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Getting Harder: Cobalt(III)-Template Synthesis of Catenanes and Rotaxanes

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Abstract: The synthesis of catenanes and rotaxanes using the hard trivalent transition metal ion cobalt(III) as a template is reported. Tridentate dianionic pyridine-2,6-dicarboxamido ligands, each with two terminal alkene groups, coordinate Co(III) in a mutually orthogonal arrangement such that entwined or interlocked molecular architectures are produced by ring-closing olefin metathesis. Double macrocyclization of two such ligands bound to Co(III) afford a non-interlocked "figure-of-eight" complex in 42% yield, the structure determined by X-ray crystallography. Preforming one macrocycle and carrying out a single macrocyclization of the second bis-olefin with both ligands attached to the Co(III) template led to the isomeric [2]catenate in 69% yield. The mechanically interlocked structure was confirmed by X-ray crystallography of both the Co(III) catenate and the metal-free catenand. A Co(III)-template [2]rotaxane was assembled in 61% yield by macrocyclization of the bis-olefin ligand about an appropriate dianionic thread. For both catenanes and rotaxanes, removal of the metal ion via reduction under acidic conditions to the more labile Co(II) gave neutral interlocked molecules with well-defined co-conformations stabilized by intercomponent hydrogen bonding.

Introduction

The use of transition metal ions as templates[1−7] and structural elements[8] were breakthrough strategies in the development of effective methods for the synthesis of mechanically interlocked architectures, but for over fifteen years the Cu(I)-bis-phenanthroline system developed in Strasbourg remained the only reliable metal template route to catenanes and rotaxanes. Recently, however, complementary and robust methodologies for the construction of rotaxanes and catenanes around other metal−ligand systems, featuring a range of metal coordination geometries and ligand types, have been developed. For example, relatively soft divalent metal ions have been used to template the assembly of catenanes[9a] and rotaxanes[9b] around octahedral metal centers (Figure 1a);[10] the two-dimensional square planar geometry of palladium(II) has been used to prepare [2]catenanes,[11a,b] [2]-,[11b] [3]-,[11d] and [4]rotaxanes[11d] and molecular shuttles;[11e] and the linear coordination mode of gold(I) has been demonstrated to template the assembly of minimally functionalized building blocks into both catenanes and rotaxanes.[12] The result is that chemists now have a diverse range of mechanically interlocked ligands and complexes that can be investigated from the point of view of their electrochemistry,[2b,5h,13] photochemistry,[5l,10e,j,14] reactivity,[15] selectivity of binding,[13a,16] and as key structural motifs in prototypes for molecular machines.[17] However, the ability of the metal to template a particular structure remains highly dependent on the nature of both the

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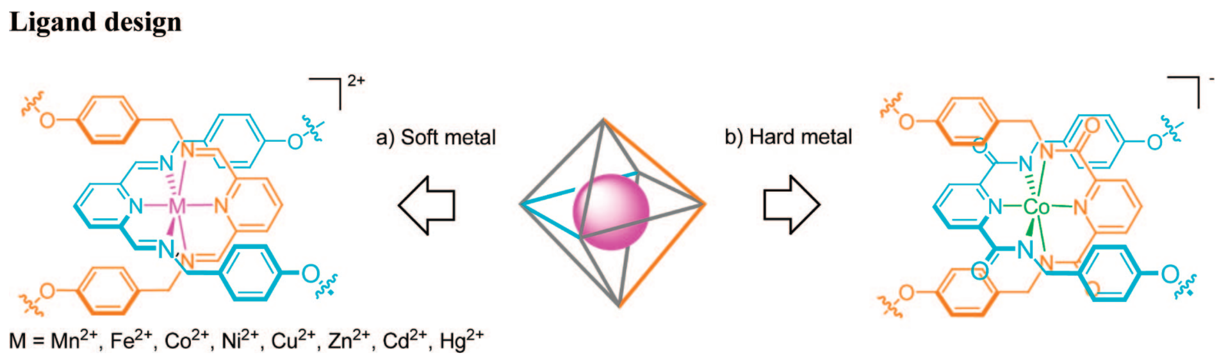

Figure 1. Tridentate ligand systems that favor orthogonal mer coordination to octahedral metal ions: (a) neutral pyridine-2,6-diimino ligands suitable for chelating "soft" divalent metal ions; (b) *bis*-anionic pyridine-2,6-dicarboxamido ligands suitable for chelating "hard" trivalent metal ions.

metal and the ligand system (and their mutual compatibility), and modest changes to either can prevent the building blocks assembling in the desired manner.[11a,b] Furthermore, mechanically interlocked ligands that have been assembled around one type of template (e.g., a soft metal ion) are generally not well-suited to binding to other types of metal ion (e.g., hard metal ions). Consequently, there is an ongoing need for new interlocked ligand motifs that enable different types of metal ions

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to be complexed. Herein we revisit the challenge of the template synthesis of mechanically interlocked architectures which bind metal ions with a preferred octahedral coordination geometry, this time utilizing the hard trivalent transition metal ion cobalt(III)[18] to preorganize two tridentate pyridine 2,6-dicarboxamido ligands in order to construct both catenanes and rotaxanes. The Co(III) template synthesis has several distinctive features which complement existing methods for interlocked molecule synthesis: (i) it utilizes two similar (rotaxane) or identical (catenane) dianionic ligands in a homotopic binding motif that makes the template complex anionic rather than cationic; (ii) the template is constructed and applied in an unusual three-step process involving, first, assembly of the ligands under thermodynamic control around kinetically labile Co(II), subsequent locking of the ligands on the metal by oxidation to nonlabile Co(III) (after which the desired template complex can be separated from other ligand−metal complexes if necessary), followed by ring-closing or cross-olefin metathesis to covalently capture the interlocked or entwined structure; (iii) the methodology is high yielding and uses readily prepared building blocks; (iv) removal of the metal ion from the interlocked product generates a free ligand that still exhibits a well-defined co-conformation as a result of intercomponent hydrogen bonding; (v) Co(III) can be reintroduced into the resulting interlocked ligands to form [2]catenane and [2]rotaxane complexes of a hard metal ion that is kinetically inert to ligand exchange.

Ligand Design. The basic design of the ligands for Co(III)-mediated assembly is derived from an earlier system successfully used to synthesize interlocked architectures around divalent metal ions (Figure 1). In that system, the mer coordination of two neutral tridentate ligands (Figure 1a) around a divalent octahedral metal center holds the ligands in an orthogonal arrangement and the shape of the ligands, supported by $\pi-\pi$ interactions between the interchelated ligands, subsequently directs interlocking macrocyclization reactions to give high yields of [2]catenates[9a] and [2]rotaxanes[9b] under either kinetic or thermodynamic control. Deprotonated carboxamide (carboxamido) groups are known to be good ligands for hard ions such as Fe(III) and Co(III) and their complexation behavior has been extensively studied because of their significance in key natural processes.[19] It appeared that replacement of the divalent-ion-coordinating imine groups with amides (Figure 1b)[20] would facilitate binding to trivalent ions while conserving the features—intercomponent π-stacking and preorganized 180° degree turn—that induce the terminal groups of each ligand to converge and form the crossover points necessary for catenane and rotaxane formation. We selected ring-closing olefin metathesis (RCM) for the reaction to covalently capture the interlocked products, as it is high yielding and tolerant to the demands imposed by macrocyclization to form very large rings (entropy loss and sufficient stability of the reactive intermediate when adoption of a geometry where ring closing can occur is a rare event). Ligand H_2**L1** (Scheme 1) appeared to have these desired features, and accordingly, the products of a series of single and double macrocyclization reactions of the ligand on a Co(III) template were investigated.

