3)	0589.3 (2)
S1	8852 (2)	0965.4 (8)	1321.2 (6)
S2	12022 (2)	0722.0 (9)	0531.0 (6)
S3	12460 (2)	2659.9 (9)	1161.1 (7)
P	8074 (2)	2607.9 (8)	−0172.0 (5)
C1	10989 (6)	2671 (3)	2086 (2)
C2	10856 (8)	3505 (4)	2177 (2)
C3	9449 (9)	3827 (4)	2321 (2)
C4	8160 (8)	3332 (4)	2391 (3)
C5	8268 (7)	2512 (4)	2313 (2)
C6	9667 (6)	2167 (3)	2153 (2)
C7	9694 (7)	1248 (3)	2070 (2)
C8	9935 (11)	0046 (4)	1213 (3)
C9	11362 (9)	0005 (4)	1031 (4)
C10	13892 (7)	1137 (4)	0982 (3)
C11	14084 (7)	2043 (4)	0951 (3)
C12	12537 (7)	2364 (4)	1911 (2)
C13	6746 (6)	3321 (3)	0117 (2)
C19	6564 (6)	1977 (3)	−0657 (2)
C25	9180 (6)	3173 (3)	−0645 (2)

[a] Multiplied by 10⁴.

**Table V.** Selected Bond Distances and Angles for [Ag(PPh₃)(TT[9]OB)][ClO₄]

Distances (Å)			
Ag–S1	2.565 (1)	Ag–S2	2.600 (1)
Ag–S3	2.554 (2)	Ag–P	2.382 (1)
S1–C7	1.808 (5)	S1–C8	1.779 (6)
S2–C9	1.805 (7)	S2–C10	1.807 (6)
S3–C11	1.805 (6)	S3–C12	1.805 (6)
P–C13	1.807 (5)	P–C19	1.817 (5)
P–C25	1.809 (5)	C1–C2	1.378 (8)
C2–C3	1.365 (8)	C3–C4	1.360 (9)
C4–C5	1.350 (8)	C5–C6	1.387 (7)
C1–C6	1.389 (7)	C6–C7	1.506 (7)
C8–C9	1.320 (9)	C10–C11	1.484 (8)
C1–C12	1.489 (7)		

Angles (deg)			
S1–Ag–S2	84.49 (4)	S1–Ag–S3	106.55 (1)
S2–Ag–S3	84.41 (5)	S1–Ag–P	122.40 (5)
S2–Ag–P	129.97 (5)	S3–Ag–P	119.24 (5)
C7–S1–C8	104.2 (3)	C9–S2–C10	100.9 (4)
C11–S3–C12	103.3 (3)	C6–C1–C12	123.7 (5)
C1–C6–C7	122.5 (5)	S1–C7–C6	111.3 (3)
S1–C8–C9	125.9 (5)	C8–C9–S2	124.9 (5)
S2–C10–C11	115.2 (4)	S3–C11–C10	116.5 (4)
S3–C12–C1	108.0 (4)		

dipotassium salt of 3-thiapentane-1,5-dithiol and α,α'-dibromo-o-xylene (eq 1). However, the Cs⁺-mediated cyclization method of Buter and Kellogg[21] (eq 2), described in this paper, allows the preparation of TT[9]OB in 5–10-g quantities with yields of 90–95%.

$$KSCH_2CH_2SCH_2CH_2SK + BrCH_2(C_6H_4)CH_2Br \xrightarrow{\text{ethanol}} TT[9]OB + 2KBr \quad (1)$$

$$HSCH_2CH_2SCH_2CH_2SH + BrCH_2(C_6H_4)CH_2Br \xrightarrow[\text{DMF}]{Cs_2CO_3} TT[9]OB + 2CsBr \quad (2)$$

The Cu(I) complex [Cu(CH₃CN)(TT[9]OB)][ClO₄] was easily prepared by displacement of three labile acetonitrile ligands from [Cu(CH₃CN)₄][ClO₄]. This product is then ideal for the incorporation of other ancillary ligands through the further displacement of the remaining acetonitrile ligand. The addition of 1 equiv of an ancillary ligand (L = PR₃, C₅H₅N, RCN) resulted in essentially quantitative formation of the new adduct [Cu(L)(TT[9]OB)][ClO₄]. No side products resulted from the competition of L with TT[9]OB were evident from spectroscopic

