293(2) K; 18793 reflections measured, 9847 unique (R(int) = 0.0612) and 5293 $I > 2\sigma(I)$; Nonius Kappa CCD, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), graphite monochromator, Lp correction. The structure was solved by direct methods and refined against F^2 with the full-matrix, least-squares method (G. M. Sheldrick, SHELXS-98, Program for Crystal Structure Analysis, University of Göttingen, Göttingen (Germany), **1998**), 583 parameters, $R1 = 0.1578$, $wR2 = 0.2990$ for all data and $R1 = 0.0892$, $wR2 = 0.2574$ for $I > 2\sigma(I)$; residual electron density 2.104/−0.579 e Å^{-3}. Owing to disorder in the BF_4^- ion, restrain distances were introduced and an occupation factor of 0.5 was applied to all B and F atoms in general positions; the highest residual electron density peaks are localized near this anion. CCDC-188436 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Towards Stepwise Cluster Assembly: A Decacopper(II) Complex Obtained by Controlled Expansion of a Metallasiloxane Cage**

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The synthesis of new magnetic clusters with unprecedented spin topologies is a central topic in the field of molecular magnetism. Among different strategies that have been developed, serendipitous assembly[1] and rational design[2] represent opposite limiting approaches. The rational construction of heptanuclear clusters with high-spin ground states has been reported starting from hexacyanometalates $[M(CN)_6]^{3-}$ (M = Cr, Fe) and mononuclear complexes bearing a capping ligand.[2] The use of robust, preformed clusters as central cores represents an even more appealing approach, which we are currently pursuing. In particular, we are focusing on metallasiloxane cages such as $[Cu_6\{(PhSiO_2)_6\}_2L_6]$[3] (where L = monodentate ligand). The $[Cu_6\{(PhSiO_2)_6\}_2]$ skeleton features a layer of six coplanar metal ions, sandwiched between two $[(PhSiO_2)_6]^{6-}$ ligands. Similar architectures containing other first-row divalent metal ions and encapsulating a chloride ion are known.[3a,4] The twelve six-membered chelate rings in the $[Cu_6\{(PhSiO_2)_6\}_2]$ structure convey a remarkable inertness and thermodynamic stability to the cluster core. In contrast, the monodentate ligands which surround the Cu_6 cage are labile and can be easily replaced in solution by open-shell units bearing suitable bridging groups. In principle, this allows a fully controlled organization of a second shell of magnetic centers around the Cu_6 unit, Figure 1.

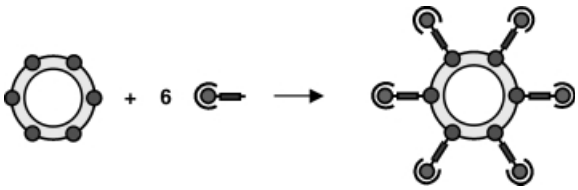

Figure 1. Addition of a second shell of magnetic centers to a central Cu_6 core.

Herein we report the successful expansion of the hexacopper(II) cage **1** through the addition of four $[Cu(tmpa)CN]^+$ (tmpa = tris(2-pyridylmethyl)amine)[5,6] units from **3** to give a decacopper(II) cluster **2**.

$[Cu_6\{(PhSiO_2)_6\}_2(n\text{BuOH})_{6-x}(H_2O)_x]$ **1**

$[Cu(tmpa)CN]PF_6$ **3**

$[Cu_6\{(PhSiO_2)_6\}_2\{NCCu(tmpa)\}_4](PF_6)_4$ **2**

Compound **2** was synthesized by reaction of **1**[3b] with the copper cyanide complex **3**[5a] in a methanol–chloroform solvent mixture (see Experimental Section).

The composition of the crystalline compound, $\mathbf{2}\cdot 2\,CHCl_3\cdot 2.75\,MeOH\cdot 0.25\,H_2O$, was established by elemental analysis and a low-temperature single-crystal X-ray diffraction investigation. The molecular structure of the cation of **2** has idealized D_2 point-group symmetry (Figures 2 and 3). The metal topology comprises an hexagonal, almost planar Cu_6 array (within ±0.0108(6) Å), plus four peripheral Cu(tmpa) units linked to the central core through cyanide bridges. Formation of the cyanide bridge induces only minor structural changes in the $[Cu(tmpa)CN]^+$ unit, the bond lengths of which are equal to within 3σ of those in **3**. On the other hand, the trigonal-bipyramidal (TB) coordination geometry of the copper(II) ion of **2** is slightly more distorted, with τ values[7] in the range 0.843(7)–0.902(7), compared with 0.943(3) in **3**.[5a] The arrangement of the bulky Cu(tmpa) units around the Cu_6 core of **2** results in significant departures from linearity in the Cu-N-C-Cu(tmpa) moieties, which have a *cisoid* conformation with N-C-Cu(tmpa) and Cu-N-C angles in the range 168.8(7)–

