

A [2]catenane quantitatively assembled *via* copper(I) and palladium(II) coordination

Christiane Dietrich-Buchecker,^{*a} Neri Geum,^b Akiko Hori,^c Makoto Fujita,^{*cd} Shigeru Sakamoto,^e Kentaro Yamaguchi^e and Jean-Pierre Sauvage^{*a}

^a Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS, Université Louis Pasteur, Faculté de Chimie, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France. E-mail: sauvage@chimie.u-strasbg.fr

^b Dankook University, 8 Hannam-dong, Yongsan-ku, Seoul 140-714, Korea

^c Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusaku, Nagoya 464-8603, Japan

^d CREST, Japan Science and Technology Corporation (JST)

^e Chemical Analysis Center, Chiba University, Yayoicho, Inageku, Chiba, 263-8522, Japan

Received (in Cambridge, UK) 13th March 2001, Accepted 4th May 2001

First published as an Advance Article on the web 13th June 2001

A [2]catenane consisting of 41-membered interlocking rings is formed quantitatively, following a two metal based [Cu(I) and Pd(II)] strategy; the compound is obtained as the thermodynamic product.

Catenanes are experiencing a spectacular revival in relation to topology as well as switches, machines and motors at the molecular level.^{1–4} Copper(I) has been extensively used as templating metal centre, allowing the preparation of simple to complex interlocking or knotted topologies.⁵ The use of coordination bonds to construct interlocking rings has been recently proposed.^{6,7} It is especially attractive when the metal-to-ligand bond is labile and the catenane is obtained as the thermodynamically most stable product, thus leading to quantitative yields of the desired species. In this respect, palladium(II) has turned out to be particularly well adapted.⁶

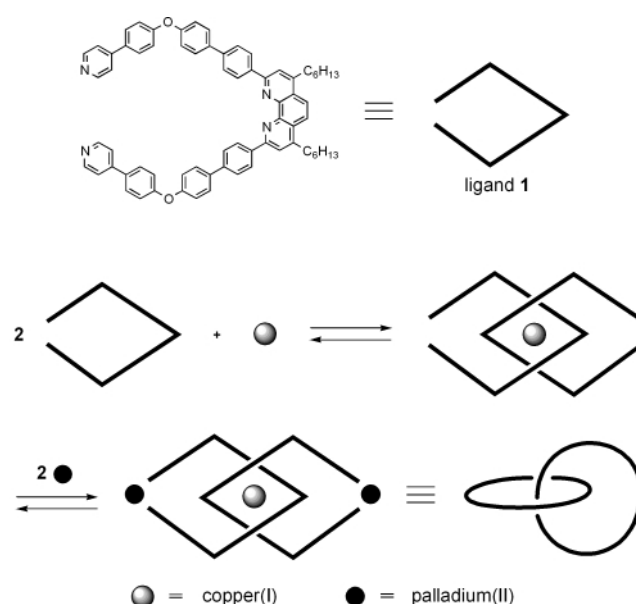
By combining copper(I) and palladium(II) in the same assembly, it has been possible to make a doubly-interlocking molecule, *i.e.* a 4-crossing [2]catenane.⁸ This unexpected structure was obtained because the organic ligand used was too short to afford a ring incorporating a single palladium(II) atom.

We would now like to report that, by utilising a sufficiently large bridging ligand, quantitative formation of a [2]catenane was observed. The strategy is depicted in Scheme 1.

According to CPK models, ligand **1** is perfectly adapted to the strategy of Scheme 1. **1** is relatively rigid, and, in particular, the distance between the two oxygen atoms of **1** is more or less fixed and does not depend on rotation about C–C bonds (O...O ~ 16 Å). After coordination of enPd²⁺ (en = 1,2-diaminoethane) two interlocking 41-membered rings are obtained. The size of the palladium(II) containing cycles is such that the final [2]catenane should not be strained, even if one considers that solubilizing groups (C₆H₁₃) have been attached at the back of the phen units.

The real reactions are represented in Fig. 1. Ligand **1** was obtained by a double Ullmann coupling reaction⁹ between 4,7-di-*n*-hexyl-2,9-bis[4-(4-hydroxyphenyl)phenyl]-1,10-phenanthroline¹⁰ and 4-(4-bromophenyl)pyridine.¹¹ The latter reaction was performed in refluxing toluene in the presence of Cs₂CO₃ and excess Cu(CH₃CN)₄·PF₆ over 3 days. After demetallation of the crude reaction mixture with KCN and purification by chromatography over silica gel, **1** was obtained in 10% yield as a pale yellow glass. It could be fully characterized by ¹H NMR and mass spectroscopy.

The reaction of **1** (0.010 mmol) and Cu(CH₃CN)₄·PF₆ (0.005 mmol) in MeCN–DMF (1:1) solution (1 ml), immediately afforded **2**, which is the precursor to catenane **3**. To this solution, enPd(NO₃)₂ (0.010 mmol) was added and the reaction was stirred for 1 h at rt. In solution, **3** was obtained quantitatively. It was isolated in 85% yield as a red micro-



Scheme 1 Ligand **1** can be regarded as an open lozenge. The 1,10-phenanthroline (phen) site reacts with copper(I) to afford an entwined complex. Cyclisation is carried out by completing the two interlocking lozenges, the 'clipping' metal being palladium(II).

