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Article

Metallomacrocycles Incorporating a Hemilabile Tröger’s Base Derived Ligand

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Tröger’s base, a chiral molecule with a rigid 90° backbone, has been incorporated into a novel hemilabile phosphinoalkyl thioether ligand. Using the Weak Link Approach, this ligand has been reacted with $Cu(CH_3CN)_4PF_6$ and $[Rh(COE)_2Cl]_x$ (COE = cyclooctene) to form metallomacrocycles. Upon reaction of the ligand with Cu^I, which prefers a tetrahedral coordination geometry, a bimetallic macrocycle was formed. Alternatively, owing to the steric restrictions imposed by the 90° backbone of the ligand and the square-planar geometry of Rh^I, when the ligand was reacted with $[Rh(COE)_2Cl]_x$, the formation of bimetallic closed macrocycles was not observed, and instead a mixture of tri- and tetrametallic closed macrocycles is formed. Introducing pyridine to the Cu^I complex causes the weak thioether–Cu bonds to break, generating a large bimetallic open macrocycle. Upon reaction of the mixture of Rh^I metallomacrocycles with CO and Cl^-, the cyclic structure of these complexes becomes flexible enough that the dimeric bimetallic macrocycle forms, along with tri- and tetrameric open complexes. The mixture of differently sized Rh^I macrocyclic complexes has been analyzed using gel permeation chromatography, and the tetramer has been characterized by a single-crystal X-ray diffraction study. These are the first examples of metallomacrocycles containing a Tröger’s base derivative.

Introduction

Tröger’s base, first synthesized by Julius Tröger in 1887,[1] has gained steady interest in recent years because of its C_2 symmetry, chirality, and rigid concave shape (Figure 1). Analogues of this molecule have been used in the fields of catalysis,[2,3] molecular recognition,[4-10] and bioorganic chemistry.[11-13] The synthetic routes to analogues of Tröger’s base have been limited because of the harsh conditions of the acid-promoted condensation reaction between aniline and formaldehyde. Despite these limitations, some progress has been made in developing organic derivatives of Tröger’s base.[13-23] In the field of coordination chemistry, very few

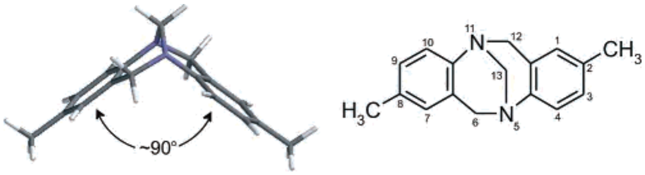

Figure 1. Optimized geometry and structural formula of Tröger’s base.

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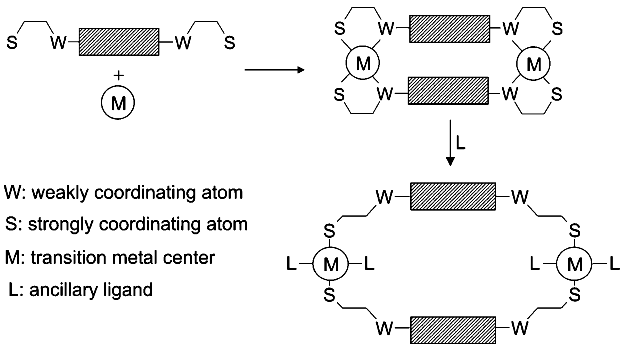

Figure 2. Weak Link Approach.

examples of Tröger's base containing molecules with transition metals have been reported, and among those, none are metallomacrocycles.[3,24−27]

The Weak Link Approach to metallomacrocycle synthesis typically leads to bimetallic macrocycles when a flexible, organic hemilabile ligand is combined in a one-to-one ratio with a monomeric late-transition-metal source (Figure 2).[28] The hemilabile ligands used contain both a strong binding phosphine moiety and a weaker binding atom, such as oxygen, sulfur, or nitrogen.[28−30] Upon addition to a transition-metal precursor, the ligand reacts in a one-to-one fashion with the transition metal to create a condensed intermediate species. This condensed intermediate, or closed macrocycle, can then be opened to create a large flexible macrocycle by selectively cleaving the bond between the metal and the weaker binding moiety in the ligand with a stronger binding ancillary ligand (i.e., CO/Cl^-). This approach has been effective for a variety of metals and ligands.[28,31−37] Most recently, the Weak Link Approach has been used to create novel allosteric catalysts that mimic the properties of ELISA detection systems by incorporation of a salen catalyst into the ligand backbone.[38−40]

The ability to synthesize large supramolecular complexes with tunable cavity dimensions is critical for fully exploring and utilizing them for host−guest chemistry and shape-selective catalysis. The generality of the Weak Link Approach makes it an ideal synthetic method to study the possible incorporation of a Tröger's base functionality into a metallomacrocycle. A fundamental issue with generating large metallomacrocyclic structures pertains to the incorporation of rigid ligands such as Tröger's base. Owing to the nearly right angle formed by the backbone of Tröger's base analogues (88.6−104.1°),[41] we hypothesized that when combined with a transition-metal center, a hemilabile ligand derived from Tröger's base may generate macrocycles of interesting geometries and higher ordered structures such as tetramers. Herein we report the facile synthesis of bimetallic Cu^I and bi-, tri-, and tetrametallic Rh^I macrocycles with backbones comprised of Tröger's base analogues.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in reagent-grade solvents, using standard Schlenk techniques or an inert-atmosphere glovebox at room temperature.[42] All other solvents were purified by published methods.[43] Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. 2,8-Dibromo-4,-10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*]diazocine (2,8-dibromo-DMDD, **2**) and $[Rh(COE)_2Cl]_x$ (COE = cyclooctene) were prepared according to literature methods.[14,44] All other chemicals were obtained from commercial sources and used as received unless otherwise noted.

