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]

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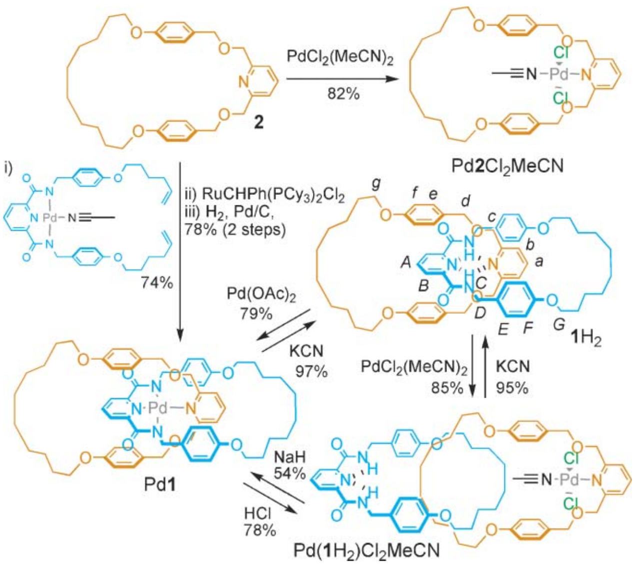
Reaction of a [2]catenane with Pd(OAc)$_2$ binds both macrocycles to the metal, locking them in position; treatment with PdCl$_2$, however, results in coordination of only one ring, producing a half-turn in the relative orientation of the [2]catenane components in both solution and the solid state.

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]catenane[2] 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.



Scheme 1 Synthesis and interconversion of Pd**1**, **1**H$_2$ and Pd(**1**H$_2$)Cl$_2$MeCN.†

The square planar coordination preference of Pd(II) can be used to direct the macrocyclization of suitable tridentate ligands around 2,6-dimethyleneoxypyridine-based threads to form rotaxanes.[5,6] We reasoned that a similar strategy could be used to make a palladium [2]catenate by incorporating the monodentate unit into a macrocycle. Pleasingly, Pd**1** 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 Pd**1** (KCN, MeOH–CH$_2$Cl$_2$, 20 → 40 °C, 1.5 h, 97%) afforded the catenane **1**H$_2$ in which pyridine–amide–pyridine H-bonding[6] holds the macrocycles in a similar position to that seen for Pd**1** in both solution and the solid state. The well defined orientation of the two fragments is clearly apparent from comparison of the ^{1}H 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 **1**H$_2$ (Fig. 1b) and Pd**1** (Fig. 1c) the upfield shift of the H$_D$, H$_E$ and H$_F$

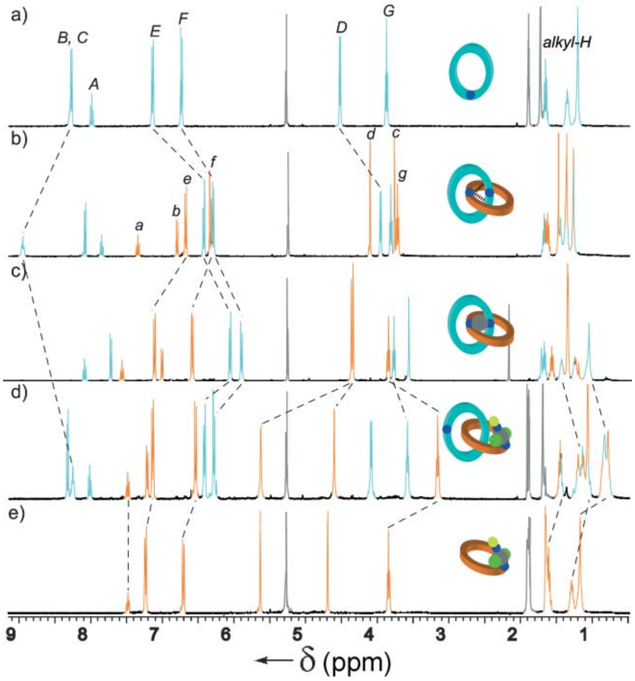


Fig. 1 ^{1}H NMR spectra (400 MHz, 9 : 1 CD$_2$Cl$_2$: CD$_3$CN, 298 K, 2.5 mM) (a) non-interlocked bis-amide macrocycle, (b) **1**H$_2$, (c) Pd**1**, (d) Pd(**1**H$_2$)Cl$_2$MeCN and (e) Pd**2**Cl$_2$MeCN (non-interlocked tetra-ether macrocycle bound to PdCl$_2$MeCN). The grey signals correspond to residual solvents. The dark blue circles in the cartoon rings indicate the position of the pyridine nitrogen atoms.

