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Olefin Cyclopropanation *via* Radical Carbene Transfer Reaction Promoted by Co(II)porphyrinates for the Active-Metal-Template Synthesis of [2]Rotaxanes

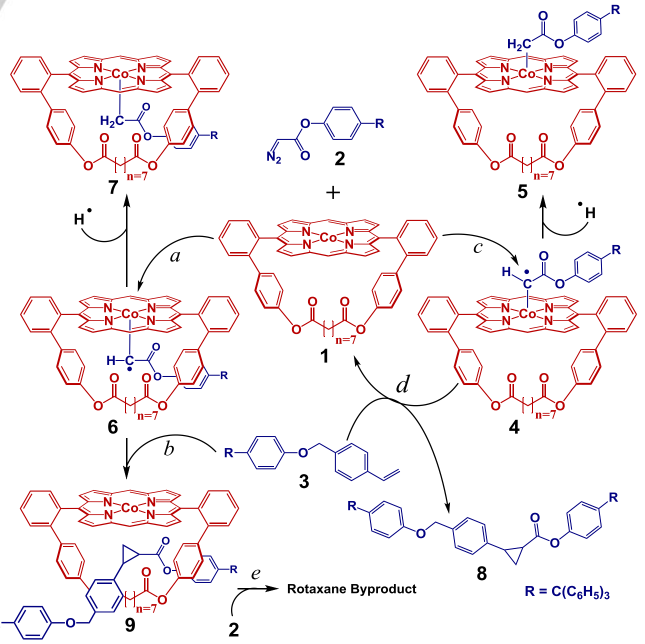
Arthur F. P. Alcântara, Liniquer A. Fontana, Vitor H. Rigolin, Yuri F. S. Andrade, Marcos A. Ribeiro, Wdeson P. Barros, Catia Ornelas and Jackson D. Megiatto Jr*

Abstract: A Co(II)porphyrinate-based macrocycle in the presence of 3,5-diphenylpyridine axial ligand functions as an endotopic ligand to direct the assembly of [2]rotaxanes from diazo and styrene half-threads *via* radical carbene transfer reactions in excellent 95% yield. The method reported herein applies the active-metal template strategy to include radical-type activation of ligands by the metal-template ion during the organometallic process that ultimately yield the mechanical bond. A careful quantitative analysis of the product distribution afforded from the rotaxane self-assembly reaction shows that the Co(II)porphyrinate subunit is still active after formation of the mechanical bond and, upon coordination of an additional diazo half-thread derivative, promotes a novel intercomponent C–H insertion reaction to yield a new rotaxane-like species. This unexpected intercomponent C–H insertion illustrates the distinct reactivity brought to the Co(II)porphyrinate catalyst by the mechanical bond.

The metal-template synthesis is a powerful methodology to prepare interlocked molecules.[1] In the so-called active-metal-template approach,[1b] the metal template ions are coordinate to endotopic macrocyclic ligands to afford active complexes that promote formation of covalent bonds between molecular fragments only through the cavity of the macrocycle to yield interlocked molecules.[2] The metal complexes explored so far in the active-template method are formal transition metal species in which the redox processes occurring during catalysis are primarily metal centered. However, further developments in transition metal complexes have opened the possibility for metal ions to share redox information with the ligands during the organometallic cycle.[3] For example, some synthetic complexes can combine 1e$^-$ redox change at the ligands with a 1e$^-$ redox change at the metal ion to enable first-row transition metal complexes to undergo the 2e$^-$ redox processes usually observed only for noble metals or multinuclear species. The cobalt(II)porphyrinate-mediated radical carbene transfer reaction are particularly noteworthy as this methodology allows formation of more nucleophilic radical carbene intermediates that easily add to olefins affording cyclopropane derivatives instead of usual coupling reactions.[4]

We reasoned that introduction of a molecular strap to a Co(II)porphyrinate would yield a porphyrin-based macrocycle with a well-defined cavity and with the two axial positions of the Co(II)porphyrinate available for further coordination of monodentate ligands and/or activation of substrates. However, the distinct size of the macrocycle's cavity would create an asymmetry on the two axial positions of the Co(II)porphyrinate due to steric hindrance. Therefore, selective coordination of strong-field and kinetically robust bulky ligands would occur only outside the cavity of the macrocycle, while leaving the internal axial site free for the activation of non-bulky substrates. Accordingly, the Co(II)porphyrinate-based macrocycle with a bulky axial ligand would function as an endotopic catalyst able to mediate radical-carbene transfer reactions between diazo and styrene half-thread derivatives to afford cyclopropane-linked rotaxanes by the active-metal-template approach.

