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## A platinum turnstile with a palladium lockt

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An organometallic molecular turnstile composed of a stator based on an  $\alpha,\omega$ -diphosphine bearing, in a symmetric fashion, the 2,6-pyridyl diamide moiety as a central tridentate chelating unit and a rotor composed of Pt(u) equipped with two pyridyl groups in *trans* configuration was designed. The switching between its open and closed states using Pd(II) was investigated both in solution and in the solid state.

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### Introduction

Dynamic molecular systems for which the intramolecular motion can be tuned is of interest for the design of molecular motors and machines.<sup>1-10</sup> Many design principles dealing with translational or rotational dynamic molecular assemblies controlled by a variety of external stimuli such as pH, photochemical or redox processes, metal binding have been reported.<sup>11-18</sup> As prototypes of rotary dynamic systems, molecular turnstiles have been reported by others<sup>19-21</sup> and by us.<sup>22-29</sup> This type of systems is based on two interconnected parts, a stator and a rotor. In the absence of external stimulus, the system is in its open state and the rotor freely rotates around the stator. In the presence of an external effector, the rotational movement is blocked and the system is in its closed state.

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In a preliminary investigation, we have reported an organometallic Pt(n) based turnstile for which the switching between the open and closed states was achieved by complexation of an Ag<sup>+</sup> cation and its removal by a Br<sup>-</sup> anion.<sup>30</sup>

Here we report on the design, synthesis and structural analysis, both in the solid state and in solution, of a new  $Pt(\pi)$ based molecular turnstile in its open (Fig. 1b) and closed states generated upon binding of Pd(II) (Fig. 1c).

#### **Experimental part**

#### **Characterization techniques**

<sup>1</sup>H-, <sup>31</sup>P- and <sup>13</sup>C-NMR spectra were recorded at 25 °C on either Bruker AV 300, Bruker AV 400 or Bruker AV 500 spectrometers in deuterated solvents and the residual solvent peak was used as the internal reference.



Fig. 1 Schematic representation of a bismonodentate podand bearing at its extremities two coordinating sites (a), its obturation by a metal centre bearing two monodentate coordinating sites in trans configuration leading to a turnstile in its open state (b) and the locking of the rotational movement by a second metal centre leading to the closed state of the turnstile (c).

Mass spectrometry was performed by the Service de Spectrometrie de Masse, University of Strasbourg.

#### Single-crystal analysis

Data were collected at 173(2) K on a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid N2 device, using graphite-monochromated Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. For both structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on  $F^2$  using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).<sup>31</sup>

Crystallographic data for 1. C<sub>126</sub>H<sub>140</sub>N<sub>10</sub>O<sub>17</sub>P<sub>4</sub> Pt<sub>2</sub>, C<sub>4</sub>H<sub>10</sub>O, M = 2580.54, triclinic, space group  $P\bar{1}$ , a = 15.7504(7) Å, b =19.2503(8) Å, c = 23.5828(10) Å,  $\alpha = 98.761(2)^{\circ}$ ,  $\beta = 92.067(2)^{\circ}$ ,  $\gamma = 107.459(2)^{\circ}$ , V = 6715.9(5) Å<sup>3</sup>, T = 173(2) K, Z = 2,  $D_c = 1.276$ Mg m<sup>-3</sup>,  $\mu$  = 2.190 mm<sup>-1</sup>, 125 016 collected reflections, 35 268 independent [ $R_{int} = 0.1063$ ], GooF = 1.060,  $R_1 = 0.0922$ , w $R_2 =$ 0.2144 for  $I > 2\sigma(I)$  and  $R_1 = 0.1587$ , w $R_2 = 0.2329$  for all data.