(21) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481–4485.
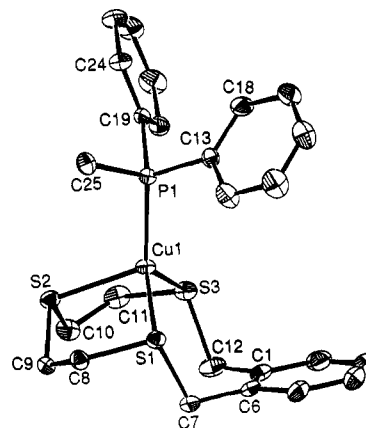
Figure 1. Perspective ORTEP drawing of the [Cu(PPh₂Me)(TT[9]OB]⁺ cation, molecule 1, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.
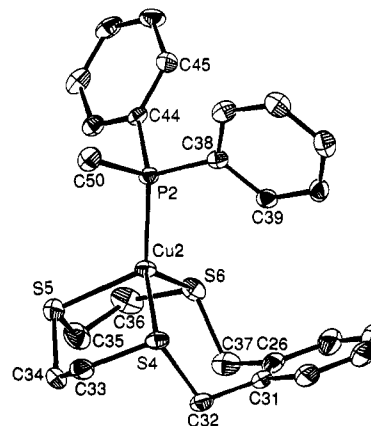
Figure 2. Perspective ORTEP drawing of the [Cu(PPh₂Me)(TT[9]OB)]⁺ cation, molecule 2, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

studies. For preparation of the Ag(I) complex [Ag(PPh₃)(TT-[9]OB)][ClO₄], the components AgClO₄, PPh₃, and TT[9]OB were simply mixed in a 1:1:1 ratio in acetonitrile and the complex was isolated directly from the reaction mixture.

X-ray Structure of [Cu(PPh₂Me)(TT[9]OB)]ClO₄]. The unit cell contains four [Cu(PPh₂Me)(TT[9]OB)]⁺ cations and four [ClO₄]⁻ anions such that the asymmetric unit contains two crystallographically independent cations and anions. Perspective views of the two [Cu(PPh₂Me)(TT[9]OB)]⁺ cations are shown in Figures 1 and 2. The two cations are geometric isomers by virtue of the rotational orientation of the PPh₂Me ligand. The basic molecular geometries are essentially identical, although some significant differences in bonding parameters are present. These differences are quite small and are attributed to subtle differences in the steric requirements of the two rotational isomers. Selected listings of interatomic distances and angles are found in Tables III and S-III (supplementary material).

The Cu(I) ion is in a tetrahedral geometry with three coordination sites occupied by facial coordination to the S atoms of the TT[9]OB ligand and the fourth site occupied by the P atom of the PPh₂Me ligand. The Cu–S distances involving the o-xylyl sulfur atoms S1, S3, S4, and S6 average 2.294 (7) Å, and the average Cu–S distance involving the central sulfur atoms S2 and S5 is 2.365 (9) Å. The S–Cu–S angles for the five-membered chelate rings average 92.9 (4)°, and S–Cu–S angles for the seven-membered chelate ring involving the o-xylyl fragment average 114.5 (10)°. The Cu–P distances average 2.228 (6) Å, and the average S–Cu–P angle is 117 (4)°. The S–C, P–C, and C–C bond distances are all within expected limits. The ClO₄⁻ anions have expected tetrahedral geometry although the variation in bond distances and angles and the large thermal parameters suggest some degree of disorder is likely.