Results and Discussion

Co(III)-Template Double Cross-Olefin Metathesis of L2 (“Figure-of-Eight” Synthesis). Initially we investigated the olefin metathesis of two molecules of H_2**L1** on a cobalt(III) template, a reaction that could potentially generate a number of different product types and topologies (Scheme 1). As ligand exchange around Co(III) centers is generally slow, it proved convenient to initially assemble the ligands around Co(II) and then to kinetically lock the system by simple air oxidation to Co(III) (the increase in oxidation state is strongly favored by the two

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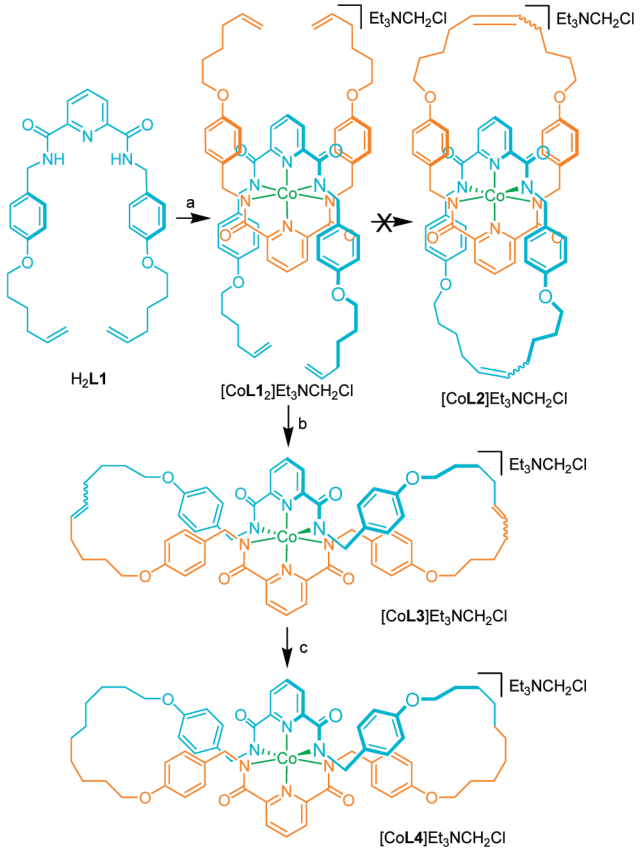
Scheme 1. Synthesis of "Figure-of-Eight" Complex [Co**L4**]$^-$ via Double Cross-Olefin Metathesis of **L2** on a Co(III) Template^a



^{a} Reagents and conditions: (a) (i) $Co(OAc)_2 \cdot (H_2O)_4$, $Et_4N(OAc)$, NaOEt, EtOH, reflux, 1 h, (ii) silica gel, CH_2Cl_2, acetone, Et_3N, 83%; (b) $(Cy_3P)_2Cl_2Ru{=}CHPh$, CH_2Cl_2, 2 d, 42%; (c) Pd/C, MeOH, H_2, 1 d, 85%.

doubly negatively charged ligands). Reaction of an ethanolic solution of H$_2$**L1** with a cobalt(II) salt ($Co(OAc)_2 \cdot (H_2O)_4$), $Et_4N(OAc)$ and NaOEt under anaerobic conditions gave an immediate color change from pink to deep purple. Exposure of the presumed divalent species, [Co**L1**$_2$]$^{2-}$, to air resulted in a second color change from purple to green (indicative of oxidation to Co(III)) over ca. five minutes. After heating at reflux for a further 1 h and work up of the reaction, purification by column chromatography on silica gel with acetone:dichloromethane:triethylamine (40:59:1) as eluent afforded complex [Co**L1**$_2$]Et$_3$NCH$_2$Cl in 83% yield (Scheme 1, step a). The unexpected countercation is apparently formed ($Et_3N + CH_2Cl_2 \rightarrow Et_3N^+CH_2Cl + Cl^-$) and introduced into the product (cation exchange with Et_4N^+) during the chromatography step.[21] Complex [Co**L1**$_2$]Et$_3$NCH$_2$Cl gave a sharp ^{1}H NMR spectrum in CD_2Cl_2 (Figure 2a),[22] confirming that the structure contained diamagnetic Co(III) rather than paramagnetic Co(II). Comparison of the ^{1}H NMR spectrum with that of the free ligand H$_2$**L1** (Figure 2b) revealed upfield shifts of H_E and H_F, indicative of the π-stacking between the benzylic groups of each ligand intended to favor catenane formation. However, subjecting [Co**L1**$_2$]Et$_3$NCH$_2$Cl to olefin metathesis with $(PCy_3)_2Cl_2Ru{=}CHPh$ (Scheme 1, step b) led to a "figure-of-eight" complex [Co**L3**]Et$_3$NCH$_2$Cl formed through interligand cross-metathesis.[10b,23] The structure was confirmed by X-ray crystallography of single crystals of the hydrogenated (H_2, Pd/C, MeOH, Scheme 1, step c) complex (Figure 3). The X-ray crystal structure shows that in order to accommodate the perpendicular alignment of the tridentate pyridine-2,6-dicarboxamido ligands around the octahedral Co(III) center, the macrocycle adopts a helical

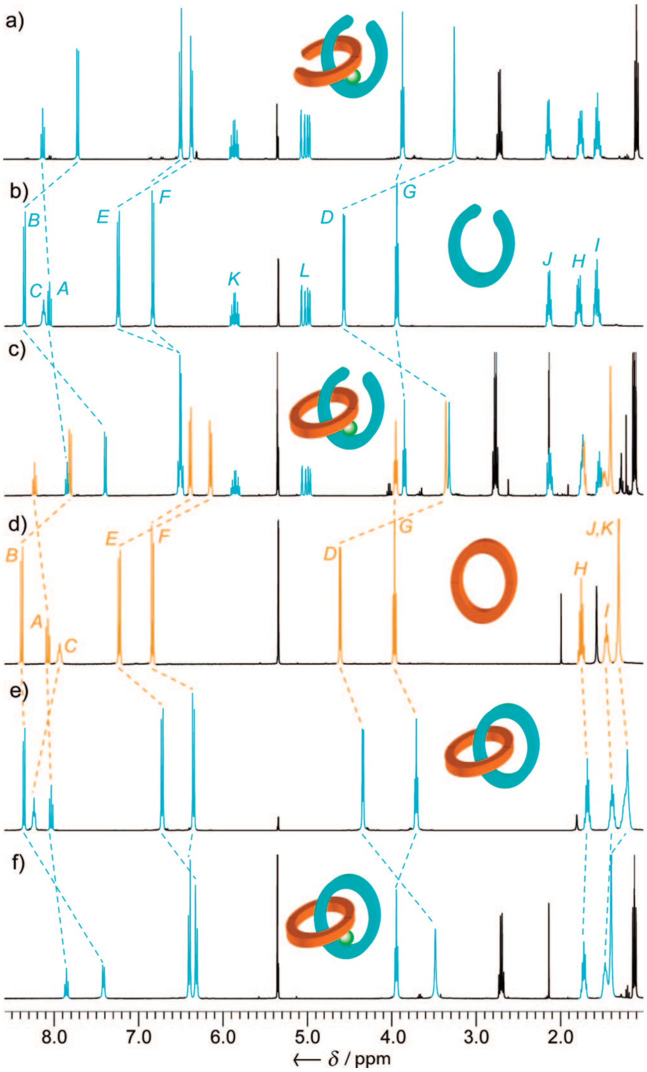


Figure 2. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 300 K) of (a) [Co**L1**$_2$]Et$_3$NCH$_2$Cl, (b) H$_2$**L1**, (c) precatenate [**L1**Co**L5**]Et$_3$NCH$_2$Cl, (d) macrocycle H$_2$**L5**, (e) [2]catenand H$_4$**L7**, and (f) [2]catenate [Co**L7**]Et$_3$NCH$_2$Cl. The assignments correspond to the lettering shown in Scheme 2.

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(21) ^{1}H NMR and mass spectrometry revealed that all of the purified Co(III) complexes had undergone cation exchange of Et_4N^+ with $Et_3N^+CH_2Cl$. This was most likely formed by reaction of Et_3N with CH_2Cl_2 (Menshutkin, N. Z. *Phys. Chem.* **1890**, *6*, 41−57). This reaction normally proceeds slowly under ambient conditions (Wright, D. A.; Wulff, C. A. *J. Org. Chem.* **1970**, *35*, 4252) but is accelerated under pressure (Almarzoqi, B.; George, A. V.; Issacs, N. S. *Tetrahedron* **1986**, *42*, 601−607). It was recently reported (Lee, J. J.; Stanger, K. J.; Noll, B. C.; Gonzalez, C.; Marquez, M.; Smith, B. D. *J. Am. Chem. Soc.* **2005**, *127*, 4184−4185) that macrocyclic hosts containing a tertiary amine and a chloride anion binding cleft can react with CH_2Cl_2. In the present case, however, the reaction takes place during the chromatographic purification procedure (silica gel, CH_2Cl_2, acetone, Et_3N).

