FULL PAPER

Dalton
www.rsc.org/dalton

Palladium(II)-directed formation of pseudo-rotaxanes : the 3 + 1 approach to threaded species using square-planar geometries

C. Hamann, J.-M. Kern * and J.-P. Sauvage *
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: jmkern@chimie.u-strasbg.fr

Received 3rd June 2003, Accepted 23rd July 2003
First published as an Advance Article on the web 29th August 2003

Palladium(II) has been used as a gathering and threading metal centre, using a terpy-incorporating ring and a string-like compound containing a monodentate ligand (pyridine derivative). Preliminary experiments show that the fourth ligand of the square planar complex can be exchanged (pyridine-based ligand/aliphatic amine) by modifying the H^+ concentration of the medium, allowing us to envision new molecular machines set in motion by protonation/deprotonation.

Introduction

Rotaxanes and catenanes constitute nowadays an important family of multicomponent molecular systems,[1] whose specific properties are promising in relation to photoinduced electron transfer[2] and controlled molecular motions,[3] in particular. Transition-metal containing rotaxanes and catenanes have been of special interest to our group in the course of the last 20 years.[4] The metal centre plays an essential gathering and templating role in the elaboration of such molecules. Its electronic properties are also important in order to control intramolecular electron transfer processes, in relation to the modelling of the photosynthetic reaction centre,[2] or to trigger electrochemically driven motions in artificial molecular machines and motors.[5] Traditionally, tetrahedral copper(I) has been the metal of choice to induce the formation of entangled structures from two coordinating molecular threads or to drive the formation of a pseudo-rotaxane from a ring and a molecular string.[4] Recently, we have also utilised octahedrally coordinated metal centres such as ruthenium(II) to assemble and preorganise the various organic fragments to be incorporated in catenanes and rotaxanes containing a three-bidentate chelate coordination site.[6] In addition, five-coordinate geometries have been exploited, based on Zn^{2+} associated to a set of ligands consisting of a terpyridine and a phenanthroline, allowing the preparation of catenanes containing a five-coordinate complexation site.[7] Besides a tetrahedron, a square pyramid, a trigonal bipyramid or an octahedron, a square is potentially an interesting transition metal complex geometry to investigate, in order to generate threaded species. Three of these template strategies are represented in a schematic fashion in Fig. 1.

We would now like to report that pseudo-rotaxanes can be prepared following strategy (c) of Fig. 1, based on palladium(II) as the assembling metal and 2,2′,6′,2″-terpyridine (terpy) as the terdentate which is incorporated into the cyclic component.

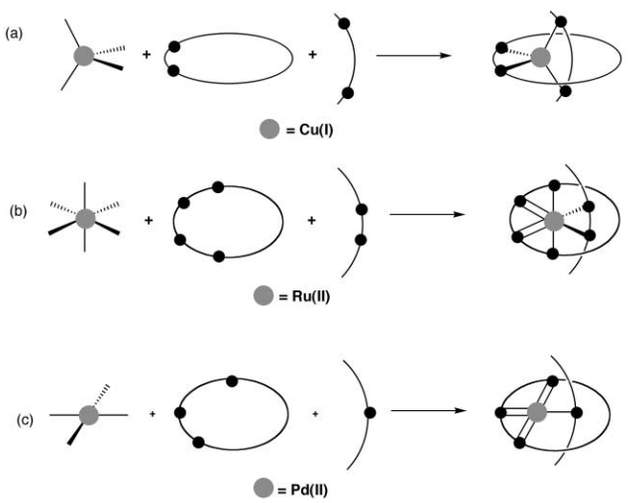

Fig. 1 Transition metal-directed threading of a ring by a coordinating molecular string. (a) The metal centre is tetrahedrally coordinated to four ligands in the final complex (two donor atoms in the ring and two in the thread). This reaction has been extensively used with copper(I). (b) The 4 + 2 approach based on an octahedral metal centre able to promote the gathering and threading process. The ring contains two bidentate chelates which must lead to a C_2 symmetry compound after coordination to the metal. The thread contains a bidentate chelate. Ru(II) has been used recently following this strategy. (c) The central metal is square planar (3 + 1 approach). The ring incorporates a terdentate chelate and the string contains a monodentate ligand.

Experimental

^{1}H NMR spectra were acquired on either a Bruker WP200 SY (200 MHz) or a Bruker AC 300 (300 MHz) spectrometer, using the deuterated solvent as the lock and residual solvent as the internal reference. Fast atom bombardment mass spectroscopy (FAB MS) data were recorded in the positive ion mode with a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a ZAB-HF mass spectrometer. A VG BIOQ triple quadripole spectrometer was used for the electrospray mass spectrometry measurements (ES-MS) also in the positive ion mode. MALDI-TOF spectra were taken on a Brücker Spectrometer Protein TOF using α-cyano-4-hydroxycinnamic acid as matrix.

