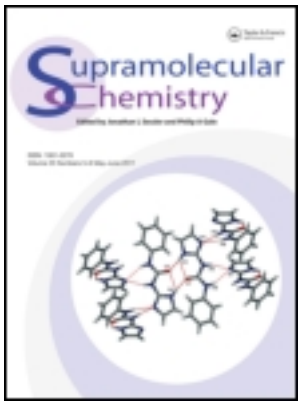


Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

A multi-component CuAAC 'click' approach to an exo functionalised pyridyl-1,2,3-triazole macrocycle: synthesis, characterisation, Cu(I) and Ag(I) complexes

Asif Noor [a], James E.M. Lewis [a], Scott A. Cameron [a], Stephen C. Moratti [a] & James D. Crowley [a]

[a] Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

Version of record first published: 21 May 2012

To cite this article: Asif Noor, James E.M. Lewis, Scott A. Cameron, Stephen C. Moratti & James D. Crowley (2012): A multi-component CuAAC 'click' approach to an exo functionalised pyridyl-1,2,3-triazole macrocycle: synthesis, characterisation, Cu(I) and Ag(I) complexes, Supramolecular Chemistry, 24:7, 492-498

To link to this article: http://dx.doi.org/10.1080/10610278.2012.688126

Supramolecular Chemistry
Vol. 24, No. 7, July 2012, 492–498

Taylor & Francis
Taylor & Francis Group

A multi-component CuAAC 'click' approach to an *exo* functionalised pyridyl-1,2,3-triazole macrocycle: synthesis, characterisation, Cu(I) and Ag(I) complexes

Asif Noor, James E.M. Lewis, Scott A. Cameron, Stephen C. Moratti and James D. Crowley*

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

(*Received 11 March 2012; final version received 11 April 2012*)

A one-pot, multi-component CuAAC reaction was exploited for the safe generation of an *exo* alcohol-functionalised pyridyl-1,2,3-triazole 'click' macrocycle in good yield. The macrocycle was characterised by elemental analysis, HR-ES-MS, ^{1}H and ^{13}C NMR spectrometry, and the molecular structure was confirmed by X-ray crystallography. Efforts to use the 'click' macrocycle in both passive and active metal template syntheses of [2]rotaxanes were unsuccessful, and this appears to be connected to the coordinating ability of the 1,2,3-triazole units in the macrocycle. The coordination chemistry of the macrocycle with Cu(I) and Ag(I) was examined. It has been demonstrated using HR-ES-MS, ^{1}H NMR spectrometry and X-ray crystallography that the macrocycle can form both discrete and polymeric coordination compounds with Cu(I) and Ag(I) and in all cases the 1,2,3-triazolyl units of the macrocycle are coordinated to the metal ions.

Keywords: macrocycles; CuAAC; click; Ag(I); 1,2,3-triazole; pyridyl

Introduction

Pyridine-containing macrocycles continue to engender great interest due to potential applications in catalysis (*1*), molecular recognition (*2*, *3*), biology (*3*, *4*) and self-assembly (*5*). One area in which the use of pyridine-containing macrocycles has seen rapid development is the synthesis of mechanically interlocked architectures (MIAs) (*6*) and molecular machines (*7*). Pyridine macrocycles such as **1** have been extensively used in both passive (*8*) and active metal template (*9*) syntheses of MIAs (Figure 1). However, the vast majority of this class of pyridine macrocycles contain no additional functionality, making it difficult to further elaborate the MIAs. As part of work towards novel MIAs, we required pyridine macrocycles that retained the core pyridine-binding motif of **1** but that also contained functional *exo* substituents. The mild and functional group tolerant Cu(I)-catalysed 1,3-cycloaddition of organic azides with terminal alkynes (*10*) (the CuAAC reaction) has recently shown great potential as an efficient, reliable method for the formation of macrocycles (*11*), and as such we postulated that it may provide a facile synthetic approach to the desired *exo* functionalised pyridine macrocycles.

Here, it is demonstrated that a one-pot, multi-component CuAAC method can be used to safely generate an *exo* functionalised pyridyl-1,2,3-triazole 'click' macrocycle (**2**, Figure 1). The potentially dangerous diazide synthon is generated *in situ* then captured by copper(I) acetylides, safely providing the desired 'click' macrocycle in good yield. Efforts to use the 'click' macrocycle in both passive and active metal template syntheses of [2]rotaxanes were unsuccessful, and this appears to be connected to the coordinating ability of the 1,2,3-triazole units within the macrocycle. In addition, the coordination chemistry of this new macrocyclic 'click' ligand with Cu(I) and Ag(I) has been examined, and it is shown that both discrete and polymeric complexes involving 1,2,3-triazolyl units can be formed.

Results and discussion

Macrocycle synthesis

The pyridyl-1,2,3-triazole 'click' macrocycle, **2**, was synthesised from the dialkyne, **3** (*12*), and dibromide, **4**, precursors using a one-pot, multi-component CuAAC method (Scheme 1) (*13–15*). The potentially explosive diazide (required for the formation of **2**) was generated *in situ* by heating dibromide **4** (1 equiv.) and NaN_3 (3 equiv.) at 90°C in DMF for 48 h. The resulting diazide (1 equiv.) solution and an equimolar DMF solution of the dialkyne, **3**, were added dropwise slowly to a solution of $CuSO_4{\cdot}5H_2O$, Na_2CO_3 and ascorbic acid in DMF–water (4:1) over a period of 16 h, resulting in a 30% yield of the macrocycle, **2**. The yield could be further improved by slowing the rate of addition of diazide and dialkyne reagents. The use of a syringe pump allowed **3** and **4** to be added to the DMF–water (4:1) solution containing the Cu(I) catalyst over a 48-h period, and this modification resulted in a respectable 44% isolated yield of **2**. The 'click' macrocycle was characterised by ^{1}H and ^{13}C NMR spectroscopy,