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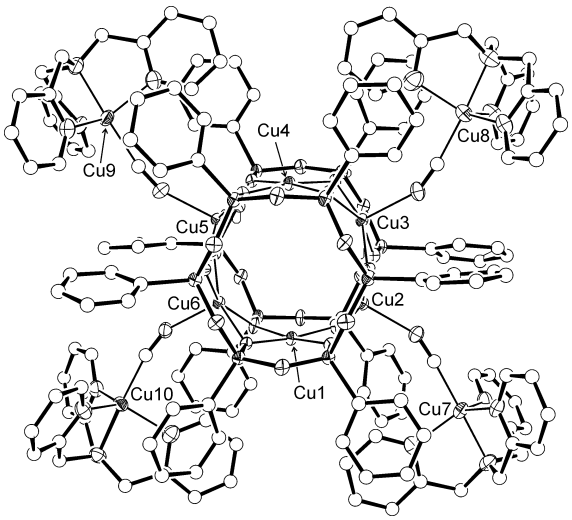

Figure 2. Molecular structure of the cation of **2** (thermal ellipsoids for the Cu, Si, O and N atoms are set at 50 %-probability). C atoms are represented as spheres of arbitrary radius. Hydrogen atoms are omitted for clarity (see Figure 3 for the atom labeling scheme).

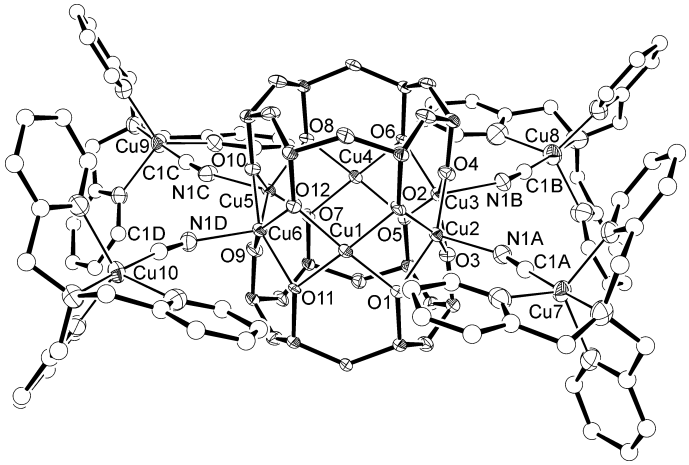

Figure 3. ORTEP[11d] plot of the cation of **2** (thermal ellipsoids for Cu, Si, O and N atoms are set at 50 %-probability). C atoms are represented as spheres with arbitrary radius. The phenyl rings of the siloxanolate ligand, as well as hydrogen atoms, have been omitted for clarity. Selected interatomic distances [Å] and interbond angles [°]: Cu1···Cu2 2.7614(12), Cu2···Cu3 2.9083(12), Cu3···Cu4 2.7598(12), Cu4···Cu5 2.7769(12), Cu5···Cu6 2.9129(11), Cu1···Cu6 2.7742(11), Cu1···Cu4 5.4164(11), Cu2···Cu5 5.7408(11), Cu3···Cu6 5.7205(11), Cu2···Cu1···Cu6 126.19(4), Cu1···Cu2···Cu3 116.77(4), Cu4···Cu3···Cu2 117.26(4), Cu3···Cu4···Cu5 126.15(4), Cu4···Cu5···Cu6 116.57(4), Cu1···Cu6···Cu5 117.05(4), Cu1-O1-Cu2 90.63(19), Cu1-O2-Cu2 90.91(19), Cu2-O3-Cu3 97.4(2), Cu2-O4-Cu3 97.9(2), Cu3-O5-Cu4 91.13(19), Cu3-O6-Cu4 90.57(18), Cu4-O7-Cu5 91.31(19), Cu4-O8-Cu5 91.84(18), Cu5-O9-Cu6 97.3(2), Cu5-O10-Cu6 96.5(2), Cu6-O11-Cu1 91.25(18), Cu6-O12-Cu1 91.04(19), Cu2-N1A-C1A 153.0(7), Cu3-N1B-C1B 153.2(7), Cu5-N1C-C1C 159.9(7), Cu6-N1D-C1D 156.3(7), N1A-C1A-Cu7 173.5(8), N1B-C1B-Cu8 171.9(8), N1C-C1C-Cu9 170.1(7), N1D-C1D-Cu10 168.8(7).

