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A bi-stable Pt(II) based molecular turnstile

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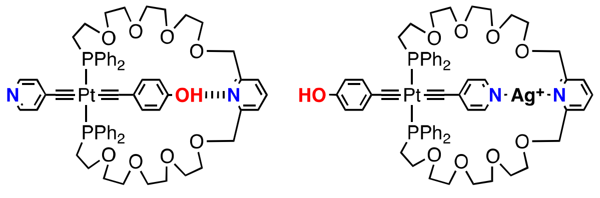
Playing with competition between H- and coordination-bonds, a bi-stable unsymmetrical organometallic turnstile was designed and its dynamic behaviour studied in solution by NMR techniques. The turnstile, bearing two differentiated interaction sites, is based on a stator, composed of a square planar Pt(II) centre equipped with one pyridyl group and one phenol moiety, connected to a symmetrical rotor bearing a pyridyl unit as either a H-bond acceptor or as a monodentate coordinating site. Whereas in the absence of a metallic effector, the turnstile is locked by a H-bond formed between the phenol moiety located on the stator and the pyridyl group of the rotor, in the presence of Ag^+ cation, the turnstile switches to another close state resulting from the simultaneous binding of the cation by both pyridyl units belonging to the stator and to the rotor. The switching process was shown to be reversible.

Controlling translational or rotational intramolecular movements within abiotic molecular entities is a topic of current interest.[1] Among many systems reported, a class of molecules called molecular turnstiles[2] is of particular interest for the design of bi-stable dynamic entities displaying an open and a closed states with the possibility of switching between the two by an external stimuli.

For some time now, our group has been investigating the design and synthesis of molecular turnstiles. Thus, we have reported a series of porphyrin based dynamic systems.[3] We have also extended our approach to organic turnstiles with optical reading of their open and close states.[4] Finally, inspired by contributions on molecular gyroscopes by Gladysz *et al.*,[5] we have reported a series of organometallic turnstiles based on Pt(II).[6] Molecular turnstiles reported so far are dynamic entities based on an open and a close states. To the best of our knowledge, no example of turnstiles undergoing a switch between two close states has been reported.

Herein we report the design, synthesis and solution study of a Pt(II)-based organometallic turnstile and the switching between its two different closed states based either on H-bonding or coordination process (Fig. 1).

The design of the turnstile **1** (Scheme 1) is based on a square planar Pt(II) centre as a hinge, bearing two different sites, a phenol as a H-bond donor and a pyridyl moiety as a monodentate coordinating site. This ensemble may be regarded as the stator. The latter is equipped with a symmetric rotor bearing also a pyridyl group as either a H-bond acceptor site or as a monodentate coordinating group. The connection of the two sites located on the Pt(II) based stator is ensured by Pt-C bonds using two alkynyl units and the position 4 of both phenol and pyridine moieties. The rotor is connected to the stator by two Pt-P bonds using an α,ω-bis-diphenylphosphine fragment bearing at its centre a pyridyl unit. The interconnection between the pyridyl moiety and the two phosphine groups is ensured by two tetraethyleneglycol spacers using positions 2 and 6 of the aromatic group. The choice of stator and rotor terminology is arbitrary and may be reversed.



1 **1**-Ag^+

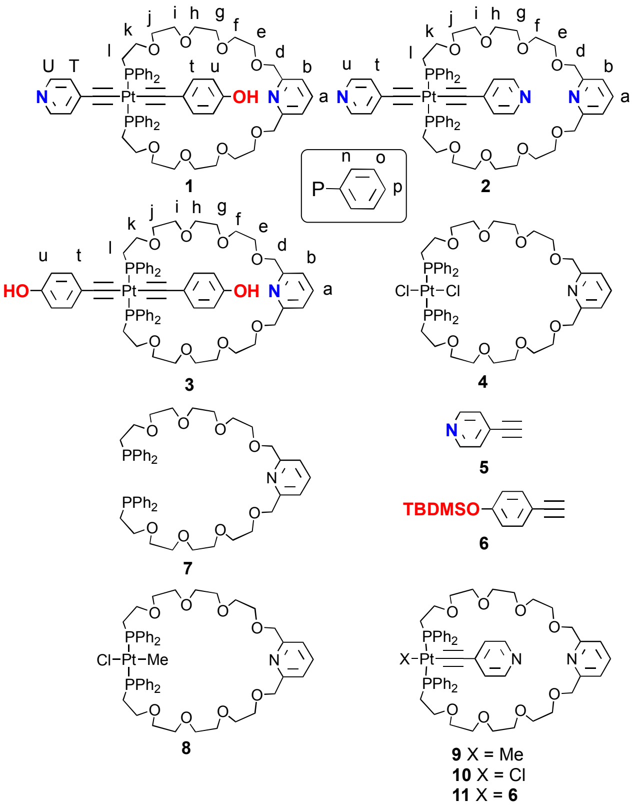
Figure 1. The two close states of the unsymmetrical turnstile **1** (C1) and its silver complex **1**-Ag^+ (C2).