Synthesis of the ligands

Oxygen- or water-sensitive reactions were conducted under a positive pressure of argon in oven-dried glassware, using Schlenk techniques. Common reagents and materials were purchased from commercial sources. The following materials were prepared according to literature procedures: **1**,[7] **2**,[7], 2-(2′-iodoethoxy)ethyl-2″-tetrahydropyranyl ether.[7]

Monofunctionalized lutidine 6. A degassed solution of 2,6-lutidine (3.01 g, 0.028 mol) in anhydrous THF (50 mL) was cooled to −78 °C. While this temperature was maintained, a freshly prepared solution of LDA (20 mmol in THF) was added *via* the canula transfer technique. The solution turned red and

DOI: 10.1039/b306277e

was stirred at −78 °C for a further 3 h. A solution of 2-(2′-iodoethoxy)ethyl-2″-tetrahydropyranyl ether (12.6 g, 0.042 mol) in freshly distilled THF was then added and the resulting solution was stirred for 24 h at room temperature. After hydrolysis with 10 mL of water, the solution turned yellow. The solvent was evaporated and the residue taken up in a CH_2Cl_2/H_2O mixture. The organic layer was separated and dried over $MgSO_4$. After the solvent was evaporated, the resulting yellow oil was chromatographed (Al_2O_3; eluent : hexane–ethyl acetate (1–3%) to give NMR-pure **6** as a pale yellow oil in 83% yield (6.47 g, 0.023 mol). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.42 (t, ^3J = 7.6 Hz, 1H, H_4); 6.91 (m, 2H, $H_{3,5}$); 4.60 (m, 1H, H_a); 3.86 (m, 2H, H_e); 3.50 (m, 6H, $H_{c',d',e'}$); 2.77 (m, 2H, $H_{a'}$); 2.47 (s, 3H, –CH_3); 2.00 (m, 2H, $H_{b'}$); 1.90–1.46 (m, 6H, $H_{b,c,d}$); (protons a, b, c, d, e correspond to the protons of the –OTHP moiety).

Lutidine-diOTHP 7. The monosubstituted lutidine **6** (3.4 g, 0.012 mol) was reacted successively with LDA (20 mmol in THF) and 2-(2′-iodoethoxy)ethyl-2″-tetrahydropyranyl ether[2] (5.7 g, 0.019 mol), following the method described for preparing **6**. After chromatographing several times using a Chromatotron® (Al_2O_3, eluent: hexane–EtOAc (98 : 2 to 90 : 10), a yellow oil (1.5 g. 0.003 mol) was obtained in 30% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45 (t, 1H, H_4, ^3J = 7.6 Hz); 6.94 (d, 2H, $H_{3,5}$, ^3J = 7.6 Hz); 4.62 (m, 2H, H_a); 3.87 (m, 4H, H_e); 3.53–3.59 (m, 12H, $H_{c',d',e'}$); 2.80 (m, 4H, $H_{a'}$), 1.98 (m, 4H, $H_{b'}$); 1.90–1.40 (m, 12H, $H_{b,c,d}$); (protons a, b, c, d, e correspond to the protons of the THP moiety).

Ligand 8. Compound **7** (395 mg, 0.87 mmol) dissolved in ethanol (30 mL), was brought to reflux under argon before 1 drop of 37% HCl was added. The solution was refluxed for 3 h and ethanol was then removed. The residue was taken up in CH_2Cl_2/H_2O. The aqueous layer was washed with a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2 (2 × 50 mL). Drying over $MgSO_4$ left, after the solvent was removed, a yellow oil whose purity was good enough (>90% by NMR) to be used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.48 (t, 1H, H_4, ^3J = 7.6 Hz); 6.94 (d, 2H, $H_{3,5}$, ^3J = 7.6 Hz); 3.67 (m, 4H, $H_{e'}$); 3.59–3.22 (m, 8H, $H_{c',d'}$); 2.93 (m, 4H, $H_{a'}$); 1.92 (m, 4H, $H_{b'}$).

Synthesis of the Pd complexes and ligand exchange reactions

Chromatography over silica gel or alumina of the palladium complexes caused the complexes to decompose. Their formation was thus observed by ^{1}H NMR spectroscopy. They were purified if necessary by precipitation with ether or by crystallization.

3(BF$_4$)$_2$. $Pd(CH_3CN)_4(BF_4)_2$ (49.5 mg, 0.11 mmol) dissolved in degassed CH_3CN (2 mL) was added under argon and at room temperature to a stirred degassed solution of **2** (70.3 mg, 0.11 mmol) dissolved in a mixture of CH_3CN–THF. A yellow coloration appeared instantly. After the solution was stirred for 1 h under argon, the solvents were removed under high vacuum to afford the complex as a bright yellow crystalline solid. NMR showed that the reaction proceeded quantitatively. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.40 (t, 1H, $H_{4'}$, ^3J = 7.65 Hz); 8.19 (m, 8H, $H_{4,6,3,3'}$); 6.98 (d, 4H, H_o, ^3J = 8.8 Hz); 6.79 (d, 4H, H_m, ^3J = 8.8 Hz); 4.01 (m, 4H, H_e); 3.66 (m, 4H, H_d); 3.52 (t, 4H, H_c, ^3J = 5.6 Hz); 2.90 (t, 4H, H_a, ^3J = 7.2 Hz); 2.00 (m, 4H, H_b); 1.52 (s, 6H, –CH_3). ^{13}C NMR ($CDCl_3$): δ 157.7; 156.9; 155.5; 155.4; 153.8; 146.6; 145.0; 144.0; 143.8; 128.4; 126.0; 124.8; 115.1; 70.2; 69.8; 68.8; 42.1; 30.9; 30.4.

