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Binuclear Copper(I) Macrocycles Synthesized via the Weak-Link Approach

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The weak-link approach has been employed to synthesize a series of bimetallic Cu(I) macrocycles in high yield. Addition of phosphinoalkylether or -thioether ligands to $[Cu(MeCN)_4]PF_6$ produces "condensed" intermediates, $[\mu\text{-}(1,4\text{-}(PPh_2CH_2CH_2X)_2Y)_2Cu_2][PF_6]_2$ (X = S, O; Y = C_6H_4, C_6F_4), containing strong P–Cu bonds and weaker O–Cu or S–Cu bonds. The weak bonds of these intermediates can be cleaved through ligand substitution reactions to generate macrocyclic structures, $[\mu\text{-}(1,4\text{-}(PPh_2CH_2CH_2X)_2Y)_2(Z)_nCu_2][PF_6]_2$ (X = S, O; Y = C_6H_4, C_6F_4; Z = pyridine, acetonitrile, diimines, isocyanide) in nearly quantitative yields. The incorporation of tetrahedral Cu(I) metal centers into these macrocycles provides a pathway to complexes that differ from analogous d^8 square planar macrocycles generated via this approach in their increased air stability, small molecule reactivity, and ability to form multiple structural isomers. Solid-state structures, as determined by single-crystal X-ray diffraction studies, are presented for condensed intermediates and an open macrocycle.

Introduction

In recent years, metallomacrocycles have received a significant amount of attention due to their encapsulating properties and potential applications in catalysis, sensing, molecular electronics, and facilitated small molecule transport.[1] A number of strategies have been employed to generate multimetallic supramolecular structures, such as the directional bonding and the symmetry interaction approaches.[2] These approaches have been used to assemble a variety of ligands and transition metal centers into sophisticated predefined two- and three-dimensional structures.

Over the past five years, our group has developed and refined a high-yield synthetic method for preparing bi-, tri-, and tetrametallic macrocycles from flexible hemilabile ligands and simple metal precursors.[3] The weak-link approach (WLA) targets condensed intermediate structures that

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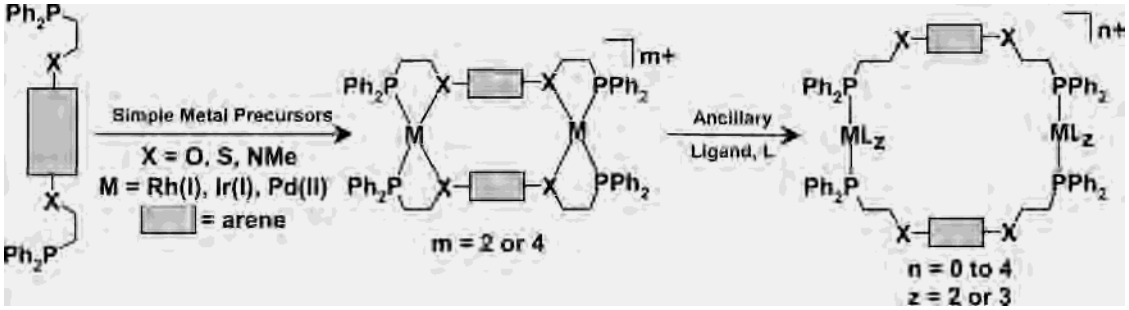
Scheme 1. Synthetic Scheme for Condensed Intermediates[3]

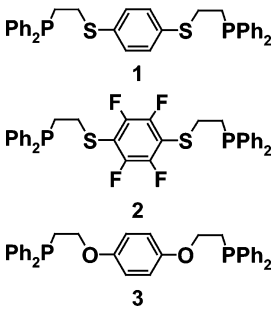


contain strategically placed strong (typically, metal−phosphine) and weak (metal−ether, −thioether, −amine, or −arene) bonds. The weak metal−heteroatom interactions can be selectively cleaved via ligand substitution reactions to afford the desired macrocyclic structures (Scheme 1). Using this approach, over 100 examples of metallomacrocycles have been synthesized with control over macrocycle size, shape, hydrophobicity, chirality, and overall charge through judicious choice of metal, hemilabile ligand, and ancillary ligands.[3] Recently, the WLA has been used to prepare a novel class of allosteric catalysts.[3n]

Although the generality of the WLA has been demonstrated with respect to a variety of hemilabile ligands, the utility of the approach thus far has been limited to square planar d^8 metal centers (Rh(I), Ir(I), Pd(II)).[3] Expanding the types of transition metal centers that can be utilized by this methodology provides another level of control over the resulting macrocyclic properties, such as air stability, charge, cavity shape, and host−guest chemistry. It also provides a route to structures with catalytic and photophysical properties that are different from the previously studied analogues.

Herein, we explore how macrocyclic structures with d^{10} Cu(I) centers can be prepared via the WLA. Copper(I) macrocycles are interesting systems to study for the following reasons: (1) The condensed intermediates generated en route to the targeted macrocycles have tetrahedral geometries around the metal centers as opposed to the square planar d^8 systems previously studied, thereby testing the versatility and tolerance of the approach to significant changes in coordination geometry about the templating metal centers. (2) The macrocycles formed should be air-stable on the basis of an analysis of isoelectronic mononuclear copper complexes with similar ligand environments.[4] All of the Rh(I) and Ir(I) systems we have synthesized are air-sensitive, which limits their utility for applications that require oxygen and water stability (e.g. many types of chemical sensors and catalysts). (3) The copper macrocycles will allow for different small molecules to be used as ancillary ligands to open the condensed intermediates into the desired macrocycles, which in turn provides an additional element of control to this approach. (4) Due to their d^{10} electronic configuration, the Cu(I) centers should have less of a quenching effect on the fluorescence of macrocycles synthesized with fluorophore-containing ligands than has been seen in the d^8 systems.[3d] As we begin to prepare fluorescent sensors based upon structures synthesized via the WLA, this will become a significant consideration that will allow for more sensitive detection.[5]

Chart 1



Experimental Section

General Procedures. Unless otherwise noted, all reactions and manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk and glovebox techniques. Tetrahydrofuran (THF), diethyl ether, CH_2Cl_2, acetonitrile (MeCN), and hexanes were purified by published methods.[6] All solvents were degassed with nitrogen prior to use. Nitromethane-d_3 was purchased from Aldrich. All other deuterated solvents were purchased and used as received from Cambridge Isotopes Laboratories. The ligands 1,4-$(PPh_2CH_2CH_2X)_2Y$ (**1**,[3e] X = S, Y = C_6H_4; **2**,[3o] X = S, Y = C_6F_4; **3**,[3a] X = O, Y = C_6H_4) (Chart 1) were prepared as previously reported. All other chemicals were obtained from commercial sources and used as received unless otherwise noted.

Physical Measurements. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian 300 MHz Gemini FT-NMR spectrometer at 121.53 MHz and referenced relative to an external 85% H_3PO_4 standard. $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian 300 MHz Gemini FT-NMR spectrometer at 282.47 MHz and referenced relative to an external $CFCl_3$ in $CDCl_3$ standard. ^1H NMR spectra were

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obtained using a Varian Gemini 300 MHz FT-NMR spectrometer and referenced relative to tetramethylsilane. All chemical shifts are reported in ppm. FT-IR spectra were obtained using a ThermoNicolet Nexus 670 FT-IR and a solution cell with NaCl windows. Electrospray (ES) mass spectra were obtained on a Micromass Quatro II triple quadrapole mass spectrometer. Elemental analyses were obtained from Quantitative Technologies Inc., Whitehouse, NJ.

