Formation of a [2]rotaxane and [2]catenane based on $PdBr_2L_2$ as a template[1]

Barry A. Blight, James A. Wisner, and Michael C. Jennings

Abstract: Previous studies have determined that neutral palladium(II) dibromide complexes template the formation of [2]pseudorotaxanes, albeit with weaker affinities than the analogous palladium(II) dichloride species. Here, the self-assembly of both [2]rotaxane (**2**) and [2]catenane (**5**) were attempted using a $PdBr_2L_2$ centre as the template, resulting in the desired interlocked structures. The structures were confirmed by NMR spectroscopy, CSI-MS, and single crystal X-ray diffraction analyses. [2]Rotaxane **2** was isolated in 53% and [2]catenane **5** in 41% yields. The lower yields observed in comparison to the chloride analogues can be attributed to the reduced template effect of the palladium(II) dibromide subunits, caused by both the poor steric fit of the bromides in the isophthalamide cleft and bromide's reduced capacity as a hydrogen bond acceptor.

Key words: rotaxane, catenane, hydrogen bonding, interlocked, supramolecular chemistry.

Résumé : Des études antérieures ont permis de déterminer que les complexes de dibromure de palladium(II) neutre peuvent être utilisés comme gabarit pour la formation de [2]pseudorotoxanes, même si leur affinité est plus faible que celle des espèces analogues à base de dichlorure de palladium(II). Dans ce travail, on a tenté de réaliser l'autoassemblage du [2]rotoxane (**2**) et du [2]caténane (**5**) en utilisant un gabarit à base de $PdBr_2I_2$ et on a obtenu les structures comportant les interrelations désirées. Les structures ont été confirmées par spectroscopie RMN, par spectrométrie de masse avec ionisation par nébulisation à froid (SM-INF) et par des analyse de diffraction des rayons X par un cristal unique. On a isolé le [2]rotoxane (**2**) avec un rendement de 53% et le [2]caténane (**5**) avec un rendement de 41%. Ces rendements plus faibles que ceux obtenus avec les analogues chlorés peuvent être attribués à l'effet de gabarit réduit des unités de dibromure de palladium(II) qui est provoqué par le mauvais ajustement stérique des bromures dans les espaces disponibles de l'isophtalamide ainsi que par la capacité réduite du bromure comme accepteur d'une liaison hydrogène.

Mots-clés : rotaxane, caténane, liaison hydrogène, interrelié, chimie supramoléculaire.

[Traduit par la Rédaction]

Introduction

The study of interlocked molecules (e.g., rotaxanes and catenanes) (1), conceptual precursors to molecular machines (2), has largely been possible because of the potentially high yields of products that self-assemble by applying modern template-based synthetic methods (1, 2). In this context, the use of transition metals in these assemblies generally falls into one of two categories. The metal may be used as a reversible connection point in the backbone of one or more of the components (3). Alternatively, the metal can participate in the template process to organize accompanying ligands in a desired spatial arrangement (4). The simultaneous use of the metal in both roles is rare but offers a possible route to further simplify syntheses of these interlocked products (5).

Received 31 March 2008. Accepted 11 April 2008. Published on the NRC Research Press Web site at canjchem.nrc.ca on 16 September 2008.

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[1]This article is part of a Special Issue dedicated to Professor R. Puddephatt.