In principle, in the absence of a metal centre as effector, the turnstile **1** should be in its closed state C1 resulting from the establishment of a H-bond between the phenol group of the stator and the pyridyl moiety belonging to the rotor. Upon addition of an effector such as Ag^+ cation, owing to the higher stability constant of the silver complex when compared to the H-bonded state, the turnstile should switch to a second closed state C2 based on the simultaneous binding of the cation by both pyridyl moieties belonging to the stator and the rotor (Fig. 1).

The synthesis (see ESI) of the unsymmetrical turnstile **1** appeared to be rather challenging and required the exploration of three different synthetic strategies. The first one, statistical in nature, was based on the condensation at 55 °C of the metallamacrocycle **4**[6a] with the ethynylpyridine **5**[7] and the protected ethynylphenol derivative **6**[8] (1.5 eq. of each) in presence of a catalytic amount of CuI in a THF/NEt_3 mixture. As expected, the reaction afforded all three macrocyclic compounds: the desired unsymmetrical compound **1**, and the two symmetrical turnstiles **2**[6a] and **3**. Unfortunately, their separation was found to be unfeasible. However, upon deprotection of the phenol moiety using TetraButylAmmonium Fluoride (TBAF) at room temperature, the separation, although very tedious, could be achieved affording thus the desired turnstile **1** in 3.5 % yield.

The second strategy, more directed, was based on the condensation of CODPtMeCl[9] with the diphenylphosphine compound 7[6a] under high dilution conditions. The reaction produced the intermediate **8** in 92 % yield. The condensation of the latter with ethynyl pyridine **5**[7] afforded the compound **9** with *ca.* 5-10 % of the symmetrical bispyridyl turnstile **2**. After substitution of the methyl group by chloride using HCl leading to the compound **10**, the latter was condensed with the protected phenol **6**.[8] Again, the purification appeared to be very tedious. In order to overcome this, the TBDMS protective group was removed. After column chromatography and several purification by PTLC, the desired turnstile **1** has been obtained in 6 % yield (over the three last synthetic steps).

Finally, a third synthetic strategy was explored. The latter was based on mono-alkylation of the Pt(II)-metallamacrocycle **4** upon its reaction with stannylated 4-ethynylpyridine, generated *in situ* upon successive additions of *n*BuLi and $SnMe_3Cl$.[10] The condensation afforded the compound **10**. The reaction of the latter with **6** afforded the protected intermediate metallamacrocycle **11** which upon deprotection using TBAF afforded the desired turnstile **1** in 13 % yield over the last three synthetic steps. The rather low yield reported for **1**, corresponds to the isolated compound and results from the purification method, mainly, chromatography which appeared to be the only possible one.



Scheme 1. Structures of compounds **1-11** and assignments of the H-atoms for turnstiles **1-3**.

The switching between the two C1 and C2 closed states of the unsymmetrical turnstile **1** (Fig. 1) was studied in CD_2Cl_2 solution by 1- and 2-D NMR techniques. All the H-atoms of **1** were assigned (Scheme 1).

