

Half-rotation in a [2]catenane *via* interconvertible Pd(II) coordination modes†

David A. Leigh,^{*a} Paul J. Lusby,^a Alexandra M. Z. Slawin^b and D. Barney Walker^a

Received (in Cambridge, UK) 27th July 2005, Accepted 15th August 2005

First published as an Advance Article on the web 13th September 2005

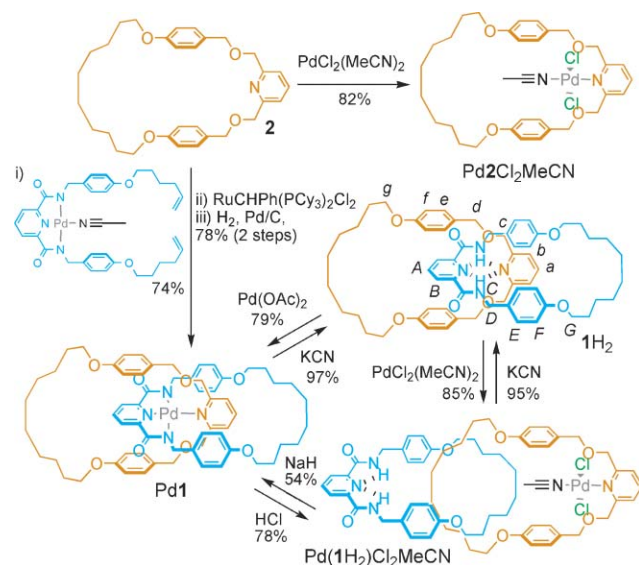
DOI: 10.1039/b510663j

Reaction of a [2]catenane with Pd(OAc)₂ binds both macrocycles to the metal, locking them in position; treatment with PdCl₂, however, results in coordination of only one ring, producing a half-turn in the relative orientation of the [2]catenane components in both solution and the solid state.

The development of novel ways to bring about changes in the relative positions of mechanically interlocked sub-molecular components is an important area of investigation in the emerging field of synthetic molecular machines.¹ In terms of rotational processes, a formal half-turn of a ring in a [2]catenane² not only corresponds to a simple mechanical switch,³ but is also a step towards the more demanding requirements of a synthetic rotary molecular motor.⁴ Here we report on a simple [2]catenane system in which the different binding modes of the interlocked rings to Pd(II) cause a major change in the position and orientation of the macrocycles in the resulting complexes.

The square planar coordination preference of Pd(II) can be used to direct the macrocyclization of suitable tridentate ligands around 2,6-dimethyleneoxy-pyridine-based threads to form rotaxanes.^{5,6} We reasoned that a similar strategy could be used to make a palladium [2]catenane by incorporating the monodentate unit into a macrocycle. Pleasingly, Pd1 was isolated in 58% yield from **2** *via* the three step (ligand coordination, ring-closing olefin metathesis, hydrogenation) reaction sequence shown in Scheme 1.⁷

De-metallation of Pd1 (KCN, MeOH–CH₂Cl₂, 20 → 40 °C, 1.5 h, 97%) afforded the catenane 1H₂ in which pyridine–amide–pyridine H-bonding⁶ holds the macrocycles in a similar position to that seen for Pd1 in both solution and the solid state. The well defined orientation of the two fragments is clearly apparent from comparison of the ¹H NMR spectra of the two catenanes (Fig. 1b and c) with those of the non-interlocked component macrocycles (Fig. 1a and 1e). In the room temperature spectra of both 1H₂ (Fig. 1b) and Pd1 (Fig. 1c) the upfield shift of the H_D, H_E and H_F



Scheme 1 Synthesis and interconversion of Pd1, 1H₂ and Pd(1H₂)Cl₂MeCN.†

^aSchool of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh, UK EH9 3JJ.

