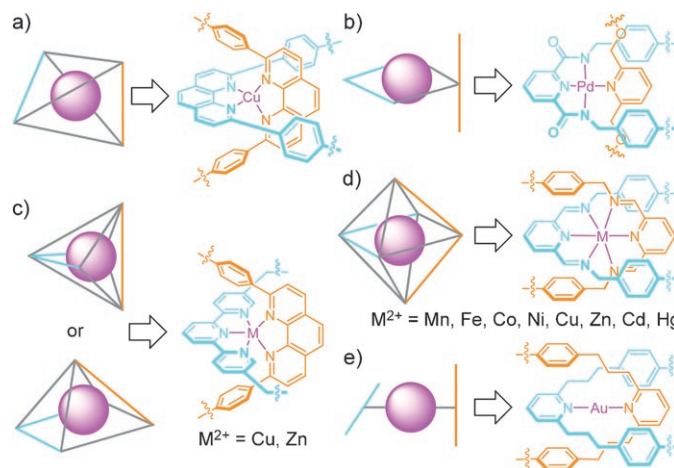


Gold(I)-Template Catenane and Rotaxane Synthesis**

Stephen M. Goldup, David A. Leigh,* Paul J. Lusby, Roy T. McBurney, and Alexandra M. Z. Slawin

Metal ions with a range of different two- and three-dimensional coordination geometries (Scheme 1 a–d) have been used as a template for the synthesis of catenanes and rotaxanes.^[1,2] The result is a rich tapestry of mechanically interlocked ligands and complexes that have been studied from the point of view of their electrochemistry,^[3] photochemistry,^[4] reactivity,^[5] selectivity,^[3b,6] and as prototypes for molecular machines.^[7] Some of these systems can be assembled under thermodynamic control,^[8] others under kinetic control.^[3–6,9] Some use sophisticated ligand systems,^[10] others relatively simple ones.^[8] Some feature homoleptic complexation modes,^[3a,8a,c,11,12] others heteroleptic ones.^[9a,c,13,14] All employ at least one multidentate ligand. Herein we report on the first use of a one-dimensional (linear) metal–ligand coordination geometry (Scheme 1 e) to template the synthesis of mechanical bonds.^[15,16] The method requires only monodentate units on each component (we have used pyridine rings but aryl–gold coordination motifs are also well known^[17]) and both homoleptic (suitable for homocircuit catenanes) and heteroleptic (suitable for heterocircuit catenanes and rotaxanes) complexes can be assembled. The approach is exemplified through the gold(I)-template synthesis of a catenane and a rotaxane by ring closing olefin metathesis (RCM) macrocyclization^[8a,11] protocols.

Although gold(III), with its square-planar coordination preference, has previously been used as a template in synthesis (to direct the assembly of aza-macrocycles^[18]), to the best of our knowledge two-coordinate gold(I) has not, despite it being an integral part of many oligomeric and polymeric supramolecular complexes, helicates, and organo-metallic structures (which often feature multiple gold–gold



Scheme 1. Metal coordination geometries successfully utilized in the metal-template synthesis of catenanes and rotaxanes. a) Four-coordinate (tetrahedral);^[3a,4e,5a,b,6,8c,9a,b,11] b) four-coordinate (square planar);^[5d,9c,13] c) five-coordinate (square-based pyramidal/trigonal bipyramidal);^[14] d) six-coordinate (octahedral);^[8a,b,12] e) two-coordinate (linear; this work).

