Rotaxanes

DOI: 10.1002/anie.200802745

An Ion-Pair Template for Rotaxane Formation and its Exploitation in an Orthogonal Interaction Anion-Switchable Molecular Shuttle**

Michael J. Barrell, David A. Leigh, Paul J. Lusby,* and Alexandra M. Z. Slawin*

Despite significant advances[1] in anion-template methods for the construction of mechanically interlocked molecules,[2] the use of anions to induce changes in the relative positions of the components of catenanes and rotaxanes has proved particularly challenging,[3] especially in comparison to the widespread success achieved with other stimuli.[4–6] The few examples of anion-switchable molecular shuttles developed to date employ competition between the same types of weak interaction in both states of the molecule to achieve switching (solvation effects[3d,e] or the anion outcompeting hydrogen-bonding acceptor groups of the macrocycle for donor groups on the thread [3e,f]). Other features of anions, such as the propensity of halides to form strong coordination bonds to various transition metals, have yet to be exploited.[7] Herein we report the serendipitous discovery of a new efficient template for rotaxane formation and its use in the assembly of a chloride-switchable molecular shuttle which exhibits excellent positional integrity (> 98 %) of the ring in both states that arises from orthogonal binding modes: direct intercomponent metal–ligand coordination in one state and a combination of tight ion pairing, aromatic stacking interactions, and CH···O and CH···Cl hydrogen bonding in the other.

The development of the new template for rotaxane formation was prompted by the chance observation that displacement of the acetonitrile ligand of [(**L1**)Pd(CH_3CN)] by the chloride ion of benzyl pyridinium chloride (**1**-Cl) was accompanied by encapsulation of the organic cation by the anionic PdCl-coordinated macrocycle [(**L1**)PdCl]$^-$ (Figure 1 a).[8] The threaded nature of the complex [(**L1**)PdCl·**1**] in $CDCl_3$ was clearly apparent from ^1H NMR spectroscopy (a distinct upfield shift in the pyridinium resonances with respect to those in **1**-Cl caused by shielding by the benzylic groups of the macrocycle, see the Supporting Information) and was also found to persist in the solid state (Figure 1 b and c) from the X-ray crystal structure of single crystals grown from a saturated CH_2Cl_2/EtOAc solution.[9]