Crystallographic data for 1-Pd. C<sub>61</sub>H<sub>63</sub>N<sub>5</sub>O<sub>8</sub>P<sub>2</sub>PdPt, C<sub>6</sub>H<sub>14</sub>O, CHCl<sub>3</sub>, M = 1579.13, triclinic, space group  $P\bar{1}$ , a = 7.9136(2) Å, b = 18.6050(4) Å, c = 23.8040(5) Å,  $\alpha = 96.7200(10)^{\circ}$ ,  $\beta =$ 90.6200(10)°,  $\gamma = 96.4710(10)°$ ,  $V = 3457.45(14) Å^3$ , T = 173(2) K, Z = 2,  $D_c = 1.517$  Mg m<sup>-3</sup>,  $\mu = 2.501$  mm<sup>-1</sup>, 85 720 collected

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reflections, 18 604 independent [ $R_{int} = 0.0682$ ], GooF = 1.024,  $R_1 = 0.0404$ , w $R_2 = 0.0812$   $I > 2\sigma(I)$  and  $R_1 = 0.0654$ , w $R_2 = 0.0901$  for all data.

#### Synthesis

THF, CH<sub>2</sub>Cl<sub>2</sub> and triethylamine were distilled over sodium, CaH<sub>2</sub> and KOH, respectively. Analytical grade CH<sub>3</sub>CN was used without further purification.

Compounds 2,<sup>25</sup> 3,<sup>32,33</sup> 4,<sup>28</sup> 5<sup>28</sup> and 8<sup>34</sup> (Scheme 1) were synthesized following described procedures.

Compound 6. Compound 5 (1.03 g, 1.52 mmol) was dissolved in 30 mL of THF at 0 °C, and KPPh2 (0.5 M in THF, 6.4 mL, 2.1 eq.) was added dropwise during 30 min. After the addition was completed, the mixture was allowed to reach slowly 25 °C. After 4 h, the solution was filtrated on Celite and evaporated to dryness. Column chromatography  $(Al_2O_3,$ CH<sub>2</sub>Cl<sub>2</sub>-MeOH 100/0 to 90/10) afforded compound 6 as a slightly yellowish oil (0.25 g, 19% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 2.31 (br t, 4H, PCH<sub>2</sub>, J = 7.5 Hz), 3.45-3.67 (m, 28H, OCH<sub>2</sub>), 7.25-7.40 (m, 20H, Ph), 7.93 (t, 1H,  ${}^{3}J$  = 7.8 Hz, pyr), 8.28 (d, 2H,  ${}^{3}J$  = 7.8 Hz, pyr), 8.40 (br, 2H, NH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  (ppm) = 28.8 (PCH<sub>2</sub>,  $J_{P-C}$  = 13.1 Hz), 39.7 (NCH<sub>2</sub>), 68.7 (PCH<sub>2</sub>CH<sub>2</sub>), 70.1, 70.2, 70.4, 70.6, 70.8 (OCH<sub>2</sub>), 125.0 (pyr), 128.6 (Ph,  $J_{P-C}$  = 6.8 Hz), 128.8 (Ph), 132.8 (Ph,  $J_{P-C}$  = 18.9 Hz), 138.4 (Ph,  $J_{P-C}$  = 13.1 Hz), 138.8 (pyr), 149.1 (pyr), 163.9 (CO);  ${}^{31}$ P-NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$ (ppm) = -22.4

**Compound 7.** Under argon and at 25 °C, 300 mL of anhydrous and degassed  $CH_2Cl_2$  was introduced into a dry 1 L three-necked round-bottomed flask and the solution was stirred. Using a syringe pump (1 mL h<sup>-1</sup>), an anhydrous and degassed  $CH_2Cl_2$  (15 mL) solution of compound **6** (250 mg, 0.29 mmol, 1 eq.) and an anhydrous and degassed  $CH_2Cl_2$  (15 mL) solution of CODPtCl<sub>2</sub> (110 mg, 0.29 mmol, 1 eq.) were