We have designed semi-rigid macrocycle **1** (Scheme 1) for our synthetic strategy. The crystal structure of **1** (CCDC number 1823132, grown from slow evaporation of a DMSO/CH_2Cl_2 solution under N_2 atmosphere, Figure 1) reveals that the pair of *ortho*-biphenyl moieties attached to the *meso*-positions of the porphyrin core and connected to each other by the flexible aliphatic ester linker create an aperture with cavity width of 10.3 Å, which is sufficient large to fit a residual DMSO molecule coordinate to the Co(II) ion. This large cavity prompts us to use the bulky 3,5-diphenylpyridine moiety as axial ligand in our studies.



Scheme 1. Proposed mechanism for the active-metal-template synthesis of rotaxanes using the radical-carbene transfer reaction to olefins promoted by Co(II)porphyrinates.[4,5]

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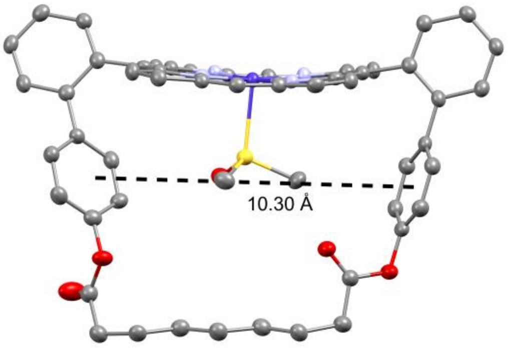

Figure 1. Crystal structure of macrocycle **1-DMSO**. Carbon atoms are shown in gray, nitrogen in light blue, cobalt in dark blue, oxygen in red and sulfur in yellow. Hydrogen atoms are omitted for clarity purposes. Ellipsoids are drawn at 50% probability levels.

We were pleased to find that just mixing macrocycle **1** with half-threads **2** and **3** (Scheme 1) in a 1:1:1 molar ratio in toluene under a nitrogen atmosphere affords rotaxane **9** (steps *a* and *b*, Scheme 1) in reasonable 45% yield after 18 h at room temperature (entry 1, Table 1). Preliminary evidence supporting the structure assignment to rotaxane **9** came from MALDI-TOF analysis (see Figure S1 in Supporting Information, S.I.). The fragmentation pattern of the mass spectrum is very characteristic of interlocked structures.[1d-f] The molecular ion peak for rotaxane **9** is observed at *m/z* 1683.28, along with the molecular ion peak for macrocycle **1** (*m/z* 854.95), indicating cleavage of the thread component upon the MALDI-TOF ionization process. Furthermore, a molecular ion peak fragment at *m/z* 1348.20 informs that cleavage of the thread probably occurs via homolytic rupture of the benzyl linkage with subsequent loss of a tritylphenoxyl moiety and coordination of the remaining radical to the Co(II)porphyrinate group on the ring component during the MALDI-TOF process.

Table 1. Experiments to determine the optimal conditions for formation of rotaxane **9** using the radical-carbene transfer cyclopropanation reaction as a metal-active-template methodology.[a,b]

Entry	Molar Ratio **1**:**2**:**3**	Thread **8** (%)[e]	Complex **5/7** (%)[f]	Rotaxane **9** (%)[f]	Rotaxane byproduct (%)[f]	Macrocycle **1** (%)
1	1:1:1	12	30	45	3	20
2[c]	1:1:5	21	17	56	2	23
3[c]	1:1.2:5	20	19	74	3	-
4[c,d]	1:1.2:5	-	-	95	3	-

[a] Reactions carried out at 0.053 M concentration with respect to **1** in toluene, under N_2 atmosphere for 18 h at room temperature. [b] Isolated yields. [c] Slow addition of half-thread **2**. [d] Addition of 1 equiv. (with respect to **1**) of 3,5-diphenylpyridine. [e] Relative to diazo **2**. [f] Relative to macrocycle **1**.