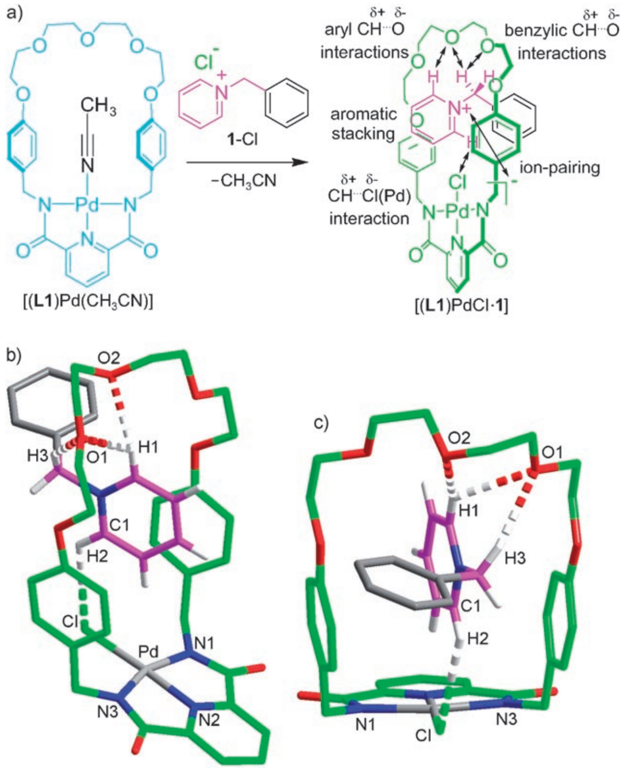


Figure 1. An allosteric anion-activated template for threading based on tight ion pairing reinforced through multiple other noncovalent interactions. a) Synthesis of pseudorotaxane [(**L1**)PdCl·**1**]. Reaction conditions: CH_2Cl_2, 1 h, quantitative yield (use of **1**-PF_6 instead of **1**-Cl, or using DMSO instead of CH_2Cl_2, does not lead to pseudorotaxane formation). b) Side-on and c) face-on views of the X-ray crystal structure of [(**L1**)PdCl·**1**].[9] N blue, O red, Pd silver, Cl and the C atoms of the macrocycle green, pyridinium purple, and other C atoms gray. Selected bond lengths [Å] and angles [°]: N1–Pd 2.04, N2–Pd 1.93, N3–Pd 2.03, Cl–Pd 2.32, O1–H3 2.47, O1–H1 2.57, O2–H1 2.37; N1-Pd-N3 160.8, N2-Pd-Cl 176.4.

The solid-state structure of [(**L1**)PdCl·**1**] indicates that a broad range of noncovalent interactions are responsible for the assembly of the threaded architecture. In addition to the tight ion pair[10] (the pyridinium nitrogen atom is within 4 Å of atoms in the first coordination sphere of the formally negatively charged metal complex), aromatic stacking interactions between the aromatic rings of the host and guest, aryl- and alkyl-CH···O hydrogen bonding between the polyether

---

[*] M. J. Barrell, Prof. D. A. Leigh, Dr. P. J. Lusby
School of Chemistry, University of Edinburgh
The King's Buildings, West Mains Road, Edinburgh EH9 3JJ (UK)
Fax: (+44) 131-650-6453
E-mail: david.leigh@ed.ac.uk
paul.lusby@ed.ac.uk
Homepage: http://www.catenane.net
Prof. A. M. Z. Slawin
School of Chemistry, University of St. Andrews
Purdie Building, St. Andrews, Fife KY16 9ST (UK)

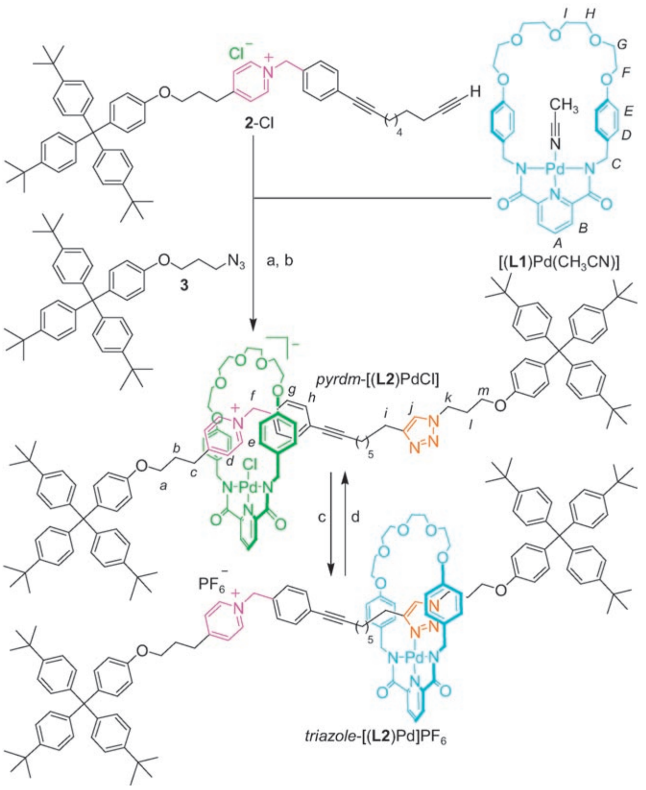
[**] We thank Michael Hoffman and Dr. Anne-Marie Fuller for initial work on ion-pair rotaxane templates in our group and the EPSRC National Mass Spectrometry Service Centre (Swansea, U.K.) for accurate mass data. This work was supported by the EPSRC. P.J.L. is a Royal Society University Research Fellow. D.A.L. is an EPSRC Senior Research Fellow and holds a Royal Society-Wolfson Research Merit Award.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802745.