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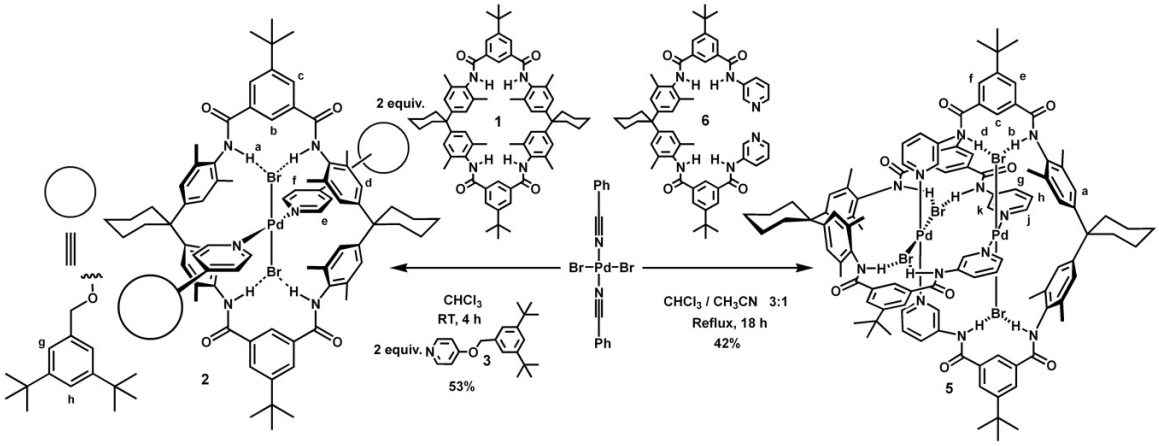
We have previously reported a study (6) that examined the complexation of *trans*-bis-pyridine palladium(II) dihalide axles by the well-known isophthalamide-based macrocycle **1** (7). Their combination resulted in [2]pseudorotaxane formation, employing second-sphere coordination of the halide ligands (hydrogen-bond acceptors) by the isophthalamide clefts (hydrogen-bond donors) of **1** as the template. It was concluded that the size of the $PdCl_2$ subunit of a *trans*-$PdCl_2Py_2$ axle was a complimentary fit to the size of the hydrogen-bond donating macrocyclic cavity (K_a = 5000 (mol/L)$^{-1}$ in $CDCl_3$ at 298 K). Nitrogen-based ligand exchange allowed us to then apply this template strategy in the facile self-assembly of palladium(II) dichloride templated [2]rotaxane (8) and [2]catenane superstructures (9).

Anion recognition studies by Crabtree and co-workers (10), Smith and co-workers (11), Beer and co-workers (12), and Gale and co-workers (13) have demonstrated that neutral isophthalamide-based acyclic receptors associate with a variety of anions through hydrogen bonding in solution. Studies specifically examining isophthalamide–halide complexation in solution revealed an inferior affinity for bromide compared with chloride, which can be rationalized by a reduced hydrogen-bond acceptor ability and a poorer steric fit of bromide anions for such receptors. [2]Pseudorotaxanes formed between **1** and a *trans*-$PdBr_2Py_2$ axle exhibit a similarly reduced affinity (K_a = 750 (mol/L)$^{-1}$ in $CDCl_3$ at 298 K) in

 doi:10.1139/V08-126

Scheme 1. Syntheses of [2]rotaxane **2** and [2]catenane **5**. Aromatic protons are labeled identically to the previously reported $PdCl_2$-based structures (8, 9) to aid in discussion of their respective ^{1}H NMR spectra.



comparison with the chloride analogue, which can be explained using similar arguments (6). To date, however, there are no literature examples of bromide anions or ligands acting as, or in, the organizational template to form a finite interlocked structure. We sought to examine this potential phenomenon by observing whether bromide can indeed be used to template interlocked products, and, if so, how they compare structurally to other bromide-bound isophthalamide-based receptors. Herein, we describe the syntheses and characterization of a [2]rotaxane (**2**) and [2]catenane (**5**) templated by second-sphere coordination of palladium(II) dibromide complexes via hydrogen bonding (Scheme 1) and rendered interlocked through first-sphere ligation.

Results and discussion

[2]Rotaxane (2)

Ligand substitution of benzonitrile from *trans*-bis-benzonitrile palladium(II) dibromide (14) by sterically demanding pyridine co-ligands (4-(3,5-di-tert-butylbenzyl)-oxypyridine) **3** (8) in the presence of **1** (2 equiv.) results in the synthesis of interlocked **2** in modest yields (Scheme 1). Its preparation proceeds via dissolution of the above three components in chloroform and allowing them to stir for 4 h at room temperature. After selective crystallization of macrocycle **1** and precipitation of the remaining liquor's contents into hexanes, flash column chromatography was required to separate the product from the reaction mixture, affording [2]rotaxane **2** in 53% yield.