(22) Pristine Co(III) complexes were found to decompose over a period of a few days in both $CDCl_3$ and $(CD_3)_2CO$; however, no decomposition was observed for CD_2Cl_2 solutions of the Co(III) complexes.

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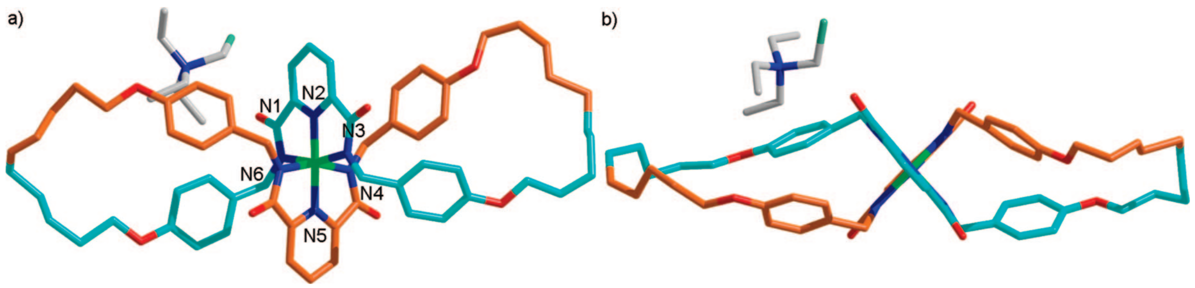
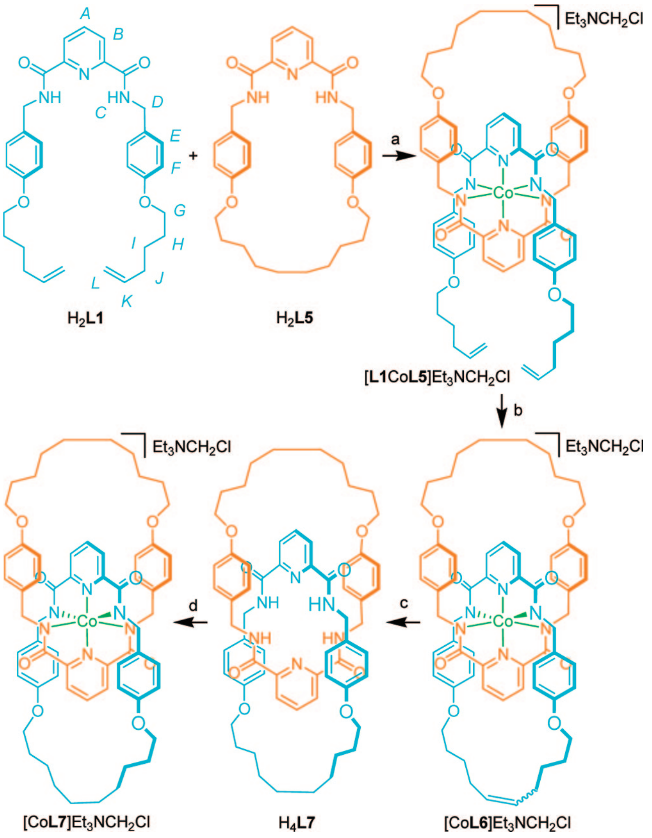


Figure 3. X-ray crystal structure of "figure-of-eight" complex [Co**L4**]Et_3NCH_2Cl. (a) Side-on view. (b) Viewed down the N2−Co−N5 axis. Selected bond lengths (Å) and angles (deg): N1−Co 1.98, N2−Co 1.85, N3−Co 1.94, N4−Co 1.96, N5−Co 1.83, N6−Co 1.96, N1−Co−N3 163.6, N4−Co−N6 163.8, N2−Co−N5 177.1. The hydrogen atoms are omitted for clarity. The carbon atoms are shown in light blue (those originating from one ligand), orange (those originating from the second ligand), and gray (countercation); cobalt(III), green; oxygen, red; nitrogen, blue; and chlorine, olive.

Scheme 2. Synthesis of [2]catenate [Co**L7**]$^-$ via Single Macrocyclization of **L1** through **L5** on a Co(III) Template[a]



[a] Reagents and conditions: (a) $Co(OAc)_2\cdot(H_2O)_4$, $Et_4N(OAc)$, NaOEt, EtOH, reflux, 1 h, 84%; (b) $(PCy_3)_2Cl_2Ru{=}CHPh$, CH_2Cl_2, 2 d, 69%; (c) (i) Pd/C, MeOH, H_2, 1 d, (ii) Zn, AcOH, MeOH, 30 min, 65%; (d) $Co(OAc)_2\cdot(H_2O)_4$, $Et_4N(OAc)$, NaOMe, EtOH, reflux, 30 min, 75%.

conformation that promotes interligand cross-metathesis rather than intraligand ring-closing metathesis.

Co(III)-Template Single Macrocyclization of L1 Through L5 ([2]catenate Synthesis). We next investigated single RCM of a complex consisting of H_2**L1** and the preformed macrocycle H_2**L5** held in a mutually orthogonal arrangement by the Co(III) template. Treatment of an ethanolic solution of H_2**L1**, H_2**L5**, $Co(OAc)_2\cdot(H_2O)_4$ and $Et_4N(OAc)$ with NaOEt (4.4 equiv.) (Scheme 2, step a) under anaerobic conditions, followed by exposure to air, gave the same series of color changes observed during the formation of [Co**L1**$_2$]$^-$ (Scheme 2, step a). The mixed-ligand Co(III) complex [**L1**Co**L5**]Et_3NCH_2Cl was isolated after chromatography (again, with cation exchange) in 84% yield. In comparison to the ^{1}H NMR of H_2**L1** (Figure 2b) and macrocycle H_2**L5** (Figure 2d) a significant shift to lower field is observed for both sets of benzylic aromatic resonances (H_E's and H_F's, Figure 2c) in [**L1**Co**L5**]Et_3NCH_2Cl, again indicating the presence of the π-stacking interactions intended to encourage catenane formation. The selectivity of the reaction for the mixed-ligand complex [**L1**Co**L5**]$^-$—neither of the homotopic complexes [**L1**$_2$Co]$^-$ or [**L5**$_2$Co]$^-$ are apparent in the product mixture—is a result of the shape and topology of the **L5** macrocycle physically preventing complexes of the type [**L5**$_2$Co]$^-$ from forming. Therefore, the only way in which all the ligands in an equimolar solution of the cobalt ion, **L1**$^{2-}$ and **L5**$^{2-}$ can be coordinated is through sole formation of the mixed-ligand complex. The thermodynamically driven rearrangement of any initially formed [**L1**$_2$Co]$^{2-}$ likely occurs before the ligands are "locked" around kinetically inert Co(III), i.e., prior to aerobic oxidation.

Ring-closing metathesis of [**L1**Co**L5**]Et_3NCH_2Cl under high dilution conditions (Scheme 2, step b) proceeded smoothly to give a new Co(III) complex, clearly different by ^{1}H NMR spectroscopy and thin layer chromatography to [Co**L3**]$^-$, in 69% yield. Subsequent hydrogenation with H_2 over Pd/C to remove the double bonds (Scheme 2, step c, i) resulted in partial abstraction of the Co(III) ion. It was therefore convenient to completely demetallate the structure with activated Zn dust in acetic acid/methanol (Scheme 2, step c, ii)[24] prior to isolation, to give the fully reduced neutral molecule H_4**L7** in 65% yield over the two steps. The ^{1}H NMR spectrum H_4**L7** in CD_2Cl_2 (Figure 2e) shows shielding of various signals (H_D, H_E, H_F, and H_G) with respect to macrocycle H_2**L5** (Figure 2d), characteristic of a catenane, an architecture that was confirmed by X-ray crystallography of single crystals grown from a saturated acetonitrile solution (Figure 4). In the solid state, each macrocycle of the catenand is involved in bifurcated hydrogen bonding to a molecule of acetonitrile. The alkyl chains of each ring are located in the center of the cavity of the other macrocycle with the amide groups positioned to the outside of each molecule, a very different co-conformation from that required for metal ion template assembly (tridentate chelating groups converging toward the metal ion at the center; alkyl groups to the outside).[25]