*Corresponding author. Email: jcrowley@chemistry.otago.ac.nz

ISSN 1061-0278 print/ISSN 1029-0478 online

http://dx.doi.org/10.1080/10610278.2012.688126
http://www.tandfonline.com

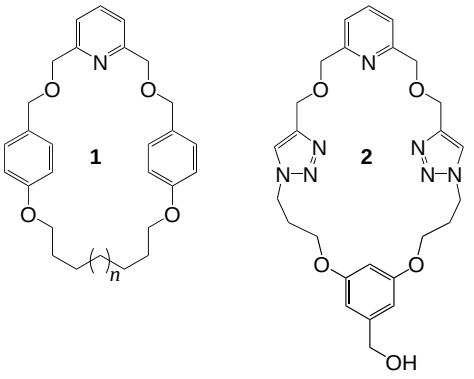
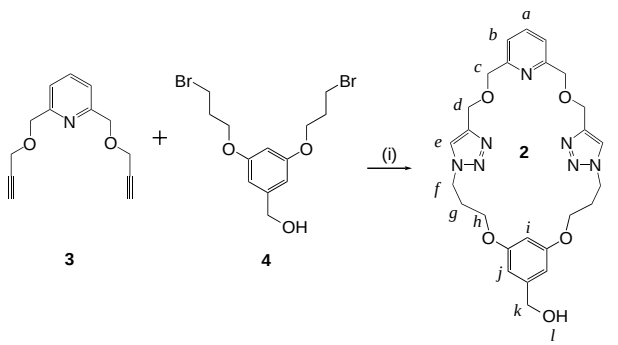


Figure 1. The pyridine-containing macrocycles **1** and **2**. The 2,6-bis[(alkyloxy)methyl]pyridine macrocycle motif, **1**, is commonly used in the passive and active template syntheses of MIAs. The CuAAC 'click' derived *exo* functionalised pyridyl-1,2,3-triazole, **2**, is a potentially readily synthesised surrogate of **1**.

elemental analysis and HR-ES-MS, and the molecular structure was confirmed using X-ray crystallography. X-ray quality crystals of **2** were obtained by vapour diffusion of diethyl ether into an acetone solution of the macrocycle. The molecular structure of the macrocycle (Figure 2) is unremarkable but demonstrates that **2** contains a large, flexible central cavity that should potentially enable its use in the syntheses of MIAs using metal template strategies.

Attempted active and passive metal template syntheses of [2]rotaxanes using the pyridyl-1,2,3-triazole 'click' macrocycle

As the parent 2,6-bis[(alkyloxy)methyl]pyridine macrocycle, **1**, has been successfully exploited to synthesise [2]rotaxanes and [3]rotaxanes using the CuAAC active metal template method (*16*, *17*), we set out to use the same approach to synthesise the alcohol-functionalised [2]rotaxane, **8**. The macrocycle, **2** (1 equiv.), azide, **5** (2 equiv.) and



Scheme 1. The one-pot, multi-component CuAAC synthesis of the *exo* functionalised pyridyl-1,2,3-triazole 'click' macrocycle, **2**; (i) (a) **4**, NaN_3 (3 equiv.), DMF, 90°C, 48 h, (b) **3**, $CuSO_4{\cdot}5H_2O$, ascorbic acid, Na_2CO_3, DMF–H_2O (4:1), RT, 48 h.

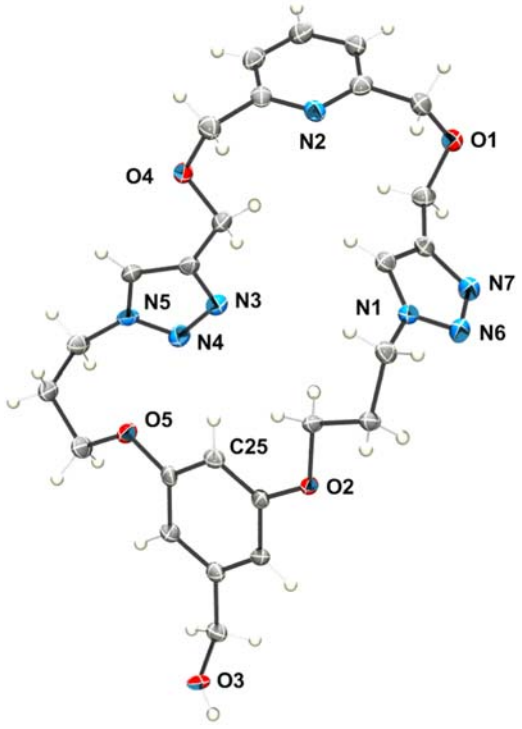
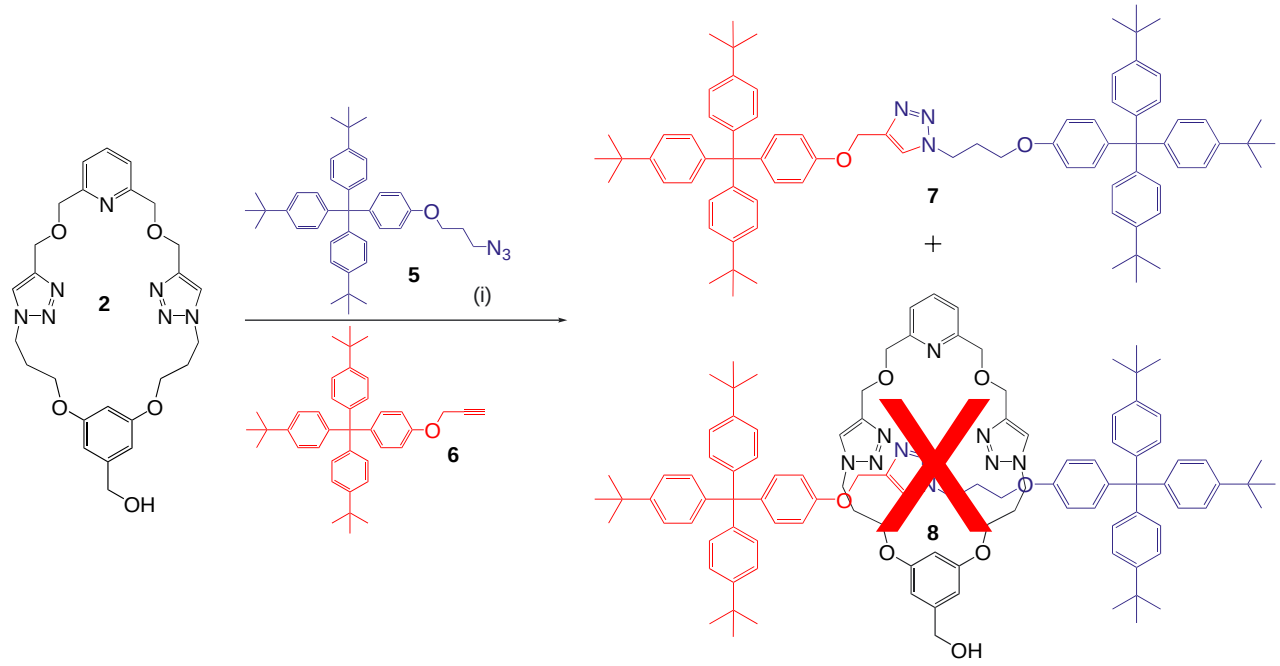