General Syntheses of [μ-(1,4-Bis[2-(diphenylphosphino)-ethylthio]benzene)$_2$Cu$_2$][PF$_6$]$_2$ (4), [μ-(1,4-Bis[2-(diphenylphosphino)ethylthio]-2,3,5,6-tetrafluorobenzene)$_2$Cu$_2$][PF$_6$]$_2$ (5), and [μ-(1,4-Bis[2-(diphenylphosphino)ethoxy]benzene)$_2$Cu$_2$][PF$_6$]$_2$ (6). In a Schlenk flask, the appropriate ligand (**1**, **2**, or **3**, 1.78 mmol) was dissolved in CH_2Cl_2 (175 mL). A solution of $Cu(MeCN)_4PF_6$ (662 mg, 1.78 mmol) in CH_2Cl_2 (175 mL) was added via cannula to the stirring ligand solution to give a colorless solution. After stirring for 2 h, solvent was removed via evacuation, and the resulting white solid was dried at 150 °C under vacuum to give a white solid. Recrystallization from CH_2Cl_2/Et_2O afforded an analytically pure compound (as determined by NMR spectroscopy) in high yield. Data for **4** (yield = 1.31 g, 0.845 mmol, 95.3%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.84 (m, C*H*$_2$PPh$_2$, 8H), 3.34 (m, SC*H*$_2$, 8H), 6.36 (bs, C$_6$*H*$_4$, 8H), 7.3−7.7 (bm, P*Ph*$_2$, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −0.05 (s), −143.16 (sept, PF_6). ES-MS (*m*/*z*) [C$_{68}$H$_{64}$P$_4$S$_4$Cu$_2$]$^{2+}$: calcd = 630.1; expt = 630.2. Anal. Calcd for C$_{68}$H$_{64}$P$_4$S$_4$Cu$_2$P$_2$F$_{12}$: C, 52.68; H, 4.16. Found: C, 52.53; H, 4.04. Data for **5** (yield = 1.44 g, 0.851 mmol, 95.6%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.76 (m, C*H*$_2$PPh$_2$, 8H), 3.36 (m, SC*H*$_2$, 8H), 7.2−7.6 (bm, P*Ph*$_2$, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 0.22 (s), −143.69 (sept, PF_6). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −130.64 (s, C$_6$*F*$_4$), −72.57, −75.09 (s, s, PF_6). ES-MS (*m*/*z*) [C$_{68}$H$_{56}$F$_8$P$_4$S$_4$Cu$_2$]$^{2+}$: calcd = 702.0; expt = 702.2. Anal. Calcd for C$_{68}$H$_{56}$F$_8$P$_4$S$_4$Cu$_2$P$_2$F$_{12}$: C, 48.20; H, 3.33. Found: C, 47.83; H, 3.25. Data for **6** (yield = 1.19 g, 0.801 mmol, 90.0%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.61 (m, C*H*$_2$PPh$_2$, 8H), 4.12 (m, OC*H*$_2$, 8H), 6.56 (bs, C$_6$H$_4$, 8H), 7.2−7.8 (bm, P*Ph*$_2$, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −14.06 (s), −143.27 (sept, PF_6). ES-MS (*m*/*z*) [C$_{68}$H$_{64}$P$_4$O$_4$Cu$_2$]$^{2+}$: calcd = 597.2; expt = 597.5. ES-MS (*m*/*z*) [C$_{68}$H$_{64}$P$_4$O$_4$Cu$_2$PF$_6$]$^+$: calcd = 1339.2; expt = 1339.5. Anal. Calcd for C$_{68}$H$_{64}$P$_4$O$_4$Cu$_2$P$_2$F$_{12}$: C, 54.96; H, 4.34. Found: C, 55.12; H, 4.31.

General Syntheses of [μ-(1,4-Bis[2-(diphenylphosphino)ethylthio]-2,3,5,6-tetrafluorobenzene)$_2$Cu$_2$(acetonitrile)$_4$][PF$_6$]$_2$ (7) and [μ-(1,4-Bis[2-(diphenylphosphino)ethoxy]benzene)$_2$Cu$_2$(acetonitrile)$_4$][PF$_6$]$_2$ (8). Method A. In a Schlenk flask, copper complex **5** or **6** (0.0322 mmol) was dissolved in CH_2Cl_2 (3.0 mL) to give a colorless solution. Acetonitrile (0.132 mmol, 4.0 equiv) was added to the stirring copper solution via syringe to give a colorless solution. After stirring for 1 h, the solvent was removed in vacuo at room temperature to yield analytically pure white solids as the sole products as determined by NMR spectroscopy.

Method B. In a Schlenk flask, the ligand (**2** or **3**, 1.78 mmol) was dissolved in CH_2Cl_2 (175 mL). A solution of $Cu(MeCN)_4PF_6$ (662 mg, 1.78 mmol) in MeCN (175 mL) was added via cannula to the stirring ligand solution to give a colorless solution. After stirring for 2 h, the solvent was removed in vacuo to give analytically pure white solids (as determined by NMR spectroscopy) in high yield. Owing to the lability of the acetonitrile ligands in **7** and **8**, resolution of the molecular ions in MS and elemental analyses of these complexes were not possible. Data for **7** (yield = 1.48 g, 0.795 mmol, 89.3%) follow. ^{1}H NMR (CD_3CN): δ 2.36 (m, C*H*$_2$-PPh$_2$, 8H), 2.81 (m, SC*H*$_2$, 8H), 7.2−7.6 (bm, P*Ph*$_2$, 40H). ^{31}P{^{1}H} NMR (CD_3CN): δ −9.02. (s), −143.52. (sept, PF_6). ^{19}F{^{1}H} NMR (CD_3CN): δ −135.15 (s, C$_6$*F*$_4$), −71.97, −74.48 (s, s, PF_6). FT-IR (CD_2Cl_2): 2254, 2275 cm^{-1} (m, w, MeCN). ES-MS (*m*/*z*) [C$_{68}$H$_{56}$F$_8$P$_4$S$_4$Cu$_2$]$^{2+}$: calcd = 702.0; expt = 702.1 (M^{2+} − 4MeCN). Data for **8** (yield = 1.38 g, 0.805 mmol, 90.4%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.02 (s, MeCN, 12 H), 2.73 (m, C*H*$_2$PPh$_2$, 8H), 4.06 (m, OC*H*$_2$, 8H), 6.58 (s, C$_6$*H*$_4$, 8H), 7.0−7.7 (bm, P*Ph*$_2$, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −11.35 (s), 143.25 (sept, PF_6). FT-IR (CH_2Cl_2): 2277, 2310 cm^{-1} (w, m, MeCN). ES-MS (*m*/*z*) [C$_{68}$H$_{64}$P$_4$O$_4$Cu$_2$]$^{2+}$: calcd = 597.2; expt = 597.3 (M^{2+} − 4MeCN). ES-MS (*m*/*z*) [C$_{68}$H$_{64}$P$_4$O$_4$Cu$_2$PF$_6$]$^+$: calcd = 1339.2; expt = 1339.4 (M$^+$ − 4MeCN).