4(BF$_4$)$_2$. Complex $\mathbf{3}^{2+}$ (10 mg, 0.01 mmol) in CH_3CN (1.5 mL) was introduced in a 5 mL flask and 1 mL of a 0.01 mol L^{-1} solution of 2,6-lutidine in CH_3CN (0.01 mmol) was added. After 15 min at room temperature, the solvent was removed under high vacuum: a yellow powder of $\mathbf{4}^{2+}$ was obtained. NMR showed that the reaction proceeded in a quantitative yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.50 (t, 1H, $H_{4'}$, ^3J = 7.4 Hz); 8.27 (m, 6H, $H_{4,3,3'}$); 7.31 (d, 4H, H_o, ^3J = 8.8 Hz); 7.07 (m, 3H; $H_{6,l4}$); 6.87 (d, 2H, H_{l3}, ^3J = 7.8 Hz); 6.79 (d, 4H, H_m, ^3J = 8.8 Hz); 3.94 (m, 4H, H_e); 3.62 (m, 4H, H_d); 3.41 (t, 4H, H_c, ^3J = 5.8 Hz); 3.04 (s, 6H, –CH_3 (l)); 2.74 (t, 4H, H_a, ^3J = 7.2 Hz); 1.83 (m, 4H, H_b); 1.75 (s, 6H, –CH_3 (**2**)).

5(BF$_4$)$_2$. Complex $\mathbf{3}^{2+}$ (10 mg, 0.01 mmol) dissolved in CH_3CN (1 mL) was introduced in a 5 mL flask and 1 mL of a 0.01 mol L^{-1} solution of diethylamine in CH_3CN (0.01 mmol) was added. After 15 min at room temperature, the solvent was removed under high vacuum: a yellow powder of $\mathbf{5}(BF_4)_2$ was obtained. NMR showed that the reaction proceeded quantitatively. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.44 (t, 1H, $H_{4'}$, ^3J = 7.4 Hz); 8.23 (m, 6H, $H_{4,3,3'}$); 7.94 (d, 2H, H_6, ^4J = 1.8 Hz); 7.12 (d, 4H, H_o, ^3J = 8.8 Hz); 6.79 (d, 4H, H_m, ^3J = 8.8 Hz); 5.41(br s, 1H, NH); 4.04 (m, 4H, H_e); 3.70 (m, 4H, H_d); 3.56 (t, 4H, H_c, ^3J = 6 Hz); 3.14 (m, 4H, H_α); 2.90 (t, 4H, H_a, ^3J = 7.4 Hz); 1.96 (m, 4H, H_b); 1.61 (s, 6H, –CH_3 (**2**)); 1.22–1.09 (m, 6H, H_β).

9(BF$_4$)$_2$. Complex $\mathbf{3}^{2+}$ (30 mg, 0.03 mmol) dissolved in acetonitrile (2 mL) was added to a solution of **8** (8.5 mg, 0.03 mmol) in acetonitrile (1 mL). The solvent was then removed to afford $\mathbf{9}(BF_4)_2$ as a yellow powder (35 mg). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.46 (t, 1H, $H_{4'}$, ^3J = 8 Hz); 8.27–8.19 (m, 6H, $H_{4,3,3'}$); 7.33 (d, 4H, H_o, ^3J = 8.8 Hz); 7.03 (m, 3H; $H_{6,l4}$); 6.82 (d, 2H, H_{l3}, ^3J = 8 Hz); 6.78 (d, 4H, H_m, ^3J = 8.8 Hz); 3.92 (m, 4H, H_e); 3.60 (m, 8H, $H_{d,a'}$); 3.37–3.31 (m, 8H, $H_{c,c'}$); 3.23 (m, 4H, $H_{e'}$); 3.15 (m, 4H, $H_{d'}$); 2.70 (t, 4H, H_a, ^3J = 6 Hz); 2.38 (t, 2H, –OH); 1.80 (m, 4H, $H_{b,b'}$); 1.75 (s, 6H, –CH_3).

X-Ray structural study

Single crystals suitable for X-ray analysis were obtained for the complex $\mathbf{3}^{2+}$ by slow diffusion of diethyl ether vapour into a solution of $\mathbf{3}^{2+}$ in acetonitrile. Crystal data and details of data collection are provided in Table 1.

CCDC reference number 213163.

See http://www.rsc.org/suppdata/dt/b3/b306277e/ for crystallographic data in CIF or other electronic format.

Results and discussion

(a) Design of the system and synthesis of the terpy-containing ring

Palladium(II) forms stable square planar complexes with a variety of ligands, this geometry being generally strongly favoured over other coordination geometries.[8] Our experience of terpy and its derivatives[9] prompted us to use this terdentate ligand and to incorporate it in a ring. The fourth donor atom was designed so as to be the central part of the thread to be passed through the ring. The choice of this monodentate ligand is critical since it has to be easily derivatized in order to be incorporated in a string-like fragment, with the donor atom oriented in such a way that the Pd-donor atom bond is roughly perpendicular to the main axis of the thread. We considered various motifs, represented in Chart 1, because of their coordinating ability towards Pd(II) but also for their structural features, which should allow us to design thread-like molecules incorporating them.