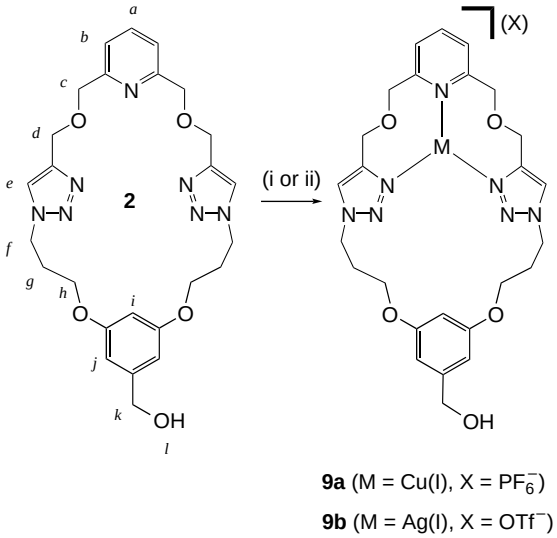
Figure 2. A labelled ORTEP diagram of the *exo* functionalised pyridyl-1,2,3-triazole 'click' macrocycle, **2**. The thermal ellipsoids are shown at the 50% probability level. Selected atom distances (Å) for **2**; N2—C25 7.819(6), N3—N1 5.789(5).

alkyne, **6** (2 equiv.) 'stoppers' were added to a CH_2Cl_2 solution containing $[Cu(CH_3CN)_4](PF_6)$ (1 equiv.), and the resulting reaction mixture was stirred at room temperature (Scheme 2). The 'click' reaction was monitored using TLC and HR-ES-MS and proceeded to completion after 48 h. However, no trace of the interlocked product, **8**, could be detected and only the non-interlocked linear thread, **7**, and macrocycle could be recovered from the reaction mixture. In an attempt to drive the formation of the [2]rotaxane, **8**, the reaction was repeated using an excess (4 equiv.) of the azide and alkyne stoppers. Once again the 'click' reaction proceeded to completion but only non-interlocked linear thread, **7**, and macrocycle, **2**, could be detected in the reaction mixture. Somewhat surprisingly, despite the structural similarity of the 'click' macrocycle, **2**, to 2,6-bis[(alkyloxy)methyl]pyridine macrocycle, **1**, no rotaxanes are formed under CuAAC active metal template conditions; this lack of formation of the expected MIA may be explained if the complexation of Cu(I) to the macrocycle is weak and therefore the metal ion does not direct the CuAAC reaction through the cavity of the macrocycle. Thus, we examined the complexation of Cu(I) and, the larger but isoelectronic, Ag(I) ions with the 'click' macrocycle using ^{1}H NMR and HR-ES-MS experiments (Scheme 3). HR-ES-MS experiments on 1:1 mixtures of either $[Cu(CH_3CN)_4](PF_6)$ (1 equiv.) or AgOTf (1 equiv.) and macrocycle, **2** (1 equiv.),



Scheme 2. Attempted CuAAC active metal template rotaxane synthesis using the *exo* functionalised pyridyl-1,2,3-triazole 'click' macrocycle, **2**; (i) $[Cu(CH_3CN)_4](PF_6)$ (1 equiv.), CH_2Cl_2, RT, 48 h.

displayed prominent peaks due to metal ion complexation at $m/z = 584$ $[\mathbf{2} + Cu]^+$ or 628 $[\mathbf{2} + Ag]^+$ along with weak peaks at $m/z = 522$ $[\mathbf{2} + H]^+$ and 544 $[\mathbf{2} + Na]^+$, suggesting that the 'click' macrocycle forms stable complexes with these metal ions. ^{1}H NMR spectra of the 1:1 mixtures were also indicative of metal ion complexation with large downfield shifts observed for the pyridyl protons H_a and H_b. A similar shift was observed for the H_e proton of the macrocycle, suggesting that the 1,2,3-triazole units are involved in the metal ion complexation (Figure 3 and Supporting Information). The ^{1}H NMR and HR-ES-MS data are consistent with 'click' macrocycle, **2**, acting as a tridentate chelating ligand and this binding mode was confirmed by X-ray crystallography. X-ray quality crystals of the AgOTf complex (**9b**) were obtained by vapour diffusion of diethyl ether into a methanol solution of the silver(I) macrocycle complex (Figure 4). The macrocycle, **2**, acts as a tridentate chelate ligand complexing the silver(I) ions through its pyridyl and 1,2,3-triazolyl donor units in a trigonal-planar coordination mode (Figure 4). Although



Scheme 3. Synthesis of Cu(I) and Ag(I) metal complexes of **2**; (i) $[Cu(CH_3CN)_4](PF_6)$ (1 equiv.), CH_2Cl_2, RT, 1 h, or (ii) AgOTf (1 equiv.), CH_2Cl_2, RT, 1 h.