Physical Measurements. ^1H NMR spectra were recorded on a Varian Mercury 300-MHz Fourier transform (FT-) NMR spectrometer and referenced relative to residual proton resonances in $CDCl_3$ or CD_2Cl_2. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300-MHz FT-NMR spectrometer at 121.4 MHz and referenced relative to an external 85% H_3PO_4 standard. All chemical shifts are reported in ppm. FT-IR spectra were obtained in solution

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with a Thermo Nicolet Nexus 670 FT-IR with NaCl cells with 0.1-mm spacers. Gel permeation chromatography (GPC) experiments were carried out on an automated Agilent 1100 series high-performance liquid chromatograph equipped with a multiwavelength detector. Samples were run in CH_2Cl_2 and monitored at 254 nm. The column used was a Phenomenex Phenogel 500-Å column packed in CH_2Cl_2 with a 7.80-mm inner diameter and 300-mm length (flow rate = 1 mL/min). Electrospray mass spectrometry (ESMS) spectra were recorded on a Micromass Quatro II triple-quadrapole mass spectrometer or a Micromass Q-Tof Ultima mass spectrometer. Electron ionization MS (EIMS) spectra were recorded on a Fisions VG 70-250 SE mass spectrometer. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

Synthesis of 2,8-Bis[2-(diphenylphosphino)ethylthio]DMDD (4). *t*-BuLi (1.7 M) in hexane (3.23 mL, 5.39 mmol) was added dropwise over 10 min to a stirred solution of **2** (0.50 g, 1.22 mmol) in THF (50 mL) at −78 °C. After 5 min of stirring, sulfur (0.117 g, 3.68 mmol) was added swiftly and the reaction mixture was allowed to reach room temperature and left to stir for 2 h. The solvent was removed in vacuo, leaving a yellow solid. (1-Chloroethyl)diphenylphosphine (0.61 g, 2.45 mmol), Cs_2CO_3 (0.079 g, 0.245 mmol), and CH_3CN (50 mL) were then added to the reaction mixture. After refluxing overnight, the solvent was removed under reduced pressure. The remaining beige solid was dissolved in CH_2Cl_2 and filtered through a short pad of Celite to remove all inorganics. Upon removal of CH_2Cl_2, the beige solid was recrystallized from CH_3CN. The resulting solid was then purified by column chromatography on silica using ethyl acetate/hexanes (1:4) as the eluent. The product was isolated as a white solid in 36% yield. ^{1}H NMR ($CDCl_3$): δ 2.27−2.39 (m, 10H, C*H*$_3$, C*H*$_2$P), 2.82−2.89 (m, 4H, C*H*$_2$S), 3.85 (d, 2H, *J* = 17.1 Hz, H-6 and H-12), 4.24 (s, 2H, H-13), 4.47 (d, 2H, *J* = 17.1 Hz, H-6 and H-12), 6.63 (s, 2H, H-1 and H-7), 6.96 (s, 2H, H-3 and H-9), 7.26−7.34 (br m, 20H, Ph-*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.6 (s). EIMS: [M] calcd, *m/z* 738.2; expt, *m/z* 737.4. Elem anal. Calcd for $C_{45}H_{44}N_2P_2S_2$: C, 73.15; H, 6.00; N, 3.79. Found: C, 72.75; H, 5.70; N, 3.74.

Synthesis of [(2,8-Bis[2-(diphenylphosphino)ethylthio]DMDD)$_2$Cu$_2$][PF$_6$]$_2$ (5). A CH_2Cl_2 solution (30 mL) of $Cu(CH_3CN)_4PF_6$ (50 mg, 0.13 mmol) was added to a CH_2Cl_2 solution (30 mL) of **4** (99 mg, 0.13 mmol), and the resulting solution was allowed to stir for 2 h at room temperature. The solvent was removed in vacuo to yield a white solid. The solid was recrystallized from CH_2Cl_2 and Et_2O, giving a white solid in 93% yield. ^{1}H NMR (CD_2Cl_2): δ 2.08 (s, 12H, C*H*$_3$), 2.60 (br m, 8H, C*H*$_2$P), 3.13 (br m, 8H, C*H*$_2$S), 3.63 (br m, 4H, H-6 and H-12), 4.07 (s, 4H, H-13), 4.27 (br m, 4H, H-6 and H-12), 6.73 (br, 4H, H-1 and H-7), 6.87 (br, 4H, H-3 and H-9), 7.01−7.63 (br m, 40H, Ph-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −0.51 (s), −143.2 (sept, PF_6). EIMS: $[M - 2PF_6]^{2+}$ calcd, *m/z* 802.4; expt, *m/z* 802.1. Elem anal. Calcd for $C_{90}H_{88}N_4P_4S_4Cu_2P_2F_{12}$: C, 57.05; H, 4.68; N, 2.96. Found: C, 56.36; H, 4.56; N, 2.85. GPC retention time: 7.76 min.