**Scheme 1** Formula of compounds **1–8** and of **1**-Pd and assignment of H atoms.

added simultaneously. The mixture was further stirred at 20 °C overnight. After the removal of the solvent under reduced pressure, the mixture was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>-MeOH 99/1 to 95/5) affording the desired compound 7 in 49% yield (160 mg) as a white solid. <sup>1</sup>H-NMR  $(CDCl_3, 300 \text{ MHz}): \delta (ppm) = 2.51 (dt, 4H, PCH_2, J = 10.9 \text{ Hz},$ J = 6.9 Hz), 3.62–3.83 (m, 24H, OCH<sub>2</sub>), 4.04 (dt, 4H, PCH<sub>2</sub>-CH<sub>2</sub>,  $J = 10.9 \text{ Hz}, J = 6.9 \text{ Hz}), 7.15-7.49 \text{ (m, 20H, PPh}_2), 7.96 \text{ (t, 1H, })$ pyr,  ${}^{3}J = 7.7$  Hz), 8.29 (d, 2H, pyr,  ${}^{3}J = 7.7$  Hz), 8.73 (br t, 2H, NH,  ${}^{3}J = 5.9$  Hz);  ${}^{13}$ C-NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 28.8$  (PCH<sub>2</sub>, virtual t,<sup>35</sup> J<sub>P-C</sub> = 46.6 Hz), 39.6 (NCH<sub>2</sub>), 67.6 (PCH<sub>2</sub>CH<sub>2</sub>), 70.2, 70.4, 70.7, 70.8, 71.0 (OCH<sub>2</sub>), 124.8 (pyr), 128.5 (Ph, virtual t,<sup>35</sup>  $J_{\rm P-C}$  = 5.3 Hz), 130.8 (Ph, virtual t, <sup>35</sup>  $J_{\rm P-C}$  = 54.8 Hz), 131.1 (Ph), 133.5 (Ph, virtual t,  ${}^{35} J_{P-C}$  = 4.9 Hz), 138.7 (pyr), 149.1 (pyr), 164.1 (CO); <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 121.5 MHz):  $\delta$  (ppm) = 3.92 ( $J_{P-Pt}$ = 3632 Hz). MS (ESI): m/z calcd for  $C_{47}H_{57}Cl_2N_3O_8P_2PtNa^+$ :  $1142.25 \text{ g mol}^{-1}$ ; found:  $1142.24 \text{ g mol}^{-1}$ .

Compound 1. Compound 7 (40 mg, 0.036 mmol) and ethynylpyridine 8 (11 mg, 0.107 mmol, 3 eq.) were dissolved in a degassed THF-NEt<sub>3</sub> 1:1 mixture (10 mL) and degassed by freeze-thaw cycles. After one cycle, CuI (1 mg, 0.005 mmol, 0.14 eq.) was added to the cold mixture. After 5 more cycles, the reaction mixture was heated to 55 °C and stirred overnight. After filtration on Celite and evaporation of the filtrate, the mixture was purified by column chromatography (SiO<sub>2</sub>,  $CHCl_3$ -MeOH 99/1 to 90/10) affording the desired product 1 in 71% yield as a yellow solid (32 mg). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):  $\delta$  (ppm) = 3.21 (m, 4H, H<sub>1</sub>), 3.38 (q, 4H, NCH<sub>2</sub>,  ${}^{3}J$  = 5.9 Hz), 3.45-3.58 (m, 20H, OCH<sub>2</sub>), 3.89 (m, 4H, H<sub>k</sub>), 6.70 (d, 4H, H<sub>t</sub>,  ${}^{3}J$  = 4.6 Hz), 7.41–7.51 (m, 12H, H<sub>o-p</sub>), 7.82 (m, 8H, H<sub>n</sub>), 8.00 (t, 1H, H<sub>a</sub>,  ${}^{3}J$  = 7.8 Hz), 8.28 (d, 2H, H<sub>b</sub>,  ${}^{3}J$  = 7.8 Hz), 8.31 (d, 4H, H<sub>u</sub>,  ${}^{3}J$  = 4.6 Hz), 9.16 (br t, 2H, H<sub>v</sub>,  ${}^{3}J$  = 6.6 Hz); <sup>13</sup>C-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz) (assignments according to HSQC and HMBC 2D <sup>1</sup>H-<sup>13</sup>C NMR experiments):  $\delta$  (ppm) = 28.9 (C<sub>1</sub>, virtual t,  ${}^{35}J_{P-C}$  = 18.8 Hz), 40.0 (C<sub>e</sub>), 67.4 (C<sub>k</sub>, virtual t,  ${}^{35}J_{P-C}$  = 4.1 Hz), 70.1, 70.7, 70.8, 70.9, 70.9 ( $C_{f-i}$ ), 109.5 ( $C_{q}$ ,  $J_{Pt-C}$  = 259.4 Hz), 115.6 (C<sub>r</sub>,  $J_{Pt-C}$  = 29.6 Hz), 124.8 (C<sub>b</sub>), 126.0 (C<sub>t</sub>), 128.7 (C<sub>o</sub>, virtual t,  $^{35}$   $J_{P-C}$  = 5.5 Hz), 131.1 (C<sub>p</sub>), 131.6 (C<sub>m</sub>, virtual t,  ${}^{35}J_{P-C}$  = 28.6 Hz), 134.0 (C<sub>n</sub>, virtual t,  ${}^{35}J_{P-C}$  = 6.2 Hz), 136.5 (C<sub>s</sub>), 139.0 (C<sub>a</sub>), 149.6 (C<sub>u</sub>), 149.7 (C<sub>c</sub>), 164.3 (C<sub>d</sub>);  $^{31}$ P-NMR  $(CD_2Cl_2, 161.98 \text{ MHz}): \delta (ppm) = 5.79 (J_{P-Pt} = 2511 \text{ Hz}).$ MS (ESI): m/z calcd for  $C_{61}H_{65}N_5O_8P_2PtH^+$ : 1253.40 g mol<sup>-1</sup>; found:  $1253.40 \text{ g mol}^{-1}$ .