173.5(8)° and 153.0(7)–159.9(7)°, respectively. Interestingly, a pyridine group of each tmpa ligand is sandwiched between two siloxanolate phenyl rings, with dihedral angles between the pyridine and phenyl mean planes ranging from 11.3(7) to 51.5(3)°.

The geometry of the cyanide bridge in **2** is fully consistent with the blue shift observed in the C–N stretching frequency (2172 cm^{-1} vs. 2147 cm^{-1} in **3**[5a]). This behavior strongly points to a quite rigid cyanide bridge acting mainly as a σ–donor toward the metal centers.[8]

The docking of the complex ligands has a dramatic impact on the geometry of the intrinsically symmetric copper–siloxanolate framework. The cyanide-nitrogen-bound copper(II) ions have a slightly distorted square-pyramidal (SP) coordination environment, with Cu–O bond lengths in the range 1.909(5)–2.005(4) Å (av. 1.96 Å) and an average shift of the copper ions of 0.41 Å from the basal planes towards the cyanide donors. In contrast, Cu1 and Cu4 have a square-planar (S) coordination environment, with Cu–O separations in the range 1.876(5)–1.922(5) Å (av. 1.90 Å) and considerably smaller deviations from the basal planes ($\leq$ 0.13 Å). The coordination number of Cu1 and Cu4 results from the steric hindrance of the tmpa ligands which precludes coordination of a fifth axial ligand to Cu1 and Cu4. Consequently, the hexacopper(II) moiety is compressed approximately along the Cu1–Cu4 vector, the distances between opposite copper ions range from 5.4164(11) to 5.7408(11) Å. The angles at the bridging siloxanolate oxygen atoms also vary considerably around the ring, with average values of 91.1(4) and 97.3(5)° for Cu_S-O-Cu_{SP} and Cu_{SP}-O-Cu_{SP}, respectively.

The magnetic properties of a microcrystalline sample of **2** were investigated as a function of temperature (T) and applied magnetic field (B). The temperature dependence of the molar magnetic susceptibility at 1 T is shown in Figure 4 (top) as a χT versus T plot. The value of χT is 4.9 emu K mol^{-1} at 300 K and increases smoothly upon lowering the temperature, which reaches a maximum (6.2 emu K mol^{-1}) at approximately 10 K, and then decreases rapidly to 4.6 emu K mol^{-1} at 2.0 K. The molar magnetization (M) measured at 2.0 and 4.5 K as a function of B is plotted versus

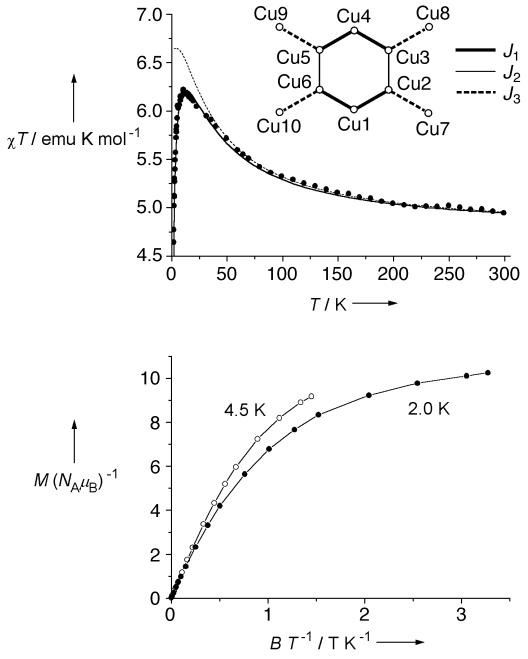

Figure 4. χT versus T (top) and M versus B/T (bottom) data for **2.** Calculated χT versus T data are also shown as solid —— ($g = 2.25$, $J_1 = -47$ cm^{-1}, $J_2 = 0$, $J_3 = 1.7$ cm^{-1}) and dashed - - - - ($g = 2.25$, $J_1 = -47$ cm^{-1}, $J_2 = 0$, $J_3 = 0$) curves.