Thread **8** is isolated from the reaction in 12% yield, confirming that the cyclopropanation reaction also occurs *exo-* to the macrocyclic cavity (steps *c* and *d*, Scheme 1). Congruently, noninterlocked macrocycle **1** is recovered from the reaction mixture in 20% yield. Two porphyrin byproducts with higher polarity on silica are also isolated from the crude mixture. The MALDI-TOF mass spectrum (Figure S2, S.I.) of the most polar byproduct shows *m/z* signals for complexes **5** and **7** along with that for macrocycle **1**. Complexes **5** and **7** are relatively stable alkyl-Co(III)porphyrinates, which are formed from radical carbene intermediates[5] **4** and **6** *via* radical hydrogen abstraction reactions; a well-known side-reaction that leads to deactivation of the Co(II)porphyrinate catalyst in the cyclopropanation process.[4] The presence of *m/z* peak for macrocycle **1** in the mass spectrum of the porphyrin byproduct should come from fragmentation of complexes **5** and/or **7** as Co–C bonds in alkyl-Co(III)porphyrinates are photosensitive[6] and can break upon the MALDI-TOF laser ionization process.

The MALDI-TOF mass spectrum of the other isolated porphyrin byproduct (Figure S3, S.I.) shows a *m/z* peak at 2059.72, along with that for rotaxane **9** and its characteristic stepwise fragmentation pattern. The mass spectrum of this byproduct corresponds to a rotaxane-like species that is formed when one extra half-thread **2** reacts with rotaxane **9** to yield a carbenoid species. The coordination of the extra half-thread **2** can occur outside or inside the cavity of the macrocycle component of rotaxane **9**. If coordination of **2** to **9** occurs *endo*- to the macrocyclic cavity, cyclopropanation reaction must yield a [3]rotaxane, which is never observed in our investigation. In contrast, transfer of the carbenoid intermediate to half-thread **3** *exo-* to the macrocyclic cavity must regenerate rotaxane **9** while forming thread **8** and no porphyrin byproduct should have been observed. Therefore, cyclopropanation reactions do not yield this rotaxane byproduct. Radical hydrogen abstraction reactions are also ruled out as those reactions should yield alkyl-Co(III)porphyrinate-based rotaxanes and the UV-Vis absorption spectrum of this porphyrin byproduct is very similar to that of rotaxane **9** (Figure S4, S.I.). Accordingly, the porphyrin byproduct is a Co(II)-based species.

We reason that this porphyrin byproduct is formed by coordination of half-thread **2** *endo-* to the macrocyclic cavity of **9** to produce the carbenoid fragment, which further reacts with the thread component *via* insertion reactions into the C–H bonds of the cyclopropane moiety or those on the benzylic position (For proposed structures for the rotaxane byproduct, see Figure S5, S.I.).[7] Those C–H insertions are not observed in the cyclopropanation reactions promoted by acyclic Co(II)porphyrinates[4] because the cyclopropane product diffuses away from the Co(II)porphyrinate catalyst after the carbenoid transfer reaction occurs. In the case of rotaxanes, the mechanical bond always keeps the thread component near the Co(II)-active center, thereby facilitating this follow up intercomponent reaction with additional half-thread **2** (step *e*, Scheme 1). Furthermore, this rotaxane byproduct is always isolated in 2-3% yield even though the concentration of **2** is lower in the reaction medium (Table 1, *vide infra*), corroborating the hypothesis of intercomponent reaction.