oxygen atoms and protons on the carbon atoms adjacent to the pyridinium nitrogen atom (C–O distances 3.19–3.36 Å), and CH···Cl(Pd) second coordination sphere interactions[7] (C–Cl distance 3.72 Å) all apparently contribute to the stability of the interpenetrated structure. Many of these primarily electrostatic interactions should be much weaker in more polar environments and, indeed, the ^{1}H NMR spectrum of [(**L1**)PdCl·**1**] (see the Supporting Information) shows the complex is largely unthreaded in [D$_6$]DMSO. The chloride anion is a vital component of the assembly process: [(**L1**)Pd(CH$_3$CN)] did not form a threaded complex when treated with **1**-PF$_6$ in CH$_2$Cl$_2$, a result which suggested that the recognition motif could also be used as the basis of an anion-selective trigger.

A pyridinium chloride salt suitable for rotaxane synthesis (**2**-Cl) was prepared in four steps from 4-pyridinepropanol (see the Supporting Information). Treatment of [(**L1**)Pd(CH$_3$CN)] with **2**-C1 in dichloromethane for one hour, followed by reaction with **3** by a Cu^I-catalyzed azide–alkyne 1,3-cycloaddition (CuAAC)[11] in the presence of tris(benzyltriazolylmethyl)amine (TBTA)[12] and diisopropylethylamine (DIPEA) led to [(**L2**)PdCl] in 64% yield (Scheme 1). The mass spectrum of this product was strongly suggestive of a rotaxane, as the major peak, which corresponds to [(**L2**)Pd]$^+$, does not fragment to the intact macrocycle and axle, as would be expected for a non-interlocked salt. The irreversible formation of a stoppered rotaxane was further confirmed when removal of palladium did not cause separation of the components (see the Supporting Information). Comparison of the ^{1}H NMR spectrum of [(**L2**)PdCl] (Figure 2b) with that of the chloride salt of the thread (Figure 2a), shows significant upfield shifts to the pyridinium resonances H$_d$, H$_e$, and H$_f$, and adjacent protons (H$_a$ and H$_c$).[13] Other signals of the thread show little change, which indicates that the anionic PdCl–macrocycle is located overwhelmingly over the pyridinium station, that is, the structure is *pyrdm*[14]-[(**L2**)PdCl] (Scheme 1).

The triazole group introduced by the CuAAC reaction can also act as a ligating station for the palladium–macrocycle.[15] Treatment of *pyrdm*-[(**L2**)PdCl] with AgPF$_6$ (1.1 equiv; Scheme 1, step c) smoothly precipitated AgCl and resulted in quantitative conversion into a new rotaxane, [(**L2**)Pd]PF$_6$, in which the chloride ligand had been replaced by the noncoordinating PF$_6^-$ counterion. A comparison of the ^{1}H NMR spectrum of [(**L2**)Pd]PF$_6$ (Figure 2c) with that of the PF$_6$ salt of the thread (Figure 2d) shows that the signals of the pyridinium station (H$_{d\text{-}f}$) appear at similar chemical shifts in the thread and rotaxane, while the triazole resonance (H$_j$) and adjacent protons (e.g., H$_i$) are shifted upfield in the rotaxane, which indicates that removal of the chloride ion from the palladium center is accompanied by translocation of the palladium–macrocycle component to



Scheme 1. Synthesis and operation of chloride-switchable molecular shuttle [(**L2**)Pd]$^+$: a) CH$_2$Cl$_2$, 1 h; b) **3** (1.1 equiv), [Cu(CH$_3$CN)$_4$]PF$_6$ (0.2 equiv), TBTA (0.25 equiv), DIPEA (1 equiv), CH$_2$Cl$_2$/CH$_3$CN (7:1), 18 h, 64% (from **2**-Cl); c) AgPF$_6$ (1.1 equiv), acetone, 18 h, quantitative; d) Bu$_4$NCl (1.5 equiv), CHCl$_3$, quantitative.