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B/T in Figure 4 (bottom). At the highest B/T ratio, the magnetization is close to $10N_A\mu_B$, which indicates the presence of a low-lying $S=5$ state. However, the highest measured χT value in Figure 4 (top) is far below that expected for a $S=5$ state (15 emu K mol^{-1} with $g=2$), which indicates that low-lying states with a lower spin multiplicity must be present.

The molar magnetic susceptibility data (χT vs T) were quantitatively analyzed using a Heisenberg hamiltonian [Eq. (1)] with three independent exchange-coupling constants, which was suggested by the different Cu_S-O-Cu_{SP} and Cu_{SP}-O-Cu_{SP} angles (see Figure 3).

$$\mathscr{H} = J_1[\mathbf{S_1}(\mathbf{S_2}+\mathbf{S_6})+\mathbf{S_4}(\mathbf{S_3}+\mathbf{S_5})]+J_2(\mathbf{S_2}\,\mathbf{S_3}+\mathbf{S_5}\,\mathbf{S_6})+J_3(\mathbf{S_2}\,\mathbf{S_7}+\mathbf{S_3}\,\mathbf{S_8}+\mathbf{S_5}\,\mathbf{S_9}+\mathbf{S_6}\,\mathbf{S_{10}}) \quad (1)$$

The observed magnetic behavior is accurately reproduced by setting $J_1 \sim -47$ cm^{-1} with J_2 and J_3 very weakly antiferromagnetic in nature (1–2 cm^{-1}) to account for the decrease of χT at $T<10$ K. A precise, independent evaluation of J_2 and J_3 is impracticable, and is further precluded by the occurrence of magnetic anisotropy and saturation effects at low temperature. The J_1 value is close to that found in $[Cu_6\{(PhSiO_2)_6\}_2(EtOH)_6]$ ($J=-42$ cm^{-1} for Cu-O-Cu = 92.8°).[3c] The small value of J_2 is consistent with a larger Cu_{SP}-O-Cu_{SP} angle (av. 97.3(5)°) compared with Cu_S-O-Cu_{SP} (av. 91.1(4)°). Finally, a small antiferromagnetic J_3 constant is expected considering: a) the poor overlap between the d orbitals that carry the unpaired electron on Cu_{SP} ($d_{x^2-y^2}$) and on Cu_{TB} (d_{z^2}), the lobes of which are directed toward the siloxanolate and the cyanide bridges, respectively; and b) the δ-type symmetry of the $d_{x^2-y^2}$ orbitals on Cu_{SP} with respect to the C–N vector.[9]

These results show that the metallasiloxane cages can be conveniently exploited as building blocks for constructing higher-nuclearity metal clusters in a controlled fashion. Furthermore, the size and properties of the resulting complexes can be manipulated through careful choice of the complex ligands employed.

The possibility of controlling the number of Cu(tmpa) units in the cluster by varying the reaction ratio between the Cu_6 cage and the complex ligand is now under investigation.

Experimental Section

n-Butanol was distilled over CaO shortly before use, while all the other solvents were used as received. Compound **3** was prepared by a literature method[5a] and characterized by elemental analysis.

1: The compound was obtained by a variation on the synthesis reported by Lindeman and co-workers:[3b] solid polyphenylsiloxane[10] (3.226 g, 0.0250 mol) and KOH 85 % (1.710 g, 0.0259 mol) were stirred together in *n*-butanol (60.0 mL) and heated to reflux on a water bath for 1 h after complete dissolution. A solution of $CuCl_2$ (1.683 g, 0.0125 mol) in *n*-butanol (30.0 mL) was added dropwise to the continuously stirred and heated reaction mixture. The solution immediately turned to green-blue, and as the addition progressed the solution darkened and a green precipitate was formed. After the addition was complete, the suspension was heated at reflux for 10 min, then left undisturbed for 15 min. The green solid was removed by filtration and the blue filtrate was stored in a closed vessel at room temperature, which afforded a crop of green-blue prisms after a few days. Elemental analysis calcd. (%) for $C_{92}H_{120}Cu_6O_{34}Si_{12}$: C 45.73, H 4.67; found (on a vacuum dried sample 0.2 mm Hg, ca. 1 h): C 45.73, H 4.81.