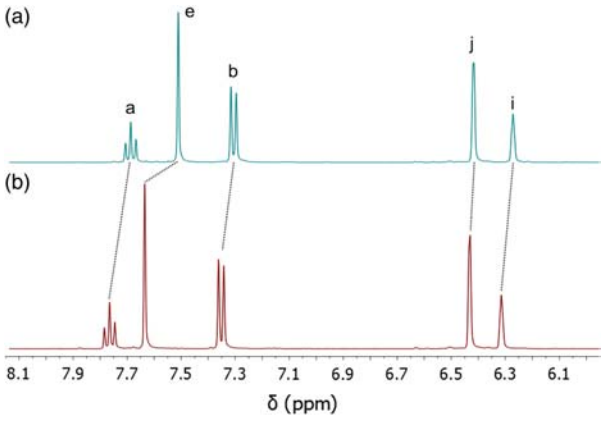


Figure 3. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 300 K) of (a) macrocycle **2**, (b) Ag(I) complex **9b**. The assignments correspond to the lettering shown in Scheme 3.

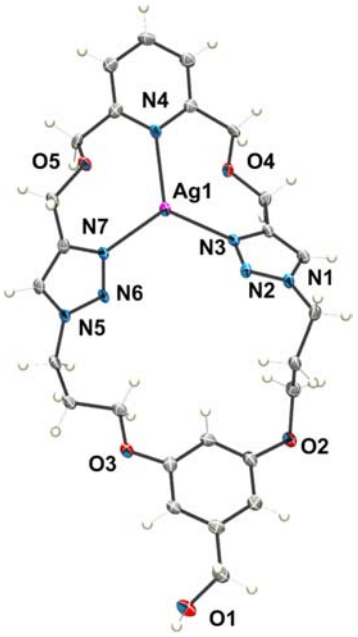


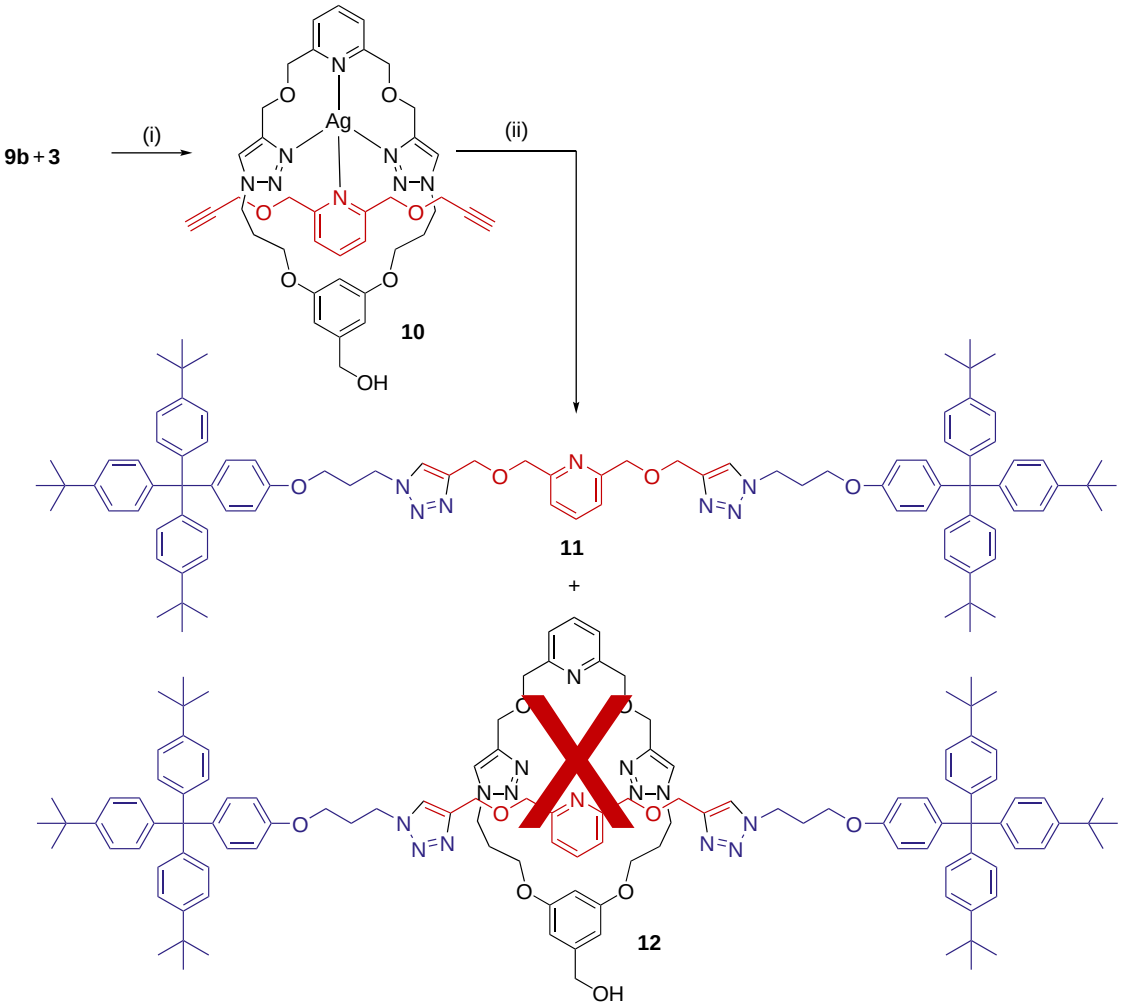
Figure 4. A labelled ORTEP diagram of 'click' macrocycle silver(I) triflate complex, **9b**. The thermal ellipsoids are shown at the 50% probability level. The solvent molecules and counter ions have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **9b**; Ag1—N7 2.245(2), Ag1—N3 2.265(2), Ag1—N4 2.303(2), Ag1—O4 2.843(2), Ag1—O5 2.923(2), N7—Ag1—N3 122.87(8), N7—Ag1—N4 116.25(8), N4—Ag1—N3 120.77(8).