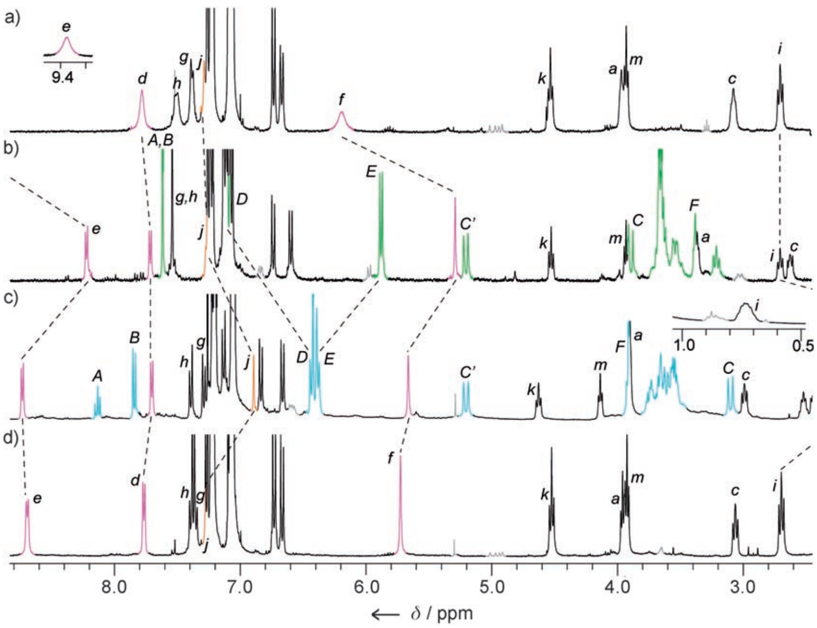


Figure 2. Partial ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectra of a) chloride salt of the thread,[13] b) *pyrdm*-[(**L2**)PdCl], c) *triazole*-[(**L2**)Pd]PF$_6$, and d) PF$_6^-$ salt of the thread. The assignments correspond to the lettering shown in Scheme 1. Signals shown in gray arise from impurities and residual solvents.

give *triazole*-[(**L2**)Pd]PF_6. Simple addition of tetrabutylammonium chloride to *triazole*-[(**L2**)Pd]PF_6 in chloroform (Scheme 1, step d) reverses this process to afford a product with identical physical and spectroscopic properties to the original rotaxane, *pyrdm*-[(**L2**)PdCl].

The chance discovery of a molecular recognition motif that is triggered by the formation of an anion–palladium coordination bond has been exploited as both an efficient rotaxane-forming template and as the basis for a chloride-switchable molecular shuttle. The use of wholly different and orthogonal binding modes in the two states of the shuttle leads to exceptional positional integrity of the ring in both forms. Anion-activated allosteric templates could lead to new developments in sensors, logic gates, transport agents, and molecular machines.

Experimental Section

Experimental procedure for the preparation of *pyrdm*-[(**L2**)PdCl]: **2**-Cl (59 mg, 0.066 mmol) and [(**L1**)Pd(CH_3CN)] (50 mg, 0.073 mmol) were stirred for 1 h in CH_2Cl_2 (7 mL) prior to the addition of **3** (43 mg, 0.073 mmol) and DIPEA (11 μL, 0.066 mmol). A solution of TBTA (9 mg, 0.017 mmol) and $[Cu(CH_3CN)_4]PF_6$ (6 mg, 0.0147 mmol) in CH_3CN (1 mL) was added and the reaction mixture allowed to stir for a further 18 h. After this time the volatile compounds were removed under reduced pressure and the residue taken up in CH_2Cl_2 (10 mL). The resulting solution was washed with saturated NH_4Cl (3 × 10 mL) and the aqueous phase re-extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were concentrated under reduced pressure and subjected to flash chromatography on silica gel (0–3 % MeOH in CH_2Cl_2 as eluent) to give *pyrdm*-[(**L2**)PdCl] as a bright yellow solid (89 mg, 64 %). For compound characterization, full synthetic details for all precursors, and the switching experiments, see the Supporting Information.

Received: June 11, 2008

Keywords: anion recognition · molecular shuttles · palladium · rotaxanes · template synthesis

---

[1] For a recent review on the anion-template synthesis of interlocked molecules, see: M. S. Vickers, P. D. Beer, *Chem. Soc. Rev.* **2007**, *36*, 211 – 225.