Synthesis of [2,8-Bis[2-(diphenylphosphino)ethylthio]DMDD)$_n$Rh$_n$][BArF]$_n$ [BArF = Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; 6 (*n* = 4) and 7 (*n* = 3)]. $[Rh(COE)_2Cl]_x$ (100 mg, 0.28 mmol) and NaBArF (248 mg, 0.28 mmol) were added to CH_2Cl_2 (10 mL), and the resulting solution was allowed to stir for 5 min. A solution of **4** (207 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) was then added dropwise over 5 min, and the reaction continued to stir for 2 h at room temperature. The solvent was removed in vacuo to yield a yellow-orange oily solid. The solid was dissolved in Et_2O (15 mL), and the solution was passed through Celite to remove all NaCl. Upon removal of Et_2O, the solid was recrystallized from CH_2Cl_2 and hexanes, giving an orange solid in 88% yield as a mixture of tetra- and trimeric complexes. ^{1}H NMR (CD_2Cl_2): δ 2.05−2.68 (br m, C*H*$_3$, C*H*$_2$S, C*H*$_2$P), 3.80 (br m, H-6 and H-12), 4.16 (s, H-13), 4.51 (br m, H-6 and H-12), 6.89 (s, H-1 and H-7), 7.01 (s, H-3 and H-9), 7.06−7.48 (br m, Ph-*H*), 7.57 (s, BArF$^-$-*H*), 7.75 (s, BArF$^-$-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 64.8 (d, $J_{\mathrm{Rh-P}}$ = 163.0 Hz), 67.0 (d, $J_{\mathrm{Rh-P}}$ = 160.5 Hz). EIMS for **6**: $[M - 3BArF]^{3+}$ calcd, *m/z* 1410.3; expt, *m/z* 1409.9; $[M - 4BArF]^{4+}$ calcd, *m/z* 841.9; expt, *m/z* 841.6. EIMS for **7**: $[M - 2BArF]^{2+}$ calcd, *m/z* 1694.5; expt, *m/z* 1694.3; $[M - 3BArF]^{3+}$ calcd, *m/z* 841.9; expt, *m/z* 841.6. Elem anal. Calcd for $(C_{77}H_{56}BF_{24}N_2P_2RhS_2)_n$ (*n* = 3 or 4): C, 54.22; H, 3.31; N, 1.64. Found: C, 54.23; H, 3.05; N, 1.68. GPC retention time: 6.33 min (**6**), 8.57 min (**7**). Crystals of **6**·9CH_2Cl_2 were grown by layering of pentane over a dilute solution of a mixture of **6** and **7** in CH_2Cl_2 at room temperature.

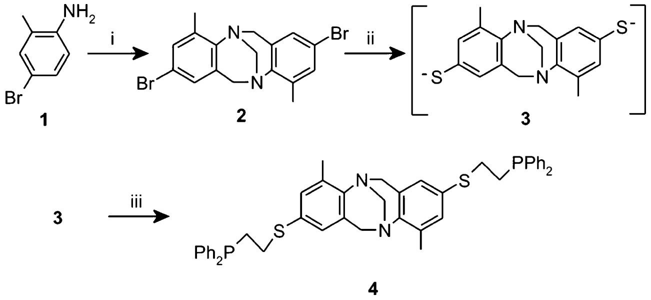
Synthesis of [(2,8-Bis[2-(diphenylphosphino)ethylthio]DMDD)$_2$Cu$_2$(pyridine)$_4$][PF$_6$]$_2$ (8). Pyridine (11 μL, 0.141 mmol, 4 equiv) was added via syringe to a stirring CH_2Cl_2 solution (3 mL) of **5** (67 mg, 0.035 mmol). The solution was allowed to stir for 1 h at room temperature. The solvent was removed in vacuo to yield a white solid in 92% yield. ^{1}H NMR (CD_2Cl_2): δ 2.10 (s, 12H, C*H*$_3$), 2.44 (br m, 8H, C*H*$_2$P), 2.88 (br m, 8H, C*H*$_2$S), 3.66 (d, 4H, *J* = 16.8 Hz, H-6 and H-12), 4.09 (s, 4H, H-13), 4.34 (d, 4H, *J* = 17.1 Hz, H-6 and H-12), 6.62 (br, 4H, H-1 and H-7), 6.80 (br, 4H, H-3 and H-9), 6.93−7.58 (br m, 48H, Ph-*H*, pyr), 7.73 (t, 4H, *J* = 5.7 Hz, pyr), 8.47 (d, 8H, *J* = 4.2 Hz, pyr). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −4.8 (s), −143.2 (sept, PF_6). EIMS: $[M - 4(\text{pyridine}) - PF_6]^+$ calcd, *m/z* 1749.9; expt, *m/z* 1749.4; $[M - 4(\text{pyridine}) - 2PF_6]^{2+}$ calcd, *m/z* 802.4; expt, *m/z* 802.1. Elem anal. Calcd for $C_{110}H_{108}N_6P_2S_2Cu_2P_2F_{12}\cdot CH_2Cl_2$: C, 58.06; H, 4.83; N, 4.88. Found: C, 58.31; H, 4.41; N, 3.82. GPC retention time: 7.66 min.