1,2,3-triazolyl coordination chemistry is now well documented in the literature (*18*), this coordination environment was somewhat unexpected as it leads to the formation of the rather rare 8- and 18-membered chelate rings. The 1,2,3-triazolyl units are coordinated to the silver(I) ion through the more electron-rich N3 nitrogen and the Ag—N distances (Ag1—N7 2.245(2), Ag1—N3 2.265(2), Ag1—N4 2.303(2)) are consistent with those previously observed for non-macrocyclic Ag(I) pyridyl-1,2,3-triazole complexes (*14*, *15*, *19*). The ether oxygen atoms of the macrocycle could also potentially coordinate to the Ag(I) ions but the Ag—O distances (Ag1—O4 2.843(2), Ag1—O5 2.923(2) Å) are outside the range that would normally constitute a bonding interaction. In the extended crystal structure, the $[(\mathbf{2})Ag]^+$ cations form a 1D slip stack (Supporting Information) that is supported by weak C—H—N hydrogen bonding interactions (*15*, *20*) between neighbouring 1,2,3-triazolyl units (H23—N2, 2.695(3), C23—N2 3.372(4) Å, C23—H23—N2 128.8(2)°, H11—N6, 2.794(2), C11—N6 3.383(2) Å, C11—H11—N2 121.0(2)°). There is no evidence of stabilising Ag(I)—Ag(I) interactions (the shortest Ag(I)—Ag(I) distance is 6.0188(4) Å).

We have been unable to generate X-ray quality crystals of the analogous Cu(I) complex (**9a**), but on the basis of the similar ^{1}H NMR and HR-ES-MS data the copper(I) ion presumably adopts a similar tridentate, trigonal-planar coordination mode when coordinated to **2**. These observations provide a rationale for the lack of rotaxane formation with **2** under the CuAAC active metal template conditions. If **2** forms a strong tridentate complex with Cu(I), it lacks the vacant coordination sites necessary to bind both azide and alkyne required for the CuAAC active metal template reaction to proceed. A similar lack of reactivity in the CuAAC active metal template reaction has been observed previously with other tridentate macrocycles (*16*).

Ag(I) complexes are known to be coordinatively flexible and are readily able to interact with two to six ligands (*21*). Furthermore, close inspection of the molecular structure of **9b** suggested that a suitably designed ligand could potentially coordinate to and thread through the centre of the tridentate silver(I) macrocycle complex to form a pseudorotaxane architecture (SPARTAN Molecular Models, Supporting Information). Based on this we reasoned that **9b** could potentially be used to synthesise [2]rotaxane **12** using a [3 + 1] (*22*) passive template approach (Scheme 4). The silver(I) complex, **9b** (1 equiv.), and pyridyl dialkyne ligand, **3** (1 equiv.), were added to CH_2Cl_2, and the resulting reaction mixture was stirred at room temperature for 1 h (Scheme 4). The azide stopper (2.5 equiv.) **5**, $[Cu(CH_3CN)_4](PF_6)$ (1 equiv.) and tris(benzyltriazolylmethyl)amine (TBTA 1 equiv.) were added to the CH_2Cl_2 solution containing **10**, and the 'click' reaction was monitored using TLC and HR-ES-MS. However, as with the CuAAC active metal template method, the [3 + 1] passive template approach (Scheme 4) only resulted in the formation of the non-interlocked linear thread, **11**, in stoichiometric yield, with no trace of the interlocked product [2]rotaxane, **12**, detected in the reaction mixture.

There are two potential reasons for the failure of the [3 + 1] passive template approach to the [2]rotaxane, **12**: (1) the silver(I)-pyridine interaction is known to be very labile; thus, the CuAAC 'click' reaction may occur on uncoordinated **3** leading to the non-interlocked linear thread, **11**, or (2) the pyridyl dialkyne ligand, **3**, has not threaded through the cavity of the silver(I) macrocycle complex to form the required pseudorotaxane architecture that would lead to capture of the mechanical bond. The ^{1}H NMR spectrum of a 1:1 mixture of **9b** and **3** (CD_2Cl_2, Supporting Information) indicates that the pyridyl dialkyne ligand, **3**, coordinates to the silver(I) macrocycle complex, **9b**. However, HR-ES-MS experiments only display prominent peaks due to a silver(I) pyridyl dialkyne ligand adduct ($m/z = 322$ $[\mathbf{3} + Ag]^+$) and the silver(I) macrocycle complex ($m/z = 628$ $[\mathbf{9b}]^+$). No ion due to the $[\mathbf{9b} + \mathbf{3}]^+$ complex could be detected suggesting that any interaction between silver(I) 'click' macrocycle complex, **9b**, and the pyridyl dialkyne ligand, **3**, is weak. Vapour diffusion of diethyl ether into a methanol solution containing a 1:1 mixture of **9b** and **3** provided X-ray quality crystals. However, the molecular structure was not the expected pseudorotaxane **10**, in fact the crystals contained none of the pyridyl dialkyne ligand, **3**. Under these



Scheme 4. Attempted [3 + 1] passive metal template rotaxane synthesis using the *exo* functionalised pyridyl-1,2,3-triazole 'click' macrocycle, **2**; (i) CH_2Cl_2, RT, 1 h, (ii) $[Cu(CH_3CN)_4](PF_6)$ (2.2 equiv.), tris(benzyltriazolylmethyl)amine (TBTA), (1 equiv.), azide stopper **5** (2.5 equiv.), CH_2Cl_2, RT, 48 h.