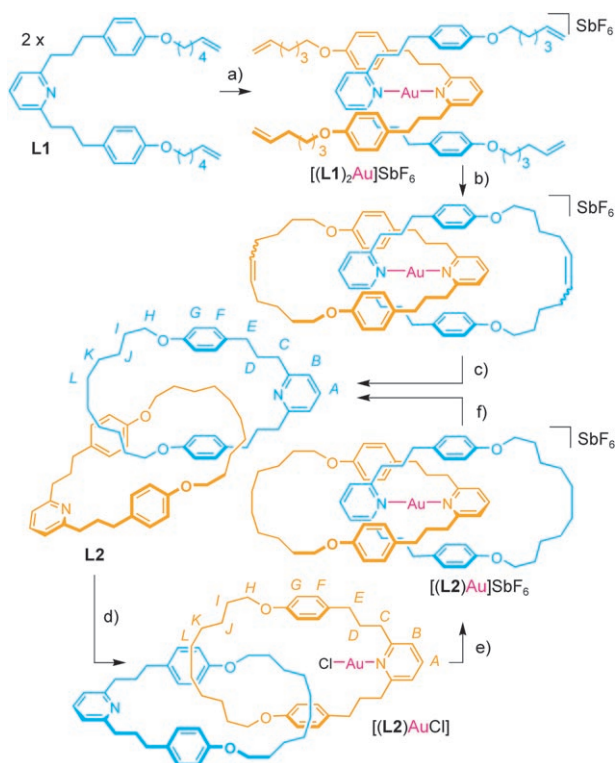
aurophilic interactions in addition to the metal–ligand interactions).^[15,19] The attractiveness of using a linear coordination mode in synthesis lies in its simplicity and the potential generality of a motif that requires just two monodentate ligands to bind the metal. However, a key design question in any metal-template catenane or rotaxane synthesis is how to promote entwining of the ligands once they are attached to the metal. With gold(I) this is particularly easy to achieve: two 2,6-dialkylpyridine ligands, which are readily accessible by metal-mediated cross-couplings with 2,6-dihalopyridines,^[20] must necessarily assemble with orthogonal orientations about the gold ion with the “arms” of each ligand pointing over the other ligand to create the required two crossover points. For our chosen ligand system (**L1**, see Scheme 2) we also introduced aromatic rings (Scheme 1 e) at positions equivalent to those found to form efficient intercomponent aromatic stacking interactions in benzylic amide and imine catenanes and rotaxanes (Scheme 1 b,d). The terminal functional groups on each ligand should thus be oriented such that macrocyclization reactions should favor interlocked products over the formation of larger macrocycles, oligomers, and polymers.

Pyridine ligand **L1** was synthesized by alkylation of a known^[2d] bis-phenol (see the Supporting Information), and a 2:1 complex with gold(I), [(**L1**)₂Au]SbF₆, assembled by treating **L1** (2 equiv) with AuCl(SMe₂) (1 equiv) followed by anion exchange with AgSbF₆ (Scheme 2, step a). Ring

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Scheme 2. Gold(I)-template catenane synthesis and subsequent chemistry. a) 1. AuCl(SMe₂), acetone, 5 min; 2. AgSbF₆, 5 min; b) [(PCy₃)₂Cl₂Ru=CHPh], CH₂Cl₂, 2 d; c) 1. 1 M HCl(aq.)/CH₂Cl₂ (1:1), 40 °C, 18 h; 2. H₂, Pd/C, THF/EtOH (1:1), 18 h; **L2** (41 % from **L1**); d) AuCl(SMe₂), acetone, 5 min; e) AgSbF₆, acetone, 5 min; > 98 %; f) 1 M HCl(aq.)/CH₂Cl₂ (1:1), 40 °C, 18 h or *hν* 400–700 nm (500 W halogen lamp), CHCl₃, 6 d; > 98 %.

closing metathesis of [(**L1**)₂Au]SbF₆ (Scheme 2, step b) afforded one major and two minor products, each as a mixture of olefin diastereomers and in both metalated and demetalated forms. To facilitate purification, the crude product mixture was fully demetalated and the olefins reduced before being subjected to column chromatography to yield the major product, later confirmed to be the desired catenane **L2**, in 41 % yield (from **L1**). Also isolated were the macrocycle resulting from simple cyclization of **L1** (20 %) and a larger macrocycle (an isomer of the catenane) formed from the 1+1 cyclization of **L1** (18 %). It is not clear whether the noninterlocked products arise from unproductive macrocyclization reactions on the gold(I) template (similar product distributions have been observed in some Pd^{II}-templated catenane syntheses^[13c]) or from reactions involving uncomplexed **L1** (a potential disadvantage of using relatively weakly binding monodentate ligands for a template synthesis is that unbound ligand can be present during the reaction).