[2] a) G. M. Hübner, J. Gläser, C. Seel, F. Vögtle, *Angew. Chem.* **1999**, *111*, 395 – 398; *Angew. Chem. Int. Ed.* **1999**, *38*, 383 – 386; b) J. A. Wisner, P. D. Beer, M. G. B. Drew, *Angew. Chem.* **2001**, *113*, 3718 – 3721; *Angew. Chem. Int. Ed.* **2001**, *40*, 3606 – 3609; c) J. A. Wisner, P. D. Beer, M. G. B. Drew, M. R. Sambrook, *J. Am. Chem. Soc.* **2002**, *124*, 12469 – 12476; d) M. R. Sambrook, P. D. Beer, J. A. Wisner, R. L. Paul, A. R. Cowley, *J. Am. Chem. Soc.* **2004**, *126*, 15364 – 15365; e) K.-Y. Ng, A. R. Cowley, P. D. Beer, *Chem. Commun.* **2006**, 3676 – 3678; f) B. Huang, S. M. Santos, V. Felix, P. D. Beer, *Chem. Commun.* **2008**, DOI: 10.1039/b808094a.

[3] For co-conformational switching induced by intramolecular anion–hydrogen bonding (which involves deprotonation of a phenol group), see: a) C. M. Keaveney, D. A. Leigh, *Angew. Chem.* **2004**, *116*, 1242 – 1244; *Angew. Chem. Int. Ed.* **2004**, *43*, 1222 – 1224; b) J. Berná, A. M. Brouwer, S. M. Fazio, N. Haraszkiewicz, D. A. Leigh, C. M. Lennon, *Chem. Commun.* **2007**, 1910 – 1912; c) K.-Y. Ng, V. Felix, S. M. Santos, N. H. Reesa, P. D. Beer, *Chem. Commun.* **2008**, 1281 – 1283. For co-conformational switching induced by anion solvation effects, see: d) B. W. Laursen, S. Nygaard, J. O. Jeppesen, J. F. Stoddart, *Org. Lett.* **2004**, *6*, 4167 – 4170; e) C.-F. Lin, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu, *Chem. Eur. J.* **2007**, *13*, 4350 – 4355. For co-conformational switching induced by intermolecular anion-hydrogen bonding, see: Ref. [3e] and f) Y.-L. Huang, W.-C. Hung, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu, *Angew. Chem.* **2007**, *119*, 6749 – 6753; *Angew. Chem. Int. Ed.* **2007**, *46*, 6629 – 6633.

[4] For examples of light-switchable molecular shuttles, see: a) A. C. Benniston, A. Harriman, *Angew. Chem.* **1993**, *105*, 1553 – 1555; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1459 – 1461; b) H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, N. Nakashima, *J. Am. Chem. Soc.* **1997**, *119*, 7605 – 7606; c) A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G. W. H. Wurpel, *Science* **2001**, *291*, 2124 – 2128; d) C. A. Stanier, S. J. Alderman, T. D. W. Claridge, H. L. Anderson, *Angew. Chem.* **2002**, *114*, 1847 – 1850; *Angew. Chem. Int. Ed.* **2002**, *41*, 1769 – 1772; e) A. Altieri, G. Bottari, F. Dehez, D. A. Leigh, J. K. Y. Wong, F. Zerbetto, Angew. Chem. **2003**, *115, 2398–2402; Angew. Chem. Int. Ed.* **2003**, *42*, 2296–2300; *Angew. Chem. Int. Ed.* **2003**, *42*, 2296–2300; f) G. Bottari, D. A. Leigh, E. M. Pérez, *J. Am. Chem. Soc.* **2003**, *125*, 13360 – 13361; g) E. M. Pérez, D. T. F. Dryden, D. A. Leigh, G. Teobaldi, F. Zerbetto, *J. Am. Chem. Soc.* **2004**, *126*, 12210 – 12211; h) H. Murakami, A. Kawabuchi, R. Matsumoto, T. Ido, N. Nakashima, *J. Am. Chem. Soc.* **2005**, *127*, 15891 – 15899; i) J.-P. Collin, D. Jouvenot, M. Koizumi, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **2005**, 1850 – 1855; j) D.-H. Qu, Q.-C. Wang, H. Tian, *Angew. Chem.* **2005**, *117*, 5430 – 5433; *Angew. Chem. Int. Ed.* **2005**, *44*, 5296 – 5299; k) S. Schmidt-Schäffer, L. Grubert, U. W. Grummt, K. Buck, W. Abraham, *Eur. J. Org. Chem.* **2006**, 378 – 398; l) V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1178 – 1183; m) W. Abraham, K. Buck, M. Orda-Zgadzaj, S. Schmidt-Schäffer, U.-W. Grummt, *Chem. Commun.* **2007**, 3094 – 3096; n) V. Serreli, C.-F. Lee, E. R. Kay, D. A. Leigh, *Nature* **2007**, *445*, 523 – 527; o) W. Zhou, D. Chen, J. Li, J. Xu, J. Lv, H. Liu, Y. Li, *Org. Lett.* **2007**, *9*, 3929 – 3932; For a recent review, see: p) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77 – 92.