For the turnstile **1**, chemical shifts (ppm) H*t* and H*u* of the phenol moiety and H*T* and H*U* of the pyridyl group appeared at 6.95, 6.62 and 6.23, 8.09 respectively. For the phenol group, the chemical shifts observed are downfield shifted when compared to signals for the symmetrical bis-phenol turnstile **3** (H*t* 6.60 and H*u* 6.51). The chemical shifts for H*T* and H*U* of the pyridyl moiety of **1** are close to those observed for the unbound pyridyl group of **2**-Ag^+ at low temperature.[6a] Finally, the chemical shifts observed for H*a* (7.75) and H*b* (7.37) atoms of the pyridyl group located on the rotor in **1** are similar to those observed for the bis-phenol turnstile **3**. These observations indicate the formation of a H-bond between the phenol moiety of the stator (H bond donor) and the pyridyl group of the rotor (H bond acceptor) leading thus to the peripheral positioning of the pyridyl unit of the stator with respect to the macrocyclic cavity.

Observations obtained by 1D ^1H-NMR investigations mentioned above were further confirmed by ^1H-^1H ROESY NMR experiments (Fig. 2). Chemical shift of signals in the regions corresponding to the aromatic and ethylene glycol H atoms shows cross-relaxation peaks between H*t* and H*u* of the phenol moiety and H*d-j-k-l* of the handle. As expected, no cross-relaxation peaks between H*T* and H*U* of the pyridyl moiety of the stator and H*d-j-k-l* atoms of the handle was observed. This indeed confirms that the turnstile **1** is locked in the close state C1.

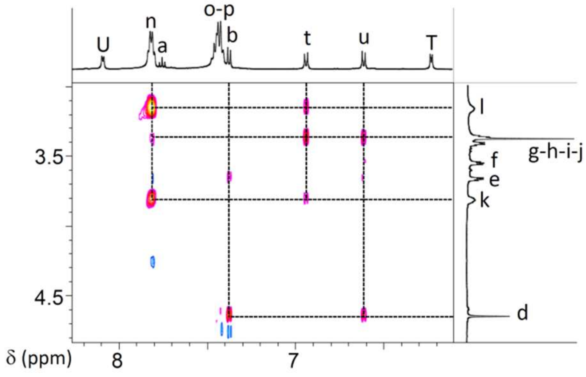


Figure 2. Portion of the ^1H-^1H ROESY spectra of **1** (CD_2Cl_2, 500 MHz, 298 K). For signals assignments see scheme 1.

The switch between the two close states C1 and C2 was achieved upon addition of Ag^+ cation as an effector. Indeed, addition of one equivalent of $AgSbF_6$ in CD_3CN to a solution of **1** in CD_2Cl_2, caused significant changes in the ^1H NMR spectra of the turnstile, especially in the aromatic region (Fig. 3 a and b, left). Hydrogen atoms of the stator are all strongly affected, with shifts (ppm) of -0.46, -0.23 and +0.36 ppm for H*t*, H*u* and H*U*, respectively. It should be noticed that the signal corresponding to H*T* is hidden under the H*o-p* signals. This is in agreement with the previous observation of the signal at 7.5 ppm for **2**-Ag^+ at low temperature.[6a] Furthermore, the signal corresponding to H*a* is downfield shifted (δ = 7.94 ppm) upon binding of Ag^+ cation. Again, this is in agreement with previous observation for **2**-Ag^+ for which the signal corresponding to H*a* appears at 7.96 ppm.[6a] These observations imply the simultaneous binding of the silver cation by both pyridyl units belonging to the stator and the rotor.

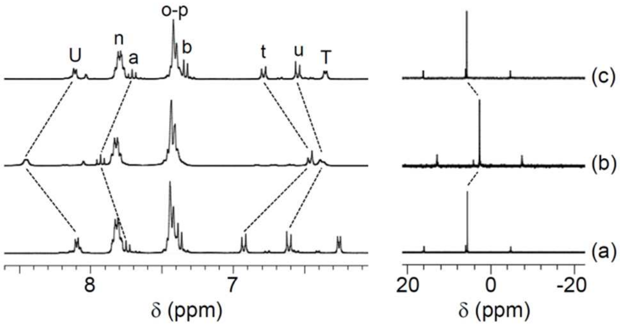


Figure 3. Portions of the ^{1}H-NMR (left) and ^{31}P-NMR (right) (CD_2Cl_2, 298 K) spectra for **1** (a), **1**-Ag^+ (b) and **1**-Ag^+ after the addition of one equivalent of Br^- anion (c). For signals assignments see scheme 1.