General Syntheses of [μ-(1,4-Bis[2-(diphenylphosphino)-ethylthio]benzene)$_2$Cu$_2$(pyridine)$_4$][PF$_6$]$_2$ (9), [μ-(1,4-Bis[2-(diphenylphosphino)ethylthio]-2,3,5,6-tetrafluorobenzene)$_2$Cu$_2$(pyridine)$_4$]-[PF$_6$]$_2$(10), and [μ-(1,4-Bis[2-(diphenylphosphino)ethoxy]benzene)$_2$Cu$_2$-(pyridine)$_4$] [PF$_6$]$_2$ (11). In a Schlenk flask, copper complex **4**, **5**, or **6** (0.0322 mmol) was dissolved in CH_2Cl_2 (3.0 mL) to give a colorless solution. Pyridine (10.5 μL, 0.130 mmol, 4.0 equiv) was added to the stirring copper solutions via syringe to give colorless solutions. After stirring for 1 h, the solvent was removed to yield an analytically pure white solid as the sole product as determined by NMR spectroscopy. The products were recrystallized from CH_2Cl_2/Et_2O. Data for **9** (yield = 56 mg, 0.0301 mmol, 93.5%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.72 (m, C*H*$_2$PPh$_2$, 8H), 3.22 (m, SC*H*$_2$, 8H), 6.60 (bs, C$_6$H$_4$, 8H), 7.31 (m, pyr, 8H), 7.42 (bm, P*Ph*$_2$, 40H), 7.74 (m, pyr, 4H), 8.45 (d, pyr, 8H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −4.61 (s), −143.21 (sept, PF_6). ES-MS (*m*/*z*) [C$_{68}$H$_{64}$P$_4$S$_4$-Cu$_2$C$_{20}$H$_{20}$N$_4$]$^+$: calcd = 787.2; expt = 787.4. Anal. Calcd for C$_{68}$H$_{64}$P$_4$S$_4$Cu$_2$C$_{20}$H$_{20}$N$_4$P$_2$F$_{12}$: C, 56.62; H, 4.54; N, 3.00. Found: C, 56.50; H, 4.68; N, 3.02. Data for **10** (yield = 63 mg, 0.0315 mmol, 97.8%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.49 (m, C*H*$_2$PPh$_2$, 8H), 2.90 (m, SC*H*$_2$, 8H), 7.0−7.4 (bm, P*Ph*$_2$, 40H), 7.46 (m, pyr, 8H), 7.82 (m, pyr, 4H), 8.37 (m, pyr, 8H). ^{31}P{^{1}H} NMR (CD_2-Cl_2): δ −7.70 (s), −143.45 (sept, PF_6). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −133.74 (s, C$_6$*F*$_4$), −72.17, −74.69 (s, s, PF_6). ES-MS (*m*/*z*) [C$_{68}$H$_{56}$F$_8$P$_4$S$_4$Cu$_2$C$_{20}$H$_{20}$N$_4$]$^{2+}$: calcd = 859.1; expt = 859.3. Anal. Calcd for C$_{68}$H$_{56}$F$_8$P$_4$S$_4$Cu$_2$C$_{20}$H$_{20}$N$_4$P$_2$F$_{12}$: C, 52.57; H, 3.81; N, 2.79. Found: C, 52.68; H, 3.78; N, 3.14. Data for **11** (yield = 54 mg, 0.0298 mmol, 92.5%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.67 (m, C*H*$_2$PPh$_2$, 8H), 3.95 (m, OC*H*$_2$, 8H), 6.34 (s, C$_6$*H*$_4$, 8H), 7.1−7.3 (bm, P*Ph*$_2$, 40H), 7.41 (m, pyr, 8H), 7.79 (m, pyr, 4H), 8.32 (d, pyr, 8H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −12.70 (s), −143.28 (sept, PF_6). ES-MS (*m*/*z*) [C$_{68}$H$_{64}$P$_4$O$_4$Cu$_2$C$_{20}$H$_{20}$N$_4$]$^{2+}$: calcd = 755.2; expt = 756.0. Anal. Calcd for C$_{68}$H$_{64}$P$_4$O$_4$Cu$_2$C$_{20}$H$_{20}$N$_4$P$_2$F$_{12}$: C, 58.64; H, 4.70; N, 3.11. Found: C, 59.41; H, 4.03; N, 3.54.

General Syntheses of [μ-(1,4-Bis[2-(diphenylphosphino)-ethylthio]benzene)$_2$Cu$_2$-η^2-(2,2′-bipyridine)$_2$][PF$_6$]$_2$ (12), [μ-(1,4-Bis[2-(diphenylphosphino)ethylthio]-2,3,5,6-tetrafluorobenzene)$_2$Cu$_2$-η^2-(2,2′-bipyridine)$_2$][PF$_6$]$_2$ (13), [μ-(1,4-Bis[2-(diphenylphosphino)ethoxy]benzene)$_2$Cu$_2$-η^2-(2,2′-bipyridine)$_2$][PF$_6$]$_2$ (14), [μ-(1,4-Bis[2-(diphenylphosphino)-ethylthio]benzene)$_2$Cu$_2$-η^2-(1,10-phenanthroline)$_2$][PF$_6$]$_2$ (15), [μ-(1,4-Bis[2-(diphenylphosphino)ethylthio]-2,3,5,6-tetrafluorobenzene)$_2$Cu$_2$-η^2-(1,10-phenanthroline)$_2$][PF$_6$]$_2$ (16), [μ-(1,4-Bis[2-(diphenylphosphino)ethoxy]benzene)$_2$-η^2-Cu$_2$(1,10-phenanthroline)$_2$][PF$_6$]$_2$ (17), [μ-(1,4-Bis[2-(diphenylphosphino)-ethylthio]benzene)$_2$Cu$_2$-η^2-(neocuproine)$_2$][PF$_6$]$_2$ (18), [μ-(1,4-Bis[2-(diphenylphosphino)ethylthio]-2,3,5,6-tetrafluorobenzene)$_2$Cu$_2$-η^2-(neocuproine)$_2$][PF$_6$]$_2$ (19), and [μ-(1,4-Bis[2-(diphenylphosphino)ethoxy]benzene)$_2$Cu$_2$-η^2-(neocuproine)$_2$][PF$_6$]$_2$ (20). In a Schlenk flask, copper complex **4**, **5**, or **6** (0.0322 mmol) and the appropriate diimine ligand (2,2′-bipyridine, 1,10-phenanthroline, neocuproine hydrate) (0.065 mmol, 2 equiv) were dissolved in CH_2Cl_2 (3.0 mL) to give yellow (**12**−