Table VI. Structural Comparison (Å and deg) of TT[9]OB and TT[9]OB Complexes of Mo(0), Cu(I), and Ag(I)

compd	M–S2	M–S[a]	S–M–S[b]	S1–M–S3	S⋯S[c]	S1⋯S3	S–C–C–S
TT[9]OB[d]					4.39 (3)	5.76 (1)	162 (4)
TT[9]OB (MM)[d]					3.31	3.64	49.5
Mo(CO)₃L[d]	2.531 (2)	2.545 (1)	81.6 (4)	96.5 (1)	3.31 (2)	3.798 (2)	54 (3)
Cu(PPh₂Me)L⁺	2.365 (9)	2.294 (7)	92.9 (4)	114.5 (10)	3.376 (3)	3.386 (2)	55 (3)
Ag(PPh₃)L⁺	2.600 (1)	2.560 (6)	84.7 (2)	106.6 (1)	3.475 (11)	4.103 (2)	59.8 (6)

[a] Average of the M–S1 and M–S3 distances. [b] Average of the S1–M–S2 and S2–M–S3 angles. [c] Average of the S1⋯S2 and S2⋯S3 nonbonding distances. [d] Structural data are taken from ref 17. MM represents the molecular mechanics calculated geometry for an all endodentate conformation as described in ref 17.
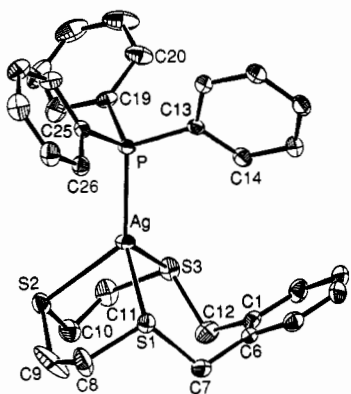

Figure 3. Perspective ORTEP drawing of the [Ag(PPh₃)(TT[9]OB)]⁺ cation, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

X-ray Structure of [Ag(PPh₃)(TT[9]OB)][ClO₄]. The unit cell contains four [Ag(PPh₃)(TT[9]OB)]⁺ cations and four [ClO₄]⁻ anions. A perspective view of the [Ag(PPh₃)(TT[9]OB)]⁺ cation is shown in Figure 3. Selected listings of interatomic distances and angles are found in Tables V and S-VII (supplementary material).

The Ag(I) ion is in a tetrahedral geometry with three coordination sites occupied by facial coordination to the S atoms of the TT[9]OB ligand and the fourth site occupied by the P atom of the PPh₃ ligand. The Ag–S distances are 2.565 (1) and 2.554 (1) Å for S1 and S3 and 2.600 (1) Å for the central S2 atom. The S–Ag–S angles for the five-membered chelate rings are 84.89 (4) and 84.41 (5)°, and the S–Ag–S angle for the seven-membered chelate ring involving the *o*-xylyl fragment is 106.55 (5)°. The Ag–P distance is 2.382 (1) Å, and the S–Ag–P angles average 124 (4)°. The S–C, P–C, and C–C bond distances are all within expected limits. The ClO₄⁻ anion has expected tetrahedral geometry, and the Cl–O bond distances and O–Cl–O angles are normal.

NMR Spectroscopy. The ¹H and ¹³C{¹H} NMR spectra of TT[9]OB show the characteristic pattern expected for *o*-xylyl substitution in the aromatic region and separate resonances due to benzylic CH₂ groups and SCH₂CH₂S chains. The only feature of note is the AA′BB′ pattern observed for the –SCH₂CH₂SCH₂CH₂S– linkage in the ¹H NMR spectrum. This is probably due to retention of the exododentate conformation and –SCH₂CH₂SCH₂CH₂S– bracket formation, which is observed in the solid state.[17] The S–C–C–S torsional angles estimated from calculated coupling constants[22] ($^2J_{HH}$ = 8.7 and 6.0 Hz) are comparable to those observed in the solid-state structure and are consistent with a significant (ca. 15°) distortion from an anti conformation.[17] We have obtained similar ¹H NMR spectra for other rigid crown thioethers in which the SCH₂CH₂SCH₂CH₂S bracket has been identified in the solid state.[23]

The ¹H NMR spectra of the [M(L)(TT[9]OB)]⁺ cations (M = Cu, L = PPh₂Me, PPh₃, pyridine, C₆H₅CN; M = Ag, L = PPh₃) show the same general features as the free TT[9]OB ligand.
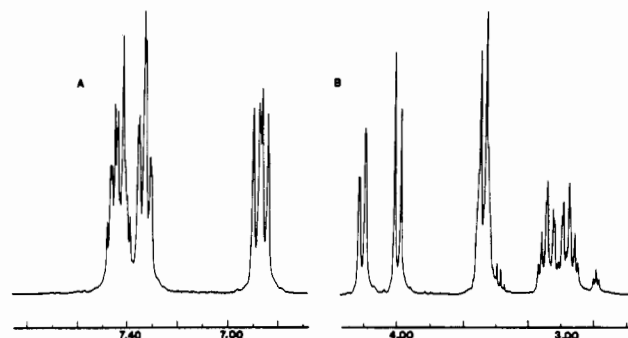