Again, the above mentioned conclusions are further confirmed by 2D NOESY experiments. Indeed, the ^{1}H-^{1}H NOESY spectrum (Fig. 4) reveals the absence of correlations between the phenolic hydrogen atoms H*t* and H*u* of the stator and hydrogen atoms of the handle. This indicates that the phenol moiety is located outside of the macrocyclic backbone. Furthermore, as expected, H*U* correlates with H*f*.

The stoichiometry of the binding of silver cation by the turnstile **1** was investigated by mass spectrometry by addition of increasing amounts of $AgSbF_6$, to a CH_2Cl_2 solution of **1** (see ESI). For the 1/1 ratio of Ag^+ and **1**, the main product is **1**-Ag^+. Upon increasing the ratio to 2 or 3, no trace of dicationic species was present, however, degradation of the complex was observed which was not further investigated.

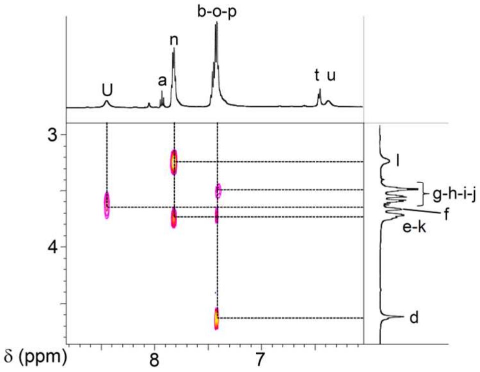


Figure 4. Portion of the ^{1}H-^{1}H NOESY spectrum for **1**-Ag^+ (CD_2Cl_2, 500 MHz, 298 K). For signals assignments see Scheme 1.

The reversibility of the switching process between the two close states C1 and C2 was achieved upon addition of one equivalent of Et_4NBr to a solution of **1**-Ag^+ followed by the filtration of the precipitated AgBr salt. The process was monitored both by ^{1}H- and ^{31}P-NMR studies (Fig. 3). Indeed, chemical shifts for signals corresponding to H*t*, H*u*, H*T*, H*U*, H*a* and H*b* atoms were identical to those observed for **1** (Fig. 3 left). The same behaviour was observed when monitoring the process by ^{31}P-NMR (Fig. 3 right).

The solution dynamic behaviour of the symmetrical bis-phenol turnstile **3** was also studied by 1- and 2-D NMR. In that case, as for the unsymmetrical turnstile **1**, one would expect a close state resulting from the formation of a H-bond between one of the two phenol units of the stator and the pyridyl group of the rotor. However, as previously observed for the other symmetrical turnstile **2** in the presence of silver cation,[6a] owing to the rather weak nature of the H bond, one would expect an oscillation between two equivalent close states. At room temperature in CD_2Cl_2, the two phenol groups were found to be equivalent as only a single set of signals was observed for the H*t* and H*u* atoms (Fig. 5). This implies either the absence of the H-bond and thus the open state of the turnstile **3** or a rapid exchange between two equivalent closed states resulting from the formation of a H bond. In order to investigate the exchange process, variable temperature NMR studies have been carried out. Unfortunately, lowering the temperature to -46 °C did not allow to observe the splitting of H atoms belonging to the two phenol groups into H*t* and H*u* and H*t′* and H*u′* as one would expect for the phenol involved in the H bond formation and the free phenol respectively. In order to enhance the strength of the H-bond, the ^{1}H-NMR spectrum was recorded in a less polar mixture of solvents (CD_2Cl_2/CCl_4 1/1). Unfortunately, the turnstile **3** appeared to be insoluble bellow -20 °C. The existence of the close state of the turnstile **3** was demonstrated by 2D ^{1}H-^{1}H NOESY NMR that clearly revealed the presence of correlations peaks between the H*t* and H*u* atoms of the phenol ring and the H atoms of $–OCH_2$- groups of the rotor (Fig. 5).