17) or orange (**18**−**20**) solutions. After stirring for 1 h, the solvent was removed to yield analytically pure yellow or orange solids as the sole products as determined by NMR spectroscopy. Data for **12** (yield = 53 mg, 0.0286 mmol, 88.8%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.29 (m, CH_2PPh$_2$, 8H), 2.53 (m, SCH_2, 8H), 6.79 (s, C$_6H_4$, 8H), 6.9−7.3 (bm, PPh_2, 40H), 7.40 (m, bipy, 4H), 7.95 (m, bipy, 4H), 8.19 (m, bipy, 4H), 8.33 (m, bipy, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −5.68 (s), −143.15 (sept, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4S_4Cu_2C_{20}H_{16}N_4]^{2+}$: calcd = 785.1; expt = 785.4. ES-MS (*m*/*z*) $[C_{68}H_{64}P_4S_4Cu_2C_{20}H_{16}N_4PF_6]^+$: calcd = 1405.1; expt = 1405.4. Anal. Calcd for $C_{68}H_{64}P_4S_4Cu_2C_{20}H_{16}N_4P_2F_{12}$: C, 56.74; H, 4.33; N, 3.01. Found: C, 56.34; H, 3.97; N, 2.97. Data for **13** (yield = 56 mg, 0.0284 mmol, 88.2%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.24 (m, CH_2PPh$_2$, 8H), 2.50 (m, SCH_2, 8H), 6.8−7.4 (bm, PPh_2, 40H), 7.38 (bm, bipy, 4H), 8.03 (bm, bipy, 4H), 8.25 (bm, bipy, 4H), 8.38 (bm, bipy, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −5.57 (s), −143.27 (sept, PF_6). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −133.82 (s, C$_6F_4$), −72.07, −74.59 (s, s, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{56}F_8P_4S_4Cu_2C_{20}H_{16}N_4]^{2+}$: calcd = 857.1; expt = 857.1. ES-MS (*m*/*z*) $[C_{68}H_{56}F_8P_4S_4Cu_2C_{20}H_{16}N_4PF_6]^+$: calcd = 1859.2; expt = 1859.3. Anal. Calcd for $C_{68}H_{56}F_8P_4S_4Cu_2C_{20}H_{16}N_4P_2F_{12}$: C, 52.67; H, 3.62; N, 2.79. Found: C, 52.57; H, 3.33; N, 2.70. Data for **14** (yield = 56 mg, 0.0311 mmol, 96.6%) follow: ^{1}H NMR (CD_2Cl_2): δ 2.49 (m, CH_2PPh$_2$, 8H), 3.61 (m, OCH_2, 8H), 6.06 (s, C$_6H_4$, 8H), 6.8−7.3 (bm, PPh_2, 40H), 7.38 (m, bipy, 4H), 7.87 (bm, bipy, 4H), 8.10 (bm, bipy, 4H), 8.32 (bm, bipy, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −8.41 (s), −143.18 (sept, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4O_4Cu_2C_{20}H_{16}N_4PF_6]^+$: calcd = 1653.6; expt = 1653.9. Anal. Calcd for $C_{68}H_{64}P_4O_4Cu_2C_{20}H_{16}N_4P_2F_{12}$: C, 58.77; H, 4.48; N, 3.12. Found: C, 58.46; H, 3.76; N, 3.03. Data for **15** (yield = 56 mg, 0.0299 mmol, 92.9%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.30 (m, CH_2PPh$_2$, 8H), 2.51 (m, SCH_2, 8H), 6.65 (s, C$_6H_4$, 8H), 6.9−7.4 (bm, PPh_2, 40H), 7.75 (m, phen, 4H), 7.92 (s, phen, 4H), 8.44 (m, phen, 4H), 8.71 (m, phen, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −5.14 (s), −143.11 (sept, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4S_4Cu_2C_{24}H_{16}N_4]^{2+}$: calcd = 809.1; expt = 809.4. Anal. Calcd for $C_{68}H_{64}P_4S_4Cu_2C_{24}H_{16}N_4P_2F_{12}$: C, 57.83; H, 4.22; N, 2.93. Found: C, 57.36; H, 3.52; N, 2.94. Data for **16** (yield = 55 mg, 0.0268 mmol, 83.4%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.30 (m, CH_2PPh$_2$, 8H), 2.50 (m, SCH_2, 8H), 6.8−7.5 (bm, PPh_2, 40H), 7.80 (m, phen, 4H), 7.99 (s, phen, 4H), 8.49 (m, phen, 4H), 8.76 (m, phen, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −4.84 (s), −143.25 (sept, PF_6). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −134.04 (s, C$_6F_4$), −71.93, −74.45 (s, s, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{56}F_8P_4S_4Cu_2C_{24}H_{16}N_4]^{2+}$: calcd = 881.1; expt = 881.2. Anal. Calcd for $C_{68}H_{56}F_8P_4S_4Cu_2C_{24}H_{16}N_4P_2F_{12}$: C, 53.78; H, 3.53; N, 2.73. Found: C, 53.99; H, 3.20; N, 2.61. Data for **17** (yield = 48 mg, 0.0260 mmol, 80.9%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.52 (m, CH_2PPh$_2$, 8H), 3.55 (m, OCH_2, 8H), 5.93 (s, C$_6H_4$), 7.1−7.5 (bm, PPh_2, 40H), 7.60 (m, phen, 4H), 7.80 (m, phen, 4H), 8.33 (m, phen, 4H), 8.68 (m, phen, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −7.62 (s), −143.14 (sept, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4O_4Cu_2C_{24}H_{16}N_4]^{2+}$: calcd = 777.2; expt = 777.4. ES-MS (*m*/*z*) $[C_{68}H_{64}P_4O_4Cu_2C_{24}H_{16}N_4PF_6]^+$: calcd = 1701.6; expt = 1701.6. Anal. Calcd for $C_{68}H_{64}P_4O_4Cu_2C_{24}H_{16}N_4P_2F_{12}$: C, 59.84; H, 4.37; N, 3.03. Found: C, 59.15; H, 4.23; N, 2.83. Data for **18** (yield = 59 mg, 0.0316 mmol, 98.0%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.30 (m, SCH_2, 8H), 2.37 (s, neoc, 12H), 2.59 (m, CH_2PPh$_2$, 8H), 6.78 (s, C$_6H_4$, 8H), 6.9−7.5 (bm, PPh_2, 40H), 7.55 (d, J_{H-H} = 7.8 Hz, neoc, 4H), 7.88 (s, neoc, 4H), 8.35 (d, J_{H-H} = 8.1 Hz, neoc, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −7.47 (s), −143.27 (sept, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4S_4Cu_2C_{28}H_{24}N_4]^{2+}$: calcd = 837.2; expt = 837.3. Anal. Calcd for $C_{68}H_{64}P_4S_4Cu_2C_{28}H_{24}N_4P_2F_{12}$: C, 58.62; H, 4.51; N, 2.85. Found: C, 58.75; H, 4.23; N, 2.96. Data for **19** (yield = 67 mg, 0.0317 mmol, 98.6%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.24 (m, SCH_2, 8H), 2.44 (s, neoc, 12H), 2.59 (m, CH_2PPh$_2$, 8H), 6.9−7.4 (bm, PPh_2, 40H), 7.60 (d, J_{H-H} = 7.8 Hz, neoc, 4H), 7.91 (s, neoc, 4H), 8.39 (d, J_{H-H} = 8.1 Hz, neoc, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −6.61 (s), −143.33 (sept, PF_6). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −133.58 (s, C$_6F_4$), −72.34, −74.86 (s, s, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{56}F_8P_4S_4Cu_2C_{28}H_{24}N_4]^{2+}$: calcd = 909.1; expt = 909.2. Anal. Calcd for $C_{68}H_{56}F_8P_4S_4Cu_2C_{28}H_{24}N_4P_2F_{12}$: C, 54.62; H, 3.82; N, 2.65. Found: C, 54.88; H, 3.52; N, 2.79. Data for **20** (yield = 52 mg, 0.0273 mmol, 84.8%) follow. ^{1}H NMR (CD_2Cl_2): δ 2.42 (s, neoc, 12H), 2.54 (bm, OCH_2, 8H), 3.58 (bm, CH_2PPh$_2$, 8H), 6.01 (s, C$_6H_4$, 8H), 7.0−7.4 (bm, PPh_2, 40H), 7.48 (d, J_{H-H} = 8.4 Hz, neoc, 4H), 7.79 (s, neoc, 4H), 8.27 (d, J_{H-H} = 8.1 Hz, neoc, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −10.48 (s), −143.28 (sept, PF_6). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4O_4Cu_2C_{28}H_{24}N_4]^{2+}$: calcd = 805.2; expt = 805.4. Anal. Calcd for $C_{68}H_{64}P_4O_4Cu_2C_{28}H_{24}N_4P_2F_{12}$: C, 60.60; H, 4.66; N, 2.94. Found: C, 60.51; H, 4.53; N, 2.96.

General Syntheses of [μ-(1,4-Bis[2-(diphenylphosphino)-ethylthio]benzene)$_2$Cu$_2$(*tert*-butylisocyanide)$_4$][PF$_6$]$_2$ (21), [μ-(1,4-Bis[2-(diphenylphosphino)ethylthio]-2,3,5,6-tetrafluorobenzene)$_2$Cu$_2$(*tert*-butylisocyanide)$_4$][PF$_6$]$_2$ (22), and [μ-(1,4-Bis[2-(diphenylphosphino)ethoxy]benzene)$_2$Cu$_2$(*tert*-butylisocyanide)$_4$][PF$_6$]$_2$ (23). In a Schlenk flask, copper complex **4**, **5**, or **6** (0.0322 mmol) was dissolved in CH_2Cl_2 (3.0 mL), and *tert*-butylisocyanide (14.6 μL, 0.129 mmol, 4.0 equiv) was added to give a colorless solution. After stirring for 1 h, the solvent was removed to yield analytically pure colorless oil (**21**) or white solid (**22**, **23**) as the sole product as determined by NMR spectroscopy. Data for **21** (yield = 51 mg, 0.0273 mmol, 84.8%) follow. ^{1}H NMR (CD_2Cl_2): δ 1.35 (s, ^{t}BuNC, 36H), 2.27 (m, SCH_2, 8H), 2.73 (m, CH_2PPh$_2$, 8H), 6.97 (s, C$_6H_4$, 8H), 7.21, 7.33, 7.42 (m, m, m, PPh_2, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −4.31 (s), −143.31 (sept, PF_6). FT-IR (CH_2Cl_2): 2170 cm^{-1} (s, ^{t}BuNC). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4S_4Cu_2C_{20}H_{36}N_4]^{2+}$: calcd = 795.2; expt = 795.3. Anal. Calcd for $C_{68}H_{64}P_4S_4Cu_2C_{20}H_{36}N_4P_2F_{12}$: C, 56.16; H, 5.36; N, 2.98. Found: C, 55.83; H, 5.43; N, 3.40. Data for **22** (yield = 61 mg, 0.0301 mmol, 93.5%) follow. ^{1}H NMR (CD_2Cl_2): δ 1.39 (s, ^{t}BuNC, 36H), 2.22 (m, SCH_2, 8H), 2.75 (m, CH_2PPh$_2$, 8H), 7.18, 7.32, 7.42 (m, m, m, PPh_2, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −4.04 (s), −143.38 (sept, PF_6). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −133.91 (s, C$_6F_4$), −72.42, −74.94 (s, s, PF_6). FT-IR (CH_2Cl_2): 2172 cm^{-1} (s, ^{t}BuNC). ES-MS (*m*/*z*) $[C_{68}H_{56}F_8P_4S_4Cu_2C_{20}H_{36}N_4]^{2+}$: calcd = 867.2; expt = 867.4. Anal. Calcd for $C_{68}H_{56}F_8P_4S_4Cu_2C_{20}H_{36}N_4P_2F_{12}$: C, 52.17; H, 4.58; N, 2.77. Found: C, 52.91; H, 4.32; N, 2.98. Data for **23** (yield = 58 mg, 0.0319 mmol, 99.0%) follow. ^{1}H NMR (CD_2Cl_2): δ 1.25 (s, ^{t}BuNC, 36H), 2.47 (m, OCH_2, 8H), 3.88 (m, CH_2PPh$_2$, 8H), 6.42 (s, C$_6H_4$, 8H), 7.2−7.5 (bm, PPh_2, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −7.88 (s), −143.35 (sept, PF_6). FT-IR (CH_2Cl_2): 2171 cm^{-1} (s, ^{t}BuNC). ES-MS (*m*/*z*) $[C_{68}H_{64}P_4O_4Cu_2C_{20}H_{36}N_4]^{2+}$: calcd = 763.3; expt = 763.2. Anal. Calcd for $C_{68}H_{64}P_4O_4Cu_2C_{20}H_{36}N_4P_2F_{12}$: C, 58.14; H, 5.55; N, 3.08. Found: C, 58.42; H, 5.59; N, 3.23.