Comparison of the ^{1}H NMR spectra of the free components macrocycle **1** and dumbbell **4** with the pale yellow powder isolated from chromatography supported the expected interlocked geometry in solution (Fig. 1). Hydrogen-bonding interactions with the bromide ligands result in the deshielding of the macrocyclic amide protons (H_a $\Delta\delta$ = 0.94 ppm). As a consequence of the interpenetrated nature of the structure, both pyridyl-protons (H_e $\Delta\delta$ = –1.44 ppm, H_f $\Delta\delta$ = –0.55 ppm) are shifted upfield from the frequency of their free components due to C-H$\cdots\pi$ interactions with the diphenylcyclohexyl sidewalls of the macrocycle, which also results in deshielding of the diphenylcyclohexyl arene protons (H_d $\Delta\delta$ = 0.23 ppm). Cold spray ionization mass spectrometry (CSI-MS) confirmed the presence of the solvated

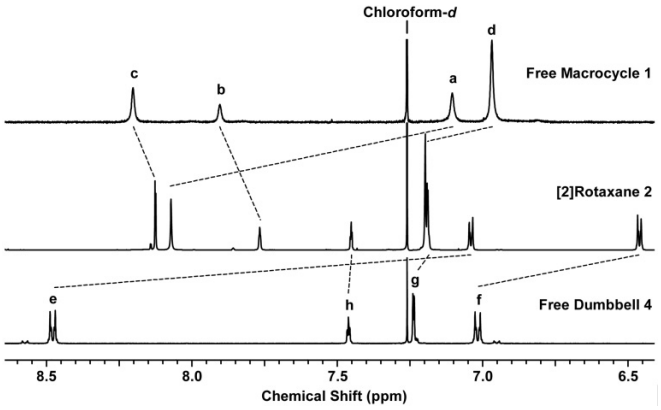
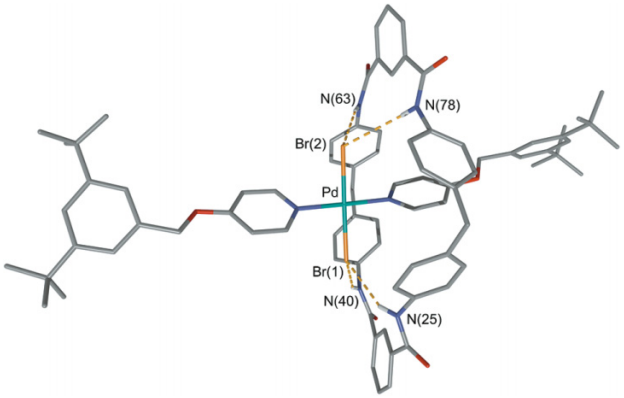


Fig. 1. The aromatic region of the ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of free macrocycle **1** (top), [2]rotaxane **2** (middle), and free dumbbell **4** (bottom). Illustrated are the observed perturbations in chemical shift between free and interlocked components (dashed lines). COSY, and ROESY NMR experiments were performed to determine individual ^{1}H NMR spectroscopic assignments.

superstructure with ions of $[M - Br]^+$ at 1797.9 amu and $[M - 2Br]^{2+}$ at 858.5.3 amu, signals that do not appear in solutions of **1** and (or) **4** subjected to the same conditions.