The cobalt(III) cation could be reintroduced into the catenand (Scheme 2, step d) to produce the [2]catenate [Co**L7**]Et_3NCH_2Cl in 75% yield. The ^{1}H NMR spectra of [Co**L7**]Et_3NCH_2Cl

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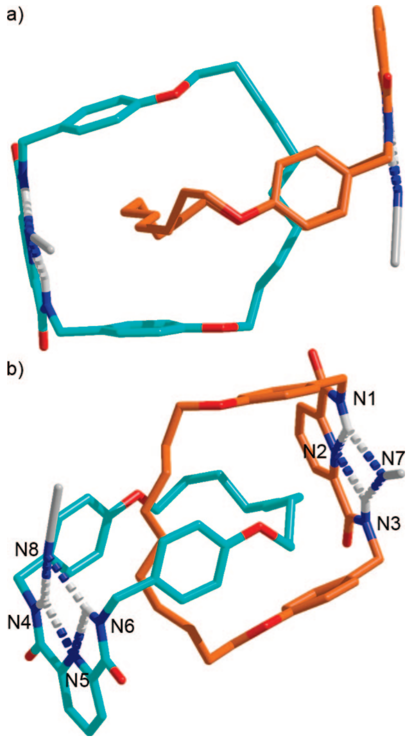

Figure 4. X-ray crystal structure of [2]catenand H_4**L7**·2MeCN viewed (a) in the plane of the pyridine rings and (b) showing the hydrogen bonding networks present. Selected bond lengths (Å) and angles (deg): NH1···N2 2.22, NH1···N7 2.32, NH3···N2 2.22, NH3···N7 2.27, NH4···N5 2.24, NH4···N8 2.28, NH6···N5 2.21, NH6···N8 2.40, N1−H1−N2 107.1, N1−H1−N7 145.7, N3−H3−N2 107.3, N3−H3−N7 145.6, N4−H4−N5 105.9, N4−H4−N8 146.7, N6−H6−N5 108.4, N6−H6−N8 143.1. The non-H-bonded hydrogen atoms are omitted for clarity. The carbon atoms are light blue (one macrocycle), orange (the second macrocycle), and gray (acetonitrile); oxygen, red; and nitrogen, blue.

(Figure 2f) shows pronounced π-stacking interaction of resonances H_E and H_F, and a decrease in the shielding for H_G, H_H, H_I, H_J, and H_K compared to H_4**L7**, indicating that complexation of the ligand to cobalt(III) fixes the alkyl chains to the outside of the catenate. Single crystals of the Co(III) catenate suitable for X-ray crystallographic analysis were grown by vapor diffusion of Et_2O into a saturated solution of the catenate in CH_2Cl_2. The crystal structure of [Co**L7**]Et_3NH (the countercation again exchanged from the one expected!)[26] (Figure 5) shows the octahedral environment of the Co(III) metal center bound to the two bis-anionic tridentate macrocycles with, as in solution, the alkyl chains of each ring positioned to the outside of the catenate. The off-set π-interactions between the benzyl groups of each macrocycle and the pyridine ring of the other component apparent by ^{1}H NMR are also present in the X-ray crystal structure.

Co(III)-Template Single Macrocyclization of L1 About L8 ([2]Rotaxane Synthesis). Having established a protocol for the formation of catenanes using pyridine-2,6-dicarboxamide ligands and a Co(III) template, the methodology was applied to the synthesis of a [2]rotaxane (Scheme 3). The bis-amide thread H_2**L8** was prepared in four steps (72% overall yield from commercial starting materials, see the Supporting Information) and when subjected to the cobalt-complexation conditions in the presence of H_2**L1** the prerotaxane complex [**L1**Co**L8**]Et_3NCH_2Cl could be isolated in 37% yield (Scheme 3, step a). Because—unlike macrocycle **L5**—thread **L8** can form a 2:1 complex with Co(III), in this case, the ligand assembly reaction was unselective for the mixed-ligand complex and [**L1**Co**L8**]$^-$ needed to be separated via column chromatography from [Co**L1**$_2$]$^-$ and [Co**L8**$_2$]$^-$. The ^{1}H NMR spectrum of [**L1**Co**L8**]Et_3NCH_2Cl in CD_2Cl_2 (Figure 6b) shows the intercomponent π-stacking interactions between **L1**$^{2-}$ and **L8**$^{2-}$ (shielding of resonances H_E, H_F, H_e, and H_f), which augured well for interlocking occurring under RCM. Indeed, macrocyclization of [**L1**Co**L8**]Et_3NCH_2Cl proceeded smoothly with $(PCy_3)_2Cl_2Ru{=}CHPh$ (Scheme 3, step b) to give [Co**L9**]Et_3NCH_2Cl in 61% yield. Following hydrogenation and demetalation (Scheme 3, step c) a single organic product was isolated which was confirmed as the metal-free rotaxane, H_4**L10**, by mass spectrometry and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the rotaxane in CD_2Cl_2 (Figure 6d) shows shielding of the thread resonances H_d, H_e, H_f, H_g, and H_h and macrocycle resonances H_D, H_E, H_F, and H_G, compared to the non-interlocked components H_2**L8** (Figure 6a) and H_2**L5** (Figure 2d). In contrast, the amide hydrogen resonances of both the thread and macrocycle are shifted to higher frequency by ~1.5 ppm in the rotaxane, indicating that the intercomponent hydrogen bonding observed in solution for the free catenand H_4**L7** also occurs with rotaxane H_4**L10**.

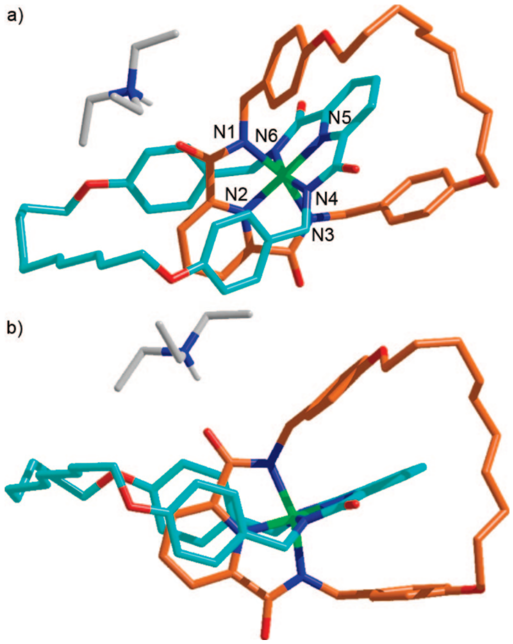

Figure 5. X-ray crystal structure of [2]catenate [Co**L7**]Et_3NH viewed (a) to show the octahedral coordination sphere of the complexed cobalt(III) ion and (b) perpendicular to the plane of the orange ring to show the two sets of intercomponent π-stacking. Selected bond lengths (Å) and angles (deg): N1−Co 1.97, N2−Co 1.85, N3−Co 1.95, N4−Co 1.97, N5−Co 1.85, N6−Co 1.97, N1−Co−N3 163.1, N4−Co−N6 163.2, N2−Co−N5 174.2. The hydrogen atoms are omitted for clarity except for the NH of the protonated Et_3N cation. The carbon atoms are shown in light blue (one macrocycle), orange (the second macrocycle), and gray (countercation); cobalt(III), green; oxygen, red; and nitrogen, blue.