**Compound 1-Pd.** To a solution of compound **1** (6 mg, 4.8 µmol) in a CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>CN 1/1 mixture (4 mL) a CH<sub>2</sub>Cl<sub>2</sub> solution (0.5 mL) of Pd(OAc)<sub>2</sub> (1.2 mg, 5.3 µmol, 1.1 eq.) was added. After 5 days at 25 °C, the mixture was evaporated to dryness under reduced pressure. The residue thus obtained was purified by preparative layer chromatography (PLC, SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>–MeOH 93/7) to yield the desired complex 1-Pd in 54% yield as a yellow solid (3.5 mg). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) = 3.03 (br t, 4H, H<sub>e</sub>, <sup>3</sup>J = 4.8 Hz), 3.25 (m, 4H, H<sub>l</sub>), 3.48–3.60 (m, 16H, OCH<sub>2</sub>), 3.65 (m, 4H, OCH<sub>2</sub>), 3.79 (m, 4H, H<sub>k</sub>), 6.22 (br d, 2H, H<sub>t</sub>, <sup>3</sup>J = 4.7 Hz), 7.45 (m, 8H, H<sub>o</sub>), 7.49 (m, 4H, H<sub>p</sub>), 7.60 (d, 2H, H<sub>t</sub>, <sup>3</sup>J = 5.2 Hz), 7.65 (d, 2H, H<sub>b</sub>, <sup>3</sup>J = 7.8 Hz), 7.81 (m, 8H, H<sub>n</sub>), 8.00 (t, 1H, H<sub>a</sub>, <sup>3</sup>J = 7.8 Hz), 8.11 (br, 2H,