Evidence supporting assignment of the major product as [2]catenane **L2** came initially from the comparison of the mass spectrometry and ¹H NMR spectroscopic data for the products (Figure 1a and b: the major product (Figure 1b) shows shielding effects similar to those found in other catenanes).^[8a,b,13c] Confirmation of the mechanically interlocked structure was obtained from X-ray crystallography of the bis-*p*-toluenesulfonic acid salt (Figure 2), in which the

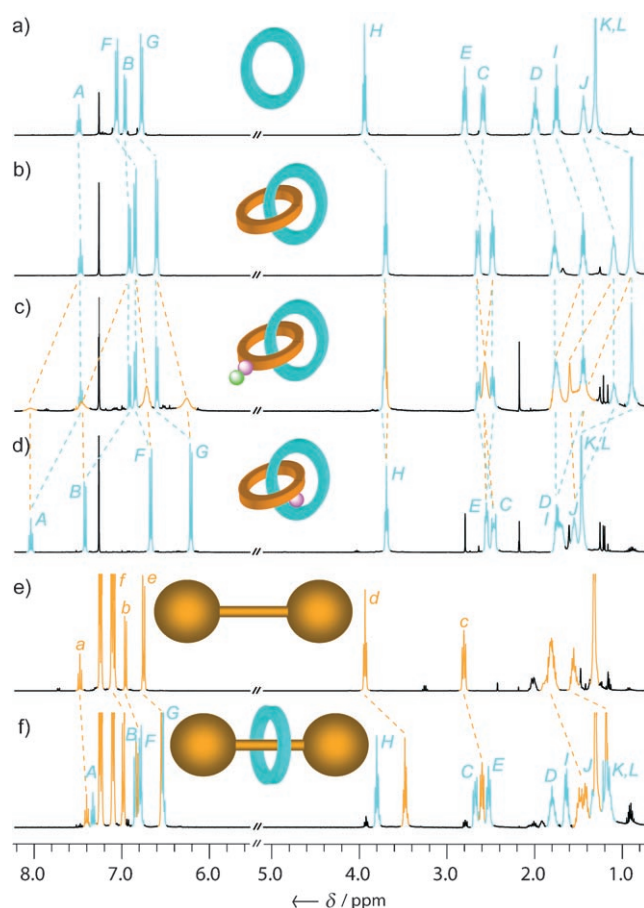


Figure 1. ¹H NMR spectra (400 MHz, CDCl₃, 300 K) of a) the non-interlocked macrocycle; b) the metal-free catenane **L2**; c) [(**L2**)Au]Cl; d) gold(I) catenane [(**L2**)Au]SbF₆; e) thread **L3**, and f) the metal-free rotaxane **L4**. The assignments correspond to the lettering shown in Schemes 2 and 3.

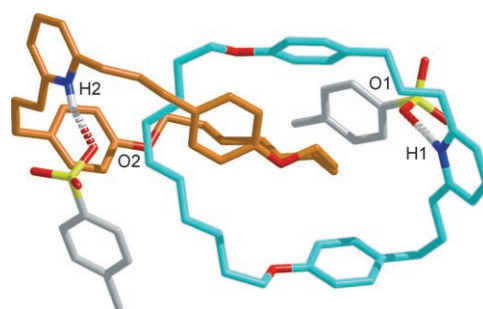


Figure 2. Molecular structure^[21] of H₂**L2**(OTs)₂ from X-ray structure analysis of a single crystal grown by vapor diffusion of diisopropyl ether into a saturated acetone solution. Carbon atoms are shown in light blue for one macrocycle and in brown for the other; O red, N blue, S yellow. Hydrogen bond lengths [Å] and angles [°]: NH1...O1 = NH2...O2 1.76; N1-H1-O1 = N2-H2-O2 163.

protonated pyridine groups lie to the outside of the catenane, with the alkyl chains of each macrocycle buried through the cavity of the other.^[21]