2: Compound **3** (0.0314 g, 0.0592 mmol) was dissolved in chloroform (10.0 mL) and slowly added dropwise to a vigorously stirred solution of **1** (0.0251 g, 0.0103 mmol) in chloroform (1.0 mL). During the addition, a few drops of methanol were immediately added whenever the solution became cloudy. After filtration, rapid diffusion of methanol vapors into the blue filtrate afforded air-stable small blue blocks of **2**·2 $CHCl_3$·2.75 MeOH·0.25 H_2O after two days (yield ca. 25 %). Prismatic crystals suitable for an X-ray diffraction study were obtained by slow diffusion of methanol vapors into the reaction mixture. Elemental analysis calcd (%) for $C_{152.75}H_{145.5}Cl_6Cu_{10}F_{24}N_{20}O_{27}P_4Si_{12}$: C 41.15, H 3.39, N 6.28; found (on a vacuum dried sample 0.1–0.2 mmHg, 90 min.): C 41.09, H 3.44, N 6.37. IR (NaBr): $\tilde{\nu}=2172$ cm^{-1} (w, CN^-).

Crystal structure data for **2**·2 $CHCl_3$·2.75 MeOH·0.25 H_2O: $C_{152.75}H_{145.5}Cl_6Cu_{10}F_{24}N_{20}O_{27}P_4Si_{12}$, $M_r=4458.51$, crystal dimensions $0.60\times0.40\times0.40$ mm, orthorhombic, space group $Pc2_1n$, $a=21.0176(2)$, $b=25.2589(2)$, $c=33.5011(3)$ Å, $V=17785.1(3)$ Å^3, $Z=4$, $\rho_{calcd}=1.660$ g cm^{-3}, $\rho=1.64(2)$ g cm^{-3}, $2\theta_{max}=57.38°$, $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=223(2)$ K. Of the 208363 reflections collected on a SMART-CCD system, 44176 were independent and were used in the structure refinement (Lorentz, polarization and absorption corrections applied, $\mu=1.48$ mm^{-1}, min./max. transmission = 0.4715/0.5900). The structure was solved by direct methods (SIR-92)[11a] and refined on F_o^2 using SHELXL-97 program[11b] implemented in the WINGX suite.[11c] The asymmetric unit comprises one cluster and four hexafluorophosphate ions along with two chloroform and disordered lattice methanol and water molecules. All non-hydrogen atoms were refined anisotropically, except for those of methanol and water molecules and for some fluorine atoms of a disordered hexafluorophosphate ion. The hydrogen atoms of the cluster were added in idealized positions and treated isotropically. The values of $R1$ and $wR2$ are 0.0648 [$I>2\sigma(I)$] and 0.1814 (all data) for 2280 parameters and 22 restraints. The maximum and minimum residual electron density are 1.15 and -1.32 e Å^{-3}, respectively. CCDC-186933 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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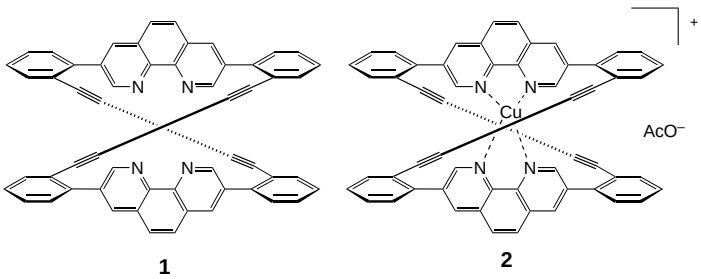


Figure 1. Phenanthrolenophane **1** and its copper(I) complex, **2**.

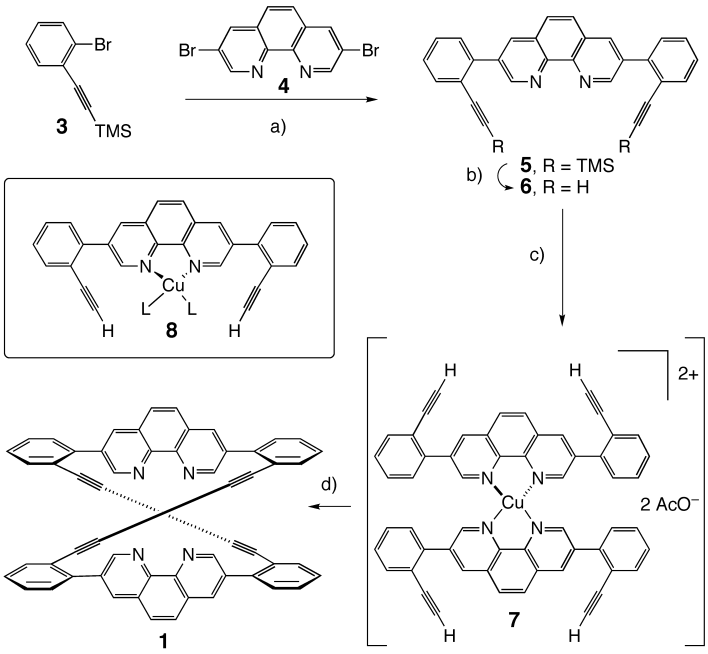
Template-Directed Synthesis of Helical Phenanthroline Cyclophanes**