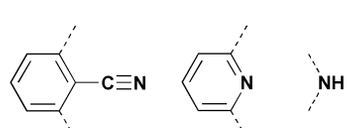

Chart 1

Table 1 X-Ray experimental data for $\mathbf{3}(BF_4)_2$

Formula	$C_{94}H_{115}B_4F_{16}N_9O_{10}Pd_2$ $\equiv 2(C_{42}H_{46}N_4O_4Pd)\cdot 4BF_4\cdot CH_3CN\cdot 2C_4H_{10}O$
Molecular weight	2091.04
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	13.1827(2)
b/Å	18.5474(2)
c/Å	20.6953(4)
α/°	101.281(5)
β/°	90.583(5)
γ/°	102.957(5)
V/Å^3	4828.2(1)
Z	2
Color	Yellow
Crystal dimensions/mm	0.20 × 0.14 × 0.10
D_c/g cm^{-3}	1.44
F(000)	2156
μ/mm^{-1}	0.465
Transmission (min./max.)	0.9626/1.0000
T/K	173
λ/Å	0.71073
Radiation	Mo-Kα graphite monochromated
Diffractometer	KappaCCD
Scan mode	'Phi scans'
hkl limits	0, 17/−24, 23/−26, 26
θ Limits/°	2.5–27.47
Number of measured data	21436
Number of data [$I > 3\sigma(I)$]	13539
Number of variables	1216
R	0.048
R_w	0.073
GOF	1.316
Largest peak in final difference map/e Å^{-3}	1.476

Table 2 Selected bond lengths (Å) and angles (°) for $\mathbf{3}(BF_4)_2$

Pd_1–N_1	2.013(4)	Pd_2–N_1	2.035(4)
Pd_1–N_2	2.030(4)	Pd_2–N_2	2.030(3)
Pd_1–N_3	1.911(3)	Pd_2–N_3	1.928(4)
Pd_1–N_4	2.029(3)	Pd_2–N_4	2.035(3)
N_2–Pd_1–N_3	81.2(1)	N_2–Pd_2–N_3	81.3(1)
N_3–Pd_1–N_4	81.1(1)	N_3–Pd_2–N_4	80.9(1)
N_1–Pd_1–N_3	179.4(1)	N_1–Pd_2–N_3	178.1(1)
N_2–Pd_1–N_4	162.3(1)	N_2–Pd_2–N_4	162.1(1)

Pd_1 and Pd_2 refer to the two independent molecules in the asymetric unit.

The terpy-incorporating macrocycle **2** and its precursor **1** are depicted in Fig. 2(a). Its synthesis was recently described.[7]

(b) Preliminary coordination chemistry studies

Before threading string-like fragments through the ring, we investigated a few simple coordination reactions with palladium(II). The acetonitrile complex $\mathbf{3}^{2+}$ was obtained quantitatively from **2** and $Pd(CH_3CN)_4(BF_4)_2$, as indicated in Fig. 2(b). $\mathbf{3}(BF_4)_2$ is a yellow crystalline solid, whose formation was first evidenced in solution by ^{1}H NMR. As expected, the signals of the terpy fragment are downfield shifted by complexation to the Pd(II) centre ($\Delta\delta$ ~0.5 ppm for the hydrogen atoms *para* to the coordinated nitrogen atoms). A single crystal was obtained by slow diffusion of diethyl ether vapour into an acetonitrile solution of the complex and the X-ray structure of $\mathbf{3}^{2+}2BF_4^-$ could be determined.

The asymetric unit contains two independent molecules, whose structures are very similar. The conformation of the dioxodiethylene chains make them slightly different. The values of the N_i–Pd–N_j angles and of the Ni–Pd distances indicated in Fig. 3 are the average values. The values concerning the Pd–Ni distances and N_i–Pd–N_j angles of the two molecules in the cell are listed in Table 2. As shown in Fig. 3, the geometry around the palladium(II) centre is roughly square-planar. The three N atoms of the terpy motif are bound to the metal and this situation originating in a noticeable ″pinching″ of the terpy as already observed for other Pd(II) terpy complexes:[10] the *ortho* substituents (at positions 2′ and 6′) of the central pyridine form an angle of 113°, to be compared to the theoretical value of 120°. In addition, significant distortion from square planar geometry around Pd(II) is observed: the N_1–Pd–N_2 and N_2–Pd–N_3 angles are ~80° instead of 90° for a true square planar situation. The fourth coordination site is occupied by a CH_3CN molecule which is located in the mean plane formed by the nitrogen atoms of the terpyridine and the palladium centre.

For the preparation of other Pd(II) macrocyclic complexes, the acetonitrile complex $\mathbf{3}^{2+}$ turned out to be a convenient starting compound. The bound CH_3CN molecule could be displaced quantitatively by other ligands, such as 2,6-lutidine or diethylamine. The substitution reaction of CH_3CN in $\mathbf{3}^{2+}$ by 2,6-lutidine is depicted in Fig. 2(c). The ^{1}H NMR spectrum of the lutidine complex, $\mathbf{4}^{2+}$, Fig. 4, provides evidence in support of the formation of this compound.