Synthesis of (2,8-Bis[2-(diphenylphosphino)ethylthio]DMDD)$_n$Rh$_n$Cl$_n$(CO)$_n$ [9 (*n* = 4), 10 (*n* = 3), and 11 (*n* = 2)]. An air-free NMR tube containing a solution of the mixture of **6** and **7** (30 mg, 8.7 μmol) and benzyltriethylammonium chloride (3.9 mg, 17.4 μmol) in CD_2Cl_2 (1 mL) was charged with CO (1 atm) at room temperature. The orange solution immediately turned yellow, giving the products **9**−**11** in quantitative yield as a mixture of tetra-, tri-, and dimeric complexes. ^{1}H NMR (CD_2Cl_2): δ 2.21 (br m, C*H*$_2$P), 2.39 (s, C*H*$_3$), 2.64 (br m, C*H*$_2$S), 3.94 (d, *J* = 16.2 Hz, H-6 and H-12), 4.34 (s, H-13), 4.51 (d, *J* = 16.8 Hz, H-6 and H-12), 6.94 (s, H-1 and H-7), 7.18 (s, H-3 and H-9), 7.27−7.57 (br m, Ph-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.45 (d, $J_{\mathrm{Rh-P}}$ = 123.2 Hz), 22.78 (d, $J_{\mathrm{Rh-P}}$ = 125.2 Hz), 24.75 (d, $J_{\mathrm{Rh-P}}$ = 124.5 Hz). EIMS for **11**: $[M - 2Cl]^{2+}$ calcd, *m/z* 869.1; expt, *m/z* 869.1. FT-IR: ν(CO) 1973 cm^{-1}. GPC retention time: 5.96 min (**9**), 8.42 min (**10**), 11.00 min (**11**).

Results

Ligand Synthesis. Wärnmark discovered that halogen-substituted anilines, such as **1**, could undergo the Tröger's base condensation reaction using paraformaldehyde and trifluoroacetic acid (TFA).[14] Accordingly, we synthesized the dibromo derivative of Tröger's base, **2**, following his protocol (Scheme 1). Upon reaction of the dibromide precursor with *t*-BuLi, the dilithiated product was formed, which was then quenched with elemental sulfur. Without isolating dithiolate **3**, (1-chloroethyl)diphenylphosphine and a small amount of base were added to the reaction mixture to yield the targeted ligand. Attempts to improve the yield of this reaction by protonating the dithiolate, **3**, and isolating the dithiol prior

Scheme 1. Synthesis of **4**[a]



[a] (i) $(CH_2O)_n$, TFA, rt; (ii) 4.4 equiv of *t*-BuLi, 3 equiv of S_8, THF, −78 °C; (iii) 2 equiv of $Cl(CH_2)_2PPh_2$, 0.2 equiv of Cs_2CO_3, CH_3CN, reflux.

to the addition of (1-chloroethyl)diphenylphosphine were unsuccessful. Owing to the near overlap in pK_a's of tertiary arylammonium salts (approximate pK_a relative to water: 3−5) and thiophenols (pK_a: 6−8), an acid with suitable strength to protonate the thiolate but not the amine could not be found.[45] Use of a stoichiometric amount of acetic acid allowed for the isolation of a small of amount of the dithiol (protonated **3**) but also resulted in protonation of the amine, leaving a large amount of the ammonium salt trapped in the water layer during extraction. Ligand **4**, which was isolated in 36% yield, is a mildly air-sensitive white solid, which has been characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies, MS, and elemental analysis. All data are consistent with its assigned structure.

Synthesis of Condensed Intermediates 5−7. The use of two metals with different preferred coordination geometries (tetrahedral for Cu^I and square planar for Rh^I) results in the formation of different condensed intermediates when monomeric sources of these metals are independently combined with ligand **4**. The condensed intermediate **5** was formed upon reaction of $Cu(CH_3CN)_4PF_6$ and ligand **4** (Scheme 2).

The CH_3CN ligands on the Cu^I starting material were replaced with the chelating phosphine/thioether moieties of **4**, resulting in quantitative formation of **5**. The product formed solely as a bimetallic macrocycle and has been fully characterized in solution by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies, MS, GPC, and elemental analysis.

Condensed intermediates **6** and **7** were formed by first combining $[Rh(COE)_2Cl]_x$ and NaBArF in a CH_2Cl_2 solution (Scheme 3).