[5] For examples of pH-switchable molecular shuttles, see: a) R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133 – 137; b) M.-V. Martínez-Díaz, N. Spencer, J. F. Stoddart, *Angew. Chem.* **1997**, *109*, 1991 – 1994; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1904 – 1907; c) P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gómez-López, M.-V. Martinez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 11932 – 11942; d) A. M. Elizarov, S.-H. Chiu, J. F. Stoddart, *J. Org. Chem.* **2002**, *67*, 9175 – 9181; e) K.-W. Cheng, C.-C. Lai, P.-T. Chianga, S.-H. Chiu, *Chem. Commun.* **2006**, 2854 – 2856; f) Y. Tokunaga, T. Nakamura, M. Yoshioka, Y. Shimomura, *Tetrahedron Lett.* **2006**, *47*, 5901 – 5904; g) D. A. Leigh, A. R. Thomson, *Org. Lett.* **2006**, *8*, 5377 – 5379; h) J. D. Crowley, D. A. Leigh, P. J. Lusby, R. T. McBurney, L.-E. Perret-Aebi, C. Petzold, A. M. Z. Slawin, M. D. Symes, *J. Am. Chem. Soc.* **2007**, *129*, 15085 – 15090; i) S. J. Vella, J. Tiburcio, S. J. Loeb, *Chem. Commun.* **2007**, 4752 – 4754; j) D. Tuncel, Ö. Özsar, H. B. Tiftika , B. Salih, *Chem. Commun.* **2007**, 1369 – 1371; k) W. Zhou, J. Li, X. He, C. Li, J. Lv, Y. Li, S. Wang, H. Liu, D. Zhu, *Chem. Eur. J.* **2008**, *14*, 754 – 763; l) J. Berná, S. M. Goldup, A.-L. Lee, D. A. Leigh, M. D. Symes, G. Teobaldi, F. Zerbetto, *Angew. Chem.* **2008**, *120*, 4464 – 4468; *Angew. Chem. Int. Ed.* **2008**, *47*, 4392 – 4396.

[6] For examples of redox-switchable molecular shuttles, see: a) N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage, B. Ventura, *J. Am. Chem. Soc.* **1999**, *121*, 4397 – 4408; b) A. Altieri,