H<sub>u</sub>), 8.90 (d, 2H, H<sub>u</sub>',  ${}^{3}J$  = 5.3 Hz);  ${}^{13}$ C-NMR (CDCl<sub>3</sub>, 125 MHz) (assignments according to HSQC and HMBC 2D  ${}^{1}$ H- ${}^{13}$ C NMR experiments):  $\delta$  (ppm) = 28.8 (C<sub>1</sub>, virtual t,  ${}^{35}$   $J_{P-C}$  = 18.5 Hz), 47.3 (C<sub>e</sub>), 67.1 (C<sub>k</sub>, virtual t,  ${}^{35}$   $J_{P-C}$  = 4.1 Hz), 70.9, 71.1, 71.1, 71.2 (C<sub>f-j</sub>), 106.9 (C<sub>r'</sub>), 111.7 (C<sub>r</sub>), 124.1 (C<sub>b</sub>), 125.3 (C<sub>t</sub>), 128.5 (C<sub>t'</sub>), 128.8 (C<sub>o</sub>, virtual t,  ${}^{35}$   $J_{P-C}$  = 5.1 Hz), 131.1 (C<sub>m</sub>, virtual t,  ${}^{35}$   $J_{P-C}$  = 28.6 Hz), 131.3 (C<sub>p</sub>), 134.0 (C<sub>n</sub>,  $J_{P-C}$  = 6.0 Hz), 139.3 (C<sub>s'</sub>), 140.7 (C<sub>a</sub>), 149.1 (C<sub>u</sub>), 152.6 (C<sub>u'</sub>), 153.2 (C<sub>c</sub>), 171.4 (C<sub>d</sub>);  ${}^{31}$ P-NMR (CDCl<sub>3</sub>, 121.5 MHz):  $\delta$  (ppm) = 3.67 ( $J_{P-Pt}$  = 2496 Hz). MS (ESI): m/z calcd for C<sub>61</sub>H<sub>63</sub>N<sub>5</sub>O<sub>8</sub>P<sub>2</sub>PdPtH<sup>+</sup>: 1357.28 g mol<sup>-1</sup>; found: 1357.29 g mol<sup>-1</sup>.

#### Results

The design of the turnstile 1 (Scheme 1) is based on our previous studies on porphyrin<sup>22-29</sup> or platinum<sup>30</sup> based turnstiles and inspired by the reported investigations by Gladysz et al. on molecular gyroscopes.<sup>21</sup> The herein reported design is based on a stator, an  $\alpha,\omega$ -bismonodentate ligand bearing in a symmetrical fashion a tridentate chelating unit (Fig. 1a) and a rotor composed of a metal centre as a hinge to which two identical monodentate coordinating sites in trans disposition are attached (Fig. 1b). In the absence of external stimulus, the rotor freely rotates around the stator defining thus the open state of the turnstile. In the presence of a metal centre as an effector offering four free coordination sites occupying the apices of a square, its simultaneous binding by the tridentate chelating units of the stator and by one of the two pyridyl groups of the rotor blocks the rotational movement (Fig. 1c) leading thus to the closed state of the turnstile. Although the design principle proposed in this contribution might appear to be rather similar to the one previously reported by us,<sup>30</sup> it nevertheless differs substantially. Indeed, the previous system was based on monodentate pyridyl groups both on the stator and on the rotor and the locking of the turnstile was achieved by a silver cation. This system was shown to oscillate between two closed states. In order to overcome this feature, the monodentate coordinating site was replaced by a tridentate chelating unit on the stator in 1 (Scheme 1). Consequently, owing to the high affinity of the chelating moiety for metal cations adopting a square planar type geometry, *i.e.* Pd(II) or Pt(II), no oscillatory movement between two closed positions should be observed.

It may be of interest to notice that the system presented above could be described as a sequential process leading from a podand to a binuclear metallamacrobicyclic architecture. Indeed, the binding of the first metal centre by the podand (Fig. 1a) leads by an obturation process to a metallamacrocycle (Fig. 1b). The complexation of the second metal centre generates the metallamacrobicycle (Fig. 1c).

The translation of the above mentioned design principle into molecules is given in Scheme 1. As the stator, the  $\alpha,\omega$ -diphosphine **6** based on the 2,6-pyridyl diamide moiety was chosen. The spacers used to connect the diphenylphosphine groups to the pyridyl derivative were  $-(CH_2)_2-O(CH_2)_2-O(CH_2)_2-O(CH_2)_2-O(CH_2)_2-O(CH_2)_2$  permit the free rotation of the rotor around the stator, was based on CPK models. As the rotor, Pt(n), used as the hinge, was equipped with two 4-ethynylpyridyl units in *trans* configuration. The choice of the C=C bond between the metal centre and the pyridyl group was made for synthetic reasons. The junction between the pyridyl groups and the metal centre was organometallic in nature and based on Pt–C bonds. Finally, as an effector, Pd(n) was used. It is worth noting that owing to the dianionic nature of the 2,6-pyridyl diamide moiety under alkaline conditions, the closed state of the turnstile 1-Pd is a neutral species.