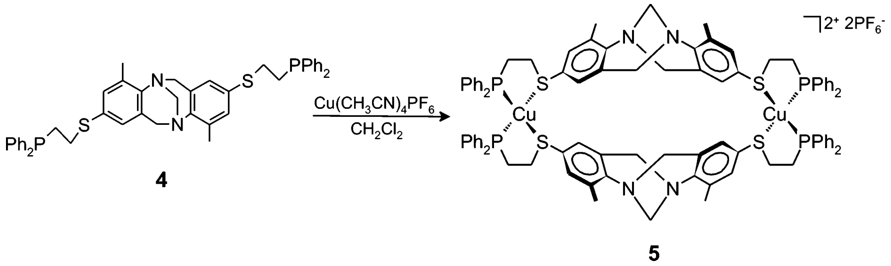
After abstraction of the chlorides on the Rh^I center with NaBArF, ligand **4** was slowly added to the reaction mixture, which resulted in the displacement of the COE ligands by the phosphine/thioether portions of **4**. A mixture of two differently sized condensed intermediates, a tetramer (**6**) and a trimer (**7**), formed as evidenced by ^{31}P{^{1}H} NMR, MS, and GPC. We were unable to separate this mixture on the preparative scale using GPC. However, the mixture has been fully characterized in solution (see the Experimental Section), and the tetrametallic condensed intermediate, **6**, has been characterized in the solid state by a single-crystal X-ray diffraction study (Figure 3 and Table 1). Attempts to change the ratio of the products in this mixture or to drive the reaction toward one product by heating resulted in no change in the distribution of products, indicating they are not involved in a dynamic equilibrium, even at 80 °C in dichloroethane.

Solid-State Characterization of Tetrametallic Complex 6·9CH$_2$Cl$_2$. Various attempts were made to crystallize **6** and **7** with different solvent systems, dilutions, and temperatures. Unfortunately, these attempts yielded only an oily substance, which fell out of solution. However, upon changing the counterion from BArF$^-$ to BF_4^-, yellow single crystals of **6**·$9CH_2Cl_2$ were grown under a variety of solvent conditions. The X-ray-quality crystal used in the diffraction study came from a CH_2Cl_2 solution of the mixture of **6** and **7** layered with pentane.

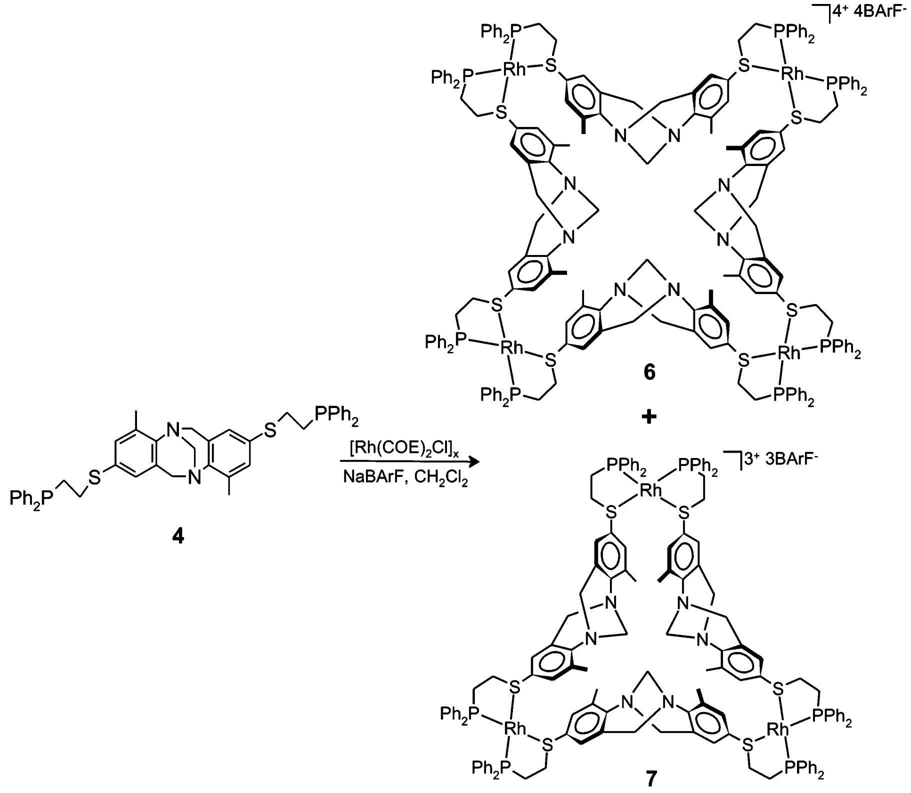
Crystals of compound **6**·$9CH_2Cl_2$ were of marginal quality, but one suitable for study was mounted on a Cryoloop with paratone-N oil. Data were collected at −173 °C on a Bruker SMART APEX system with Mo Kα radiation. Data were corrected for absorption using *SADABS*. The structure was solved by direct methods and refined by successive Fourier least squares on F^2. All phenyl rings were refined as rigid hexagons and carbon atoms C6, C7, C8, C9, and C12, as well as boron atom B2 and fluorine atoms F5, F6, F7, and F8, were refined isotropically. The bond distances B2−F5, B2−F6, B2−F7, and B2−F8 and the six intrafluorine distances F5−F6, F5−F7, F5−F8, F6−F7, F6−F8, and F7−F8 were fixed at 1.38 and 2.26 Å, respectively. All other non-hydrogen atoms were refined anisotropically. To account for the unresolved CH_2Cl_2 solvent, the program *SQUEEZE* (*PLATON*) was used. After the use of *SQUEEZE*, initial R1 and wR2 values of 24.20 and 58.89 were reduced to 9.53 and 27.95. These large R1 and wR2 values are most likely due to the poor crystalline quality of the sample. The nine CH_2Cl_2 solvent molecules were found only in the solved structure of the crystal. Neither solution data nor elemental analysis of the solid shows evidence for CH_2Cl_2 molecules trapped in the void space of the molecule.