F. G. Gatti, E. R. Kay, D. A. Leigh, D. Martel, F. Paolucci, A. M. Z. Slawin, J. K. Y. Wong, *J. Am. Chem. Soc.* **2003**, *125*, 8644 – 8654; c) G. Cooke, J. F. Garety, B. Jordan, N. Kryvokhyzha, A. Parkin, G. Rabani, V. M. Rotello, *Org. Lett.* **2006**, *8*, 2297 – 2300; d) T. D. Nguyen, Y. Liu, S. Saha, K. C.-F. Leung, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2007**, *129*, 626 – 634; e) S. Nygaard, K. C.-F. Leung, I. Aprahamian, T. Ikeda, S. Saha, B. W. Laursen, S.-Y. Kim, S. W. Hansen, P. C. Stein, A. H. Flood, J. F. Stoddart, J. O. Jeppesen, *J. Am. Chem. Soc.* **2007**, *129*, 960 – 970; f) S. Saha, A. H. Flood, J. F. Stoddart, S. Impellizzeri, S. Silvi, M. Venturi, A. Credi, *J. Am. Chem. Soc.* **2007**, *129*, 12159 – 12171; g) I. Aprahamian, W. R. Dichtel, T. Ikeda, J. R. Heath, J. F. Stoddart, *Org. Lett.* **2007**, *9*, 1287 – 1290; h) F. Durola, J.-P. Sauvage, *Angew. Chem.* **2007**, *119*, 3607 – 3610; *Angew. Chem. Int. Ed.* **2007**, *46*, 3537 – 3540; i) G. Fioravanti, N. Haraszkiewicz, E. R. Kay, S. M. Mendoza, C. Bruno, M. Marcaccio, P. G. Wiering, F. Paolucci, P. Rudolf, A. M. Brouwer, D. A. Leigh, *J. Am. Chem. Soc.* **2008**, *130*, 2593 – 2601; j) Y.-L. Zhao, I. Aprahamian, A. Trabolsi, N. Erina, J. F. Stoddart, *J. Am. Chem. Soc.* **2008**, *130*, 6348 – 6350.

[7] For the exploitation of second-sphere coordination of metal–halide and thiocyanate bonds in rotaxane and catenane assembly, see: a) B. A. Blight, K. A. Van Noortwyk, J. A. Wisner, M. C. Jennings, *Angew. Chem.* **2005**, *117*, 1523 – 1528; *Angew. Chem. Int. Ed.* **2005**, *44*, 1499 – 1504; b) B. A. Blight, J. A. Wisner, M. C. Jennings, *Chem. Commun.* **2006**, 4593 – 4595; c) B. A. Blight, J. A. Wisner, M. C. Jennings, *Angew. Chem.* **2007**, *119*, 2893 – 2896; *Angew. Chem. Int. Ed.* **2007**, *46*, 2835 – 2838; d) B. A. Blight, X. Wei, J. A. Wisner, M. C. Jennings, *Inorg. Chem.* **2007**, *46*, 8445 – 8447.

[8] In a two-step process, carbon monoxide and chloride coordination to rhodium has been used to change the shape and charge of a "weak-link approach" macrocycle, which thereby promotes subsequent pseudorotaxane formation with viologens, see: J. Kuwabara, C. L. Stern, C. A. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 10074 – 10075.

[9] The X-ray crystal data and experimental details of the structural refinement for [(**L1**)PdCl·**1**] are provided in the Supporting Information. CCDC 689628 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] For other examples of rotaxane formation aided by ion-pairing, see: a) D. J. Hoffart, J. Tiburcio, A. de La Torre, L. K. Knight, S. J. Loeb, *Angew. Chem.* **2008**, *120*, 103 – 107; *Angew. Chem. Int. Ed.* **2008**, *47*, 97 – 101; b) E. Lestini, K. Nikitin, H. Müller-Bunz, D. Fitzmaurice, *Chem. Eur. J.* **2008**, *14*, 1095 – 1106.

[11] a) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057 – 3064; b) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708 – 2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596 – 2599.

[12] T. R. Chan, R. Hilgraf, K. B. Sharpless, V. V. Fokin, *Org. Lett.* **2004**, *6*, 2853 – 2855.

[13] The broad appearance of the H_d, H_e, and H_f resonances of the chloride salt of the thread (Figure 2 a) is probably a result of multiple chloride positions within the tight ion pair.

[14] The prefix indicates the position of the macrocycle on the thread: *pyrdm*- noncovalent bonding to the pyridinium group; *triazole*- coordinated through the palladium ion to the triazole ring.

[15] V. Aucagne, J. Berná, J. D. Crowley, S. M. Goldup, K. D. Hänni, D. A. Leigh, P. J. Lusby, V. E. Ronaldson, A. M. Z. Slawin, A. Viterisi, D. B. Walker, *J. Am. Chem. Soc.* **2007**, *129*, 11950 – 11963.