crystallisation conditions, a coordination polymer between AgOTf and the 'click' macrocycle, **2**, is formed (Figure 5(a)). There are two different silver(I) coordination environments in the coordination polymer; one silver(I) ion (Ag2) is sandwiched between two 'click' macrocycles and coordinated to four 1,2,3-triazolyl nitrogen atoms (two from each macrocycle) in a distorted tetrahedral arrangement ($\tau_4 = 0.89$) (*23*) forming a $[(\mathbf{2})_2Ag]^+$ cation (Figure 5(b)). Each one of these sandwiched cations is linked to a neighbouring $[(\mathbf{2})_2Ag]^+$ unit by a second silver(I) ion (Ag1). This silver ion is coordinated to two pyridyl units (one from each adjacent macrocycle) in a linear fashion linking adjacent $[(\mathbf{2})_2Ag]^+$ cations and generating the coordination polymer (Figure 5(a)). Two ether oxygen atoms make close contacts to Ag1 (Ag1—O4 2.586(4), Ag1—O34 2.631(4)), but the coordination environment is best described as linear two coordinate (N4—Ag1—N34 179.4(2), Figure 5(c)) – a motif that is common in Ag(I)-pyridyl complexes (*21*). Based on the observed results, we postulate that the lack of templation to form the desired [2]rotaxane using the [3 + 1] passive template approach is connected to both the lability of the Ag(I)–pyridyl interaction and the coordinative flexibility of the 'click' macrocycle **2**.

Conclusion

It has been demonstrated that a one-pot, multi-component CuAAC method can be used to safely generate an *exo* functionalised pyridyl-1,2,3-triazole 'click' macrocycle (**2**) in good yield. Efforts to use the 'click' macrocycle in both passive and active metal template syntheses of [2]rotaxanes were unsuccessful, and this appears to be connected to the coordinating ability of the 1,2,3-triazolyl units in the macrocycle. Two different silver(I) triflate complexes of the 'click' macrocycle were characterised using single crystal X-ray diffraction. The coordination chemistry of the 'click'

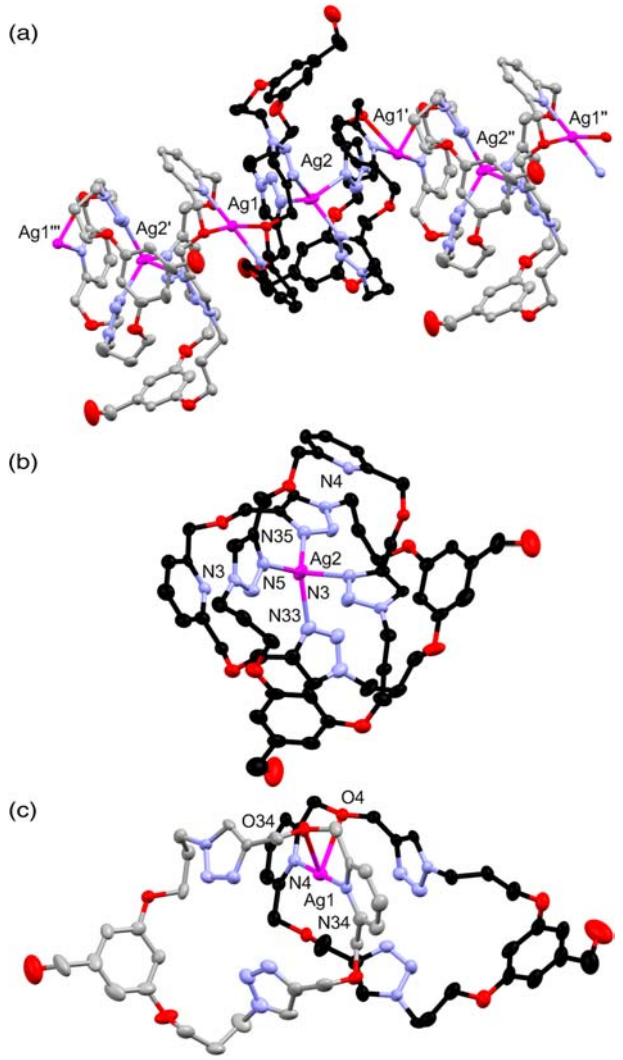


Figure 5. Labelled MERCURY diagrams of the coordination polymer formed between the 'click' macrocycle **2** and silver(I) triflate, (a) the extended coordination polymer, (b) $[(\mathbf{2})_2Ag]^+$ cation showing the coordination environment of Ag2 ion and (c) the coordination environment of Ag1 ion. The thermal ellipsoids are shown at the 50% probability level. The solvent molecules and counterions have been omitted for clarity. Selected bond lengths (Å) and angles (°) for silver(I) triflate **2** coordination polymer; Ag1—N4 2.197(5), Ag1—N34 2.186(5), Ag2—N3 2.422(4), Ag2—N5 2.289(5), Ag2—N33 2.349(5), Ag2—N35 2.272(5), Ag1—O4 2.586(4), Ag1—O34 2.631(4), N4—Ag1—N34 179.4(2), N3—Ag2—N5 93.3(3), N3—Ag2—N33 91.4(2), N3—Ag2—N35 116.3(2), N5—Ag2—N33 117.2(2).

macrocycle **2** is complicated, with both discrete and polymeric complexes obtained under very similar conditions. However, in both cases the 1,2,3-triazolyl units of the macrocyclic ligand are coordinated to the silver(I) ions. These results indicate that pyridyl-1,2,3-triazole 'click' macrocycles could potentially be used in both passive and active metal template syntheses of MIAs, but the positioning of the 1,2,3-triazolyl units within macrocyclic architectures needs to be carefully designed in order to enable the desired templation effects. Efforts towards these types of 'click' macrocycles are now underway.