The synthesis of 1 required 9 synthetic steps (Scheme 1, see the Experimental section). Intermediates 2,  $^{25}$  3,  $^{32,33}$  4,  $^{28}$  5<sup>28</sup> and  $8^{34}$  were synthesized following described literature procedures.

The condensation of the diacylchloride pyridine derivative 2 with the oligoethyleneglycol bearing an amino group 3 in  $CH_2Cl_2$  in the presence of  $Et_3N$  afforded the diol 4 which was activated into its dimesylate derivative 5 upon treatment with mesylchloride (MsCl) in THF in the presence of  $Et_3N$  as a base and *para*-dimethylaminopyridine (DMAP) as a catalyst.

Dropwise addition of a solution of KPPh<sub>2</sub> in dry THF into a solution of 5 in dry THF at 0 °C afforded compound 6 in 19% yield. Attempts to improve the yield by performing the reaction at -78 °C or by increasing the number of equivalents of KPPh<sub>2</sub> from 2.1 to 4.2 were unsuccessful. The obtained low yield may be attributed to the presence of acidic H atoms of the amide groups. Upon condensation of the podand 6 with CODPtCl<sub>2</sub> (1,5-cyclooctadiene = COD) under high dilution conditions in CH<sub>2</sub>Cl<sub>2</sub>, the metallamacrocycle 7 was obtained in 49% yield. Finally, the substitution of the two chloride anions by two ethynylpyridines 8, prepared following a published procedure,<sup>29</sup> was achieved in a NEt<sub>3</sub>-THF 1:1 mixture, affording the turnstile 1 in its open state in 71% yield.

The metallation of the turnstile **1**, leading to its closed state **1**-Pd, was achieved in 54% yield by treatment of **1** with 1.1 eq. of  $Pd(OAc)_2$  in a  $CH_2Cl_2$ - $CH_3CN$  1/1 mixture at 25 °C.

The structure of both the turnstiles in its open state **1** and in its closed state **1**-Pd was established in the solid state by X-ray diffraction on single crystals. In both cases, crystals were obtained at 25 °C upon slow diffusion of  $Et_2O$  or  $iPr_2O$ vapours into a CHCl<sub>3</sub> solution of **1** or **1**-Pd respectively (see the Experimental section).

For the turnstile 1, the crystal (triclinic,  $P\bar{1}$ ) is composed of 1 and Et<sub>2</sub>O solvent molecule (Fig. 2). Since the latter was found to be disordered, the structure was solved using the squeeze command.<sup>36</sup> The Pt(n) centre adopts a slightly distorted square-planar geometry with P–Pt–C angle in the 86.2–92.0° range and P–Pt–P and C–Pt–C angles of 177.11(9) and 176.6(4)° respectively. The Pt(n) centre is surrounded by two C and two P atoms in *trans* dispositions with Pt–P and Pt–C distances of 2.298(2), 2.295(2) Å and 1.999(7), 2.010(10) Å respectively. For the ethynylpyridyl moieties, the Pt–C–C and C–C–C angles are in the 175.9–177.6° and 179.2–176.3° range respectively. The two amide groups are in *trans* configuration with OCNH dihedral angles of *ca.* 179.1 and 178 9° and C=O and



**Fig. 2** Crystal structure of **1** showing the establishment of H bonds between the two amide NH groups and the pyridyl moiety connected to the Pt(II) centre (green) by an ethynyl spacer. H atoms except the two involved in H-bonding patterns and solvent molecules are not represented for clarity. For bond distances and angles see the text.

N–C bond distances in the *ca*. 1.24–1.25 Å and *ca*. 1.31–1.32 Å range respectively. Interestingly, two H bonds between the H atom of the two amide groups and one of the two ethynylpyridyl moieties pointing towards the handle are observed in the solid state with NH–N distances of *ca*. 2.33 and 2.37 Å.