Determination of the solid-state structure by single crystal X-ray diffraction analysis confirmed the solution evidence for the interlocked geometry (Fig. 2). Colorless plate-like single crystals were grown by slow diffusion of diisopropylether into a concentrated chloroform solution of **2**. The anticipated interlocked architecture crystallized in space group *P*(-1) and contained structural similarities to isophthalamide–bromide complexes in the existing literature (10–13). In these cases, hydrogen-bond contacts are slightly longer (3.42 to 3.63 Å) than the sums of the Van der Waals radii (3.40 Å), with the exception of one isophthalamide–bromide conjugate reported by Smith and co-workers (3.28 and 3.39 Å) and are in agreement with those measured in **2**. The larger size of bromide anions (or ligands) also causes each amide nitrogen from these examples, including **2**, to deviate from coplanarity from the central isophthalamide ring in the direction of bromide (by >20°) resembling a perching-type geometry. This also results in a 2.11 Å dis-

Fig. 2. Stick representation of [2]rotaxane **2** in the solid state. All methyl, cyclohexyl, and *t*-butyl groups of the macrocycle and all C-H hydrogen atoms have been removed for clarity. Hydrogen bonds and weak contacts have been represented by yellow dashed lines. Color code: C gray, H white, N blue, O red, Br orange, Pd teal.



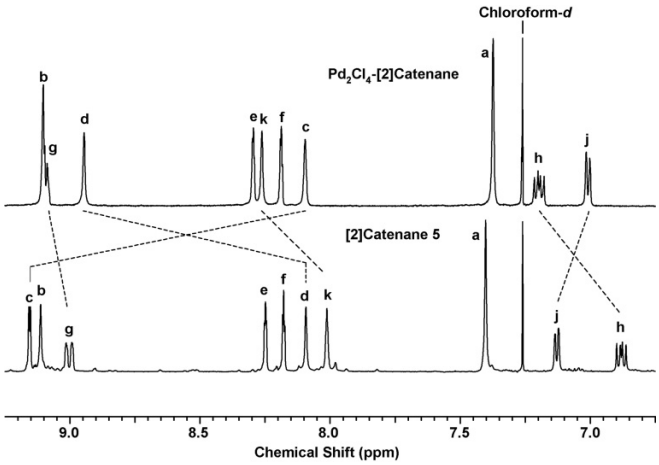
placement of the palladium centre from the least-squares plane of the macrocyclic ring (plane defined by the four carbonyl carbons), caused by the poor steric fit of the bromide ligands in the isophthalamide clefts of **1**. The dissymmetric geometry of **2**, in the solid state, prompted us to investigate its potential shuttling activity in solution (15). However, low temperature ^{1}H NMR showed no sign of exchange broadening down to –50 °C (248 K). Contact distances and angles of interest include: N(25)···Br(1) = 3.46 Å (N-H···Br = 156°), N(40)···Br(1) = 3.45 Å (N-H···Br = 153°), N(63)···Br(2) = 3.57 Å (N-H···Br = 164°), N(78)···Br(2) = 3.67 Å (N-H···Br = 150°).

[2]Catenane (5)

[2]Catenane **5** is designed to employ a *trans*-bidentate ligand **6** (9) that incorporates the structural components of both macrocycle **1** and the required pyridine co-ligands (Scheme 1). A chloroform–acetonitrile solution of **6** and *trans*-bis-benzonitrile palladium(II) dibromide (14) were refluxed for 18 h. The reaction mixture was concentrated, precipitated into hexanes to remove residual benzonitrile, and the resulting orange solid subjected to column chromatography to afford [2]catenane **5** (a yellow powder) in 41% yield.