Unlike other tetrametallic macrocycles formed via the Weak Link Approach,[46,47] the structure of **6**·$9CH_2Cl_2$ does not have a square-shaped void space. While the square-planar

Scheme 2



Scheme 3



coordination geometry is maintained about the Rh^I atoms, the complex forms a crosslike structure. The average Rh−Rh distance along the diagonal is 18.5 Å, and from corner to corner, it is 13.1 Å. The angle of the Tröger's base backbone, 94°, falls within the expected range for analogues of Tröger's base.[41] The structure also illustrates that, in the solid state, each macrocycle is equally comprised of both the *R,R* and *S,S* enantiomers of the Tröger's base ligand.

Synthesis of Open Macrocycles 8−11. The open cationic Cu^I macrocycle, **8**, was synthesized by the addition of a stoichiometric amount of pyridine (4 equiv) to a CH_2Cl_2 solution of **5** (Scheme 4).

The complex remained a dimeric macrocycle and formed in quantitative yield. Complex **5** has been fully characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies, GPC, and elemental

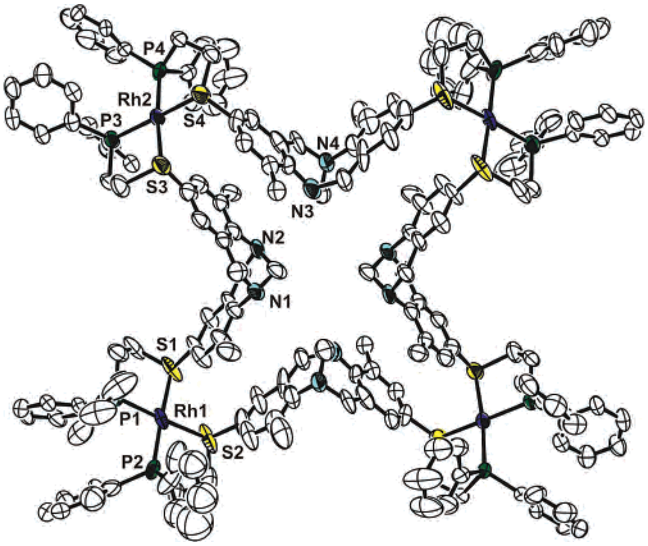


Figure 3. ORTEP drawing of $\mathbf{6}\cdot 9CH_2Cl_2$, (2,8-bis[2-(diphenylphosphino)-ethylthio]DMDD)$_4$Rh$_4$[BF$_4$]$_4$, showing the labeling scheme of selected atoms. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

Table 1. Crystal Data and Structural Refinement for $\mathbf{6}\cdot 9CH_2Cl_2$

empirical formula	$C_{189}H_{194}B_4Cl_{18}F_{16}N_8P_8Rh_4S_8$
formula weight	4478.74
temperature	100(2) K
wavelength	0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimensions	$a = 14.1695(10)$ Å, $\alpha = 78.0130(10)°$ $b = 16.0351(11)$ Å, $\beta = 76.9800(10)°$ $c = 23.1750(15)$ Å, $\gamma = 81.4300(10)°$
volume	4989.4(6) Å^3
Z	1
density (calculated)	1.491 Mg/m^3
abs coeff	0.782 mm^{-1}
F(000)	2282
crystal color, habit	yellow, block
cryst size	0.40 × 0.30 × 0.20 mm^3
θ range for data collection	0.92−24.00°
index ranges	$-16 \le h \le 16$, $-18 \le k \le 18$, $-26 \le l \le 26$
reflns collected	33 358
independent reflns	15 579 [*R*(int) = 0.0263]
completeness to $\theta = 24.00°$	99.4%
abs correction	none
max and min transmn	0.8593 and 0.7451
refinement method	full-matrix least squares on F^2
data/restraints/param	15 579/10/855
GOF on F^2	1.064
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0954, wR2 = 0.2792
R indices (all data)	R1 = 0.1137, wR2 = 0.2980
largest diff peak and hole	+3.229 and −0.955 e/Å^3