E-mail: David.Laigh@ed.ac.uk; Fax: +44-131-667-9085

^bSchool of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife, UK KY16 9ST

† Electronic supplementary information (ESI) available: Experimental procedures and X-ray crystallographic data. See <http://dx.doi.org/10.1039/b510663j>

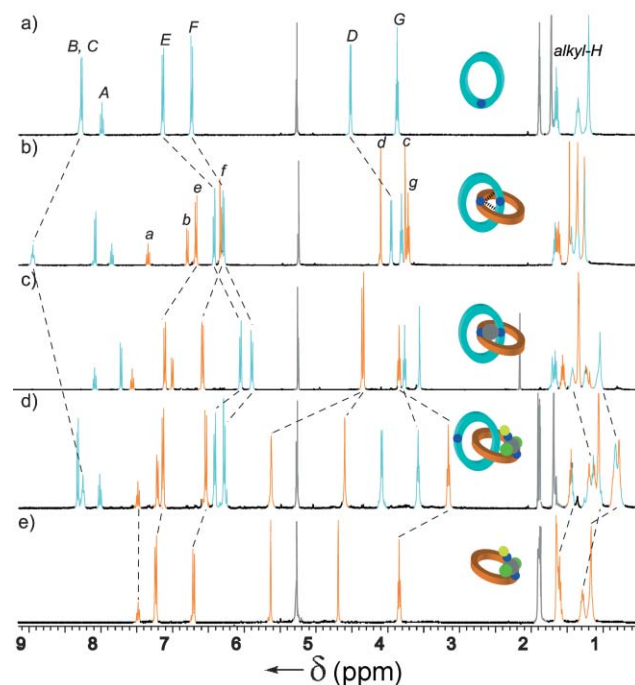


Fig. 1 ¹H NMR spectra (400 MHz, 9 : 1 CD₂Cl₂ : CD₃CN, 298 K, 2.5 mM) (a) non-interlocked bis-amide macrocycle, (b) 1H₂, (c) Pd1, (d) Pd(1H₂)Cl₂MeCN and (e) Pd2Cl₂MeCN (non-interlocked tetra-ether macrocycle bound to PdCl₂MeCN). The grey signals correspond to residual solvents. The dark blue circles in the cartoon rings indicate the position of the pyridine nitrogen atoms.