Reintroduction of Co(III) into rotaxane H_4**L10** to give [Co**L10**]Et_3NCH_2Cl (Scheme 3, step d) was far more sluggish and low yielding (16% cf 75% for [Co**L7**]$^-$) than the catenane system.[27] As observed in the prerotaxane complex [**L1**Co**L5**]Et_3NCH_2Cl, the ^{1}H NMR spectrum of the Co(III)-complexed

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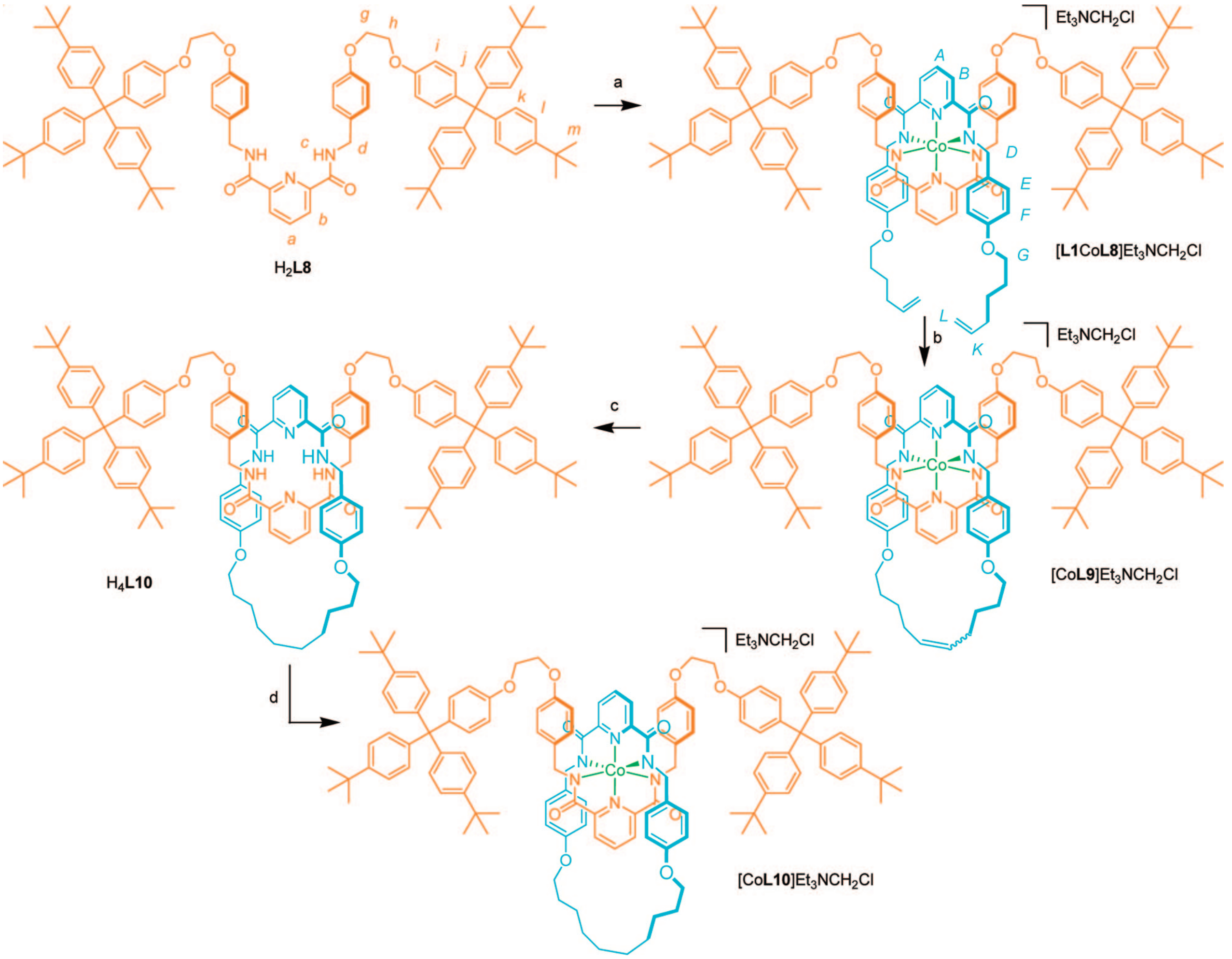
(26) Elucidation of the crystal structure revealed that another cation exchange had occurred, with Et_3NCH_2Cl being replaced by Et_3NH.

Scheme 3. Synthesis of [2]Rotaxane $[\mathrm{Co}\mathbf{L10}]^{-}$ via Single Macrocyclization of **L1** about **L8** on a Co(III) Template[a]



[a] Reagents and conditions: (a) H_2**L1**, $Et_4N(OAc)$, $Co(OAc)_2\cdot(H_2O)_4$, NaOMe, THF, EtOH, reflux, 1 h, 37%; (b) $(Cy_3P_2)Cl_2Ru{=}CHPh$, CH_2Cl_2, 2 d, 61%; (c) (i) Zn, AcOH, MeOH, 30 min; (ii) Pd/C, THF, H_2, 2 d, 83%; (d) $Co(OAc)_2\cdot(H_2O)_4$, $Et_4N(OAc)$, NaOMe, EtOH, reflux, 30 min, 16%.

rotaxane [Co**L10**]Et_3NCH_2Cl in CD_2Cl_2 (Figure 6c) provides evidence (larger shifts) of a significantly stronger π-stacking interaction between the benzylic units of the more flexible thread with the macrocycle's pyridine moiety compared to that between the benzyl groups of the (more rigid) macrocycle and the thread's pyridine unit.

Conclusions

A [2]catenane, [2]rotaxane and a "figure-of-eight" complex have been synthesized about a Co(III) template by exploiting the affinity of tridentate pyridine-2,6-biscarboxamido ligands for hard trivalent metal ions. In an unusual three-step template process, the lability of Co(II) coordination allows thermodynamically controlled assembly of the ligands on the metal and subsequent oxidation to Co(III) kinetically traps the template complex. The interlocked or entwined architectures are then covalently captured by cross-metathesis or ring-closing metathesis. In each case, decomplexation via reduction of the metal to Co(II) and protonation of the anionic ligands generated the metal-free neutral molecules. Cobalt could be reintroduced into the free ligands to form Co(III) complexes that were characterized unambiguously by mass spectrometry, NMR spectroscopy and, in some cases, X-ray crystallography. The methodology allows access to a new class of interlocked chelating ligand for hard metal cations, which adds to the growing toolbox of passive- and active-metal template[28] protocols for catenane and rotaxane synthesis. The binding of different metal types (hard and soft, different oxidation numbers and geometries, etc.) may

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(27) During the initial stages of the remetallation reaction, addition of pink crystals of Co(II) to a solution of H_4**L10** and $Et_4N(OAc)$ in THF and EtOH resulted in an immediate color change, giving a green solution indicating spontaneous oxidation of Co(II) to Co(III).

(28) For "active-metal template" rotaxane synthesis, in which the metal acts as both a template and a catalyst for covalent bond formation and thus generally changes oxidation state, coordination number, and/or geometry during the reaction, see: (a) Aucagne, V.; Hänni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 2186–2187. (b) Saito, S.; Takahashi, E.; Nakazono, K. *Org. Lett.* **2006**, *8*, 5133–5136. (c) Berná, J.; Crowley, J. D.; Goldup, S. M.; Hänni, K. D.; Lee, A.-L.; Leigh, D. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5709–5713. (d) Aucagne, V.; Berná, J.; Crowley, J. D.; Goldup, S. M.; Hänni, K. D.; Leigh, D. A.; Lusby, P. J.; Ronaldson, V. E.; Slawin, A. M. Z.; Viterisi, A.; Walker, D. B. *J. Am. Chem. Soc.* **2007**, *129*, 11950–11963. (e) Crowley, J. D.; Hänni, K. D.; Lee, A.-L.; Leigh, D. A. *J. Am. Chem. Soc.* **2007**, *129*, 12092–12093. (f) Goldup, S. M.; Leigh, D. A.; Lusby, P. J.; McBurney, R. T.; Slawin, A. M. Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 3381–3384. (g) Berná, J.; Goldup, S. M.; Lee, A.-L.; Leigh, D. A.; Symes, M. D.; Teobaldi, G.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 4392–4396.