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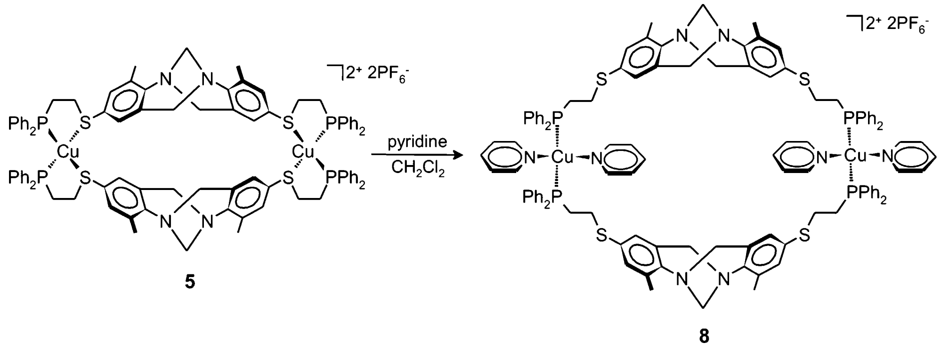
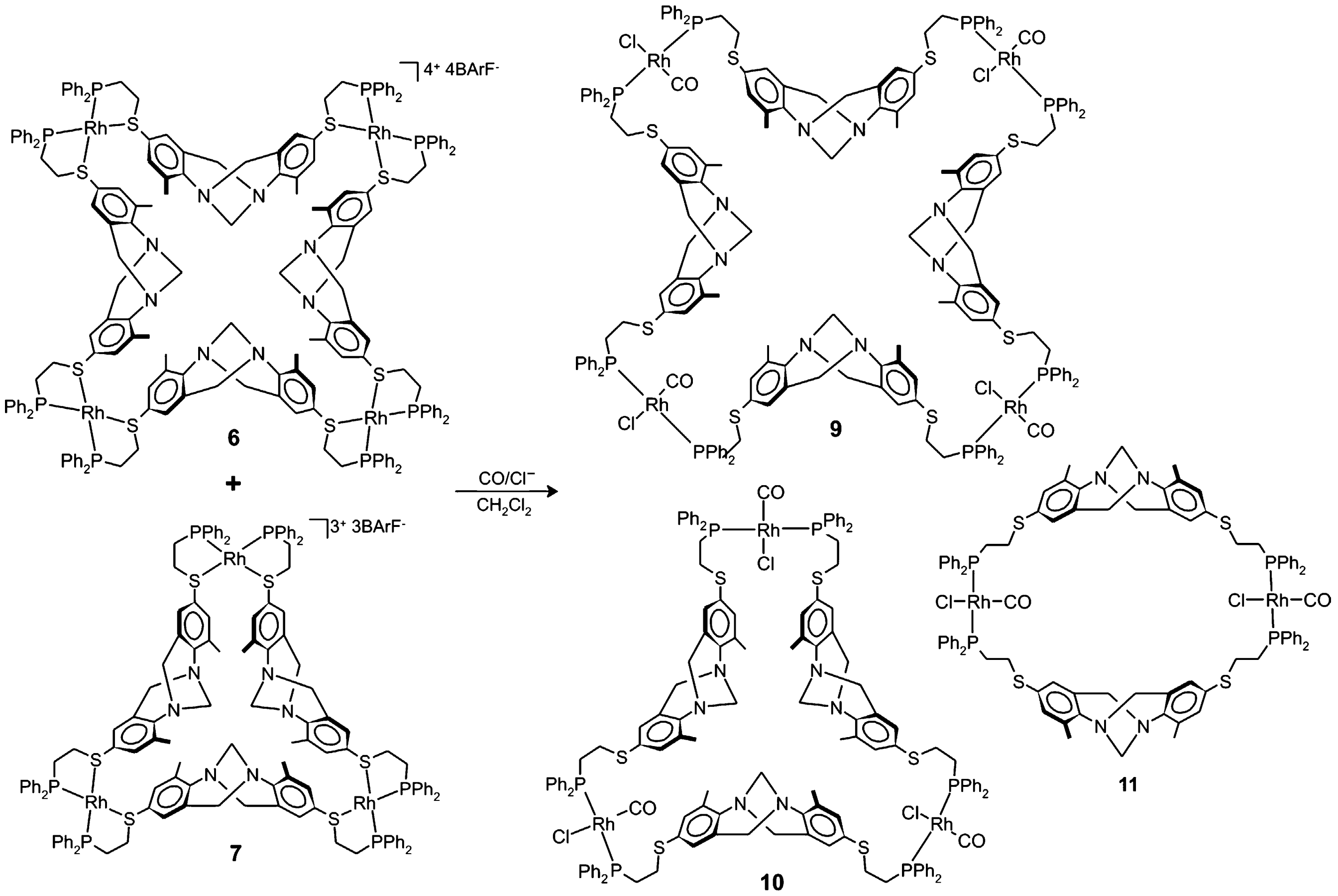
(45) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed.; John Wiley & Sons: New York, 2001.

Scheme 4



Scheme 5



analysis. Owing to the lability of the pyridine ligands, MS experiments exhibited an M^{2+} ion associated with the core structure without pyridines.

A mixture of open macrocycles **9**−**11** was synthesized by the addition of benzyltriethylammonium chloride to a CH_2Cl_2 solution of **6** and **7**. Upon charging this solution with 1 atm of CO, the neutral complexes **9**−**11** formed in quantitative yield, as a mixture of tetra-, tri-, and dimeric complexes (Scheme 5).

The CO and Cl^- ligands act to selectively cleave the thioether−Rh^I bonds. Owing to the strained geometry in the rigid closed complexes **6** and **7**, formation of a bimetallic closed complex is not observed. However, upon opening, the macrocycle becomes much more flexible and, indeed, forms the bimetallic complex (**11**), along with the tri- and tetrametallic complexes (**10** and **9**, respectively). These products have been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies, MS, and GPC. Because of the labile nature of the CO and Cl^- ligands, characterization by elemental analysis was not possible.