In particular, the protons of the lutidine nucleus (l_3, l_4) undergo a significant upfield shift (−0.1 and −0.46 ppm, respectively) by coordination to Pd(II) in spite of the electron-withdrawing character of Pd(II), whereas the protons of the two methyl groups connected to the same nucleus at positions 2 and 6 undergo a remarkable downfield shift of +0.6 ppm. A similar effect is observed for the 6 and 6″ protons of the terpy fragment. These observations tend to indicate that a mutual interaction between the macrocyclic part and the lutidine nucleus is taking place, locating certain protons of a given component in the shielding region of the other one, as suggested by the drawing of Fig. 2(c): the ring current effects of the lutidine fragment and the bis-phenol A motif induce upfield shifts of H_6, $H_{6''}$ and l_3, l_4.

The diethylamine complex $\mathbf{5}^{2+}$ was prepared similarly to $\mathbf{4}^{2+}$ by adding a stoichiometric amount of $HNEt_2$ to $\mathbf{3}^{2+}$ in acetonitrile. Here again, the substitution turned out to be quantitative. ^{1}H NMR provides evidence in support of the formation of the complex (see Experimental section). Interestingly, the 2,6-lutidine ligand of $\mathbf{4}^{2+}$ can also be displaced by $HNEt_2$ in a quantitative fashion, as shown by ^{1}H NMR. This is not surprising in view of the respective pK_a values[11] of lutidine (pK_a ~5)