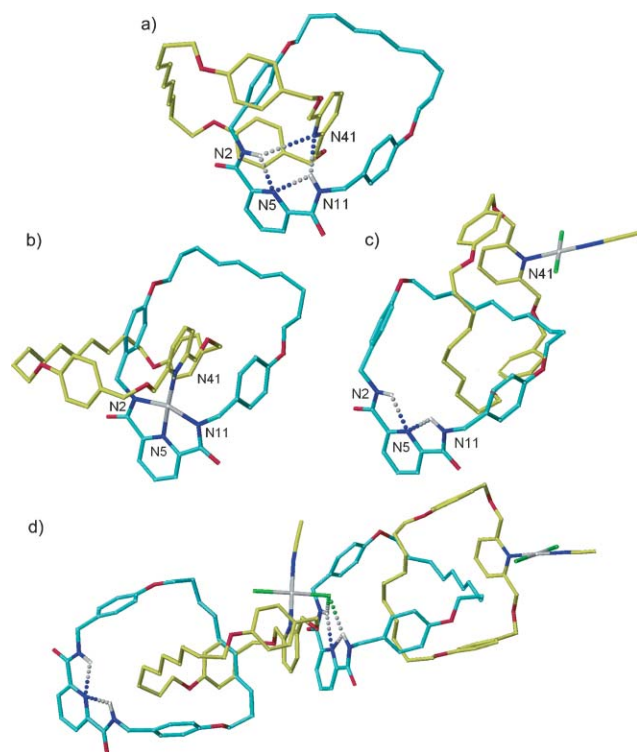


Fig. 2 X-Ray crystal structures of: (a) $1H_2$,⁶ (b) $Pd1$,⁷ (c) $Pd(1H_2)Cl_2MeCN$ ⁸ (single molecule view; note the change of position and orientation of the yellow macrocycle compared to $Pd1$ and $1H_2$) and (d) adjacent molecules of $Pd(1H_2)Cl_2MeCN$ showing intermolecular $Pd-Cl \cdots HN$ hydrogen bonding. Carbon atoms of the bis-amide macrocycle are shown in light blue and those of the tetra-ether macrocycle and coordinated acetonitrile molecule in yellow; oxygen atoms are red, nitrogen dark blue, hydrogen white, palladium grey, chlorine green. For clarity only amide hydrogen atoms are shown. Selected bond lengths for $Pd(1H_2)Cl_2MeCN$ [Å]: N2H–N5 2.21; N11H–N5 2.31; N5–N41 12.93. Selected bond angles for $Pd(1H_2)Cl_2MeCN$ [°]: N2–H–N5 108.8; N11–H–N5 104.1.

resonances indicate a π -stacking arrangement between the benzylic amide rings of the ‘blue’ macrocycle and the pyridine group of the ‘orange’ macrocycle. In contrast, the alkyl chain protons are not shielded by interactions with aromatic rings in either catenane. The solution geometries suggested by 1H NMR studies correspond well to the solid state structures of $1H_2$ (Fig. 2a) and $Pd1$ (Fig. 2b) determined by X-ray crystallography. Reaction of $1H_2$ with $Pd(OAc)_2$ (MeCN, 60 °C, 4 h, 79%) re-forms the co-conformationally locked catenane, $Pd1$.

Reaction of $1H_2$ with $PdCl_2(MeCN)_2$ in MeCN (20 °C, 1 h, 85%) afforded a second catenane $Pd(II)$ complex in which the amide protons (H_C) of the ‘blue’ macrocycle were clearly still present (Fig. 1d). X-Ray crystallography (Fig. 2c and d) on a single crystal obtained from slow cooling a saturated acetonitrile solution confirmed this complex to be $Pd(1H_2)Cl_2MeCN$, in which only one of the macrocyclic rings is coordinated to the palladium metal ion, presumably as a consequence of both the greater strength of the $Pd-Cl$ bond compared to $Pd-OAc$ and the poor basicity of the Cl^- ion.

The effect of the different coordination mode on the relative positions and orientations of the two macrocycles in the catenane

is dramatic. In the 1H NMR spectrum of $Pd(1H_2)Cl_2MeCN$ (Fig. 1d) the resonances corresponding to H_G , H_g and H_{alkyl} are shifted significantly upfield, indicating that each macrocycle is located preferentially over the aliphatic region of the other.⁹ The X-ray crystal structure (Fig. 2c and d) shows a similar geometry exists in the solid state. An additional feature of the X-ray crystal structure of $Pd(1H_2)Cl_2MeCN$ is the presence of intermolecular $Pd-Cl \cdots HNCO$ hydrogen bonds between adjacent molecules (Fig. 2d). The negligible change in the chemical shift of the amide protons (H_C) between $1H_2$ (Fig. 1a) and $Pd(1H_2)Cl_2MeCN$ (Fig. 1d) suggests this interaction is weak in solution,⁶ nevertheless it has been successfully utilised¹⁰ to direct the formation of pseudorotaxanes.

The three catenanes $1H_2$, $Pd1$ and $Pd(1H_2)Cl_2MeCN$ are all directly interconvertible (Scheme 1): the palladium complexes are de-metallated with KCN; $Pd(1H_2)Cl_2MeCN$ is converted into $Pd1$ by treatment with NaH, and the reverse reaction is promoted by HCl in MeCN.¹¹ It is interesting to note the macrocycles adopt similar positions and orientations in $Pd1$ and $1H_2$ but in the former they are locked in place by a coordination bond whereas in the latter they are held in the thermodynamic minimum only by weak and dynamic H-bonds. The preferred co-conformation of $Pd(1H_2)Cl_2MeCN$ is very different to the other two, presumably on steric grounds, and as such its formation from either of the others corresponds to a large amplitude rotational switch. It is rare to find such a rich variation in structure and dynamics made possible through simple manipulation of coordination modes.