X-ray Crystal Structure Determination of 4, 5, and 8. Diffraction intensity data were collected with Bruker SMART APEX (**4**) and SMART-1000 (**5**, **8**) CCD diffractometers equipped with a graphite-monochromated Mo Kα radiation source. The data collected were processed to produce conventional intensity data by the program SAINT-NT (Bruker). The intensity data were corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS[7] empirical method (T_{min}/T_{max}= 0.857 (**4**), 0.801 (**5**), and 0.852 (**8**)). The structures were solved using the Patterson function (**4**) and by direct methods (**5**, **8**), completed by subsequent difference Fourier syntheses and

Table 1. Crystallographic Data for **4**, **5**, and **8**

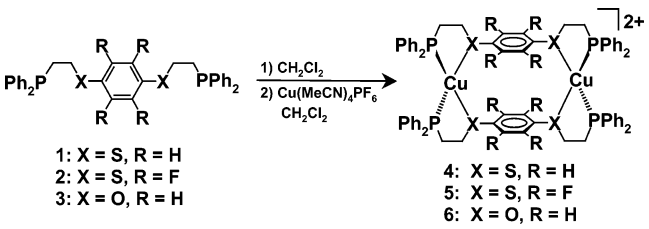
	4·CH_2Cl_2·$0.5C_4H_{10}O$	**5**·$2CH_2Cl_2$	**8**·$2CH_3CN$
formula	$C_{71}H_{71}Cl_2Cu_2F_{12}O_{0.5}P_6S_4$	$C_{70}H_{60}Cl_4Cu_2F_{20}P_6S_4$	$C_{80}H_{82}Cu_2F_{12}N_6O_4P_6$
fw	1672.32	1864.12	1732.42
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbcn*	*P*2(1)/*c*	$P\bar{1}$
a (Å)	32.951(2)	12.170(1)	13.158(1)
b (Å)	14.456(1)	27.843(2)	13.158(1)
c (Å)	32.267(2)	11.704(1)	13.305(1)
α (deg)	90	90	64.871(1)
β (deg)	90	106.97(1)	83.773(1)
γ (deg)	90	90	79.858(1)
V (Å^3)	15370(2)	3793.3(4)	2051.4(3)
Z	8	2	1
$2\theta_{max}$ (deg)	55.1	58.0	57.9
temp, K	100(2)	153(2)	153(2)
X-radiation (*λ*, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
indep reflns	17616 [R_{int} = 0.0705]	9189 [R_{int} = 0.0333]	9628 [R_{int} = 0.0265]
$R(F)^a$, $R(wF^2)^b$ (%)	6.73, 17.05	3.45, 8.76	5.05, 13.12
largest diff peak and hole (e Å^{-3})	1.295, −0.482	0.862, −0.670	1.278, −0.626
GOF	1.092	1.049	1.047

refined by full matrix least-squares procedures on F^2. Unless otherwise noted, all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at calculated positions and treated as isotropic contributions with thermal parameters defined as 1.2 or 1.5 times that of the parent atom. The space groups were chosen on the basis of the systematic absences and intensity statistics in the diffraction data. In the structure of **4**, one of the PF_6 anions and the CH_2Cl_2 and ether solvate molecules are highly disordered and were treated by SQUEEZE.[8] Correction of the X-ray data by SQUEEZE (1154 electrons/cell) was close to the required values (1056 electrons/cell) for the PF_6 anion, CH_2Cl_2, and $0.5(C_4H_{10}O)$ solvent molecules (the ether molecule is disordered around a center of symmetry). The methylene groups and the phenyl rings of the ligand are disordered over two positions in the structure of **4**. The disordered carbon atoms were refined with isotropic thermal parameters, and the H atoms of the disordered groups were not taken into consideration. All software and sources of scattering factors are contained in the SHELXTL program package (version 5.10, G. Sheldrick, Bruker-AXS, Madison, WI). Crystallographic data for **4**, **5**, and **8** are given in Table 1.

Results and Discussion

The bimetallic copper(I) metallomacrocycles reported herein demonstrate how the WLA can be adapted to metals other than d^8 square planar centers, such as Rh(I), Ir(I), and Pd(II). This class of macrocycles provides insight into the flexibility of the WLA and provides several advantages over d^8 metal centers. Interestingly, the Cu(I) metal centers have pseudotetrahedral coordination environments in the condensed intermediates **4**−**6**, which demonstrates that the directionality imparted by a square planar metal center is not required for the WLA to work. In addition, the tetrahedral nature of Cu(I) metal ions has been used to assemble bis(bidentate) diimine ligands into binuclear systems that are helical in topology.[9] This structure type has previously not been observed in macrocycles generated via the WLA. Also,

Scheme 2. Synthetic Scheme for Complexes **4**−**6**[a]



[a] All reactions were performed at 25 °C. All counterions are PF_6^-.

the Cu(I)-containing macrocycles are significantly more stable in the presence of air than previous Rh(I) and Ir(I) analogues, which allows for easier handling and makes them more amenable to catalytic and sensing applications. Finally, the d^{10} electron configuration of Cu(I) ensures that quenching of fluorescence in the appropriate macrocycles will not occur to the same degree as in their Rh(I) analogues.[3d,5]

Condensed Intermediates, 4−6. The copper condensed intermediates **4**−**6** were synthesized via methodologies similar to published procedures for the synthesis of mononuclear Cu(I) bis-thioetheralkylphosphine compounds (Experimental Section, Scheme 2).[10] In methylene chloride, solutions of $Cu(MeCN)_4PF_6$ were added to solutions of ligands **1**−**3** at room temperature followed by removal of the solvent at 150 °C to generate complexes **4**−**6**, respectively, in high yield (>90%). In this reaction, the stronger binding P, O, and S atoms of ligands **1**−**3** displace the labile acetonitrile ligands. These complexes have been fully characterized in solution (see Experimental Section), and complexes **4** and **5** have been characterized in the solid state via single-crystal X-ray diffraction studies (vide infra).