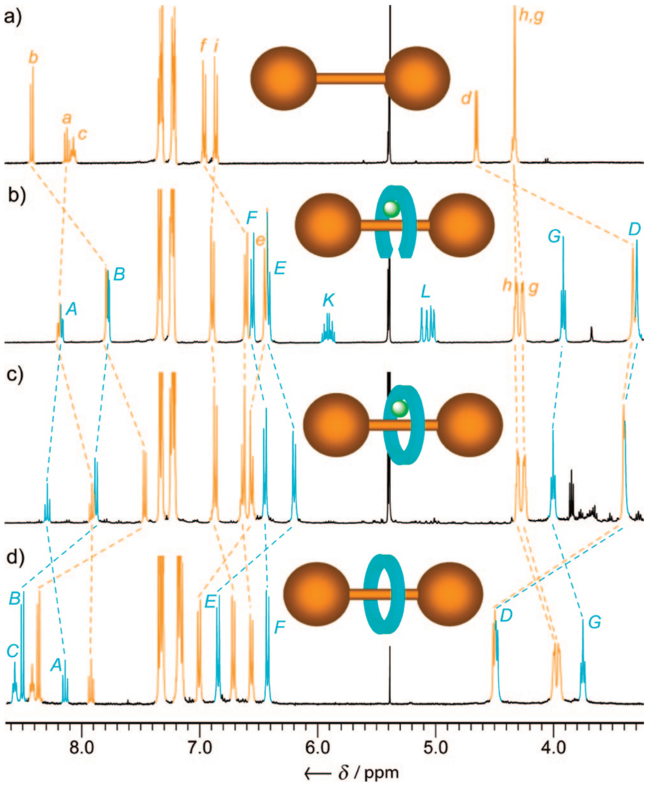

Figure 6. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 300 K) of (a) thread H_2**L8**, (b) prerotaxane [**L1**Co**L8**]Et_3NCH_2Cl, (c) Co(II) rotaxane [Co**L10**]Et_3NCH_2Cl, and (d) metal-free rotaxane H_4**L10**. The assignments correspond to the lettering shown in Scheme 3.

prove useful in the development of new synthetic molecular machine systems.[17]

Experimental Section

Synthesis of [CoL1$_2$]Et$_3$NCH$_2$Cl and Selected Spectroscopic Data. A suspension of H_2**L1** (0.993 g, 1.83 mmol), $Et_4N(OAc)$ (0.241 g, 0.92 mmol), and $Co(OAc)_2.(H_2O)_4$ (0.229 g, 0.92 mmol) in EtOH (10 mL) was heated at reflux under nitrogen to give a clear, pale pink solution. To this was added a solution of sodium ethoxide in ethanol, generated by the careful addition of NaH (0.162 g of 60% dispersion in oil, 4.05 mmol) to ethanol, resulting in a color change to deep purple. Upon exposure to air, the color of the solution changed to green over about 5 min after which it was refluxed for a further 1 h. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (40:1:59 Me_2CO:Et_3N:CH_2Cl_2 as eluent) to yield [Co**L1**$_2$]Et_3NCH_2Cl as a green oil (0.979 g, 83%), which was used without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.09 (t, J = 7.3 Hz, 9H, $H_{NCH_2C\underline{H}_3}$), 1.55 (m, 8H, $H_{I'}$), 1.76 (m, 8H, $H_{H'}$), 2.13 (m, 10H, $H_{J',NC\underline{H}_2Cl}$), 2.72 (q, J = 7.3 Hz, 6H, $H_{NC\underline{H}_2}$), 3.25 (s, 8H, $H_{D'}$), 3.86 (t, J = 6.6 Hz, 8H, $H_{G'}$), 5.02 (m, 8H, $H_{L'}$), 5.86 (m, 4H, $H_{K'}$), 6.37 (d, J = 8.7 Hz, 8H, $H_{E'}$), 6.50 (d, J = 8.7 Hz, 8H, $H_{F'}$), 7.72 (d, J = 7.7 Hz, 4H, $H_{B'}$), 8.13 (t, J = 7.7 Hz, 2H, $H_{A'}$); LRESI-MS (CH_2Cl_2) m/z = 1138 [M]$^-$, 150 [Et_3NCH_2Cl]$^+$.

Synthesis of [CoL3]Et$_3$NCH$_2$Cl and Selected Spectroscopic Data. To a solution of precatenate [Co**L1**$_2$]Et_3NCH_2Cl (0.500 g, 0.388 mmol) in CH_2Cl_2 (500 mL) was added Grubbs' first-generation olefin metathesis catalyst (0.056 g, 0.068 mmol). The solution was stirred for 2 days in the dark, after which the solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (40:1:59 Me_2CO:Et_3N:CH_2Cl_2 as eluent) to yield [Co**L3**]Et_3NCH_2Cl as a green solid (0.201 g, 42%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 300 K): δ 1.15 (t, J = 7.3 Hz, 9H, $H_{NCH_2C\underline{H}_3}$), 1.35 (m, 8H, H), 1.46 (m, 8H, H_H), 1.62 (m, 12H, $H_{D',I}$), 2.01 (s, 2H, $H_{NC\underline{H}_2Cl}$), 3.04 (q, J = 7.3 Hz, 6H, $H_{NC\underline{H}_2CH_3}$), 3.78 (m, 8H, H_G), 4.12 (t, J = 12.4 Hz, 4H, H_D), 5.24 (m, 4H, H_K), 6.27 (d, J = 1.8 Hz, 8H, H_E), 6.28 (d, J = 1.8 Hz, 8H, H_F), 7.88 (d, J = 7.8 Hz, 4H, H_B), 8.31 (t, J = 7.8 Hz, 2H, H_A); LRFAB-MS (3-NOBA matrix): m/z = 1082 [MH_2]$^+$.

Synthesis of [CoL4]Et$_3$NCH$_2$Cl and Selected Spectroscopic Data. To a solution of [Co**L3**]Et_3NCH_2Cl (0.142 g, 0.1 mmol) in methanol (30 mL) was added 10% w/w Pd/C (0.020 g). The resulting suspension was repeatedly degassed and purged with N_2 before being repeatedly degassed and purged with H_2 and stirred for 18 h under an atmosphere of H_2. The reaction mixture was filtered through celite and the solvent removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel (40:1:59 Me_2CO:Et_3N:CH_2Cl_2 as eluent) to yield [Co**L4**]Et_3NCH_2Cl as a green solid (0.106 g, 85%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 300 K): δ 1.15 (t, J = 7.3 Hz, 9H, $H_{NCH_2C\underline{H}_3}$), 1.35 (m, 16H, $H_{J,K}$), 1.70 (m, 8H, H_I), 2.01 (s, 2H, $H_{NC\underline{H}_2Cl}$), 2.05 (m, 12H, $H_{D',H}$), 3.04 (q, J = 7.3 Hz, 6H, $H_{NC\underline{H}_2CH_3}$), 3.92 (m, 8H, H_G), 4.29 (d, J = 12.3 Hz, 4H, H_D), 6.25−6.48 (m, 16H, $H_{E,F}$), 7.88 (d, J = 7.7 Hz, 4H, H_B), 8.31 (t, J = 7.7 Hz, 2H, H_A); LRFAB-MS (3-NOBA matrix): m/z = 1087 [MH_2]$^+$; HRFAB-MS (3-NOBA matrix): m/z = 1087.474 [MH_2]$^+$ (calcd for $C_{62}H_{72}CoN_6O_8$, 1087.474).

Synthesis of [L1CoL5]Et$_3$NCH$_2$Cl and Selected Spectroscopic Data. A suspension of H_2**L1** (0.507 g, 0.936 mmol), H_2**L5** (0.483 g, 0.936 mmol), $Co(OAc)_2\cdot(H_2O)_4$ (0.233 g, 0.936 mmol), and $Et_4N(OAc)$ (0.245 g, 0.936 mmol) was heated at reflux in EtOH (20 mL) under nitrogen to give a clear, pale pink solution. To this was added a solution of sodium ethoxide in ethanol, generated by the careful addition of NaH (0.165 g of 60% dispersion in oil, 4.12 mmol) to ethanol, resulting in a color change from pink to deep purple. Upon exposure to air, the color changed to green over about 5 min, after which the solution was refluxed for a further 25 min.. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (40:1:59 Me_2CO:Et_3N:CH_2Cl_2 as eluent) to yield [**L1**Co**L5**]Et_3NCH_2Cl as a green oil (1.130 g, 84%) which was used without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.12 (t, J = 7.3 Hz, 9H, $H_{NCH_2C\underline{H}_3}$), 1.41 (br, 8H, $H_{J,K}$), 1.48 (m, 4H, H_I), 1.54 (m, 4H, $H_{I'}$), 1.74 (m, 8H, $H_{H,H'}$), 2.14 (m, 6H, $H_{J',NC\underline{H}_2Cl}$), 2.77 (q, J = 7.3 Hz, 6H, $H_{NC\underline{H}_2CH_3}$), 3.32 (s, 4H, $H_{D'}$), 3.36 (s, 4H, H_D), 3.85 (t, J = 6.6 Hz, 4H, $H_{G'}$), 3.95 (t, J = 6.3 Hz, 4H, H_G), 5.01 (m, 4H, $H_{L'}$), 5.85 (m, 2H, $H_{K'}$), 6.15 (d, J = 8.6 Hz, 4H, H_E), 6.39 (d, J = 8.6 Hz, 4H, H_F), 6.50 (m, 8H, $H_{E',F'}$), 7.39 (d, J = 7.7 Hz, 2H, $H_{B'}$), 7.81 (d, J = 7.8 Hz, 2H, H_B), 7.85 (t, J = 7.7 Hz, 1H, $H_{A'}$), 8.23 (t, J = 7.8 Hz, 1H, H_A); LRESI-MS (CH_2Cl_2) m/z = 1138 [M]$^-$, 150 [Et_3NCH_2Cl]$^+$; HRFAB-MS (3-NOBA matrix) m/z = 1113.490 [MH_2]$^+$ (calcd for $C_{64}H_{64}CoN_6O_6$, 1113.490).

