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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 [4₄](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 metalion complexation.^[10] [2]Catenanes have been assembled by employing copper(t)–phenanthroline units,^[11] and copper(t)–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 ZnBr₂ (Scheme 1). Addition of [Pd(PPh₃)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 K₂CO₃ in MeOH/THF provided **6** in 85% yield.

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Scheme 1. Synthesis of phenanthrolenophanes **1** and **2**. a) 1) *n*BuLi, THF, $-78\,^{\circ}$ C; 2) ZnBr₂, 0 $^{\circ}$ C, 15 min; 3) **4**, [Pd(PPh₃)₄], THF/DMF (1/1), Δ , 72 h, 87%; b) K₂CO₃, CH₂Cl₂, MeOH, H₂O, 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), CH₂Cl₂, 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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template in these oxidative couplings was revealed by the diminished yield of **2** (15%) when the reaction was conducted with direct exposure of **6** to Cu(OAc)₂ (6 equiv, pyridine/diethyl ether).^[19]

The parent cyclophane 1, was liberated from the copper(1)-coordinated phenanthroline cyclophane 2 upon treatment with aqueous potassium cyanide. Unfortunately, cyclophane 1 was only sparingly soluble in a range of organic solvents. The synthesis of the N,N-dibutylamine-substituted analogue 11 was investigated in an attempt to circumvent this difficulty and provide a substituted member of this series for comparison of the electronic properties. In addition, the butyl groups are diastereotopic in helical (chiral) cyclophane conformations and this should be

reflected in the ¹³C NMR spectrum, thus allowing the conformational behavior of the cyclophane to be probed.^[20]

A very direct synthesis of **11** has been developed to improve the preparation of these compounds. Dibromide **4** was treated with known iodide **9**^[18] through a parallel palladium coupling sequence to generate diacetylene **10** (Scheme 2). Compound **10** was transformed into the metal-free cyclophane **11** in a single reaction vessel by a sequential in situ desilylation/ dimerization/decomplexation protocol related to the experiments we have developed recently.^[21] These steps culminated in an aqueous potassium cyanide work-up to give **11** in 39% yield. Cyclophane **11** was soluble in a variety of chlorinated solvents.

Copper(I) complexes **2** and **12** were prepared independently as above, but crystals suitable for X-ray analysis were not obtained. However, molecular modeling studies (Figure 2) revealed the twisted nature and key features of the phenanthrolenophane copper complex **2** (Figure 1).^[22] The heterocyclic rings displayed an orthogonal disposition with respect to each other and created a pseudotetrahedral coordination site for copper(I) or other electronically related metal ions. The helical nature of cyclophane **12** resulted from our synthetic protocol and the bridges selected.^[1d-f]

Variable temperature ¹³C NMR analysis of **12** indicated the helical isomerization barrier was 13.6 kcal mol⁻¹, an increase of approximately 4 kcal mol⁻¹ relative to the uncomplexed cyclophane **11** (Figure 3). Different metals and substituent combinations may increase this barrier sufficiently to inhibit isomerization and facilitate resolution of the individual enantiomers.

Electronic absorption (Figure 4) were obtained for cyclophanes 1, 2, 11, and 12 and compared to related compounds (Table 1). Copper template 7 absorbed in the 600 to 700 nm range, which is indicative of copper(Π) complexes. Emission spectra (Figure 5) of 1 and 11 were recorded but the metallocyclophanes (2 and 12) did not fluoresce.

In summary, we have developed a short, efficient syntheses of a series of functionalized acetylenic phenanthroline cyclophanes by Pd- and Cu-mediated coupling reactions. Molecular modeling studies have established the nature of the



Scheme 2. Synthesis of phenanthrolenophanes **11** and **12**. a) 1. **9**, *n*BuLi, THF, -78 °C; 2. ZnBr₂, 0 °C, 15 min; 3. **4**, [Pd(PPh₃)₄], THF/DMF (1/1), Δ , 72 h, 70 %; b) 1. TBAF, diethyl ether/py, 15 min; 2. Cu(OAc)₂ (0.5 equiv), diethyl ether/py, 2 h; 3. Cu(OAc)₂ (5.5 equiv), diethyl ether/py, 2 h; 4. KCN (aq), 39%; c) [Cu(MeCN)₄PF₆], CH₂Cl₂, 15 min, 97%; d) KCN (aq), CH₂Cl₂, 5 min, 97%. py = pyridine.



Figure 2. Molecular models of cyclophanes 1 and 2.