^{1}H NMR spectral comparison of the reaction product to the previously synthesized Pd_2Cl_4-based [2]catenane (9) confirmed in solution that the desired interlocked geometry was likely obtained using palladium(II) dibromide to template [2]catenane formation (Fig. 3). Similar chemical shifts of protons H_a, H_b, H_e, H_f, H_g, H_h, H_j, and H_k between **5** and its Pd_2Cl_4-counterpart lead us to this conclusion. In this case, however, H_h is more shielded ($\Delta\delta$ = –0.32 ppm) and H_j is less shielded ($\Delta\delta$ = 0.13 ppm) than observed in the Pd_2Cl_4-based [2]catenane, which may be attributed to stronger and (or) more frequent C-H···π interactions of H_h (resulting in weaker interactions with H_j) with the diphenylcyclohexyl cavity of the opposing macrocycle. Unexpectedly, amide proton H_d is extremely shielded ($\Delta\delta$ = –0.87 ppm) and H_c deshielded ($\Delta\delta$ = 1.07 ppm) in comparison with the Pd_2Cl_4-[2]catenane, and although examination of the ^{1}H NMR evidence could not explain these two proton assignments, a reasonable explanation presented itself upon receipt of the solid-state structure. CSI-MS also confirmed the presence of [2]catenane **5** in solution with ions of $[M + H]^+$ at 2300.8 amu and $[M + 2H]^{2+}$ at 1150.3 amu. Compound **5** was then dissolved in 1 mol/L of DMSO-d_6 and monitored by ^{1}H NMR spectroscopy in an attempt to disassemble it into its degenerate macrocyclic components. Unfortunately, the system completely degrades under these conditions, giving rise to a mixture of unidentifiable polymeric materials.

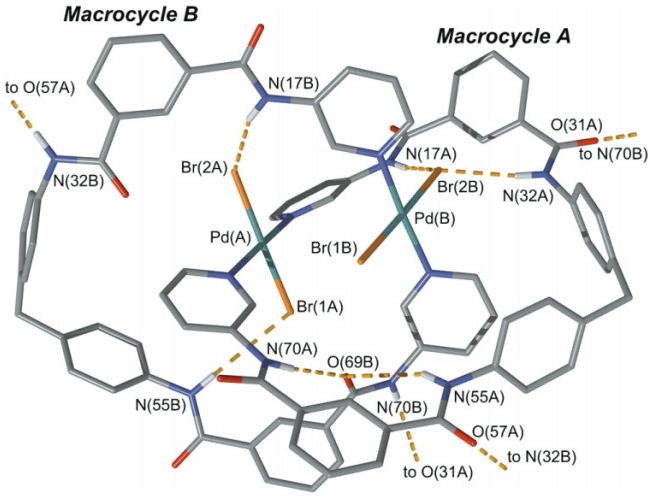
Fig. 3. The aromatic region of the ^{1}H NMR spectra (600 MHz, 298 K) of Pd_2Cl_4-[2]catenane (top), and [2]catenane **5** (bottom). Individual proton assignments are compared between the two superstructures (dashed lines). NOESY, and ROESY NMR experiments were performed to determine individual ^{1}H NMR assignments.



Orange platelike single crystals were grown from a concentrated chloroform solution of **5** by slow diffusion of diisopropyl ether crystallizing in space group *P*2(1)/*c* and subjected to single crystal X-ray diffraction analysis. Structural elucidation of **5** established the desired interlocked geometry in the solid state (Fig. 4), which unexpectedly contained two exotopically arranged amide functionalities (with respect to the NH groups) in the structure of *macrocycle B* (all eight amide NHs of the Pd_2Cl_4-[2]catenane are endotopic). We posit that competition for hydrogen-bond acceptors ($PdBr_2$ subunits and the carbonyl-oxygen atoms in the backbone of each macrocyclic component) by the hydrogen-bond donating clefts results in an overall geometry containing a blend of structural elements from Crabtree's isophthalamide–bromide complex (10) and the amide-based [2]catenanes of Hunter (16), Vögtle and co-workers (17), and Leigh and co-workers (18) in the solid state.