Synthesis of [CoL6]Et$_3$NCH$_2$Cl and Selected Spectroscopic Data. To a solution of precatenate [**L1**Co**L5**]Et_3NCH_2Cl (1.130 g, 0.877 mmol) in CH_2Cl_2 (900 mL) was added Grubbs' first-generation olefin metathesis catalyst (0.100 g, 0.121 mmol). The solution was stirred for 2 days in the dark, after which the solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (40:1:59 Me_2CO:Et_3N:CH_2Cl_2 as eluent) to yield [Co**L6**]Et_3NCH_2Cl as a green oil (0.750 g, 69%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 300 K): δ 1.20 (t, J = 7.3 Hz, 9H, $H_{NCH_2C\underline{H}_3}$), 1.28 (br, 8H, $H_{J,K}$), 1.39 (m, 8H, $H_{I,I'}$), 1.59 (m, 8H, $H_{H,H'}$), 2.01 (s, 2H, $H_{NC\underline{H}_2Cl}$), 2.09 (br, 4H, $H_{J'}$), 3.09 (q, J = 7.3 Hz, 6H, $H_{NC\underline{H}_2CH_3}$), 3.31 (br, 8H, $H_{D,D'}$), 3.84 (m, 8H, $H_{G,G'}$), 5.28 (t, J = 4.7 Hz, 1H, $H_{K'cis/trans}$), 5.45 (t, J = 3.8 Hz, 1H, $H_{K'cis/trans}$), 6.16 (m, 8H, $H_{E,E'}$), 6.28 (m, 8H, $H_{F,F'}$), 7.38 (m, 4H, $H_{B,B'}$), 7.95 (m, 2H, $H_{A,A'}$).

Synthesis of H$_4$L7 and Selected Spectroscopic Data. To a solution of catenate [Co**L6**]Et_3NCH_2Cl (0.698 g, 0.565 mmol) in MeOH (10 mL) was added 10% w/w Pd/C (0.060 g). The resulting suspension was repeatedly degassed and purged with N_2 before being repeatedly degassed and purged with H_2 and stirred for 18 h under an atmosphere of H_2. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The crude residue was redissolved in MeOH (5 mL) and AcOH (5 mL) and activated Zn (0.050 g) was added and the resulting suspension was stirred for 30 min. under an atmosphere of air. The solvent was removed under reduced pressure and the crude residue was redissolved in $CHCl_3$ (50 mL) and washed with a 17.5% NH_3 solution saturated with Na_4EDTA (50 mL). The aqueous layer was extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$) and purified by column chromatography on silica gel (3:7 EtOAc:CH_2Cl_2 as eluent) to yield H_4**L7** as a colorless solid (0.379 g, 65%). Single crystals suitable for X-ray crystallography were grown from a saturated solution of the catenand in MeCN. Mp = 231 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 1.25 (br, 16H, $H_{J,K}$), 1.41 (m, 8H, H_I), 1.70 (qt, J = 6.7 Hz, 8H, H_H), 3.62 (t, J = 6.7 Hz, 8H, H_G), 4.39 (t, J = 5.6 Hz, 8H, H_D), 6.23 (d, J = 8.5 Hz, 8H, H_F), 6.67 (d, J = 8.5 Hz, 8H, H_E), 8.02 (t, J = 7.8 Hz, 2H, H_A), 8.29 (t, J = 5.6 Hz, 4H, H_C), 8.40 (d, J = 7.8 Hz, 4H, H_B); LREI-MS: m/z = 1031 $[M]^+$; HREI-MS m/z = 1030.556 (calcd for $C_{62}H_{74}N_6O_8$, 1030.555).

Synthesis of [CoL7]Et_3NCH_2Cl and Selected Spectroscopic Data. To a suspension of catenand H_4**L7** (0.299 g, 0.29 mmol) and $Et_4N(OAc)$ (0.076 g, 0.29 mmol) in EtOH was added $Co(OAc)_2 \cdot (H_2O)_4$ (0.072, 0.029 mmol). The suspension was heated under nitrogen at reflux to give a clear, pale pink solution to which NaOMe (0.069 g, 1.28 mmol) was added. The solution was then opened to the air and heated at reflux for 30 min. until only one spot (green) was observed by thin layer chromatography (silica gel, 1:39:60 Et_3N:Me_2CO:CH_2Cl_2). The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (1:39:60 Et_3N:Me_2CO:CH_2Cl_2 and then 1:99 Et_3N:Me_2CO as eluent) to yield a green oil. Acetone was added to induce crystallization, and the solvent was then removed under reduced pressure to yield [Co**L7**]Et_3NCH_2Cl as a green solid (0.268 g, 75%). Single crystals suitable for X-ray crystallography were grown by vapor diffusion of Et_2O into a concentrated solution of catenate [Co**L7**]Et_3NCH_2Cl in CH_2Cl_2. Mp = 162 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.12 (t, J = 7.3 Hz, 9H, $H_{NCH_2CH_3}$), 1.40 (br, 16H, $H_{J,K}$), 1.47 (br, 8H, H_I), 1.73 (m, 8H, H_H), 2.14 (s, 2H, H_{NCH_2Cl}), 2.70 (q, J = 7.3 Hz, 6H, $H_{NCH_2CH_3}$), 3.48 (s, 8H, H_D), 3.95 (t, J = 6.3 Hz, 8H, H_G), 6.31 (d, J = 8.6 Hz, 8H, H_E), 6.40 (d, J = 8.6 Hz, 8H, H_F), 7.42 (d, J = 7.7 Hz, 4H, H_B), 7.85 (t, J = 7.7 Hz, 2H, H_A); LRESI-MS (CH_2Cl_2) m/z = 1085 $[M]^-$; HRESI-MS m/z = 1087.472 $[MH_2]^+$ (calcd for $C_{62}H_{72}CoN_6O_8$, 1087.473).

Synthesis of [L1CoL8]Et_3NCH_2Cl and Selected Spectroscopic Data. To a solution of H_2**L1** (0.385 g, 0.71 mmol), H_2**L8** (1.023 g, 0.71 mmol), and $Et_4N(OAc)$ (0.186 g, 0.71 mmol) in EtOH (7 mL) and THF (7 mL) was added a solution of $Co(OAc)_2 \cdot (H_2O)_4$ (0.177 g, 0.71 mmol) in EtOH (3 mL), and the resulting pale pink solution was heated at reflux under nitrogen for 1 h. NaOMe (0.169 g, 3.124 mmol) was added and the color changed to deep purple and, following exposure to air, to green, accompanied by formation of a suspension. The reaction was heated at reflux for a further 1 h. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (1:19:80 Et_3N:Me_2CO:CH_2Cl_2 and then 1:39:60 Et_3N:Me_2CO:CH_2Cl_2 then 1:99 Et_3N:Me_2CO as eluent) to yield [**L1**Co**L8**]Et_3NCH_2Cl as a green solid (0.573 g, 37%). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.11 (t, J = 7.3 Hz, 9H, $H_{NCH_2CH_3}$), 1.33 (br, 54H, H_m), 1.55 (m, 4H, H_I), 1.76 (m, 4H, H_H), 2.13 (m, 6H, H_{J,NCH_2Cl}), 2.78 (q, J = 7.3 Hz, 6H, $H_{NCH_2CH_3}$), 3.25 (br, 4H, H_D), 3.28 (br, 4H, H_d), 3.87 (t, J = 6.6 Hz, 4H, H_G), 4.21 (m, 4H, H_g), 4.27 (m, 4H, H_h), 5.02 (m, 4H, H_L), 5.87 (m, 2H, H_K), 6.38 (m, 8H, $H_{e,E}$), 6.50 (d, J = 8.6 Hz, 4H, H_F), 6.56 (d, J = 8.6 Hz, 4H, H_f), 6.84 (d, J = 8.9 Hz, 4H, H_i), 7.19 (m, 16H, $H_{j,k}$), 7.29 (d, J = 8.6 Hz, 12H, H_l), 7.74 (m, 4H, $H_{b,B}$), 8.14 (m, 2H, $H_{a,A}$); LRESI-MS (CH_2Cl_2) m/z = 2035 $[M]^-$, 150 $[NEt_3CH_2Cl]^+$; HRFAB-MS (3-NOBA matrix) m/z = 2037.063 $[MH_2]^+$ (calcd for $C_{132}{}^{13}CH_{148}CoN_6O_{10}$, 2037.062).