Figure 4. ¹H NMR spectrum of [Cu(PPh₂Me)(TT[9]OB)][ClO₄] in CD₃CN at 235 K: (A) aromatic resonances; (B) benzylic and –SCH₂CH₂SCH₂CH₂S– resonances.

The major differences are that the AA′BB′ pattern associated with the SCH₂CH₂S portion of the molecule has separated into two distinct multiplets and the benzylic protons are inequivalent due to the adoption of axial and equatorial positions in the seven-membered chelate ring. In the room-temperature spectra, these features are all broadened slightly due to ligand lability and ⁶³Cu quadrupole contributions in the case of the Cu(I) complexes. However, at lower temperatures well-resolved spectra are observed and most couplings can be resolved.

One interesting feature is the observation of additional splitting of the downfield benzylic protons when the ancillary ligand is PPh₂Me or PPh₃. For example, in the complex [Cu(PPh₃)(TT-[9]OB)]⁺ axial and equatorial benzylic protons couple to produce a pair of doublets ($^2J_{HH}$ = 11.3 Hz), but the downfield signals are split further, producing a doublet of doublets for these protons (Figure 4). The source of this extra feature is found in the aromatic portion of the spectrum. The splitting is a result of π contributions to coupling ($^4J_{HH}$) between benzylic and aromatic protons of the TT[9]OB ligand. The magnitude of this long-range coupling can be estimated from the ESR hyperfine coupling constants and is proportional to $\cos^2 \theta$, where θ is the torsional angle between the benzylic proton and the p orbitals of the unsaturated system.[24] The dependence on the $\cos^2$ term results in large π contributions when θ approaches 0 or 180° and negligible contributions when θ approaches 90 or 270°. It can then be concluded that the downfield benzylic resonances are due to the axial protons. The observed values of $^4J_{HH}$ (2.2 Hz) compare well to ^4J values found for similar basic structures[24] and may be useful in the assignment of this coordination mode for the TT[9]OB ligand. The fact that similar splittings are not observed for the complexes in which L = pyridine, acetonitrile, or benzonitrile may simply indicate that resolution is not possible due to nitrogen, quadrupolar relaxation effects.

Discussion

The structural studies of [Cu(PPh₂Me)(TT[9]OB)]⁺ and [Ag(PPh₃)(TT[9]OB)]⁺, described herein, confirm the potentially tridentate thioether ligand TT[9]OB is capable of adopting a facial coordination mode in a tetrahedral geometry. The use of Ag(I), in addition to Cu(I), allows determination of the conformational effects of varying metal ion size, as the Ag⁺ ion is considerably larger than the Cu⁺ ion. Ag(I) is also known to have weak

(22) Jackman, L. M.; Sternhell, S. In *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Barton, D. H. R., Doering, W., Eds.; Pergamon: Oxford, England, 1969; pp 280–301.
(23) de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1989**, *28*, 3573–3578.

(24) Günther, H. *NMR Spectroscopy*; John Wiley & Sons: New York, 1985.

stereochemical demands[3] so the Ag(I) complex of TT[9]OB shows a conformation for TT[9]OB that is dominated by the conformational requirements of the ligand rather than a conformation enforced by the bonding demands of the metal.

Table VI compares some of the ligand and metal–ligand bonding parameters for TT[9]OB (X-ray and molecular mechanics structures) and the complexes Mo(CO)₃(TT[9]OB, [Ag-(PPh₃)(TT[9]OB)]⁺, and [Cu(PPh₂Me)(TT[9]OB)]⁺. As we have noted previously,[17] TTOB must convert from the exodentate form, observed in the X-ray structure of the free ligand, to the endodentate form, in order for facial coordination to be possible. Thus, the large differences in the parameters for free and coordinated TT[9]OB reflect this change. The differences in the coordinated conformations of TT[9]OB are primarily due to (1) the metal geometry, octahedral for Mo(0) and tetrahedral for Cu(I) and Ag(I), and (2) the size of the metal ion, Ag(I) > Mo(0) > Cu(I).