Identification of compounds **5** and **7** as well as the rotaxane byproduct in the mixture by MALDI-TOF provide important information for optimization of the reaction conditions. The usual protocols for cyclopropanation reactions promoted by Co(II)porphyrinates require no slow addition of the diazo derivative, while the olefin counterpart is the limit reactant.[4] However, Co(II)porphyrinates are used in catalytic amounts in the traditional one-pot methods. In our case, macrocycle **1** is a stochiometric reactant and its Co(II)porphyrinate subunit is still active after formation of rotaxane **9**. If concentration of half-thread **2**, a potential radical hydrogen source,[4] is high in the reaction medium, the deleterious radical hydrogen abstraction reactions and intercomponent carbenoid insertions are favored. On the other hand, increasing the concentration of half-thread **3** in the medium should kinetically favor the cyclopropanation process over those side-reactions.[4]

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Performing the reaction in the presence of 5-fold excess of half-thread **3** (with respect to **1**, entry 2, Table 1) with portion-wise addition of half-thread **2** (0.20 equiv. every 2h) to lower its concentration in the reaction medium, improves the yield of rotaxane **9** from 45% to 56%, while reducing the yield of byproduct **5+7** from 30% to 17%. Thread **8** is also isolated in 21% yield and informs that the cyclopropanation reactions occurring *exo-* to the macrocyclic cavity are consuming considerable amount of half-thread **2**. Therefore, total interlocking of macrocycle **1** seems impossible with stoichiometric amounts of **2**. Running the reaction with a small excess of **2** (1.20 equiv. with respect to **1**) while keeping the slow addition (0.20 equiv. every 2h) and the 5-fold excess of **3** allows isolation of rotaxane **9** in good 74% yield (entry 3, Table 1) along with 20% of thread **8**, and total conversion of macrocycle **1**.

Addition of 1.00 equiv. of 3,5-diphenylpyridine to the reaction medium (entry 4, Table 1) under the optimized conditions boosts the yield of rotaxane **9** to impressive 95% (with respect to **1**) along with 3% of the rotaxane byproduct. This unequivocally shows that coordination of the 3,5-diphenylpyridine axial ligand to macrocycle **1** mitigates formation of byproduct **7** by accelerating the cyclopropanation reaction,[4a,c] while protecting the external axial coordination site that promotes the deleterious formation of thread **8** and byproduct **5**. However, UV-Vis investigation on the rotaxane isolated from the experiment with addition of 3,5-diphenylpyridine reveals that the axial ligand is lost during the purification process and that rotaxane **9** is the isolated product (see Figure S6 and its caption for further discussion, S.I.).

To investigate the structure of the rotaxane by NMR spectroscopy, we use $AgBF_4$ as oxidizing agent in the presence of imidazole as axial ligand to convert the paramagnetic Co(II)porphyrinate-based rotaxane **9** into the diamagnetic Co(III)porphyrinate-based **10** (Figure 2).[8] Comparison of the ^1H NMR spectra of rotaxane **10**, thread **8** and that of the free-base porphyrin macrocycle precursor of **1**[9] (Figure 3) provide unequivocal evidence for the interlocked architecture. The pyrrolic nuclei (H_B) resonances split in several signals, while the *meso*-ones (H_A) and those of the *ortho*-biphenyl rings ($H_{C\text{-}H}$) appear duplicate in **10** because of the unsymmetrical threaded axle that renders the porphyrinate protons magnetically inequivalent. Imidazole axial coordination is confirmed by the large shielding observed for protons H_U, H_V and H_V' as they experience the strong ring-current effect of the porphyrin aromatic system. Resonances for protons associated with the cyclopropane moiety (H_R, H_S and H_T) are significantly shielded in the rotaxane compared to noninterlocked thread **8**, with H_T dramatically shifting upfield ($\Delta\delta$ = 6.21 ppm). This is indicative of the cyclopropane ring on the axle being held very close to the Co(III)porphyrinate subunit. On the other hand, the signals for H_O, H_P and H_Q show much smaller shielding ($\Delta\delta$ = 0.49, 0.37 and 0.74 ppm, respectively) than those observed for the cyclopropane moiety. Therefore, the macrocycle component seems to preferentially stay over the half-thread bearing the carbonyl group. Congruently, the protons on the trityl-stoppering groups (H_L, H_M, H_N and $H_{N'}$) experience distinct chemical environments in **10** and split into multiple signals, with $H_{N'}$ shifting upfield ($\Delta\delta$ = 3.47 ppm), informing that the macrocycle component partially encapsulates the phenoxy-ester ring on the trityl-stopper group. Two dimensional NOESY NMR analysis (Figure S7, S.I.) reveals NOEs between protons H_R, H_S, H_T and $H_{N'}$ of the thread component and nuclei H_G of the macrocycle subunit, confirming the proposed structure for rotaxane **10**. Under the conditions investigated, ^1H NMR investigation informs that macrocycle **1** selectively yields both thread **8** and rotaxane **10** as the *trans*-diastereoisomer.[4]