The $^{31}P\{^1H\}$ NMR spectra of **4**−**6** exhibit signals for the diphenylphosphine moieties that are shifted downfield from the corresponding free ligands (>6 ppm). These resonances are slightly broadened singlets due to the interaction of the phosphorus atoms with the quadrupolar ^{63}Cu and ^{65}Cu nuclei ($I = {}^3/_2$).[10] The $^{31}P\{^1H\}$ chemical shifts for **4** (δ −0.05) and **5** (δ 0.22) compare well with those for mononuclear Cu(I) complexes with alkylthioetherphosphine ligands, which fall within the range of −2.3 to 3.4 ppm.[10,11] The resonance for **6** (δ −14.06) is similar to that for a mononuclear Cu(I)−alkyletherphosphine complex (δ −16.2).[12] FT-IR analyses show no evidence of Cu(I)-bound acetonitrile (2500−3000 cm^{-1}) for compounds **4**−**6** in CH_2Cl_2. ^1H NMR spectroscopy, mass spectrometry, and elemental analyses are consistent with the proposed formulations of **4**−**6**. Complex **4** is indefinitely stable in air in solution (CH_2Cl_2 or CH_3CN) and the solid state. While complexes **5** and **6** are indefinitely stable in air in the solid state, these complexes slowly degrade in CH_2Cl_2 under ambient conditions (∼2 weeks).

Solid State Characterization of 4 and 5. Colorless single crystals of **4** were grown by diffusion of Et_2O into a

(7) Sheldrick, G. M. *SADABS* (2.01); Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998.
(8) van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, 194.
(9) (a) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005. (b) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457 and references therein.
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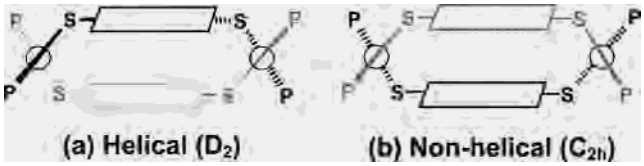

Figure 1. Schematic illustration of the formation of (a) helical and (b) nonhelical structures.

concentrated CH_2Cl_2 solution of **4**. Colorless single crystals of **5** were grown by cooling a saturated CD_2Cl_2 solution of **5** to −10 °C. Single-crystal X-ray diffraction studies of **4** and **5** show that each Cu(I) metal center is bound to two phosphines and two thioethers in a pseudotetrahedral geometry (Figures 2 and 3). Selected bond distances and angles are shown in Tables 2 and 3. The average Cu−P and Cu−S distances in **4** are 2.24 and 2.35 Å, respectively, while those in **5** are 2.26 and 2.35 Å, respectively. Similar distances are observed in both mononuclear Cu(I) complexes with thioetherphosphine ligands (av Cu−P = 2.22 Å; av Cu−S = 2.34 Å)[10,11,13] and complexes generated via this approach using ligand **1** in combination with Rh(I) (M−P = 2.25 Å; M−S = 2.35 Å) and Pd(II) (M−P = 2.30 Å; M−S = 2.40 Å) starting materials.[3f] The Cu−Cu distances in **4** and **5** are 8.58 and 8.53 Å, respectively, and the arene−arene distances are 3.65 and 4.13 Å, respectively. For the d^8 analogues of compound **4**, the metal−metal distances (Rh, 8.38 Å; Pd, 8.00 Å) and arene−arene distances (Rh, 3.51 Å; Pd, 3.53 Å) are very similar.[3f]

Due to the tetrahedral geometry of the copper(I) center, two possible [2 + 2] complexes can be formed, i.e. helical and/or nonhelical complexes (Figure 1).[14] In the structures of both **4** and **5**, the arenes are aligned in a parallel planar arrangement; however the protons on the arene rings of complex **4** are staggered, while in complex **5** the fluorine atoms on the arene are eclipsed. Although the structures appear quite different, it is interesting that the only geometric differences lie in the torsion angles for the bonds about the thioether centers. If the difference between the fluorine and hydrogen substituents on the arene are neglected, examination of molecular models shows that the two structures can be interconverted without breaking or stretching bonds, but merely by rotation about the Cu−S and S−arene bonds. The two structures may thus be regarded as stereoconformers showing helical and nonhelical structures. On the basis of the similarities of the NMR spectra for complexes **4** and **5**, the various conformers likely undergo rapid interconversion in solution. However, the interconverting species are signal averaged even at low temperatures (−65 °C) in the NMR spectra in CD_2Cl_2.

Bimetallic Cu(I) Macrocycles Synthesized via the WLA. The key step in the WLA is the breaking of the weak metal−heteroatom bonds in the condensed intermediates with stronger binding σ-donors and/or π-acceptors to generate the desired open macrocyclic structures. The Cu(I)-based condensed intermediates (**4**−**6**) can be opened with small molecules that are different from those used to open their Rh and Pd analogues. For example, bimetallic Rh(I) condensed intermediates have been synthesized with ligands **1**−**3** and have been subsequently opened with small molecules, such as nitriles, isonitriles, CO, and/or halides, to form a variety of large macrocyclic ring structures.[3a,c−e,o] The Cu−X bonds of **4**−**6** proved to be substitutionally inert under most conditions that result in displacement of these moieties in the Rh(I) intermediates. However, complexes **5** and **6** (with weaker Cu−S and Cu−O bonds than the Cu−S bonds in **4**) can be opened with acetonitrile to generate cationic structures (**7** and **8**, vide infra). Also, compounds **4**−**6** can be opened with isonitriles to form cationic macrocycles (**21**−**23**, vide infra), although, unlike their square planar analogues, they do not require a donating ligand (e.g. nitrile).[3d,o]

Cationic Macrocycles via Addition of Acetonitrile, 7 and 8. A number of reports have shown that stable complexes of Cu(I) can be synthesized with phosphines and acetonitrile as ligands.[4b,g,15] The success of acetonitrile as an opening ligand is dependent on the nature of the weak-binding moieties of the macrocyclic precursors (**4**−**6**). For instance, the Cu−S bond that is formed in the reaction of ligand **1** with the copper starting material is strong enough to preclude acetonitrile from coordinating to the copper metal centers even when present in large excess. However, under these conditions, the intermediates with Cu−X (X = O, S) bonds intact are not isolated when ligands **2** and **3** are employed. Instead, cationic macrocycles **7** and **8** (Scheme 3) are formed where each copper metal center is bound to two phosphines and two acetonitrile ligands. Alternatively, complexes **7** and **8** can be generated by addition of a stoichiometric amount of acetonitrile to condensed intermediates **5** and **6**, respectively, followed by evacuation. Compounds **7** and **8** have been characterized by multinuclear NMR and FT-IR spectroscopies, and mass spectrometry. The labile nature of the acetonitrile ligands prohibits elemental analysis and the presence of the molecular ion corresponding to the metal complex with bound acetonitrile ligands in the mass spectrum. The $^{31}P\{^1H\}$ NMR spectra of these compounds exhibit resonances (singlets) that are shifted from the closed complexes **5** and **6** (**7**, δ −9.02; **8**, δ −11.35) that compare well with mononuclear Cu(I) bisphosphine bis(nitrile) complexes (δ −9.5 to −12.7).[4b,g] The presence of the coordinated MeCN molecules is evidenced by the

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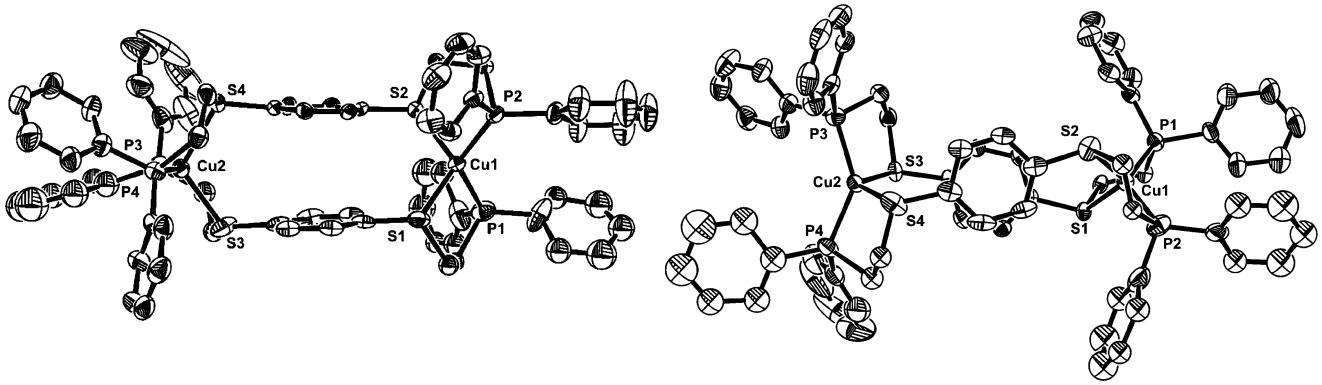