Supporting information

Full experimental details, molecular models, spectroscopic and crystallographic data are available free of charge via the Internet at http://pubs.acs.org. The CIF files for the compounds have been deposited with the Cambridge Crystallographic Data Centre (CCDC 871005 - 871007). These data may be obtained free of charge on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel: +44-1233-336408; Fax: +44-1233-336033; E-mail: deposit@ccdc.cam.uk.

References

(1) Castano, B.; Pedrazzini, T.; Sisti, M.; Gallo, E.; Ragaini, F.; Casati, N.; Caselli, A. *Appl. Organometal. Chem.* **2011**, *25*, 824–829; Korendovych, I.V.; Kryatova, O.P.; Reiff, W.M.; Rybak-Akimova, E.V. *Inorg. Chem.* **2007**, *46*, 4197–4211.

(2) Gong, H.-Y.; Rambo, B.M.; Karnas, E.; Lynch, V.M.; Keller, K.M.; Sessler, J.L. *J. Am. Chem. Soc.* **2011**, *133*, 1526–1533; Abe, H.; Chida, Y.; Kurokawa, H.; Inouye, M. *J. Org. Chem.* **2011**, *76*, 3366–3371; Lüning, U.; Mak, E.; Zindler, M.; Hartkopf, B.; Herges, R. *Eur. J. Org. Chem.* **2010**, *2010*, 4932–4940; Kilah, N.; Beer, P., Pyridine and Pyridinium-Based Anion Receptors Anion Recognition in Supramolecular Chemistry. In Topics in heterocyclic chemistry, Gale, P.A., Dehaen, W., Eds.; Springer: Berlin/Heidelberg, 2010; Vol. 24, pp 301–340; Huang, D.; Holm, R.H. *J. Am. Chem. Soc.* **2010**, *132*, 4693–4701; Mullen, K.M.; Beer, P.D. *Chem. Soc. Rev.* **2009**, *38*, 1701–1713.

(3) Fernandes, A.S.; Cabral, M.F.; Costa, J.; Castro, M.; Delgado, R.; Drew, M.G.B.; Félix, V. *J. Inorg. Biochem.* **2011**, *105*, 410–419.

(4) Rzuczek, S.G.; Pilch, D.S.; Liu, A.; Liu, L.; LaVoie, E. J.; Rice, J.E. *J. Med. Chem* **2010**, *53*, 3632–3644; Drahoš, B.; Kotek, J.; Císařová, I.; Hermann, P.; Helm, L.; Lukeš, I.; Tóth, É. *Inorg. Chem.* **2011**, *50*, 12785–12801; Al-Salahi, R.; Al-Omar, M.; Amr, A.E.-G. *Molecules* **2010**, *15*, 6588–6597.

(5) Yamasaki, R.; Shigeto, A.; Saito, S. *J. Org. Chem.* **2011**, *76*, 10299–10305; Roy, K.; Wang, C.; Smith, M.D.; Dewal, M.B.; Wibowo, A.C.; Brown, J.C.; Ma, S.; Shimizu, L.S. *Chem. Commun.* **2011**, *47*, 277–279.

(6) Forgan, R.S.; Sauvage, J.-P.; Stoddart, J.F. *Chem. Rev.* **2011**, *111*, 5434–5464; Olson, M.A.; Botros, Y.Y.; Stoddart, J.F. *Pure Appl. Chem.* **2010**, *82*, 1569–1574; Fahrenbach, A.C.; Stoddart, J.F. *Chem. Asian J.* **2011**, *6*, 2660–2669; Durola, F.; Lux, J.; Sauvage, J.-P.; Wenger, O.S. *Supramol. Chem.* **2011**, *23*, 42–52; Mateo-Alonso, A. *Chem. Commun.* **2010**, *46*, 9089–9099; Sauvage, J.-P.; Collin, J.-P.; Durot, S.; Frey, J.; Heitz, V.; Sour, A.; Tock, C. *C. R. Chim.* **2010**, *13*, 315–328; Haenni, K.D.; Leigh, D.A. *Chem. Soc. Rev.* **2010**, *39*, 1240–1251; Fang, L.; Olson, M.A.; Benitez, D.; Tkatchouk, E.; Goddard, W.A., III; Stoddart, J.F. *Chem. Soc. Rev.* **2010**, *39*, 17–29; Gassensmith, J.J.; Baumes, J.M.; Smith, B.D. *Chem. Commun.* **2009**, 6329–6338; Stoddart, J.F. *Chem. Soc. Rev.* **2009**, *38*, 1802–1820;