The isophthalamide subunit of *macrocycle A* participates in the mutual recognition of Br(2B) (N(17A)···Br(2B) = 3.37 Å (N-H-Br = 165°), N(32A)···Br(2B) = 3.36 Å (N-H-Br = 166°)), resembling those of the isophthalamide–bromide conjugates previously discussed (10–13), as well as **2**. The second isophthalamide subunit of *macrocycle A* bifurcates O(69B) of *macrocycle B* with its NH groups (N(55A)···O(69B) = 3.75 Å (N-H-O = 158°), N(70A)···O(69B) = 2.95 Å (N-H-O = 171°), while the exotopically arranged NHs of *macrocycle B* are independently engaged in hydrogen bonding with adjacent *macrocycle A* units through the crystal lattice (N(32B)···O(57A) =

Fig. 4. Stick representation of [2]catenane **5** in the solid state. All C-H hydrogen atoms, methyl, cyclohexyl, and *t*-butyl groups have been removed for clarity. Hydrogen bonds and weak contacts have been represented by yellow dashed lines. Color code: C gray, H white, N blue, O red, Br orange, Pd teal.



2.91 Å (N-H-O = 158°), N(70B)···O(31A) = 2.98 Å (N-H-O = 141°)) and are both features of the mentioned amide-based [2]catenanes in the solid state. Each isophthalamide subunit of *macrocycle B* is singularly engaged in weak hydrogen-bond contacts with the opposing bromide ligands of *macrocycle A* (N(17B)···Br(2A) = 3.67 Å (N-H-Br = 151°), N(55B)···Br(2A) = 3.99 Å (N-H-Br = 155°). As in **2,** the Br-Pd-Br subunits in **5** are also too large for the macrocyclic cavity, which forces the displacement of each $PdBr_2$ from the centre of its respective host macrocycle (macrocyclic-plane-A···Pd(B) = 1.48 Å, macrocyclic-plane-B···Pd(A) = 2.40 Å). This results in perched geometries of both $PdBr_2$ subunits in the mouths of their respective macrocyclic components, with all amides engaged in bromide–ligand contacts deviating from coplanarity with their respective isophthalamide phenyl ring (>20°) but one. Finally, from the solid-state structure we can postulate that the unusual upfield ^{1}H NMR shift of H_d (N(32A), N(55A), N(32B), N(55B)) is likely due to this hydrogen-bond competition resulting in increased exposure to the bulk solvent, while the downfield shift of H_c (C(21A), C(59A), C(21B), C(59B)) may be the result of positioning in the deshielding cone of a neighboring endotopically arranged carbonyl-oxygen atom.

Conclusion

In summary, palladium(II) dibromide metal centres have been used successfully to self-assemble both a [2]rotaxane and [2]catenane despite the reduced magnitude of the template interactions present in comparison with previously reported palladium(II) dichloride analogues. The reduced ability of the macrocycle to hydrogen bond to the bromide ligands of the metal complex gives rise to distortions of the resulting interlocked molecules from the planned template geometry, yielding recognizable structural elements from other known isophthalamide-containing supramolecules in the solid state. The [2]catenane generated using the PdBr2 template was unstable to attempts to dissociate the two catenated rings, using DMSO as a competitive solvent for both hydrogen bonding and ligand exchange.

Experimental

General

All reactions were performed in dry solvents and under an inert $N_{2(g)}$ atmosphere. All organic reagents, including palladium(II) dibromide, were purchased from Sigma-Aldrich Chemical Company and all were used without further purification. 1D NMR spectral analyses of **4** for characterization purposes were performed on a Varian Mercury 400MHz instrument. 1D NMR and 2D NMR spectral analyses of **2** and **5** or individual assignments were performed on a Varian Inova 600MHz instrument. Cold-spray ionization mass determinations were performed with Micromass LCT instrumentation with carrier gases cooled to 200 K.

