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Improved dynamics and positional bias with a second generation palladium(II)-complexed molecular shuttle

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Abstract

A second generation palladium(II)-complexed molecular shuttle, featuring structural changes to the size and shape of the macrocycle, shows significantly increased rates of shuttling and improved co-conformational bias compared to the original system.

Introduction

An understanding of how structural variations affect the positional bias and the kinetics of shuttling is important for developing rotaxane systems that possess a level of control over motion beyond that of simple switches. We recently described the synthesis and dynamics of a pH-responsive Pd(II)-complexed molecular shuttle—only the second class of rotaxane system (following Sauvage’s use of Cu(I) and Cu(II)/Zn(II)) in which co-conformational switching is dependent upon the energetics of metal-ligand coordination. A notable feature of rotaxane L1Pd was its metastability; changing the chemical state of the thread did not immediately cause a change in the macrocycle’s position. Whilst this allowed the system to be held in an out-of-equilibrium state—something that is difficult to achieve using molecular shuttles that rely on weaker non-covalent interactions—elevated temperatures and extended times were required to overcome the energy barrier to shuttling (up to 16 hours at 383 K to reach equilibrium). Furthermore, the positional bias of the Pd-macrocycle between the 4-dimethylaminopyridine (DMAP) and pyridine (Py) stations was somewhat modest in both the neutral (ca. 6:1) and protonated (ca. 1:8) states of the rotaxane thread (Scheme 1a).

Scheme 1. Operation conditions and positional bias of (a) 1st generation L1Pd and (b) 2nd generation L2Pd molecular shuttles.
Here we report on a second generation molecular shuttle, L2Pd (Scheme 1b), in which the benzylic amide macrocycle is replaced by a larger and differently shaped bis-anilide ring. The alteration of the steric environment around the palladium(II) centre in the rotaxane leads to greatly enhanced rates of macrocycle shuttling and improved positional bias in both chemical states of the thread. In addition to the minimum energy co-conformers of the two switched systems, two metastable out-of-equilibrium positional isomers were sufficiently stable to be isolated and characterised by 1H NMR spectroscopy.

L2Pd was prepared by a threading-and-stoppering procedure, first treating a palladium-macrocycle-acetonitrile complex with an unstoppered-DMAP-end thread precursor, and the resulting pseudo-rotaxane reacted with an excess of a phenol-based stopper under Mitsunobu conditions to afford the [2]rotaxane (see Supporting Information).

Comparison of the 1H NMR spectra of the free thread (Figure 1a) and the rotaxane isolated from the stoppering reaction (Figure 1b) showed that the signals assigned to the DMAP station (Hₖ and Hₘ) were split and shifted upfield by around 0.4 ppm in the rotaxane. In contrast, those of the Py station (Hₓ, Hᵧ, and Hₖ) were unchanged relative to their positions in the free thread, indicating that the co-conformation of the isolated [2]rotaxane was DMAP-L2Pd, i.e. with the palladium-macrocycle component coordinated to the DMAP station.

← Figure 1. 1H NMR spectra (400 MHz, [D₇]DMF, 300 K) of [2]rotaxane [L2Pd] in four different protonated and co-conformational states and, for comparison, the free thread. a) Thread; b) DMAP-[L2Pd]; c) DMAP-[HL2Pd]OTs; d) Py-[HL2Pd]OTs (97% + 3% DMAP-[HL2Pd]OTs); e) Py-[L2Pd] (97% + 3% DMAP-[L2Pd]). The lettering in the figure refers to the assignments in Scheme 1.
Addition of one equivalent of p-toluenesulfonic acid (TsOH) to DMAP-L2Pd in [D$_7$]DMF gave DMAP-[downfield shifting of the signals associated with the protonated Py station -[HL2Pd]OTs, evidenced (Figure 1c) by broadening and (H$_x$ by 0.9 ppm and H$_y$ and H$_z$ each by ~0.8 ppm). The positions of the DMAP unit peaks (H$_x$ and H$_y$) were virtually unchanged relative to DMAP-L2Pd (Figure 1b).

After one hour at room temperature in [D$_7$]DMF, small changes to the $^1$H NMR spectrum of this sample gave an indication that the activation barrier to macrocycle movement in the second generation molecular shuttle was significantly lower than for DMAP-[HL1Pd]OTs,$^2$ and after four hours at 323 K a new equilibrium co-conformation had been fully realised (i.e. no further spectral changes were observed). The $^1$H NMR now showed (Figure 1d) a protonated DMAP signal at around 13 ppm for the major positional isomer present, shielding of the pyridine station signals (H$_x$, H$_y$ and H$_z$) and a downfield shift of the DMAP heterocyclic signals (H$_k$ and H$_m$), all of which indicated that the Pd-macrocycle was now bound to the pyridine station and a proton to the DMAP site. Integration indicated that the distribution of co-conformers at equilibrium was ~3:97 DMAP:Py-[HL2Pd]OTs. Deprotonation of the dimethylaminopyridinium group by addition of Na$_2$CO$_3$ gave an out-of-equilibrium co-conformational mixture of ~3:97 DMAP:Py-L2Pd, apparent through changes to the $^1$H NMR spectrum (Figure 1e) the most notable of which were a return of the DMAP signals (H$_x$ and H$_y$) to positions similar to those of the free thread (Figure 1a) and the disappearance of the protonated DMAP signal at 13 ppm. Again, slow isomerisation of the sample (~5% an hour) was observed at room temperature in [D$_7$]DMF but not in non-coordinating solvents such as CDCl$_3$, supporting a solvent-mediated switching mechanism for translocation of the Pd-coordinated macrocycle between the Py and DMAP units. Raising the temperature to 323 K in [D$_7$]DMF brought about the energetically downhill shuttling of the Pd-macrocycle from the Py to the DMAP station, yielding an equilibrium ratio of 92:8 DMAP:Py-L2Pd after just 2 hours.

The associative nature of palladium(II) substitution reactions, and the faster shuttling rate of L2Pd compared to L1Pd, suggests that the bis-anilide macrocycle provides a less sterically demanding environment around the metal ion and thus easier access for an incoming coordinating solvent molecule or TsO$^-$ counter-anion. In the protonated state, the better positional bias of [HL2Pd]$^+$ with respect to [HL1Pd]$^+$ suggests that the Pd-(bis-anilide) macrocycle binds less strongly to the track than the Pd-(benzylic amide) component (the relative pK$_a$'s of the protonated stations dominate the co-conformational energetics of [HL2Pd]$^+$). This weaker interaction might also result in a longer Pd-N(thread) bond and increased access to the metal centre, which would also be consistent with the lower activation barrier to shuttling. Whilst the weakening of this interaction might be expected to produce a poorer co-conformational bias in the absence of acid, in fact the bias for L2Pd is 12:1 DMAP:Py in comparison to 6:1 for L1Pd (Schemes 1a and 1b). The reasons for the rather counter-intuitive improved positional discrimination in this neutral state of the thread are probably a subtle balance of solvation, metal-ligand coordination and π-stacking effects.
In conclusion, we have described a second generation pH-switchable Pd(II)-complexed molecular shuttle which shows significantly increased rates of shuttling compared to the first generation system and also exhibits better positional discrimination of the macrocycle, somewhat surprisingly, in both chemical states of the rotaxane thread. The improved level of control should prove useful for the development of switchable, metastable, components for advanced molecular machinery, including Brownian ratchets$^1$ and synthetic molecular walkers$^9$.
Notes and references


[8] The italicised prefix (*DMAP*- or *Py*) refers to the position of the macrocycle in the rotaxane.