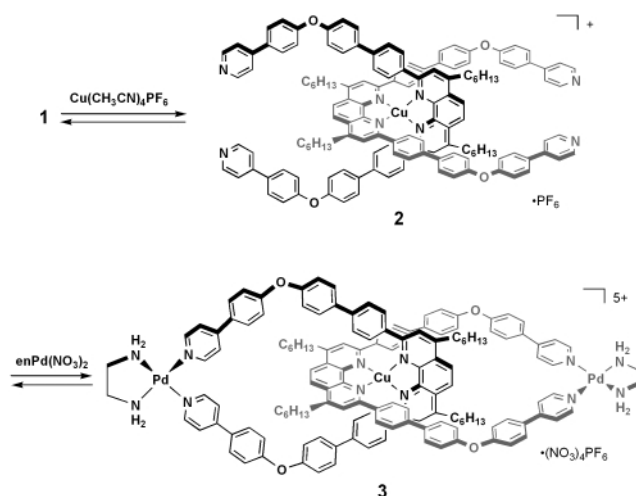


Fig. 1 Quantitative formation of catenane **3** in two steps from **1**, by successive addition of Cu(I) and Pd(II).

crystalline solid by addition of diethyl ether. **2** and **3** are formed as thermodynamic products since copper(I) complexes and, especially palladium(II) compounds are substitutionally labile.

The formation of **2** and **3** as single products was confirmed by both ¹H NMR and CSI-MS (Cold Electro Spray Ionization Mass Spectroscopy).¹² The ¹H NMR spectrum of **2** in CD₃CN–DMF-*d*₇ solution showed the expected signals for the aromatic protons, in accordance with the symmetric structure of **2**, except for the protons borne by the two pyridine nuclei which are probably too broad to lead to clear signals. CSI-MS of **2** in MeCN–DMF solution showed a prominent peak at *m/z* 2046, [M-(PF₆)]⁺.

The ¹H NMR spectrum of **3** in CD₃CN–DMF-*d*₇ is also in agreement with its structure. The chemical shifts of the peaks are slightly different from those of **2**. Not surprisingly, the pyridinic protons α to the Pd(II)-coordinated N atoms appear at low field ($\delta = 9.67$). CSI-MS of **3** in CH₃CN–DMF solution at 20 mM concentration showed predominant peaks for [M-(PF₆)-(NO₃)_{*n*}]^{(*n*+1)⁺}(dmf)_{*m*}: e.g. *m/z* 548, [M-(PF₆)-(NO₃)₄]⁵⁺(dmf)₅; 646, [M-(PF₆)-(NO₃)₃]⁴⁺(dmf)₂; 834, [M-(PF₆)-(NO₃)₂]³⁺. Interestingly, **3** is obtained quantitatively, regardless of the concentration of **2** and enPd(NO₃)₂. This is in contrast with other previous examples for which catenane dissociation to simple rings was observed at low concentration.¹³ In MeCN–DMF, **3** does not dissociate over the concentration range investigated (0.005 to 20 mM). This particularly high stability suggests that no dissociation takes place during the MS measurements. It is probably due to the excellent fit of the ligand to coordination of Pd(II) and especially to the appropriate length of the 4 sides of the constitutive 'lozenges' of **3**.

The results presented in this work together with those discussed in reference 8 (synthesis of a 4-crossing [2]catenane) highlight the utmost importance of the nature of the ligands used in directed syntheses involving both copper(I) and palladium(II)

coordination. The balance between the structural parameters (length, angles, flexibility, steric hindrance) of the ligands and stereoelectronic requirements of both metals clearly appears highly crucial and narrow, therefore dictating irrevocably the very nature of the molecular assembly generated by means of such methodology.

We thank the CNRS for its financial support.

Notes and references

- 1 J.-P. Sauvage, C. Dietrich-Buchecker and G. Rapenne, in *Molecular Catenanes, Rotaxanes and Knots*, ed. J.-P. Sauvage and C. Dietrich-Buchecker, Wiley-VCH, Weinheim, 1999.
- 2 V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348.
- 3 J.-P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611.
- 4 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.
- 5 *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn, J.-P. Sauvage and M. W. Hosseini, vol. 9, *Templating, self-assembly and self-organization*, 1996.
- 6 M. Fujita, *Acc. Chem. Res.*, 1999, **32**, 5.
- 7 D. J. Cárdenas, P. Gaviña and J.-P. Sauvage, *Chem. Commun.*, 1996, 1915.
- 8 F. Ibukuro, M. Fujita, K. Yamaguchi and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1999, **121**, 11 014.
- 9 A. V. Kalinin, J. F. Bower, P. Riebel and V. Snieckus, *J. Org. Chem.*, 1999, **64**, 2986.
- 10 J.-M. Kern, J.-P. Sauvage, J.-L. Weidmann, N. Armaroli, L. Flamigni, P. Ceroni and V. Balzani, *Inorg. Chem.*, 1997, **36**, 5329.
- 11 M. Fujita, H. Oka and K. Ogura, *Tetrahedron Lett.*, 1995, **36**, 5247.
- 12 S. Sakamoto, M. Fujita, K. Kim and K. Yamaguchi, *Tetrahedron*, 2000, **56**, 955.
- 13 M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720.