Matthew A. Heuft and Alex G. Fallis*

Recently the synthesis and study of assorted carbocyclic cyclophanes and cage compounds[1] has been augmented by novel heterocyclic arrays. Representative examples include bis-2,2′-bipyridine units in twisted diyne dehydroannulenes for spectroscopic detection of metal ions,[2] butadiyne-bridged [4_4](2,6)pyridinophanes,[3] rigid cross-conjugated acetylenic macrocycles as a cyclic alternative for 4,4′-bipyridine functionalities for metal complexation,[4] and related thiophene-bridged macrocycles.[5]

Phenanthroline-based investigations involve studies of copper complex induced DNA cleavage,[6] the mechanism of strand scission,[7] enhancement of Diels–Alder reactions,[8] and applications of a cationic platinum–phenanthroline complex.[9] Substituted 1,10-phenanthrolines are highly fluorescent and the spectra are modulated by protonation or metal-ion complexation.[10] [2]Catenanes have been assembled by employing copper(I)–phenanthroline units,[11] and copper(I)–biphenanthrolines have provided scaffolds for molecular grids.[12]

We report here the synthesis of the helical 1,10-phenanthroline-capped cyclophanes **1** (Figure 1) and **11** (Scheme 2), which possess the potential for complexation with various metals, as illustrated by the insertion of copper(I) ions in **2** and **12**. Bromosilylacetylene **3** was converted into its organozincate[1e–g,13] by in situ halogen metal exchange with *n*BuLi, followed by transmetalation with $ZnBr_2$ (Scheme 1). Addition of [$Pd(PPh_3)_4$] and 3,8-dibromophenanthroline (**4**)[14] afforded **5** in 87% yield when DMF was used as a co-solvent.[15] Suzuki couplings also provide 3,8-diaryl-1,10-phenanthrolines.[14c,16] Deprotection of **5** with K_2CO_3 in MeOH/THF provided **6** in 85% yield.



Scheme 1. Synthesis of phenanthrolenophanes **1** and **2**. a) 1) *n*BuLi, THF, −78 °C; 2) $ZnBr_2$, 0 °C, 15 min; 3) **4**, [$Pd(PPh_3)_4$], THF/DMF (1/1), Δ, 72 h, 87%; b) K_2CO_3, CH_2Cl_2, MeOH, H_2O, 72 h, 85%; c) $Cu(OAc)_2$ (0.5 equiv), diethyl ether/py, 2 h; d) 1. $Cu(OAc)_2$ (5.5 equiv), diethyl ether/py, 18 h; 2. KCN (aq), CH_2Cl_2, 5 min, 70%.

We anticipated that controlled addition of copper(II) acetate to **6** (diethyl ether/pyridine) would initially generate the intermediate complex **7**. This "copper template" would then facilitate the desired coupling reaction and circumvent the competing formation of acetate **8** from direct coordination with $Cu(OAc)_2$.[17] The geometric environment of intermediate **8** will inhibit the desired reaction relative to that of **7** in which the terminal acetylene groups are suitably disposed for intermolecular coupling. In addition, polymerization pathways often observed in similar dimerizations should be diminished.[18]

Experimentally, addition of copper(II) acetate (initially 0.5 equiv) in a mixture of pyridine/diethyl ether initiated the reaction and allowed for the formation of **7**. Subsequent addition of excess reagent (5.5 equiv) completed the coupling and afforded the copper(I)-complexed cyclophane **2** in 84% yield (Scheme 1). Supporting evidence for this mechanism was provided by the observed color changes from yellow (**6**) to red (**7**) to green after an excess of $Cu(OAc)_2$ was added. Further confirmation of the importance of the copper

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