The most interesting and widely varying parameters are those associated with the *o*-xylyl fragment, the S1–M–S3 bond angle and the S1⋯S3 distance. These values provide a measure of the conformational flexibility of TT[9]OB. For example, the seven-membered chelate ring that contains the *o*-xylyl fragment shows "bite" angles of 96.5 (1)° for Mo(0) in octahedral geometry and 106.5 (1) and 114.5 (10)° for Ag(I) and Cu(I) in tetrahedral geometry. Thus, while the other five-membered chelate rings are relatively limited in their ability to adapt to different coordination environments, the larger *o*-xylyl-containing ring appears to be capable of providing any flexibility required for adaptation to a particular geometry or ion size.

The coordination of TT[9]OB to Cu(I) and Ag(I) yields only monomeric, tetrahedral products of the general formula [M-(L)(TT[9]OB)]⁺, in which the TT[9]OB ligand is coordinated facially to the metal center. This differs slightly from what is found for the coordination of 9S3 with these metals and is significantly different from what is observed for similar crown thioether ligands such as 12S3.

12S3, like TT[9]OB, has an exodentate conformation in the free ligand and must convert all three exodentate sulfur donors to endodentate in order to coordinate to a single metal ion. Although 12S3 has been shown to be capable of attaining this coordination mode, in the case of Ag(I), 12S3 retains the exodentate conformation found for the free ligand and coordinates via three exodentate sulfur atoms to three different Ag(I) centers producing an oligomeric structure. This is very different from what is observed for TT[9]OB. Although TT[9]OB has an exodentate conformation for the free ligand, the ligand converts to an endodentate conformation in bonding to Cu(I) and Ag(I).

For 9S3, the product formed in the reaction of [Cu-(CH₃CN)₄][X] with 9S3 depends critically on the nature of the anion X. If X is I⁻, PF₆⁻, BF₄⁻, or ClO₄⁻, the products formed are [Cu(I)(9S3)],[11] [Cu(9S3)₂][PF₆],[4] [Cu₂(9S3)₃][BF₄],[4] and [Cu₃(9S3)₃][ClO₄],[11] respectively. Only in the case of the soft anion I⁻ was a simple species of the formula [Cu(9S3)(L)] found. The difference between this behavior for 9S3 and what we observe for TT[9]OB is that, at least in the case of CH₃CN as the ancillary ligand, the formation of a secondary M–S bond to an adjacent [M(9S3)]⁺ (M = Cu, Ag) fragment is favored over the stabilization of the simple [M(9S3)(CH₃CN)]⁺ adduct. Whereas, for TT[9]OB, we find that the [M(TT[9]OB)(L)]⁺ fragment is stable with simple ancillary ligands such as CH₃CN. This is likely a sterically related phenomenon, since the larger [M(TT[9]OB)]⁺ fragment may be too hindered to allow the type of aggregation observed for [M(9S3)]⁺.

Summary and Conclusion

The chemistry of TT[9]OB emphasizes the role of ligand conformation in determining coordination chemistry. Although the conformation of the free ligand has all of the sulfur donor atoms exodentate to the ring, detailed analysis of structural parameters (X-ray and molecular mechanics) showed that significant strain was inherent in this conformation and that rearrangement to an endodentate conformation might be facile.[17] For example, the coordination chemistry of 9S3 has been attributed to its conformational predisposition to chelation[3] and it has been stated that the driving force behind the formation of complexes such as [Ag(9S3)(I)] originates in the unique conformation of the nine-membered ring. Also, the square, exodentate conformation found for 12S3 has been viewed as a deterrent to chelation. The coordination chemistry of TT[9]OB is therefore an intermediate case for crown thioether ligands, since the free ligand exodentate conformation resembles 12S3 but the facial coordination to Mo(0), Cu(I), and Ag(I) resembles 9S3. Further studies in our laboratories are underway to determine whether TT[9]OB is capable of producing some of the unique reaction and redox chemistry found for complexes of 9S3.