For 1-Pd, the crystal (triclinic,  $P\bar{1}$ ) in addition to the turnstile contained iPr<sub>2</sub>O and CHCl<sub>3</sub> solvent molecules (Fig. 3). As in the case of 1, the  $Pt(\pi)$  centre adopts nearly the same geometry with some slightly different metrics (P-Pt-C angle in the 88.44-91.99° range and P-Pt-P and C-Pt-C angles of 172.22(4) and 177.92(16)° respectively). The metal centre is connected to two C and two P atoms in trans dispositions with Pt-P and Pt-C distances of ca. 2.31 and 1.99 Å respectively. For the ethynylpyridyl moieties, the Pt-C-C and C-C-C angles are ca. 177.4, 178.6° and 179.2, 180.0° respectively. The two amide groups are again in trans configuration with OCNPd dihedral angles of ca. -171.2 and -177.5° and C=O and N-C bond distances of ca. 1.24 Å and ca. 1.34 Å respectively. The Pd(II) centre adopts a distorted square planar geometry with  $\ominus N_{Pv}$ -Pd-N<sub>Pv</sub> = 180.0°,  $\ominus N_{amide}$ -Pd-N<sub>amide</sub> = 160.8°,  $\ominus N_{amide}$ -Pd-N<sub>Py</sub> in the 80.4–80.5° range and  $\ominus N_{amide}\text{-Pd-}N_{Pyethynyl}$  in the 99.0–100.2° range. The distortion is brought by the tridentate chelating unit which imposes one short N<sub>Py</sub>-Pd distance of 1.93 Å and



**Fig. 3** Crystal structure of the Pt (green)–Pd (orange) heterobinuclear metallamacrobicycle **1**-Pd showing the locking of the turnstile upon binding of Pd(II). H atoms and solvent molecules are not represented for clarity. For bond distances and angles see the text.



Fig. 4 A portion (aromatic region) of the <sup>1</sup>H-NMR spectra (500 MHz,  $CD_2CI_2$ , 298 K) between 6 and 9.2 ppm of 1 (bottom) and of 1-Pd (top). For hydrogen atoms assignments see Scheme 1.

two longer  $N_{amide}$ -Pd distances of *ca.* 2.05 Å. The last  $N_{PtPy}$ -Pd distance is *ca.* 2.03 Å. Finally, the Pt-Pd distance within the heterobinuclear species is 9.46 Å.

Both compounds 1 and 1-Pd were fully characterised in solution in CD<sub>2</sub>Cl<sub>2</sub> and their dynamic behaviour studied by 1- and 2-D NMR. For both compounds all hydrogen atoms have been assigned (Scheme 1). The <sup>1</sup>H-NMR spectrum of the turnstile 1 at 25 °C was found to be well resolved and displayed only two doublets for H<sub>u</sub> and H<sub>t</sub> atoms (Fig. 4, bottom). This observation implies either a fast free rotation of the rotor around the stator or a rapid oscillatory movement, with respect to the NMR time scale. The oscillation should take place between two closed states of the same energy for symmetry reasons by the formation of H-bonds between the two amide NH donor sites and the pyridyl moiety of the rotor. This, as mentioned above, is substantiated by the solid state structure of 1 (Fig. 2). In order to investigate the nature of the movement, *i.e.* free rotation or oscillation, compound 1 was studied by 2D ROESY NMR (Fig. 5, top). The latter experiment revealed in addition to the expected correlations between chemically connected H atoms, such as H<sub>v</sub> and H<sub>e</sub>, H<sub>n</sub> and H<sub>i-l-k</sub>, through space correlations between H<sub>u</sub> and H<sub>t</sub> hydrogen atoms of the pyridyl moiety of the rotor and H atoms of the stator. This indicates that, at 25 °C, the rotor oscillates between two positions. This type of behaviour has been previously observed for porphyrin based molecular turnstiles.<sup>27</sup> The decrease in temperature from 25 °C to -85 °C, although leading to broadening of signals, did not cause the splitting of H<sub>u</sub> and H<sub>t</sub> doublets into two sets of signals corresponding to  $H_u$ ,  $H_{u'}$  and  $H_t$ ,  $H_{t'}$ implying that the oscillatory process was not blocked at -85 °C.