Haussmann, P.C.; Stoddart, J.F. *Chem. Rec.* **2009**, *9*, 136–154.
(7) Coskun, A.; Banaszak, M.; Astumian, R.D.; Stoddart, J.F.; Grzybowski, B.A. *Chem. Soc. Rev.* **2012**, *41*, 19–30; Qu, D.-H.; Tian, H. *Curr. Phys. Chem.* **2011**, *1*, 261–274; Ambrogio, M.W.; Thomas, C.R.; Zhao, Y.-L.; Zink, J.I.; Stoddart, J.F. *Acc. Chem. Res*. **2011**, *44*, 903–913; Credi, A.; Venturi, M.; Balzani, V. *ChemPhysChem* **2010**, *11*, 3398–3403; Coti, K.K.; Belowich, M.E.; Liong, M.; Ambrogio, M.W.; Lau, Y.A.; Khatib, H.A.; Zink, J.I.; Khashab, N.M.; Stoddart, J.F. *Nanoscale* **2009**, *1*, 16–39; Balzani, V.; Credi, A.; Venturi, M. *Chem. Soc. Rev.* **2009**, *38*, 1542–1550; Kay, E.R.; Leigh, D.A.; Zerbetto, F. *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191.
(8) Beves, J.E.; Blight, B.A.; Campbell, C.J.; Leigh, D.A.; McBurney, R.T. *Angew. Chem. Int. Ed.* **2011**, *50*, 9260–9327.
(9) Crowley, J.D.; Goldup, S.M.; Lee, A.-L.; Leigh, D.A.; McBurney, R.T. *Chem. Soc. Rev.* **2009**, *38*, 1530–1541.
(10) Hein, J.E.; Fokin, V.V. *Chem. Soc. Rev.* **2010**, *39*, 1302–1315; Meldal, M.; Tornoe, C.W. *Chem. Rev.* **2008**, *108*, 2952–3015; Wu, P.; Fokin, V.V. *Aldrichim. Acta* **2007**, *40*, 7–17; Rostovtsev, V.V.; Green, L.G.; Fokin, V.V.; Sharpless, K.B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599; Tornoe, C.W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064.
(11) Zahran, E.M.; Hua, Y.; Lee, S.; Flood, A.H.; Bachas, L.G. *Anal. Chem.* **2011**, *83*, 3455–3461; Ramabhadran, R.O.; Hua, Y.; Li, Y.-J.; Flood, A.H.; Raghavachari, K. *Chem. Eur. J.* **2011**, *17*, 9123–9129; Hua, Y.; Ramabhadran, R.O.; Uduehi, E.O.; Karty, J.A.; Raghavachari, K.; Flood, A.H. *Chem. Eur. J.* **2011**, *17*, 312–321; Zahran, E.M.; Hua, Y.; Li, Y.; Flood, A.H.; Bachas, L.G. *Anal. Chem.* **2010**, *82*, 368–375; McDonald, K.P.; Hua, Y.; Flood, A.H. *Top. Heterocycl. Chem.* **2010**, *24*, 341–366; Hua, Y.; Flood, A.H. *Chem. Soc. Rev.* **2010**, *39*, 1262–1271; Bandyopadhyay, I.; Raghavachari, K.; Flood, A.H. *ChemPhysChem* **2009**, *10*, 2535–2540; Li, Y.; Pink, M.; Karty, J.A.; Flood, A.H. *J. Am. Chem. Soc.* **2008**, *130*, 17293–17295; Li, Y.; Flood, A.H. *Angew. Chem. Int. Ed.* **2008**, *47*, 2649–2652; Li, Y.; Flood, A.H. *J. Am. Chem. Soc.* **2008**, *130*, 12111–12122; Li, Y.; Flood, A.H. *Angew. Chem. Int. Ed.* **2008**, *47*, 2649–2652; Lewandowski, B.; Jarosz, S. *Synth. Commun.* **2011**, *41*, 2161–2168; Zhao, Y.; Li, Y.; Li, Y.; Huang, C.; Liu, H.; Lai, S.-W.; Che, C.-M.; Zhu, D. *Org. Biomol. Chem.* **2010**, *8*, 3923–3927; Bogdan, A. R.; James, K. *Org. Lett.* **2011**, *13*, 4060–4063; Bogdan, A.R.; James, K. *Chem. Eur. J.* **2010**, *16*, 14506–14512; Binauld, S.; Hawker, C.J.; Fleury, E.; Drockenmuller, E. *Angew. Chem. Int. Ed.* **2009**, *48*, 6654–6658.
(12) Lewandowski, B.; Jarosz, S. *Org. Lett.* **2010**, *12*, 2532–2535.
(13) Feldman, A.K.; Colasson, B.; Fokin, V.V. *Org. Lett.* **2004**, *6*, 3897–3899.
(14) Crowley, J.D.; Bandeen, P.H.; Hanton, L.R. *Polyhedron* **2010**, *29*, 70–83.
(15) Crowley, J.D.; Bandeen, P.H. *Dalton Trans.* **2010**, *39*, 612–623.
(16) 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.
(17) Aucagne, V.; Hänni, K.D.; Leigh, D.A.; Lusby, P.J.; Walker, D.B. *J. Am. Chem. Soc.* **2006**, *128*, 2186–2187.
(18) Crowley, J.D.; McMorran, D.A. 'Click-Triazole' Coordination Chemistry: Exploiting 1,4-Disubstituted-1,2,3-Triazoles as Ligands. In Topics in heterocyclic chemistry, Kosmrlj, J. Ed.; Springer: Berlin/Heidelberg, 2012; pp 1–53. DOI: 10.1007/7081_2011_67; Struthers, H.; Mindt, T.L.; Schibli, R. *Dalton Trans.* **2010**, *39*, 675–696.
(19) Gower, M.L.; Crowley, J.D. *Dalton Trans.* **2010**, *39*, 2371–2378; Fleischel, O.; Wu, N.; Petitjean, A. *Chem. Commun.* **2010**, *46*, 8454–8456.
(20) Schweinfurth, D.; Strobel, S.; Sarkar, B. *Inorg. Chim. Acta* **2011**, *374*, 253–260.
(21) Young, A.G.; Hanton, L.R. *Coord. Chem. Rev.* **2008**, 252, 1346–1386; Steel, P. J.; Fitchett, C.M. *Coord. Chem. Rev.* **2008**, *252*, 990–1006; Chen, C.-L.; Kang, B.-S.; Su, C.-Y. *Aust. J. Chem.* **2006**, *59*, 3–18; Khlobystov, A.N.; Blake, A.J.; Champness, N.R.; Lemenovskii, D.A.; Majouga, A.G.; Zyk, N.V.; Schroder, M. *Coord. Chem. Rev.* **2001**, *222*, 155–192.
(22) Leigh, D.A.; Lusby, P.J.; Slawin, A.M.Z.; Walker, D.B. *Chem. Commun.* **2005**, 4919–4921; Leigh, D.A.; Lusby, P.J.; Slawin, A.M.Z.; Walker, D.B. *Angew. Chem. Int. Ed.* **2005**, *44*, 4557–4564; Fuller, A.-M.; Leigh, D.A.; Lusby, P.J.; Oswald, I.D. H.; Parsons, S.; Walker, D.B. *Angew. Chem. Int. Ed.* **2004**, *43*, 3914–3918.
(23) Yang, L.; Powell, D.R.; Houser, R.P. *Dalton Trans.* **2007**, 955–964.