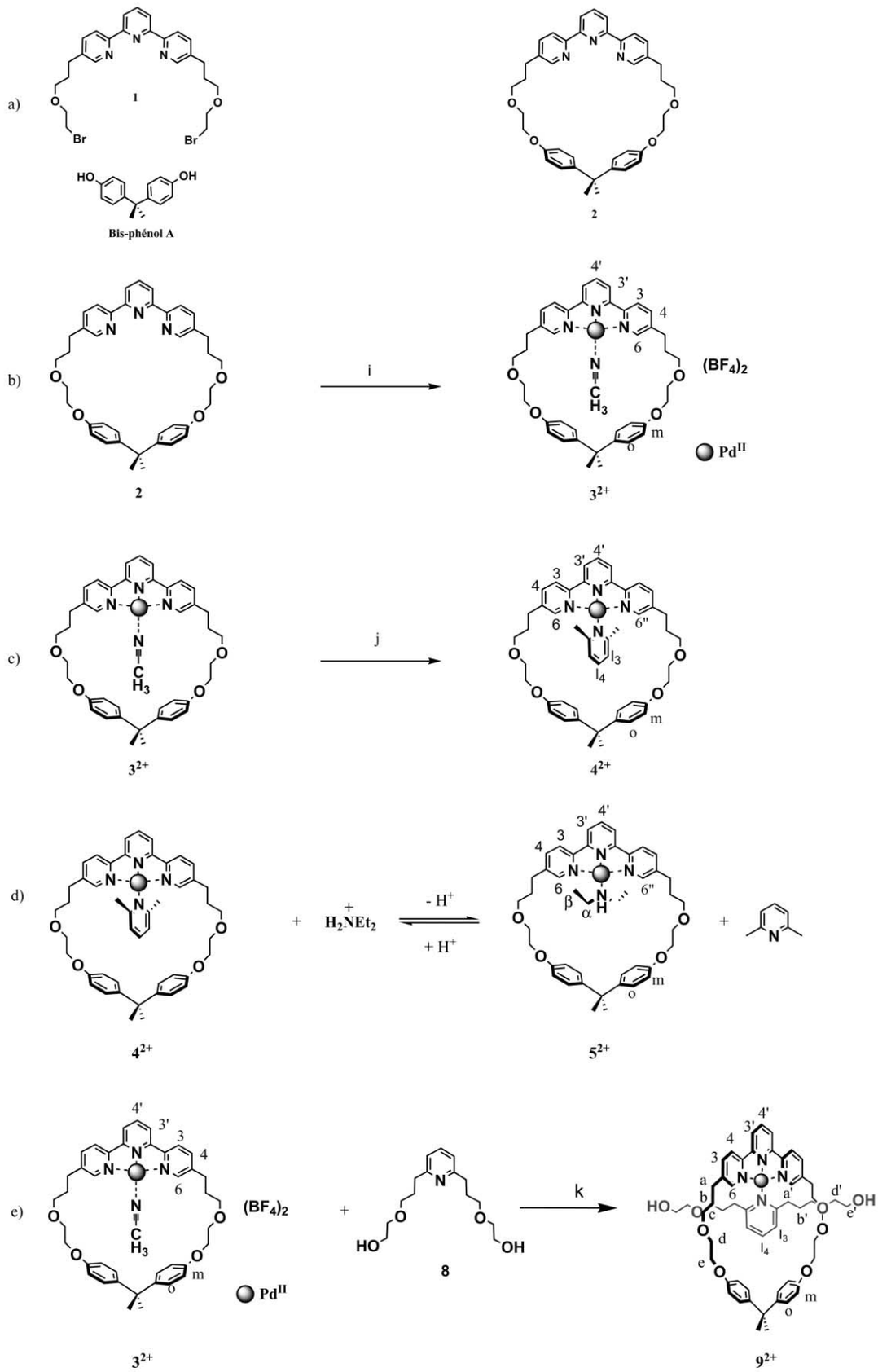

Fig. 2 (a) The terpyridine containing 34-membered ring **2** and its ultimate precursors **1** and the "bisphenol A". (b) Preparation of the macrocyclic Pd(II) complex $\mathbf{3}^{2+}$. i: $Pd(CH_3CN)_4(BF_4)_2$, CH_3CN–THF, 100%. (c) Substitution of the CH_3CN ligand by 2,6-lutidine. j: 2,6-lutidine, CH_3CN, 100%. (d) Protonation/deprotonation-induced exchange of the fourth ligand. The 2,6-lutidine nucleus of complex $\mathbf{4}^{2+}$ is quantitatively expelled by addition of $HNEt_2$ but the reverse is true under less basic conditions: addition of $[2,6\text{-lutidine-H}]^+$ to $\mathbf{5}^{2+}$ displaces quantitatively $HNEt_2$ to afford its protonated form and $\mathbf{4}^{2+}$. (e) The threading reaction affording the pseudo-rotaxane $\mathbf{9}^{2+}$ quantitatively. k: CH_3CN.

and $HNEt_2$ (pK_a ~11.5). Preliminary studies show that clean ligand exchange can easily be driven by changing the pH. Under very basic conditions, diethylamine is preferred, whereas, by lowering the apparent pH of an acetonitrile solution of $\mathbf{5}^{2+}$ in the presence of lutidine or by adding one equivalent of a 2,6-lutidinium salt to $\mathbf{5}^{2+}$, ligand exchange on the palladium(II)

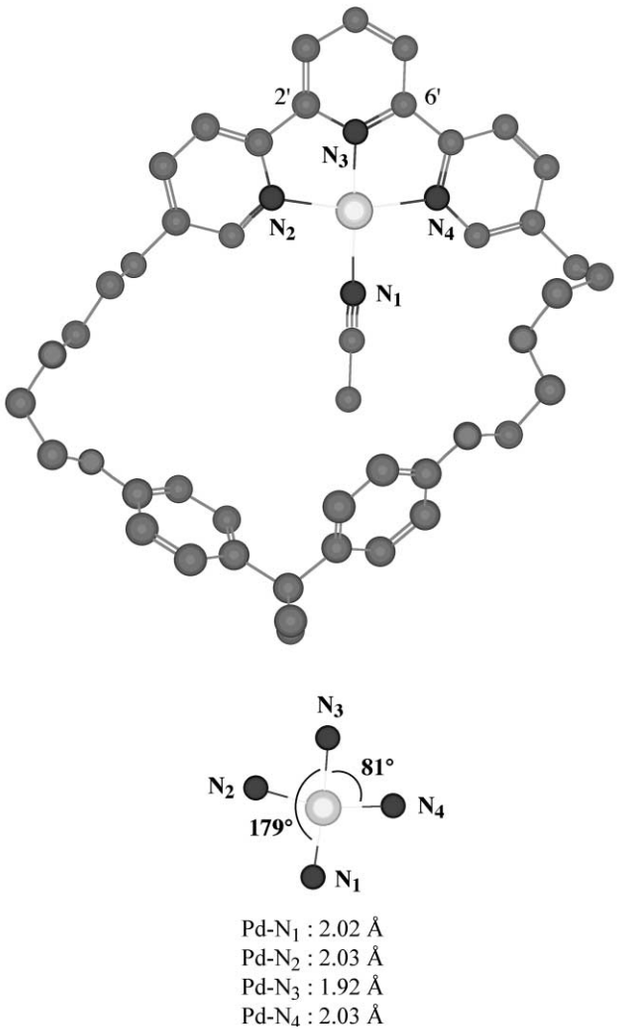

Fig. 3 X-Ray crystal structure of the macrocyclic Pd(II) complex $\mathbf{3}^{2+}$.

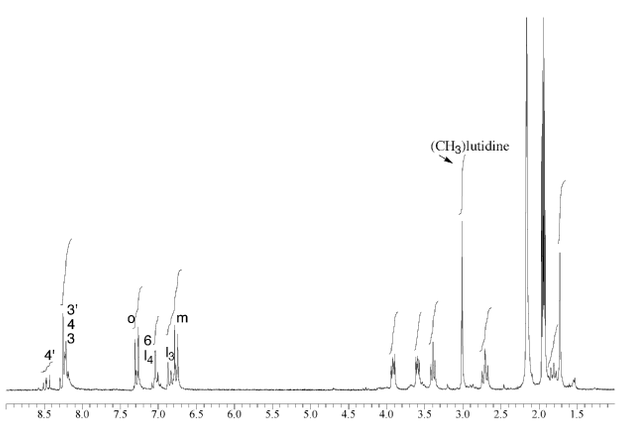

Fig. 4 ^{1}H NMR spectrum of $\mathbf{4}^{2+}$.

centre takes place simultaneously with proton transfer from the protonated lutidine to $HNEt_2$. The ligand exchange reaction is represented in Fig. 2(d).