Synthesis of [CoL9]Et_3NCH_2Cl and Selected Spectroscopic Data. To a solution of [**L1**Co**L8**]NEt_3CH_2Cl (0.261 g, 0.119 mmol) in CH_2Cl_2 (100 mL) was added Grubbs' first generation olefin metathesis catalyst (0.020 g, 0.024 mmol). The solution was stirred for 1 day, at which time more catalyst was added (0.020 g, 0.024 mmol) and the solution stirred for a further 2 days. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (1:39:60 Et_3N:Me_2CO:CH_2Cl_2 as eluent) to yield [Co**L9**]Et_3NCH_2Cl as a green oil (0.156 g, 61%). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.14 (t, J = 7.3 Hz, 9H, $H_{NCH_2CH_3}$), 1.32 (br, 54H, H_m), 1.54 (m, 4H, H_I), 1.74 (m, 4H, H_H), 2.10 (s, 2H, H_{NCH2Cl}), 2.11−2.23 (m, 4H, H_J), 2.79 (q, J = 7.3 Hz, 6H, $H_{NCH_2CH_3}$), 3.36 (m, 8H, $H_{d,D}$), 3.96 (t, J = 6.4 Hz, 4H, H_G), 4.19 (m, 4H, H_g), 4.25 (m, 4H, H_h), 5.47 (t, J = 4.6 Hz, 1H, $H_{Kcis/trans}$), 5.56 (m, 1H, $H_{Kcis/trans}$), 6.12 (m, 4H, H_E), 6.37 (m, 4H, H_F), 6.52 (d, J = 8.6 Hz, 4H, H_e), 6.58 (d, J = 8.6 Hz, 4H, H_f), 6.81 (d, J = 8.9 Hz, 4H, H_i), 7.18 (m, 16H, $H_{j,k}$), 7.28 (d, J = 8.7 Hz, 12H, H_l), 7.40 (d, J = 7.7 Hz, 2H, H_b), 7.85 (m, 3H, $H_{a,B}$), 8.24 (t, J = 7.8 Hz, 1H, H_A); LRESI-MS (CH_2Cl_2) m/z = 2007 $[M]^+$, 150 $[Et_3NCH_2Cl]^+$; HRFAB-MS (3-NOBA matrix) m/z = 2008.023 $[MH_2]^+$ (calcd. for $C_{130}H_{144}CoN_6O_6$, 2008.026).

Synthesis of H_4L10 and Selected Spectroscopic Data. To a solution of [Co**L9**]NEt_3CH_2Cl (0.146 g, 0.0677 mmol) in CH_2Cl_2 (5 mL) and AcOH (5 mL) was added activated zinc dust (0.146 g) and the suspension was stirred for 30 min under an atmosphere of air. The reaction mixture was neutralized with a 17.5% NH_3 solution saturated with Na_4EDTA (50 mL) and the organic phase was extracted into CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was redissolved in THF (5 mL) and 10% w/w Pd/C was added (0.030 g) the suspension was repeatedly degassed and purged with N_2 before being repeatedly degassed and purged with H_2 and stirred for 2 days under an atmosphere of H_2. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure; the crude residue was then purified by column chromatography on silica gel (1:9 EtOAc:CH_2Cl_2 as eluent) to yield H_4**L10** as a colorless solid (0.110 g, 83%). Mp = 137 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.32 (br, 8H, $H_{J,K}$), 1.35 (br, 54H, H_m), 1.42 (m, 4H, H_J), 1.67 (m, 4H, H_I), 3.72 (t, J = 6.6 Hz, 4H, H_G), 3.93 (m, 4H, H_g), 3.95 (m, 4H, H_h), 4.46 (m, 8H, $H_{d,D}$), 6.39 (d, J = 8.6 Hz, 4H, H_F), 6.53 (d, J = 8.6 Hz, 4H, H_f), 6.68 (d, J = 8.9 Hz, 4H, H_i), 6.81 (d, J = 8.6 Hz, 4H, H_E), 6.97 (d, J = 8.6 Hz, 4H, H_e), 7.13 (m, 16H, $H_{j,k}$), 7.29 (d, J = 8.6 Hz, 12H, H_l), 7.89 (t, J = 7.8 Hz, 1H, H_a), 8.11 (t, J = 7.8 Hz, 1H, H_A), 8.33 (d, J = 7.8 Hz, 2H, H_b), 8.39 (t, J = 5.9 Hz, 2H, H_c), 8.47 (d, J = 7.8 Hz, 2H, H_B), 8.54 (t, J = 5.7 Hz, 2H, H_C); LREI-MS m/z = 1954 $[MH]^+$; HRFAB-MS (3-NOBA matrix) m/z = 1954.134 $[MH]^+$ (calcd for $C_{130}H_{149}N_6O_{10}$, 1954.133).

Synthesis of [CoL10]Et_3NCH_2Cl and Selected Spectroscopic Data. To a solution of rotaxane H_4**L10** (0.110 g, 0.056 mmol) and $Et_4N(OAc)$ (0.015 g, 0.056 mmol) in EtOH (5 mL) and THF (5 mL) was added $Co(OAc)_2 \cdot (H_2O)_4$ (0.017 g, 0.067 mmol). To this was added NaOMe (0.013 g, 0.246 mmol) and the solution was opened to air and heated at reflux for a further 1 h. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (1:39:60 Et_3N:Me_2CO:CH_2Cl_2 as eluent) to yield [Co**L10**]Et_3NCH_2Cl as a green solid (0.019 g, 16%). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.11 (t, J = 7.3 Hz, 12H, $H_{NCH_2CH_3}$), 1.28 (br, 4H, H_K), 1.31 (br, 54H, H_m), 1.41 (br, 4H, H_J), 1.47 (m, 4H, H_I), 1.74 (m, 4H, H_H), 2.14 (s, 2H, H_{NCH_2Cl}), 2.76 (q, J = 7.3 Hz, 6H, $H_{NCH_2CH_3}$), 3.35 (m, 8H, $H_{d,D}$), 3.95 (t, J = 6.3 Hz, 4H, H_G), 4.20 (m, 4H, H_g), 4.25 (m, 4H, H_h), 6.14 (d, J = 8.6 Hz, 4H, H_E), 6.39 (d, J = 8.6 Hz, 4H, H_F), 6.51 (d, J = 8.7 Hz, 4H, H_e), 6.58 (d, J = 8.7 Hz, 4H, H_f), 6.81 (d, J = 9.0 Hz, 4H, H_i), 7.18 (m, 16H, $H_{j,k}$), 7.28 (d, J = 8.7 Hz, 12H, H_l), 7.41 (d, J = 7.58 Hz, 2H, H_b), 7.82 (d, J = 7.8 Hz, 2H, H_B), 7.86 (t, J = 7.8 Hz, 1H, H_a), 8.24 (t, J = 7.8 Hz, 1H, H_A); LRESI-MS (CH_2Cl_2) m/z = 2008 $[M]^-$, 150 $[Et_3NCH_2Cl]^+$; HRFAB-MS

(3-NOBA matrix) m/z = 2011.047 $[MH_2]^+$ (calcd for $C_{130}{}^{13}CH_{146}CoN_6O_{10}$, 2011.047).

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Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds (PDF); full crystallographic details of [Co**L4**]Et_3NCH_2Cl, H_4**L7**·2MeCN, and [Co**L7**]Et_3NH (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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