Gold(I) could be re-introduced into catenane **L2** in a two-step process. Treatment with AuCl(SMe₂) quantitatively

generated the interesting complex $[(\mathbf{L2})\text{AuCl}]$, the ^1H NMR spectrum of which (Figure 1 c) shows inequivalent resonances for the two macrocycles indicating that gold is coordinated to just one ring. Subsequent addition of AgSbF_6 and filtration through celite generated $[(\mathbf{L2})\text{Au}]\text{SbF}_6$, whose ^1H NMR spectrum (Figure 1 d) shows only one set of macrocycle resonances, enhanced shielding for aromatic protons H_F and H_G , and reduced shielding of the alkyl-chain protons, indicating that a significant co-conformational rearrangement takes place for both rings to bind to the gold ion. Crystals of the gold(I) catenate suitable for X-ray crystallography were obtained by vapor diffusion of diisopropyl ether into a saturated acetone solution of the complex.^[21] The solid state structure of $[(\mathbf{L2})\text{Au}]\text{SbF}_6$ (Figure 3), in which the pyridine

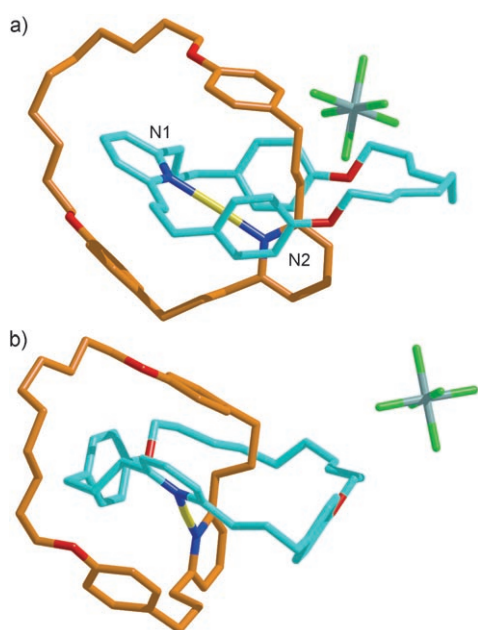
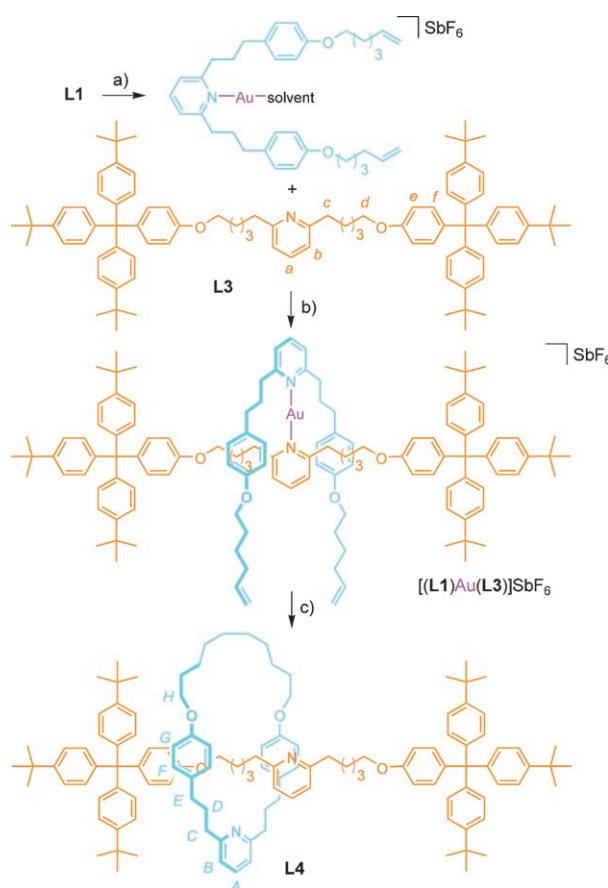


Figure 3. X-ray crystal structure^[22] of gold(I) catenate $[(\mathbf{L2})\text{Au}]\text{SbF}_6$, viewed a) parallel to the N–Au–N bond, b) close to the axis of the N–Au–N bond. Carbon atoms are shown in light blue for one macrocycle and in brown for the other; O red, N blue, Au^I gold, Sb grey, F green. Selected bond lengths [Å] and angles [°]: N1–Au 2.05, N2–Au 2.06; N1–Au–N2 175.3; closest Au...Au contact 11.31 Å.

groups are now internal to the catenate so that both can bind the metal ion, with the alkyl chains to the outside, shows the close-to-linear (175.3°) coordination geometry of the pyridine–gold(I)–pyridine motif and some of the offset inter-component aromatic stacking interactions introduced to aid catenane formation. The gold ion is fully encapsulated within the organic framework and thus prevented from making auophilic gold–gold interactions^[19] (the shortest Au...Au distance in $[(\mathbf{L2})\text{Au}]\text{SbF}_6$ in the solid state is more than one nanometer).