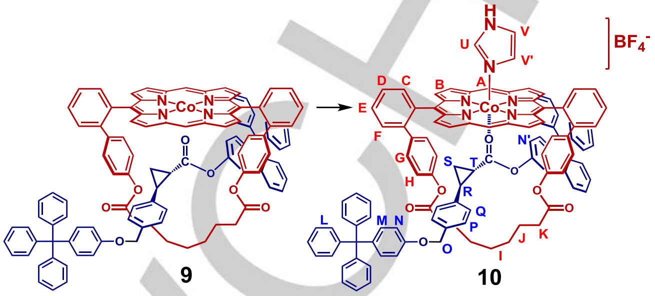

Figure 2. Conversion of paramagnetic rotaxane **9** to the diamagnetic rotaxane **10** by oxidation with $AgBF_4$ in the presence of imidazole as axial ligand for NMR investigation.

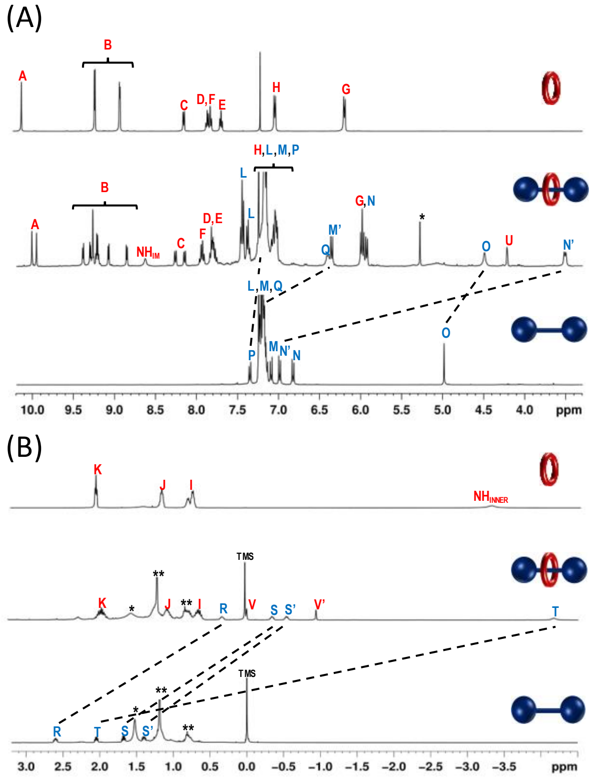

Figure 3. ^1H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the free-base porphyrin macrocycle precursor of **1**,[9] rotaxane **10** and thread **8**. (A) aromatic region; (B) aliphatic region. Proton assignments were based on 2D-NMR spectroscopy (S.I.) and they correspond to labelling shown in Figure 2. TMS = Tetramethylsilane. *residual chloroform (7.26 ppm), dichloromethane (5.29 ppm) and water (1.56 ppm) molecules; ** aliphatic impurities.