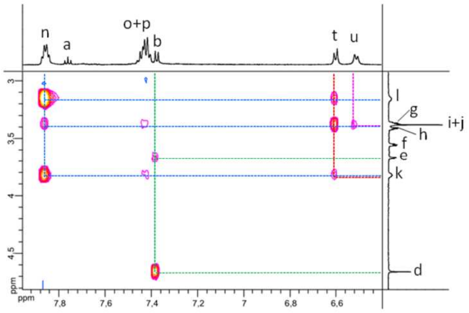


Figure 5. Portion of the ^{1}H-^{1}H ROESY spectra (CD_2Cl_2, 600 MHz, 298 K) for the turnstile **3**. For signals assignments see Scheme 1.

In conclusion, the unsymmetrical organometallic turnstile **1**, based on a Pt(II) centre bearing a phenol and a pyridyl and connected to a symmetrical handle, displays two distinct close states resulting either from the establishment of a H-bond between the phenol moiety and the pyridyl unit (C1) or the simultaneous binding of silver cation by both pyridyl units belonging to the stator and the rotor. The switching between the two states is reversible and may be achieved by adding Br^- anion, which leads to the precipitation of the insoluble AgBr salt. Based on the principle described in this contribution, the design of other organometallic turnstiles and metallic effectors is currently under investigation.

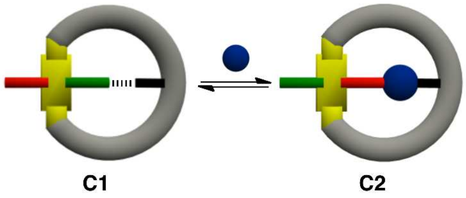


Figure 6. Schematic representations of the two closed states C1, based on a H-bond between the phenol of the stator and the pyridyl unit of the

rotor, and C2 resulting from the simultaneous binding of silver cation by both pyridyl groups belonging to the stator and the rotor.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [experimental details, full characterisation of new compounds, NMR and Mass spectra]. See DOI: 10.1039/b000000x.