X-ray crystallographic analyses

Single crystal X-ray diffraction data, for both **2** and **5** (grown from a concentrated chloroform solution of **2** or **5** by slow vapor diffusion of diisopropyl ether), was obtained from a programmed hemisphere scan routine on a Nonius Kappa-CCD diffractometer. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998). The solution for **2** was solved by Patterson methods, and the solution for **5** by direct methods, followed by difference Fourier syntheses to find the remaining atoms in each subsequent structure. Refinement was with full-matrix least-squares methods using SHELXTL-NT 6.1 (G.M. Sheldrick, Madison, Wisconsin, USA, 2000). The organic material and the metal center(s) were very well resolved in both structures. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. A summary of the data collection, solution, and refinement parameters are listed in Table 1.[3]

Procedures

[2]Rotaxane (2)

Macrocycle **1** (50 mg, 0.049 mmol) and *trans*-bis-benzonitrile palladium(II) dibromide (14) (12 mg, 0.025 mmol) were dissolved in chloroform (10 mL) in a 25 mL round-bottomed flask and stirred for 10 min. 4-(3,5-Di-*tert*-

[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3817. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 672440 (**2**) and 672439 (**5**) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystal data, solution, and refinement parameters for [2]rotaxane **2** and [2]catenane **5**.

Compound	**2**	**5**
CCDC number	672440	672439
Empirical formula	$C_{122}H_{164}Br_2Cl_6N_6O_8Pd$	$C_{122}H_{146}Br_4Cl_3N_{12}O_{9.5}Pd_2$
	(**2**·2 $CHCl_3$·2 isopropyl ether)	(**5**·1 $CHCl_3$·1.5 isopropyl ether)
Formula mass	2321.51	2571.3
Crystal description	Colorless plates	Orange plates
Crystal size (mm)	0.50 × 0.06 × 0.04	0.33 × 0.10 × 0.05
Crystal system	Triclinic	Monoclinic
Space group	P (-1)	*P*2(1)/*c*
a (Å)	17.415(2)	15.2868(5)
b (Å)	20.501(3)	32.6803(12)
c (Å)	21.0011(17)	24.8098(8)
α (°)	107.372(6)	90
β (°)	100.449(6)	95.628(2)
γ (°)	113.911(5)	90
Z	2	4
V (Å^3)	6 136.3(12)	12 334.7(7)
D_{calcd} (gcm^{-3})	1.256	1.385
μ (mm^{-1})	0.988	1.712
Independent reflections (R_{int})	20 709 (0.0780)	21 137 (0.187)
Data, restraints, parameters	20 709, 0, 1340	21 137, 22, 1370
Goodness-of-fit on F^2	1.056	0.921
Final R_1 [$F^2 > 2\sigma F^2$]	0.0985	0.091
Final wR_2 [$F^2 > 2\sigma F^2$]	0.1836	0.2089
Final R_1 (all data)	0.219	0.3346
Final wR_2 (all data)	0.2404	0.2959
Residuals peak, hole (e, Å^3)	0.994, –0.794	1.248, –0.784

butylbenzyl)-oxypyridine **3** (15 mg, 0.049 mmol) was dissolved in chloroform (2 mL) and added dropwise via pipette. The solution was stirred for 4 h, followed by cooling in the freezer to selectively crystallize unreacted macrocycle. The precipitate was isolated via vacuum filtration, and volume of the filtrate reduced under reduced pressure to approximately 2 mL of solvent. This concentrated solution was then added dropwise to a beaker of hexanes to precipitate the product away from the high-boiling benzonitrile. The precipitate was collected via vacuum filtration. The crude product was then chromatographed (5% EtOAc in DCM, leading band) to afford 24 mg (0.013 mmol, 53% yield) of pure [2]rotaxane **2**. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.13 (d, 4H, 6 Hz), 8.07 (s, 4H), 7.77 (t, 4H, 6 Hz), 7.45, (t, 2H, 5 Hz), 7.20 (s, 8H), 7.19 (d, 4H, 5 Hz), 7.04 (d, 4H, 12 Hz), 6.46 (d, 4H, 12 Hz), 5.07 (s, 4H), 2.48 (bs, 8H), 2.10 (s, 24H), 1.70 (bs, 8H), 1.57 (bs, 4H), 1.37 (s, 18H), 1.30 (s, 36H). ^{13}C NMR ($CDCl_3$, 600 MHz) δ: 166.13, 166.00, 153.49,152.91, 151.91, 135.11, 134.53, 133.11, 131.56, 129.00, 123.38, 123.11, 121.70, 112.20, 71.82, 35.26, 34.90, 34.73, 31.40, 31.36, 31.20, 22.79, 19.30, 19.19. LR CSI-MS (MeOH matrix in $CHCl_3$) $[M - 2Br]^{2+}$ *m*/*z*: 858.5.3, $[M - Br]^+$ *m*/*z*: 1797.9.