The ligand exchange process of Fig. 2(d) may open the gate to molecular motions induced by changing the pH of the medium.[12] Incorporation of both aliphatic amines and pyridinic fragments into rings or open-chain compounds may be envisaged, which could afford new molecular machines if used in conjunction with the coordinating ring **2** and Pd(II).

In order to test the feasibility of such an approach, a string-like compound containing a central pyridine nucleus was made

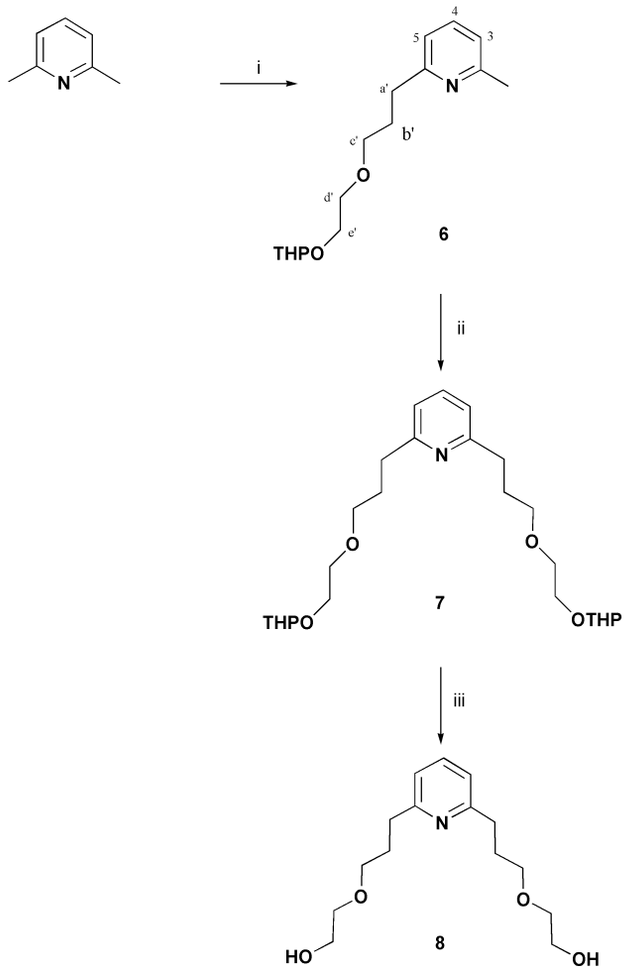

Fig. 5 Synthesis of the string-like compound **8**. i: LDA, $ICH_2CH_2OCH_2CH_2OTHP$, THF, −78 °C, 83%. ii: LDA, $ICH_2CH_2OCH_2CH_2OTHP$, THF, −78 °C, 30%. iii: cat. HCl, EtOH (reflux), 95%.

and reacted under "threading" conditions. The sequence of reactions leading to the 2,6-lutidine derivative used in the threading reactions is indicated in Fig. 5.

Unfortunately, the disubstitution of the starting 2,6-lutidine could not be carried out in one step. In a two step procedure, the protected compound **7** was obtained. Diol **8** was thus prepared in 23% yield from 2,6-lutidine, in a three-step procedure.

The pseudo-rotaxane $\mathbf{9}^{2+}$ was prepared quantitatively by threading **7** through the ring of complex $\mathbf{3}^{2+}$ (Fig. 2(e)). The reaction is a simple ligand exchange whose principle is identical to the conversion of $\mathbf{3}^{2+}$ to $\mathbf{4}^{2+}$ in the presence of 2,6-lutidine (Fig. 2(d)). The main difference is that the fourth ligand is now incorporated in a string-like compound (19 atoms in the thread from one end to the other). The coordination reaction forces the acyclic fragment to pass through the ring in a way similar to previously reported reactions utilising copper(I) or ruthenium(II) as templating metal.

Full assignment of the ^{1}H NMR signals of $\mathbf{9}^{2+}$ was made with the help of 2D (ROESY) NMR. By comparing the spectra of the string **8** and of the pseudo-rotaxane $\mathbf{9}^{2+}$, the same effects as those noticed in the formation of $\mathbf{4}^{2+}$ are observed: upfield shift of the pyridinic protons l_3, l_4 (0.12 and 0.45 ppm, respectively) and of the terpy protons 6 and 6″ (1.51 ppm).

Conclusion

Stable complexes of Pd(II) were prepared with a 35-membered macrocycle containing a terpyridine motif. A few square-planar complexes have been obtained by varying the nature of the fourth ligand. In particular, the CH_3CN complex could be

crystallized and studied by X-ray crystallography, thus confirming the expected geometry of the compounds. Ligand exchange reactions between the very basic ligand $HNEt_2$ and the much less basic compound 2,6-lutidine are easily triggered by modifying the H^+ concentration in the medium, opening the way to new protonation/deprotonation-driven molecular machines. Finally, by threading a long string-like fragment through the ring, a pseudo-rotaxane could be made. The synthesis of multisite molecular strings is presently underway as well as the elaboration of real rotaxanes, by attaching bulky groups at both ends of the thread.

Acknowledgements

We thank the European Commission for financial support and the French Ministry of Education for a fellowship (CH).