Figure 2. Thermal ellipsoid drawings of **4** showing the labeling scheme for selected atoms and ellipsoids at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

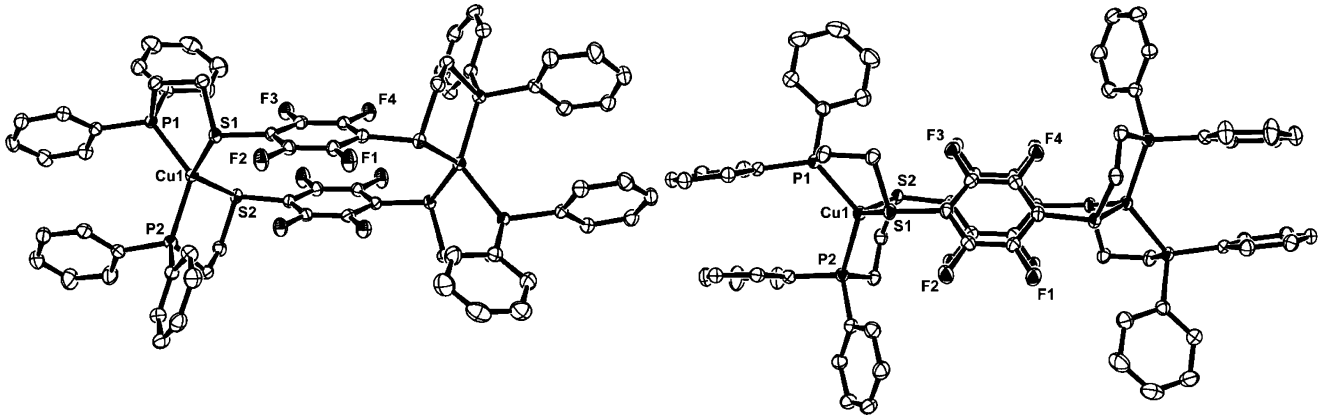


Figure 3. Thermal ellipsoid drawings of **5** showing the labeling scheme for selected atoms and ellipsoids at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

Table 2. Selected Structural Properties for $[\{1,4\text{-}(Ph_2PCH_2CH_2S)_2\text{-}C_6H_4\}_2Cu_2][PF_6]_2\cdot CH_2Cl_2\cdot 0.5C_4H_{10}O$ (**4**·CH_2Cl_2·$0.5C_4H_{10}O$)

	Distances (Å)		
Cu(1)−Cu(2)	8.581	C_6F_4(centroid)−C_6F_4(centroid)	3.636
Cu(1)−S(1)	2.340(1)	Cu(2)−S(3)	2.342(1)
Cu(1)−S(2)	2.339(1)	Cu(2)−S(4)	2.380(1)
Cu(1)−P(1)	2.245(1)	Cu(2)−P(3)	2.224(1)
Cu(1)−P(2)	2.263(1)	Cu(2)−P(4)	2.220(1)
	Angles (deg)		
∠S(1)−Cu(1)−S(2)	116.06(4)	∠S(3)−Cu(2)−S(4)	116.41(5)
∠P(1)−Cu(1)−S(1)	89.98(5)	∠P(3)−Cu(2)−S(3)	89.64(5)
∠P(1)−Cu(1)−S(2)	117.34(5)	∠P(3)−Cu(2)−S(4)	108.78(5)
∠P(2)−Cu(1)−S(1)	119.10(5)	∠P(4)−Cu(2)−S(3)	112.58(5)
∠P(2)−Cu(1)−S(2)	90.12(4)	∠P(4)−Cu(2)−S(4)	90.64(4)
∠P(1)−Cu(1)−P(2)	126.84(5)	∠P(3)−Cu(2)−P(4)	140.50(5)

Table 3. Selected Structural Properties for $[\{1,4\text{-}(Ph_2PCH_2CH_2S)_2\text{-}C_6F_4\}_2Cu_2][PF_6]_2\cdot 2CH_2Cl_2$ (**5**·$2CH_2Cl_2$)

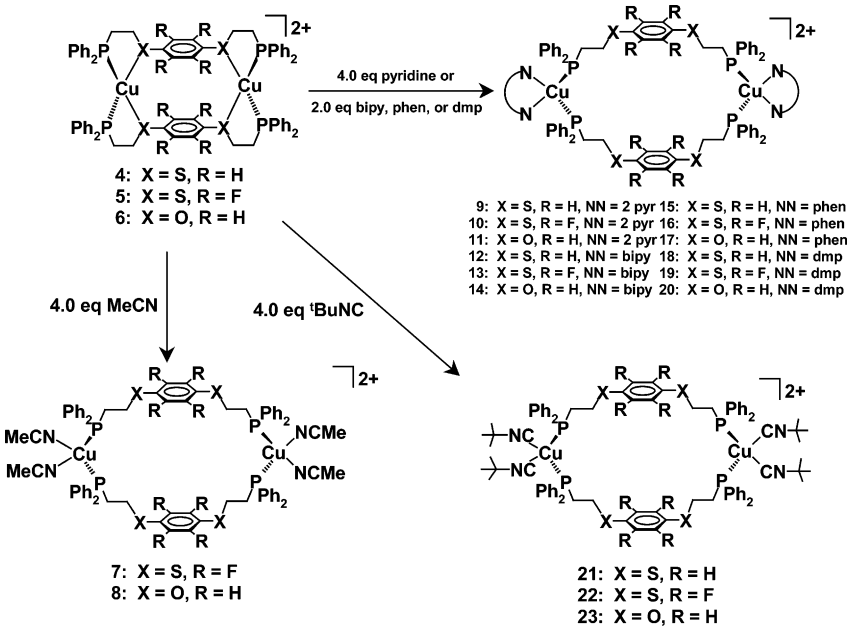
distances (Å)		angles (deg)	
Cu−Cu	8.529	∠S(1)−Cu(1)−S(2)	122.75(2)
C_6F_4(centroid)−C_6F_4(centroid)	4.125	∠P(1)−Cu(1)−S(1)	88.97(2)
Cu(1)−S(1)	2.341(1)	∠P(1)−Cu(1)−S(2)	112.68(2)
Cu(1)−S(2)	2.361(1)	∠P(2)−Cu(1)−S(1)	118.61(2)
Cu(1)−P(1)	2.268(1)	∠P(2)−Cu(1)−S(2)	90.95(2)
Cu(1)−P(2)	2.252(1)	∠P(1)−Cu(1)−P(2)	126.19(2)

appearance of two ν(CN) absorption bands (**7**, 2254, 2275 cm^{-1}; **8**, 2277, 2310 cm^{-1}) in the FT-IR spectra of these complexes. The downfield shift and the integration of the acetonitrile signals in the ^1H NMR spectra also support the structures shown in Scheme 2.

Solid State Characterization of 8. Colorless single crystals of **8** were grown by diffusion of Et_2O into a concentrated CH_2Cl_2 solution of **8**. A single-crystal X-ray diffraction study of **8** shows that each Cu(I) metal center is bound in a pseudotetrahedral geometry to two phosphines and two acetonitrile ligands (Figure 4). Selected bond lengths and angles are given in Table 4. The average Cu−P and Cu−N distances in **8** are 2.26 and 2.05 Å, respectively. Similar distances are observed in both mononuclear Cu(I) complexes with acetonitrile and phosphine ligands (Cu−P = 2.27−2.29 Å; Cu−N = 2.00−2.16 Å)[4b,15a] and macrocycles generated via opening the intermediate formed from the reaction of ligand **3** in combination with Pd(II) starting materials (M−P = 2.27 Å; M−N = 2.09 Å).[3f] The Cu−Cu distance in **8** (9.46 Å) and the arene−arene distance (7.38 Å) are within the range expected by comparison to previously synthesized macrocycles using similar benzene-based ligands.[3] The Cu−O distances (4.29 Å) are clearly nonbonding. Similar to the structure of **5**, the ligands in **8** are bound in a nonhelical manner.