The strong shielding experienced by H_T and $H_{N'}$ suggests that the Co(II)porphyrinate should be axially coordinate to the carbonyl group on the thread to form a heteroleptic hexacoordinate complex.[10] ^{13}C NMR investigation confirms this intercomponent interaction in solution (Figure S8, S.I.). The carbonyl resonances of the free-base porphyrin macrocycle precursor of **1**[9] and thread **8** appear at 171.4 and 172.1 ppm, respectively, whereas the spectrum of **10** shows three resonances for its carbonyl groups. The signals at 170.9 and 170.8 ppm are assigned to the carbonyl groups on the ring component, which are magnetically inequivalent due to the unsymmetrical threaded axle, whereas the carbonyl resonance on the thread shifts upfield to 170.6 ($\Delta\delta$ = 1.5 ppm) when compared to noninterlocked **8**, confirming its proximity to the porphyrin core. This intercomponent interaction is also present in the solid state. The FTIR-ATR spectrum of **10** (Figure S9, S.I.) shows two distinct and intense ester carbonyl stretching bands at $\nu_{\mathrm{COstretch}}$ = 1754 cm^{-1} and $\nu_{\mathrm{COstretch}}$ = 1667 cm^{-1}, which we attribute to the carbonyl moieties on the macrocycle and thread components, respectively. The carbonyl stretching mode occurring at lower frequency indicates weakening of the C=O bond on the thread and strongly suggests donation of electronic density to the Co(III) ion by the oxygen atom.[10]

In conclusion, a Co(II)porphyrinate-based macrocycle with a bulky pyridine axial ligand can efficiently mediate radical carbene transfer reactions between diazo and styrene half-thread derivatives to yield rotaxanes through the active-metal-template method. This work opens the possibility to use redox non-innocent ligands in the synthesis of interlocked molecules and introduces Co(II)porphyrinate-based macrocycles to the family of endotopic ligands suitable for the active-metal-template strategies for the formation of mechanical bonds.

Acknowledgements

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Keywords: porphyrinates • radical carbenes • rotaxanes • supramolecular chemistry • template-synthesis

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[5] The accepted cyclopropanation mechanism[4d] claims that the radical carbene intermediate exists as two isomers in dynamic equilibrium: the active "terminal carbene" configuration, which has a single Co–C bond with a large unpaired spin density delocalized over the carbon atom, and the dormant "bridging carbene" state, which has the carbene moiety bound to the metal and a pyrrole nitrogen atom with the unpaired spin density delocalized primarily over the metal ion. We only represent the active "terminal carbene" intermediate state in Scheme 1 for clarity purposes.

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[8] Performing the oxidizing reaction on **9** without addition of strong-field ligands yields Co(III)-based rotaxanes whose ^{1}H NMR spectra are complex. However, running the oxidizing reaction in the presence of 1.5 equiv. (with respect to **9**) of nitrogen-based ligands affords Co(III)-based rotaxanes that yield clean ^{1}H NMR spectra. We chose imidazole as the axial ligand for the NMR investigation of our rotaxanes instead of the 3,5-diphenylpyridine used in the rotaxane assembly reaction as the former yields simpler ^{1}H NMR spectrum than the latter.

[9] We use the ^{1}H NMR spectrum of the free-base macrocycle precursor of **1** for comparison as **1** itself is a paramagnetic compound.

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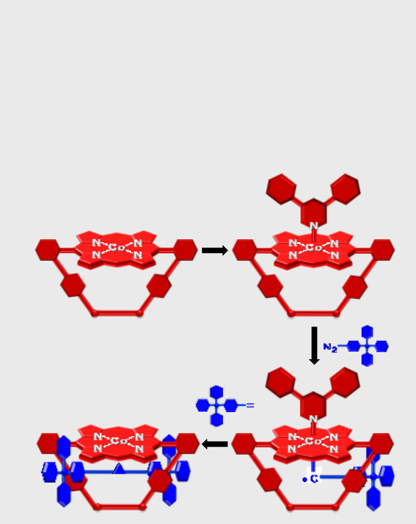
Layout 1:

COMMUNICATION

Radical approach to mechanical bonds: Coordination of axial nitrogen ligands to Co(II)porphyrinate-based macrocycles yields endotopic catalysts able to promote radical carbene transfer reactions to olefins to efficiently afford cyclopropane-linked rotaxanes.



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Layout 2:

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