1. (a) J.-P. Sauvage, *Science,* 2001, **291**, 2105; (b) J.-P. Sauvage, *Acc. Chem. Res*., 1998, **31**, 611; (c) J.-P. Sauvage, in *Molecular machines and motors*, *Structure and bonding*, Vol. 99, (Ed.: J.-P. Sauvage), Springer, Berlin, Heidelberg, 2001, pp. 1-282; (d) V. Balzani, M. Venturi and A. Credi, in *Molecular devices and machines: a journey into the nanoworld*, Wiley-VCH, Weinheim, 2003, pp. 1-457; (e) T. R. Kelly, in *Molecular machines, Topics in Current Chemistry*, Vol. 262, (Ed.: T. R. Kelly), Springer, Berlin, Heidelberg, 2005, pp. 1-227; (f) Y. Shirai, J.-F. Morin, T. Sasaki, J. M. Guerrero and J. M. Tour., *Chem. Soc. Rev.,* 2006, **35**, 1043, (g) E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem. Int. Ed.*, 2007, **46**, 72, (h) N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152; (i) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2000, **39**, 3348; (j) C. A. Schalley, K. Beizai and F. Vögtle, *Acc. Chem. Res.* 2001, **34**, 465J; (k) Michl and E. C. H. Sykes, *ACS Nano*, 2009, **3**, 1042; (l) G. Vives and J. M. Tour, *Acc. Chem. Res.* 2009, **42**, 473; (m) N. Weibel, A. Mishchenko, T. Wandlowski, M. Neuburger, Y. Leroux and M. Mayor, *Eur. J. Org. Chem.* 2009, **35**, 6140; (n) S. Sengupta, M. E. Ibele and A. Sen, *Angew. Chem. Int. Ed.*, 2012, **51**, 8434; (o) C. Clavel, C. Romuald, E. Brabet, F. Coutrot, *Chem. Eur. J.*, 2013, **19**, 2982.
2. (a) T. C. Bedard and J. S. Moore, *J. Am. Chem. Soc.,* 1995, **117**, 10662; (b) A. Carella, J. Jaud, G. Rapenne and J.-P. Launay, *Chem. Commun.,* 2003, 2434; (c) N. Weibel, A. Mishchenko, T. Wandlowski, M. Neuburger, Y. Leroux and M. Mayor, *Eur. J. Org. Chem.,* 2009, **35**, 6140
3. (a) A. Guenet, E. Graf, N. Kyritsakas, L. Allouche and M. W. Hosseini, *Chem. Commun.*, 2007, 2935; (b) A. Guenet, E. Graf, N. Kyritsakas and M. W. Hosseini, *Inorg. Chem.*, 2010, **49**, 1872; (c) A. Guenet, E. Graf, N. Kyritsakas and M. W. Hosseini, *Chem. Eur. J.*, 2011, **17**, 6443; (d) T. Lang, A. Guenet, E. Graf, N. Kyritsakas and M. W. Hosseini, *Chem. Commun*., 2010, **46**, 3508; (e) T. Lang, E. Graf, N. Kyritsakas and M. W. Hosseini, *Dalton Trans.*, 2011, **40**, 3517; (f) T. Lang, E. Graf, N. Kyritsakas and M. W. Hosseini, *Dalton Trans.*, 2011, **40**, 5244; (g) T. Lang, E. Graf, N. Kyritsakas and M. W. Hosseini, *Chem. Eur. J.*, 2012, **18**, 10419; (h) T. Lang, E. Graf, N. Kyritsakas, M. W. Hosseini, *New J. Chem.*, 2013**, 37**, 112.
4. N. Zigon, P. Larpent, A. Jouaiti, N. Kyritsakas, M. W. Hosseini, *Chem. Commun.,* 2014, **50**, 5040.
5. (a) A. J. Nawara, T. Shima, F. Hampel and J. A. Gladysz, *J. Am. Chem. Soc.*, 2006, **128**, 4962; (b) K. Skopek, M. C. Hershberger, J. A. Gladysz, *Coord. Chem. Rev*., 2007, **251**, 1723, (c) T. Shima, E. B. Bauer, F. Hampel and J. A. Gladysz, *Dalton Trans.*, 2004, 1012, (d) E. B. Bauer, F. Hampel and J. A. Gladysz, *Organometallics*, 2003, **22**, 5567; (e) P. D. Zeits, G. P. Rachiero, F. Hampel, J. H. Reibenspies, J. A. Gladysz, *Organometallics*, 2012, **31**, 2854.
6. (a) N. Zigon, A. Guenet, E. Graf, M. W. Hosseini, *Chem. Commun.* 2013, **49**, 3637; (b) N. Zigon, A. Guenet, E. Graf, N. Kyritsakas, M. W. Hosseini, *Dalton Trans.* 2013, **43**, 9740; (c) N. Zigon, N. Kyritsakas, M. W. Hosseini, *Dalton Trans.* 2013, **43**, 152.
7. L. Yu, J. S. Lindsey, *J. Org. Chem.* 2001, **66**, 7402.
8. (a) G. Y. Fang, V. K. Aggarwal, *Angew. Chem. Int. Ed.* 2007, **46**, 359, (b) T. Ogawa, K. Ohta, T. Iijima, T. Suzuki, S. Ohta, Y. Endo, *Bioorg. Med. Chem.* 2009, **17**, 1109, (c) S. K. Chitneni, C. M. Deroose, J. Balzarini, R. Gijsbers, S. Celen, Z. Debyser, L. Mortelmans, A. M. Verbruggen, G. M. Bormans, *J. Med. Chem.* 2007, **50**, 6627.
9. G. P. C. M. Dekker, A. Buijs, C. J. Elsevier, K. Vrieze, P. W. N. M. Van Leeuwen, W. J. J. Smeets, A. L. Spek, Y. F. Wang, C. H. Stam, *Organometallics* 1992, **11**, 1937.
10. M. Hissler, A. Harriman, A. Khatyr, R. Ziessel, *Chem. Eur. J.* 1999, **5**, 3366.

Graphical abstract

Playing with competition between H- and coordination-bonds, a bi-stable unsymmetrical organometallic turnstile may be swithched between to close states.