Figure 3. Potential energy diagram for the enantiomerization of cyclophanes **2** and **12**. $\Delta G_2^+ < 9.4 \text{ kcal mol}^{-1}$, $\Delta G_{12}^+ = 13.6 \text{ kcal mol}^{-1}$, $\Delta \Delta G^+ > 4.2 \text{ kcal mol}^{-1}$.



Figure 4. UV/Vis absorption spectra of 1, 11, and 12.^[23]



Figure 5. Normalized fluorescence spectra of 1 and 11 (n: counts).^[24]

Table 1. UV/Vis absorption maxima of phenanthroline compounds and copper-phenanthrolic complexes.



13		
Compound	$\lambda_{max}(abs) [nm]$	$\lambda_{\max}(em) [nm]$
13 $(R = H)^{[25]}$	440	
$[Cu(13)_2]^+ (R = H)^{[26]}$	458	
13 $(R = C \equiv C - Ph)^{[10]}$	346	376, 395
13 $(R = C \equiv C - (p - PhNMe_2))^{[10]}$	410	523
1	307 (sh)	416
2 $[Cu(1)_2]^+$	473, 553 (sh)	
7 [Cu(6) ₂] ²⁺	462	
11	383	584
12 $[Cu(11)_2]^+$	407	

copper-complexed core. In addition, resolution of the helical isomers may be feasible with additional ring substituents and metal complexation. The synthetic protocol above will facilitate the preparation of new derivatives that may possess unusual optical properties, while modification of the acetylene spacers offers some control of the helical conformation.

Experimental Section

Sequential in situ desilylation/dimerization/decomplexation procedure (11): A solution of tetrabutylammonium fluoride (TBAF) (1M in THF, 1.32 mL, 1.32 mmol, 2.5 equiv) was added in one portion to a stirred solution of 10 (500 mg, 0.53 mmol, 1 equiv) in pyridine/diethyl ether (3/1, 20 mL). After stirring the solution for 15 min, a solution of $Cu(OAc)_2$ (48 mg, 0.26 mmol, 0.5 equiv) in pyridine/diethyl ether (3/1, 20 mL) was added over 2.5 h by syringe pump. Once the addition was complete, additional Cu(OAc)₂ (530 mg, 2.92 mmol, 5.5 equiv) was added to the reaction and the solution turned green immediately. The reaction was stirred for 18 h at room temperature and partitioned between CH₂Cl₂ and water. The aqueous phase was extracted with CH_2Cl_2 (×3) and the combined extracts were washed with KCN (10%, aq) and water, filtered through celite, and concentrated. Following chromatography on silica gel (CH₂Cl₂/MeOH, 30/1), **11** was isolated as an orange solid (130 mg, 39%). 1: m.p. 150 °C slow decomp.; ¹H NMR (500 MHz, [D₆]DMSO, 25 °C, TMS): $\delta = 9.33$ (brs, 4H), 8.87 (brs, 4H), 7.82–7.77 (m, 12H), 7.63 (brs, 4H), 7.40 ppm (brs, 4H); ¹³C NMR (125 MHz, [D₆]DMSO, 25 °C, TMS): $\delta =$ 150.4 (d), 144.3 (s), 140.0 (s), 135.9 (d), 133.7 (s), 133.1 (d), 132.3 (d), 131.4 (d), 130.8 (d), 127.7 (s), 126.9 (d), 118.9 (s), 81.4 (s), 76.3 ppm (s); MS (ES) m/z (%): 757.0 (1), 579.1 (2), 279.0 (4), 141.9 (53).

2: m.p. > 260 °C; IR (CH₂Cl₂): $\tilde{v} = 3049.9$, 1604.0, 1436.7, 1266.8, 1119.7 cm⁻¹; ¹H NMR (500 MHz, [D₆]DMSO, 25 °C, TMS): $\delta = 9.25$ (brs,

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4 H), 8.84 (brs, 4 H), 8.37 (brs, 4 H), 7.65 (brs, 4 H), 7.41 ppm (brs, 12 H); ¹³C NMR (125 MHz, [D₆]DMSO, 25 °C, TMS): δ = 149.2 (d), 141.6 (s), 139.8 (s), 136.7 (d), 136.4 (s), 133.5 (d), 130.8 (d), 129.8 (d), 129.0 (d), 128.7 (s), 127.7 (d), 118.9 (s), 81.3 (s), 76.0 ppm (s); MS (70 eV): *m/z* (%): 819.3 (100) [*M*⁺], 136.0 (55).