Notes and references

- V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348; J.-P. Sauvage, *Chem. Commun.*, 2005, 1507; K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377.
- For examples of catenanes which undergo stimuli-induced half-rotations see: M. Cesario, C. O. Dietrich-Buchecker, J. Guilhem, C. Pascard and J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1985, 244; A. Livoreil, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 9399; D. B. Amabilino, C. O. Dietrich-Buchecker, A. Livoreil, L. Pérez-García, J.-P. Sauvage and J. F. Stoddart, *J. Am. Chem. Soc.*, 1996, **118**, 3905; D. A. Leigh, K. Moody, J. P. Smart, K. J. Watson and A. M. Z. Slawin, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 306; A. Livoreil, J. P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni and B. Ventura, *J. Am. Chem. Soc.*, 1997, **119**, 12114; C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172; V. Balzani, A. Credi, S. J. Langford, F. M. Raymo, J. F. Stoddart and M. Venturi, *J. Am. Chem. Soc.*, 2000, **122**, 3542; D. W. Steuerman, H. R. Tseng, A. J. Peters, A. H. Flood, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart and J. R. Heath, *Angew. Chem., Int. Ed.*, 2004, **43**, 6486; B. Korybut-Daszkiewicz, A. Wiećkowska, R. Bilewicz, S. Domagala and K. Wóźniak, *Angew. Chem., Int. Ed.*, 2004, **43**, 1668.
- A ‘switch’ influences a system as a function of state; a ‘motor’ influences a system as a function of trajectory. For a discussion see: E. R. Kay and D. A. Leigh, *Top. Curr. Chem.* (in press).
- D. A. Leigh, J. K. Y. Wong, F. Dehez and F. Zerbetto, *Nature*, 2003, **424**, 174; J. V. Hernández, E. R. Kay and D. A. Leigh, *Science*, 2004, **306**, 1532.
- A.-M. Fuller, D. A. Leigh, P. J. Lusby, I. D. H. Oswald, S. Parsons and D. B. Walker, *Angew. Chem., Int. Ed.*, 2004, **43**, 3914; Y. Furusho, T. Matsuyama, T. Takata, T. Moriuchi and T. Hirao, *Tetrahedron Lett.*, 2004, **45**, 9593.
- D. A. Leigh, P. J. Lusby, A. M. Z. Slawin and D. B. Walker, *Angew. Chem., Int. Ed.*, 2005, **44**, 4557.
- For various synthetic routes to $Pd1$ see: A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin and D. B. Walker, *J. Am. Chem. Soc.* web release date 17th August 2005.

- 8 Crystallographic data for Pd(1H₂)Cl₂MeCN: Rigaku MM007/Mercury diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å), 93 K. C₆₄H₇₉Cl₂N₅O₈Pd·CH₃CN, M = 1264.68, triclinic, space group $P\bar{1}$, a = 9.8106(8), b = 25.305(2), c = 26.820(2) Å α = 73.971(4), β = 82.771(6), γ = 88.050(6)°, V = 6348.3(9) Å³, Z = 4, D_c = 1.323 Mg m⁻³, μ = 0.435 mm⁻¹. Of 40751 measured data, 21993 were unique (R_{int} = 0.0258) and 18202 observed ($I > 2\sigma(I)$) to give R_1 = 0.0524 and wR_2 = 0.1226. CCDC 279771. See <http://dx.doi.org/10.1039/b510663j> for crystallographic data in CIF or other electronic format.
- 9 The downfield shift of H_c and H_d in Pd(1H₂)Cl₂MeCN compared to 1H₂ is probably caused by coordination of the Pd rather than the absence of macrocyclic shielding. Similar chemical shifts are observed in Pd2Cl₂MeCN (Fig. 1e).
- 10 B. A. Blight, K. A. Van Noortwyk, J. A. Wisner and M. C. Jennings, *Angew. Chem., Int. Ed.*, 2005, **44**, 1499.
- 11 For an unusual C-metallated Pd(II) catenate, see: A. J. Blake, C. O. Dietrich-Buchecker, T. I. Hyde, J.-P. Sauvage and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1989, 1663.