The closed state of the turnstile **1** was generated upon binding of Pd(II) playing the role of an effector. The complexation event led to a less symmetric species **1**-Pd as shown by the <sup>1</sup>H-NMR spectrum (Fig. 4, top). In particular, the two doublets corresponding to H<sub>t</sub> (6.70 ppm) and H<sub>u</sub> (8.31 ppm) in **1** are, as expected, split into four doublets H<sub>t</sub> (6.22 ppm) and H<sub>u</sub> (8.11 ppm) and H<sub>t'</sub> (7.60 ppm) and H<sub>u'</sub> (8.90 ppm) corresponding to H atoms of the unbound and bound pyridyl units of the rotor respectively.

Owing to coordination of the Pd atom,  $H_{t^\prime}$  and  $H_{u^\prime}$  are downfield shifted. The upfield shift observed for the  $H_t$  and



**Fig. 5** Portions of the 2D-NMR correlation maps ( ${}^{1}H{-}^{1}H$  ROESY, CD<sub>2</sub>Cl<sub>2</sub>, 298 K, 500 MHz) showing, in addition to the expected cross peaks, through space correlations between the rotor and the stator parts of the turnstile in its open (**1**, top) and closed states (**1**-Pd, bottom).

 $H_u$  atoms might be due to the shielding effect brought by the close proximity of phenyl groups located on the P atom. Furthermore,  $H_b$  and  $H_e$  signals are significantly upfield shifted with  $\Delta \delta = -0.63$  and -0.35 ppm. Finally, the signal at 9.16 ppm corresponding to  $H_v$  (NH of the amide groups) in 1 disappears implying also the binding of the Pd( $\mu$ ) cation.

Observations on 1-Pd in the solid state by X-ray diffraction and in solution by <sup>1</sup>H-NMR were further substantiated by 2D ROESY experiments in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C (Fig. 5, bottom). Indeed, the bidimensional NMR study revealed, in addition to the expected correlation peaks, through space interactions between the H<sub>t'</sub> and H<sub>u'</sub> atoms of the pyridine of the rotor coordinated to the Pd(II) centre and H atoms belonging to the stator (H<sub>t'</sub> with H<sub>l</sub>, H<sub>k</sub> and H<sub>j-f</sub> and H<sub>u'</sub> with H<sub>e</sub> and H<sub>j-f</sub>). Furthermore, as expected, no correlation peaks between H<sub>t</sub> and H<sub>u</sub> atoms of the unbound pyridine of the rotor and H atoms of the stator were observed. These features clearly demonstrate that, upon the binding of Pd cation, the turnstile is locked without oscillation between two sites as observed for the turnstile **1** discussed above.

Owing to the design of the turnstile, in particular the presence of Pt–P junctions, the  $CN^-$  anion as a competing ligand with the pyridyl unit of the rotor could not be used since it would lead to the destruction of the complex. The opening of the system was attempted using acidic conditions in order to protonate the pyridyl moiety of the rotor. Unfortunately, the presence of H<sup>+</sup> led to the decomposition of the complex.

#### Conclusions

In conclusion, the Pt(II) based molecular turnstile **1** was designed, synthesised and characterised and its dynamic behaviour in solution was established by 1- and 2-D NMR experiments. Owing to the presence of H-bond donor sites on the stator (two NH amide groups) and acceptor site (pyridyl moiety) on the rotor, both in the solid state and in solution an intramolecular H-bond is formed. Since the turnstile **1** is equipped with two identical coordinating sites (pyridyl units) on the rotor, the turnstile oscillates between two positions at 25 °C. The locking of the turnstile was achieved using Pd(II) as an effector. The structure of **1**-Pd was established both in the solid state by X-ray diffraction and in solution by NMR investigations. Based on the design principles reported here, other organometallic turnstiles using different metal centres and effectors are currently under investigation.

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