References

1 (*a*) For early work, see: G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York and London, 1971; (*b*) *Molecular Catenanes, Rotaxanes and Knots*, ed. J.-P. Sauvage and C. Dietrich-Buchecker, Wiley-VCH, Weinheim, 1999; (*c*) for recent review articles, see: D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725; J.-C. Chambron, C. Dietrich-Buchecker and J.-P. Sauvage, in *Templating Self-Assembly and Self-Organisation*, ed. J.-P. Sauvage and M. W. Hosseini, *Comprehensive Supramolecular Chemistry 9*, Pergamon, New York 1996, pp. 43–83; G. A. Breault, C. A. Hunter and P. C. Mayers, *Tetrahedron*, 1999, **55**, 5265; F. Vögtle, T. Dünnwald and T. Schmidt, *Acc. Chem. Res.*, 1996, **29**, 451.

2 (*a*) M. Andersson, M. Linke, J.-C. Chambron, J. Davidsson, V. Heitz, L. Hammarstroem and J.-P. Sauvage, *J. Am. Chem. Soc.*, 2002, **124**, 347–4362; (*b*) M.-J. Blanco, M. Consuelo Jimenez, J.-C. Chambron, V. Heitz, M. Linke and J.-P. Sauvage, *Chem. Soc. Rev.*, 1999, **28**, 293–305; (*c*) M. Linke, J.-C. Chambron, V. Heitz and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1997, **119**, 11329–11330; (*d*) N. Watanabe, N. Kihara, Y. Furusho, T. Takata, Y. Araki and O. Ito, *Angew. Chem., Int. Ed.*, 2003, **42**, 681–683.

3 (*a*) *Acc. Chem. Res.,* 2001, **34**(6); special issue on Molecular Machines; (*b*) *Struct. Bonding (Berlin)*, 2001, **99**; special issue on Molecular Machines and Motors; (*c*) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim 2001; (*d*) 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; (*e*) *Molecular Switches* . ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001; (*f*) J.-P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611–619; (*g*) V. Balzani, M. Gomez-Lopez and J. F. Stoddart, *Acc. Chem. Res.*, 1998, **31**, 405–414.

4 (*a*) C. O. Dietrich-Buchecker, J.-P. Sauvage and J.-P. Kintzinger, *Tetrahedron Lett.*, 1983, **24**, 5091–5094; (*b*) C. O. Dietrich-Buchecker, J.-P. Sauvage and J.-M. Kern, *J. Am. Chem. Soc.*, 1984, **106**, 3043–3045; (*c*) J.-C. Chambron, C. Dietrich-Buchecker, J.-P. Sauvage, *Comprehensive Supramolecular Chemistry*; Pergamon Press, Oxford, 1996, vol. 9, p. 43; (*d*) J.-C. Chambron, *Perspectives in Supramolecular Chemistry*, vol. 5 : Transition Metals in Supramolecular Chemistry, ed. J.-P. Sauvage John Wiley & Sons, 1999.

5 (*a*) A. Livoreil, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 9399–9400; (*b*) J.-P. Collin, P. Gavina and J.-P. Sauvage, *New J. Chem.*, 1997, **21**, 525–528; (*c*) L. Raehm, J.-M. Kern and J.-P. Sauvage, *Chem. Eur. J.*, 1999, **5**, 3310–3317.

6 (*a*) P. Mobian, J.-M. Kern and J.-P. Sauvage, *J. Am. Chem. Soc.*, 2003, **125**, 2016–2017; (*b*) J.-P. Collin, D. Pomeranc, D. Jouvenot, V. Heitz, J.-C. Chambron and J.-P. Sauvage, *Chem. Eur. J.*, 2003, **9**, 4247–4254.

7 (*a*) C. Hamann, J.-M. Kern and J.-P. Sauvage, *Inorg. Chem.*, 2003, **42**, 1877–1883.

8 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988.

9 (*a*) N. Belfrekh, C. Dietrich-Buchecker and J.-P. Sauvage, *Inorg. Chem.*, 2000, **39**, 5169–5172; (*b*) G. Rapenne, J.-P. Sauvage, B. T. Patterson and F. R. Keene, *Chem. Commun.*, 1999, **18**, 1853–1854; (*c*) D. J. Cardenas, P. Gavina and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1997, **119**, 2656–2664.

10 (*a*) R. Buchner, C. T. Cunningham, J. S. Field, R. J. Haines, D. R. McMillin and G. C. Summerton, *J. Chem. Soc., Dalton Trans.*, 1999, 711–718; (*b*) E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 69–121.

11 *Hanbook of Chemistry and Physics*, The Chemical Rubber Publishing Co., Cleveland, OH, 44th edn., 1962.

12 (*a*) P. R. Ashton, R. Ballardini, V. Balzani, M. Gomez-Lopez, S. E. Lawrence, M. V. Martinez-Diaz, M. Montalti, A. Piersanti, L. Prodi, J. F. Stoddart and D. J. Williams, *J. Am. Chem. Soc.*, 1997, **119**, 10641–10651; (*b*) J. Wook Lee, K. Kim and K. Kim, *Chem. Commun.*, 2001, 1042–1043.