Cationic Macrocycles via Addition of Pyridine-Based Ligands, 9−20. Mixed monometallic copper(I) phosphine complexes with a variety of heterocyclic N-donors are abundant in the literature owing to their interesting photophysical and photochemical properties.[16] Hence, N-donors, such as pyridine, 2,2′-bipyridine, or 1,10-phenanthroline,

Scheme 3. Synthetic Scheme for Cationic Macrocycles **7**−**23**[a]



[a] All reactions were performed in CH_2Cl_2 at 25 °C. All counterions are PF_6^-.

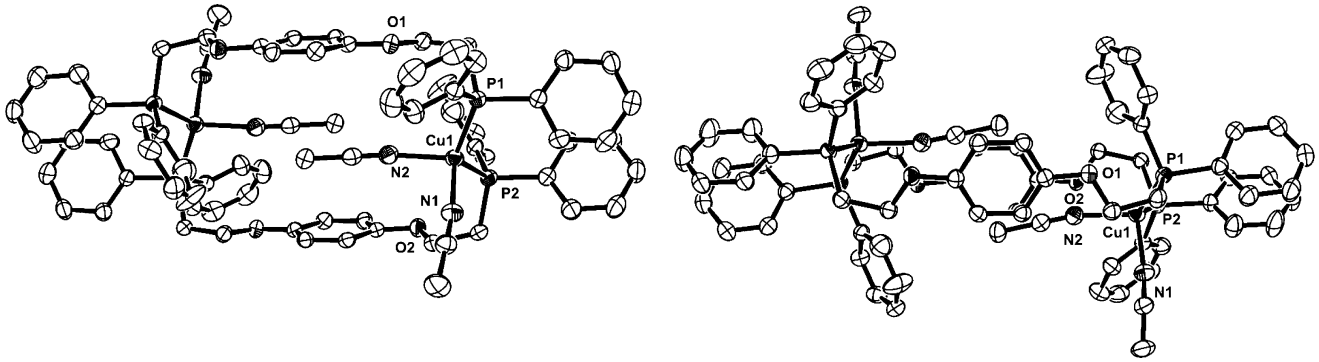


Figure 4. Thermal ellipsoid drawings of **8** showing the labeling scheme for selected atoms and ellipsoids at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

Table 4. Selected Structural Properties for [{1,4-$(Ph_2PCH_2CH_2O)_2$-C_6H_4}$_2$$Cu_2(CH_3CN)_4$][$PF_6$]$_2$·2$CH_3CN$ (**8**·2CH_3CN)

distances (Å)		angles (deg)	
Cu−Cu	9.464	∠N(1)−Cu−N(2)	95.15(9)
C_6H_4(centroid)−C_6H_4(centroid)	7.381	∠P(1)−Cu−N(1)	111.21(7)
Cu(1)−N(1)	2.029(2)	∠P(1)−Cu−N(2)	109.78(6)
Cu(1)−N(2)	2.065(2)	∠P(2)−Cu−N(1)	105.52(7)
Cu(1)−P(1)	2.253(1)	∠P(2)−Cu−N(2)	111.88(7)
Cu(1)−P(2)	2.268(1)	∠P(1)−Cu−P(2)	120.30(3)

were chosen to open the Cu(I) condensed intermediates. Successful displacement of the Cu−S or Cu−O bonds in **4**−**6** was achieved via the stoichiometric addition of pyridine, which results in the quantitative formation of the colorless cationic macrocycles (**9**−**11**) in high yield (Scheme 3). Compounds **9**−**11** have been characterized by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis. The $^{31}P\{^1H\}$ NMR spectra of these compounds exhibit resonances (singlets) that are shifted upfield from the closed complexes **4**−**6** (**9**, −1.61 ppm; **10**, −7.70 ppm; **11**, −12.70 ppm) that are similar to those of mononuclear Cu(I) bisphosphine bispyridine complexes.[17] In addition, the chemical shifts in the ^1H NMR spectra of **9**−**11** differ from those of free pyridine (upfield shift in the *o*-H) and also complexes **4**−**6**, indicating that pyridine binding has occurred. The mass spectra and elemental analyses of these compounds also support the assigned structures for each of these complexes (Scheme 3).

Stoichiometric addition of bidentate diimine ligands, such as 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and neocuproine (2,9-dimethyl-1,10-phenanthroline, dmp), also results in the formation of 26-membered macrocycles **12**−**20** in high yield (Scheme 3). These macrocycles have been characterized by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis. Similar to **9**−**11**, compounds **12**−**20** exhibit upfield chemical shifts in the $^{31}P\{^1H\}$ NMR spectroscopy as compared to the spectroscopy for closed complexes **4**−**6**. The $^{31}P\{^1H\}$ NMR chemical

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shifts of these compounds compare well with analogous mononuclear Cu(I) complexes bearing two phosphine ligands and the appropriate bidentate diimine ligand.[4c,18] Again, the ^{1}H NMR chemical shifts suggest that binding of the ancillary ligands has occurred as the resonances for all protons have shifted from the free diimine ligand (upfield for protons in the ortho positions to the nitrogen) and the condensed intermediate. Unlike the pyridine adducts, complexes **12**−**20** are colored species ranging from yellow to orange. The color of these complexes is due to a metal-to-ligand charge transfer band which relies on the d^{10} configuration of the metal center and the accessible π^* orbitals of the metal bound ligands.[19]

Cationic Macrocycles via Addition of Isocyanide, 21−**23.** *tert*-Butylisocyanide has been used to open **4**−**6** to give the colorless cationic macrocycles **21**−**23** (Scheme 3). These macrocycles have been characterized by multinuclear NMR and FT-IR spectroscopies, mass spectrometry, and elemental analysis. The ^{31}P{^{1}H} NMR chemical shifts of these compounds are shifted significantly (**21**, −4.31 ppm; **22**, −4.04 ppm; **23**, −7.88 ppm) from those of the closed complexes **4**−**6**. The ^{31}P{^{1}H} NMR chemical shifts of these compounds compare well with those of analogous mononuclear Cu(I) complexes bearing two phosphine ligands and two isocyanides.[4h] The ^{1}H NMR spectra of these complexes exhibit signals that are shifted from those of the free isocyanide and the condensed intermediates. The FT-IR spectra of these complexes exhibit strong signals in the range of 2170−2172 cm^{-1}, consistent with Cu(I)-bound *tert*-butylisocyanide.[4h,20] While ES-MS data for these compounds gives a mass corresponding to the dicationic complex with two isocyanide ligands, the ^{1}H NMR integration and elemental analysis suggests that there are four ligands bound in each complex (Scheme 3).

Conclusions

Herein, we have shown that the WLA can be used to synthesize a variety of bimetallic Cu(I) macrocycles in high yield from simple ligands and metal precursors. The WLA to Cu(I) macrocycles and the WLA to the previous square planar examples are similar, but the reactivity differences of the Cu(I) and the analogous d^8 Rh(I), Ir(I), Pd(II) condensed intermediates requires different ancillary ligands to open such structures into macrocycles. In particular, pyridine, diimines, acetonitrile, and isocyanides all can be used to open condensed structures formed from Cu(I). This provides an important additional level of control in macrocycle synthesis via the WLA, especially in view of the large number of nitrile, imine, and amine ligands available to the coordination chemist. In addition, the ability to use metal centers that prefer tetrahedral geometries demonstrates the versatility and robustness of this approach to metallomacrocycle synthesis and shows that square planar sites are not essential to achieve the directionality required to template macrocycle formation. Indeed, the basic principle of the WLA drives the formation of all of these metallomacrocycles: a hemilabile ligand can template the high yield formation of a binuclear intermediate that can be selectively opened into a macrocycle through judicious choice of small molecule, ring expanding ligands.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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