Dumbbell (4)

In a 10 mL round-bottomed flask, *trans*-bis-benzonitrile palladium(II) dibromide (14) (40.0 mg, 0.085 mmol) was dissolved in dry acetonitrile (3 mL) and allowed to stir for 5 minutes. 4-(3,5-Di-*tert*-butylbenzyl)-oxypyridine **3** (14) (50.5 mg, 0.17 mmol) was dissolved in dry acetonitrile (1 mL) and added dropwise to the bulk solution. The reaction was stirred for 30 min to allow ample time for precipitation of the desired product. The product was isolated via vacuum filtration (65.1 mg, 0.076mmol, 88% Yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.48 (d, 4H, 8 Hz), 7.46 (t, 2H, 4 Hz), 7.24 (d, 4H, 4 Hz), 7.02 (d, 4H, 8 Hz), 5.10 (s, 4H), 1.34 (s, 36H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 166.28, 154.90, 151.51, 133.42, 123.09, 122.31, 111.89, 71.69, 34.88, 31.39. LR-ESI MS (MeOH matrix in $CHCl_3$) $[M - Br]^+$ *m*/*z*: 781.2, $[M - 2Br + H]^+$ *m*/*z*: 699.3.

[2]Catenane (5)

Dipyridyl ligand **6** (50 mg, 0.057 mmol) was dissolved in a 3:1 chloroform/acetonitrile solvent mixture (10 ml). A chloroform solution (2 ml) of *trans*-bis-benzonitrile palladium(II) dibromide (14) (27 mg, 0.057 mmol) was added dropwise to the reaction mixture, and the reaction refluxed for 18 h. The crude reaction mixture was filtered through celite to remove any precipitate, and solvent removed under reduced pressure. The resulting solid was dissolved in a minimum amount of dichloromethane and precipitated into hexanes to remove residual benzonitrile. The precipitate was collected via vacuum filtration and the crude product was then chromatographed (5% EtOAc in DCM, leading band) to afford 27 mg (0.012 mmol, 42% yield) of pure [2]catenane **5**. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 9.16 (d, 4H, 1.8 Hz), 9.12 (s, 4H), 9.01 (d, 4H, 8.4 Hz), 8.26 (dd, 4H, 1.8 and 1.8 Hz), 8.18 (dd, 4H, 1.8 Hz and 1.8 Hz), 8.09 (s, 4H), 8.02 (s, 4H), 7.40 (s, 8H), 7.14 (d, 4H, 5.4 Hz), 6.88 (dd, 4H, 8.4 Hz and 5.4 Hz) 2.61 (bs, 8H), 2.22 (s, 24H), 1.77 (bs 8H), 1.61 (bs,

4H), 1.34 (s, 36H). ^{13}C NMR ($CDCl_3$, 600 MHz) δ: 165.48, 164.78, 153.68, 148.22, 146.41, 143.20, 138.25, 135.45, 134.35, 133.50, 131.52, 130.49, 129.75, 129.17, 126.27, 125.93, 120.67, 44.98, 35.19, 34.63, 31.03, 26.34, 22.79, 19.34. LR CSI-MS (MeOH matrix in $CHCl_3$) $[M + 2H]^{2+}$ *m/z*: 1150.3, $[M + H]^+$ *m/z*: 2300.8.

Acknowledgements

We are grateful for the financial support provided by the Natural Sciences and Engineering Research Council of Canada and the University of Western Ontario.

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