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[a] *School of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh, UK EH9 3JJ.*
E-mail: David.Leigh@ed.ac.uk; Fax: +44-131-667-9085
[b] *School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife, UK KY16 9ST*

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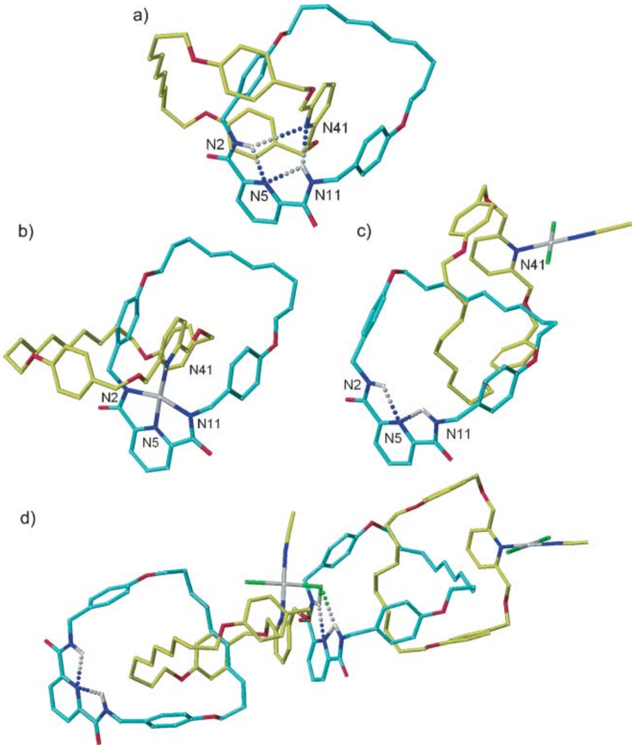

Fig. 2 X-Ray crystal structures of: (a) **1**H$_2$,[6] (b) Pd**1**,[7] (c) Pd(**1**H$_2$)Cl$_2$MeCN[8] (single molecule view; note the change of position and orientation of the yellow macrocycle compared to Pd**1** and **1**H$_2$) and (d) adjacent molecules of Pd(**1**H$_2$)Cl$_2$MeCN showing intermolecular Pd–Cl···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(**1**H$_2$)Cl$_2$MeCN [Å]: N2H–N5 2.21; N11H–N5 2.31; N5–N41 12.93. Selected bond angles for Pd(**1**H$_2$)Cl$_2$MeCN [°]: 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 ^{1}H NMR studies correspond well to the solid state structures of **1**H$_2$ (Fig. 2a) and Pd**1** (Fig. 2b) determined by X-ray crystallography. Reaction of **1**H$_2$ with Pd(OAc)$_2$ (MeCN, 60 °C, 4 h, 79%) re-forms the co-conformationally locked catenate, Pd**1**.

Reaction of **1**H$_2$ 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(**1**H$_2$)Cl$_2$MeCN, 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 ^{1}H NMR spectrum of Pd(**1**H$_2$)Cl$_2$MeCN (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(**1**H$_2$)Cl$_2$MeCN is the presence of intermolecular Pd–Cl···HNCO hydrogen bonds between adjacent molecules (Fig. 2d). The negligible change in the chemical shift of the amide protons (H$_C$) between **1**H$_2$ (Fig. 1a) and Pd(**1**H$_2$)Cl$_2$MeCN (Fig. 1d) suggests this interaction is weak in solution,[6] nevertheless it has been successfully utilised[10] to direct the formation of pseudorotaxanes.

The three catenanes **1**H$_2$, Pd**1** and Pd(**1**H$_2$)Cl$_2$MeCN are all directly interconvertible (Scheme 1): the palladium complexes are de-metallated with KCN; Pd(**1**H$_2$)Cl$_2$MeCN is converted into Pd**1** 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 Pd**1** and **1**H$_2$ 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(**1**H$_2$)Cl$_2$MeCN 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.

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8 Crystallographic data for Pd(**1**H_2)Cl_2MeCN: Rigaku MM007/Mercury diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), 93 K. $C_{64}H_{79}Cl_2N_5O_8Pd \cdot CH_3CN$, 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) Å^3, 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(**1**H_2)Cl_2MeCN compared to **1**H_2 is probably caused by coordination of the Pd rather than the absence of macrocyclic shielding. Similar chemical shifts are observed in Pd**2**Cl_2MeCN (Fig. 1e).

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