11: m.p. 138–140 °C; IR (CH₂Cl₂): $\tilde{\nu} = 2960.9$, 1596.2, 1369.8, 847.2 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): $\delta = 9.27$ (s, 4 H), 8.46 (s, 4 H), 7.40 (d, J = 8.6 Hz, 4H), 7.03 (s, 4H), 6.91 (s, 4H), 6.75 (d, J = 6.9 Hz, 4H), 3.29 (t, J=7.1 Hz, 16H), 1.62–1.53 (m, 16H), 1.41–1.32 (m, 16H), 0.96 ppm (t, J = 7.2 Hz, 24 Hz); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): $\delta = 150.6$ (d), 147.5 (s), 144.3 (s), 134.9 (d), 134.3 (s), 130.6 (d), 127.8 (s), 127.7 (s), 126.5 (d), 120.8 (s), 116.5 (d), 113.5 (d), 81.9 (s), 75.6 (s), 50.7 (t), 29.3 (t), 20.3 (t), 13.9 ppm (q); MS (ES) 1266.5 (1) [M⁺], 579 (1.2), 279.0 (48), 186.1 (100). **12**: m.p. > 250 °C (decomp); IR (CH₂Cl₂): $\tilde{\nu} = 2960.9, 1596.2, 1369.8, 847.2,$ 769.8 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): $\delta = 9.18$ (br s, 4 H), 8.30 (brs, 4H), 8.08 (brs, 4H), 7.19 (brs, 4H), 6.71 (s, 4H), 6.62 (brs, 4H), 3.21 (brs, 16H), 1.51 (brs, 16H), 1.32 (brs, 16H), 0.92 ppm (brs, 24 Hz); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): $\delta = 150.0$ (d), 148.1 (s), 141.6 (s), 137.8 (s), 134.8 (d), 130.5 (d), 128.9 (s), 127.3 (d), 126.6 (s), 120.5 (s), 115.4 (d), 113.7 (d), 81.9 (s), 75.4 (s), 50.6 (t), 29.6 (t), 20.2 (t), 13.9 ppm (q); MS (ES) 1328.5 (6) $[M^+-PF_6]$, 342.1 (10), 186.2 (24).

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In recent years, macrocyclic musks^[1,2] have gained renewed interest for their excellent odor qualities (warm, sensual, animal, natural), and for their better biodegradability than benzenoid musks.^[2,3]

In particular, there is still a great need to find efficient syntheses for the construction of C-15 macrocyclic ketones possessing specific unsaturation. We herein report the first application of a new synthetic strategy in which the target compounds are obtained from an appropriately functionalized tricyclic system by two consecutive fragmentations. This approach is complementary to the metathesis-based annulations, which are often more direct but require high dilution and generally afford E/Z mixtures.^[4]

Access to the targeted tricyclic fragmentation precursor was provided by the ready availability of the known dihydroxy ketone **1**, which was prepared in one pot from cyclohexanone and cyclopropanone (Scheme 1).^[5] Despite a reported yield of 67%, it was only after modification of the experimental procedure that we were able to attain a reproducible yield of 44% (see Experimental Section).

The 1,3,5-functionalization of **1**, in which one oxygen atom is adjacent to a bridgehead and the two other oxygen atoms are situated at bridgehead positions, is ideally suited for cascade Grob fragmentations^[6] and should allow, via inter-

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Scheme 1. Synthesis of ketone 1.^[5]



Scheme 2. Projected route to unsaturated C-15 macrocyclic ketones.

mediates **a**, ready access to new unsaturated C-15 macrocyclic ketones of type **b** (Scheme 2).

Reduction of **1** with LiAlH₄ afforded a 74:26 mixture of triols **2** and **3** (Scheme 3), whereas by using Red-Al[®] in THF at low temperature the all-*cis* triol **2** was obtained almost quantitatively in a highly diastereoselective manner (99:1). On the other hand, reduction with BH₃·SMe₂ followed the opposite facial selectivity with an equally high diastereoselectivity (98:2), affording triol **3** in 81 % yield (Scheme 3).^[7]

For the conversion of alcohol 2 into tosylate 4, whereas the application of classical conditions (TsCl, pyridine) gave rise to partial epimerization (by successive substitutions) and chloride formation, deprotonation of 2 with *n*BuLi followed by rapid treatment with TsCl gave the best results (Scheme 4).



Scheme 3. Diastereoselective reductions of ketone **1**. a) $LiAlH_4$ (1.15 equiv), THF, $-70^{\circ}C$ to $-50^{\circ}C$; b) Red-Al[®] (3.0 equiv), THF, $-70^{\circ}C$ to room temperature; c) BH_3 ·SMe₂ (0.71 equiv), THF, room temperature.

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