Discussion

The use of a Tröger's Base analogue in metallomacrocycle synthesis has led to several interesting results. Because of the nearly right angle incorporated into the backbone of ligand **4**, once the ligand is combined with a metal center, macrocycles with unusual geometries can form. For example, with a Cu^I starting material, a dimeric macrocycle, **5**, forms,

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(46) Liu, X. G.; Stern, C. L.; Mirkin, C. A. *Organometallics* **2002**, *21*, 1017−1019.

(47) Gianneschi, N. C.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 5326−5328.

which is typical of metallomacrocycles formed via the Weak Link Approach. The tetrahedral geometry about the Cu^I center allows for enough flexibility that, despite the steric restrictions imposed by the rigid Tröger's base ligand, a bimetallic macrocycle can still form. This observation is consistent with findings by Harding et al., in which a ligand with a geometry similar to that of Tröger's base was reacted with Zn^{II}, another metal preferring a tetrahedral coordination environment, to form bimetallic macrocycles.[48] When the Cu^I macrocycle **5** is converted to open macrocycle **8** by selective cleavage of the weak thioether−metal bonds with pyridine, a much more flexible structure is formed. Both **5** and **8** are stable structures because there is no evidence for fluxional interconversion with other isomers or oligomers by variable-temperature NMR and GPC (see the Supporting Information).[49]

In contrast with observations made regarding the Cu^I macrocycles, attempts to make analogous complexes with four-coordinate, square-planar Rh^I yielded very different results. For example, when combined with the Tröger's base ligand, **4**, a mixture of two different products, as evidenced by ^{31}P NMR spectroscopy, is formed. GPC confirms the existence of two differently sized supramolecular complexes (see the Supporting Information). MS experiments showed that these complexes are the tetra- and trimetallic species. The identity of the tetrametallic species, **6**, in the solid state was confirmed by a single-crystal X-ray diffraction experiment (Figure 3 and Table 1).

Because ligand **4** was used as a racemic mixture, the possibility existed that the macrocycles would form as a mixture of enantiomers or diastereomers. The $^{31}P\{^1H\}$ NMR spectrum of the mixture of **6** and **7** displays only two doublets, each attributed to a differently sized complex, thereby ruling out the possibility of diastereomer formation. The crystal structure of $\mathbf{6}\cdot 9CH_2Cl_2$ shows that the macrocycle forms without enantiomeric recognition and is comprised equally of the *R*,*R* and *S*,*S* enantiomers.

Upon introduction of a chloride source and CO, closed complexes **6** and **7**, which form as a mixture, open to three new complexes, **9**−**11**, as evidenced by three doublets in the $^{31}P\{^1H\}$NMR spectrum of the solution. Each resonance has a chemical shift in the 20−25 ppm range and a coupling constant of approximately 124 Hz, consistent with other complexes that contain phosphorus atoms in similar chemical environments.[29] GPC was used to confirm that the mixture consisted of three differently sized species (see the Supporting Information). Comparing the GPC traces obtained from the mixture of **6** and **7** to the mixture of **9**−**11**, we find that two of the species in the mixture of open complexes (**9**−**11**) have roughly the same retention times as those of the closed complexes **6** and **7** (approximately 6 and 8.5 min). From this, we conclude that two of the macrocycle sizes in the mixture of **9**−**11** correspond to the tetrameric (**9**) and trimeric (**10**) complexes. The additional peak in the GPC traces of **9**−**11** with a retention time of 11 min can be attributed to the bimetallic species (**11**). The presence of **11** also has been confirmed by MS.

It has been demonstrated that, with thioether/Rh^I macrocycles generated via the Weak Link Approach, the opening and closing process is reversible.[29] Once open complexes are exposed to reduced pressure, the CO and Cl^- ligands are typically displaced on the Rh centers by the thioether moieties in the hemilabile ligand, and the complex recloses. However, the macrocycles comprised of the Tröger's base ligand do not display the same behavior. This phenomenon can be attributed to steric effects that do not allow the Tröger's base ligand to form a dimeric closed macrocycle in the square-planar Rh^I case.

Conclusion

In conclusion, we have synthesized a novel class of metallomacrocycles incorporating a Tröger's base containing ligand. This work addresses the effect of ligand and metal coordination geometry on the overall macrocycle formation. As a result of the rigid right angle formed by the backbone of each ligand, the formation of the typical bimetallic macrocycle produced by the Weak Link Approach was possible when tetrahedral Cu^I was used but was not possible with square-planar Rh^I, thereby forcing the formation of higher ordered structures. The ability to create these supramolecular structures containing Tröger's base derived ligands could lead to structures with novel molecular recognition and shape-selective catalytic properties.

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Supporting Information Available: GPC traces and X-ray crystallographic files (including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for tetrametallic Rh complex $\mathbf{6}\cdot 9CH_2Cl_2$; in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC052000B

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(48) Anderberg, P. I.; Turner, J. J.; Evans, K. J.; Hutchins, L. M.; Harding, M. M. *Dalton Trans.* **2004**, 1708−1714.

(49) Graves, C. R.; Merlau, M. L.; Morris, G. A.; Sun, S. T.; Nguyen, S. T.; Hupp, J. T. *Inorg. Chem.* **2004**, *43*, 2013−2017.