To extend the methodology to rotaxane formation required the assembly of a heteroleptic complex about the gold(I) center (Scheme 3). Treatment of **L1** with $\text{AuCl}(\text{SMe}_2)$ (1 equiv), followed by AgSbF_6 and **L3**, attached both the macrocycle precursor and the thread to the same gold ion,



Scheme 3. Gold(I)-template rotaxane synthesis. a) 1. $\text{AuCl}(\text{SMe}_2)$, acetone, 5 min; 2. AgSbF_6 , acetone, 5 min; b) acetone, 5 min; c) 1. $[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}]$, CH_2Cl_2 , 2 d; 2. 1 M $\text{HCl}(\text{aq})/\text{CH}_2\text{Cl}_2$ (1:1), 40°C , 18 h; 3. H_2 , Pd/C , THF/EtOH (1:1), 18 h, **L4** (26% from **L1**).

generating $[(\mathbf{L1})\text{Au}(\mathbf{L3})]\text{SbF}_6$ (Scheme 3, steps a and b). Subsequent RCM (Scheme 3, step c) captured the interlocked architecture. As with the catenane synthesis, the metal was removed and the double bond hydrogenated prior to purification by column chromatography, which yielded metal-free rotaxane **L4** in 26% yield (from **L1**) together with 14% of catenane **L2** (arising from ligand-scrambling of $[(\mathbf{L1})\text{Au}(\mathbf{L3})]\text{SbF}_6$). The ^1H NMR spectrum of rotaxane **L4** (Figure 1 f) shows shielding with respect to the spectra of its noninterlocked components (macrocycle, Figure 1 a, and thread, Figure 1 e) similar to that observed for catenane **L2** (Figure 1 b).

It is easy to forget that prior to Sauvage's original Cu^{I} -template synthesis^[9a] the construction of mechanically interlocked molecules was a task of almost Herculean proportions.^[22] A quarter of a century on, the gold(I)-template synthesis of [2]catenane **L2** and [2]rotaxane **L4** marks the last of the simple metal coordination geometries (linear) to join the family of metal–ligand arrangements that can direct the formation of mechanical bonds. The ability to form both homoleptic and heteroleptic complexes, and the simplicity of the monodentate ligands required, suggests that gold(I) could prove to be a particularly versatile template for the synthesis of interlocked molecular structures.

Experimental Section

Gold(I)-template synthesis of catenane **L2**: To a stirred solution of **L1** (0.178 g, 0.348 mmol) in acetone (5 mL) was added AuCl(SMe₂) (0.0513 g, 0.174 mmol). After 5 min AgSbF₆ (0.0598 g, 0.174 mmol) was added and the resulting grey-blue suspension stirred for a further 5 min before filtration through a pad of celite and removal of the solvent under reduced pressure. The crude residue was redissolved in CH₂Cl₂ (100 mL) and Grubbs' first-generation olefin metathesis catalyst added (0.058 g, 0.070 mmol). The resulting purple solution was stirred for two days under a stream of N₂. The solvent was removed under reduced pressure, the crude residue redissolved in CH₂Cl₂ (10 mL) and 1M HCl(aq) (10 mL), and heated at 40 °C for 18 h. The mixture was neutralized with saturated aqueous sodium bicarbonate (100 mL) and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were washed with brine (50 mL), dried (MgSO₄), and concentrated under reduced pressure. The crude residue was taken up in THF (5 mL) and EtOH (5 mL) and 10% w/w Pd/C (0.070 g) added. The reaction vessel was repeatedly degassed and purged with N₂, then repeatedly degassed and purged with H₂ and its content stirred for 18 h. The reaction mixture was then filtered through a pad of celite, concentrated under reduced pressure, and purified by column chromatography (0–10% EtOAc in CH₂Cl₂ gradient elution; silica gel) to yield catenane **L2** (0.069 g, 41%) as a colorless solid.

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