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Dual Stimuli-Responsive Interconvertible Heteroleptic Platinum Coordination Modes**

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^[†]Electronic Supplementary Information (ESI) available: Synthesis and characterisation of all new compounds, details of all irradiative and non-irradiative ligand exchange experiments. See <http://dx.doi.org/10.1039/C0CC01668C>

Graphical abstract:

Abstract

The exchange between different equilibrium and out-of-equilibrium platinum coordination modes can be orthogonally controlled thermodynamically with a proton input and kinetically using light.

Main text

The operational basis for devices and smart materials, such as molecular machines¹ and switchable polymers², is often a non-covalent (supramolecular) or transition metal-ligand motif which undergoes reversible change in response to an external stimulus. In almost all cases,³ the stimulus functions by adjusting the thermodynamic position of the equilibrium; in systems that rely upon exclusively weak interactions such as hydrogen-bonding or π - π interactions,^{1a-c} re-equilibration often occurs very quickly such that out-of-equilibrium states cannot be easily detected. In contrast, systems which utilise transition metal-ligand interactions often occur on a much slower timescale, minutes, hours or even days.^{4,5} As such, metastable states, which have been shown to be important in molecular electronics⁶ and machine ratcheting mechanisms⁷, can be observed or even isolated and these systems often require the input of heat to overcome the kinetic barrier to re-equilibration.^{5,8,9} However, heat does not alter the magnitude of this barrier and so cannot be thought of as a “kinetic stimulus”. Here we report the switchable behaviour of heteroleptic, acceptor-donor-type platinum coordination complexes in which we orthogonally use a proton input to adjust the equilibrium position and exploit light to selectively lower the energetic barrier to equilibration.

The system under study aimed to combine the preference of group 10 transition metals to selectively bind heterocycles as a function a basicity,^{2b,5} a thermodynamic bias that can be reversed by the addition of an equivalent of acid,⁵ with the known photochemical lability of 2nd and 3rd row transition metals. While light-promoted ligand exchange is well documented for Ru(II),¹⁰ in particular, it has recently been shown that the rates of Pt(II) substitution can also be increased upon photoirradiation.¹¹ In order to control the selective exchange of just a single ligand, we chose to investigate the neutral platinum motif¹² [LPt(PyR)] (Scheme 1) as it was envisaged that the tridentate, doubly charged L^{2-} would not undergo dissociation from the platinum centre on exposure to light. Initially, the thermodynamically downhill exchange of *N,N'*-dimethylaminopyridine (PyNMe₂) for the pyridine ligand of [LPt(PyH)] was investigated (Scheme 1a). Upon broad band 275-375 nm irradiation (with a λ_{max} of 312 nm, see Supporting information) of a 0.01 M solution of [LPt(PyH)] and PyNMe₂ in 1:1 [D₇]DMF:CD₂Cl₂, a steady-state equilibrium of 17:83 [LPt(PyH)]:[LPt(PyNMe₂)] was obtained after 10.5 h. To investigate the effect an increase in the pK_a difference of the two exchangeable heterocycles would have on both the thermodynamic bias and the rate of equilibration, the reaction of PyNMe₂ and [LPt(PyCF₃)] was also investigated (Scheme 1a). Under the same conditions (0.01 M, 1:1 [D₇]DMF:CD₂Cl₂) 4.5 h irradiation gave a steady-state ratio of 11:89

[LPt(PyCF₃)]:[LPt(PyNMe₂)]. In both cases, the exchange experiment was followed directly by ¹H NMR spectroscopy (Figure 1). To assess the effect of light, both reactions were also carried out under identical conditions (0.01 M in 1:1 [D₇]DMF:CD₂Cl₂, 313 K) but in the dark. The reaction of PyNMe₂ with [LPt(PyCF₃)] took 44 h to reach an equilibrium ratio of 15:85, within error of the ratio obtained under irradiative conditions,¹³ indicating that light significantly lowers the activation barrier to exchange without perturbing the relative ground state energies. In the absence of light, equilibration of [LPt(PyH)] with PyNMe₂ at the same temperature (313 K) gave a ratio of 28:72 after 11 days. However, the sluggishness of the thermal exchange process (even at 333 K), coupled with the slow but steady decomposition of the complexes that occurred after further, prolonged heating, ensured that this reaction could not be followed to completion.

Scheme 1. Dual stimuli-responsive exchange between Pt coordinated PyNMe₂ and PyR (R = H or CF₃) as a function of light and protons. All reactions carried out at 0.01 M in 1:1 [D₇]DMF:CD₂Cl₂ at 313 K, either in the presence or absence of light (broad band 275-375 nm). The ratios correspond to the equilibrium ratios

obtained after x h starting from (a) [LPt(PyR)]; (b) [*cis*-HLPt(PyR)(PyNMe₂)]OTs; (c) [*cis*-HLPt(PyNMe₂)(S)]OTs.¹⁵ ^aRatio taken prior to equilibration due to increasing decomposition caused by prolonged heating.^b264 h at 313 K and then 264 h at 333 K.¹⁵ ^c312 h at 313 K and then 264 h at 333 K.

Figure 1. ¹H NMR spectra (400 MHz, 1:1 [D₇]DMF:CD₂Cl₂, 300 K) of the photochemical reaction between [LPt(PyCF₃)] and PyNMe₂ over time. The *ortho* pyridyl protons of [LPt(PyNMe₂)] and free PyNMe₂ are highlighted in blue and the *ortho* pyridyl protons of [LPt(PyCF₃)] and free PyCF₃ in red.

The platinum-binding preference of the heterocycles cannot be reversed with just one equivalent of acid as addition of a stoichiometric amount of *para*-toluenesulfonic acid (TsOH) to a mixture of [LPt(PyNMe₂)] and PyR (R = H or CF₃) results in protonation of the C[^]N[^]C complexes to give [*trans*-HLPt(PyNMe₂)(PyR)]OTs (Scheme 1b).¹⁴ Furthermore, we reasoned that the stereochemical relationship of the PyNMe₂ and PyR ligands with respect to the strong *trans* influence of the phenylato group of HL⁻ would lead to isomers of noticeably different energy. To investigate this, [LPt(PyR)] (R = H or CF₃) were initially treated with TsOH and then with PyNMe₂ to give the presumed higher energy [*cis*-HLPt(PyR)(PyNMe₂)]OTs isomers. Upon light irradiation of these samples, it could be roughly observed that an increase in [*trans*-HLPt(PyNMe₂)(PyR)]OTs was accompanied by a decrease in [*cis*-HLPt(PyR)(PyNMe₂)]OTs (Scheme 1b). However, the complexity of these NMR spectra, caused in part by the unsymmetrical nature of the C[^]N complexes, prohibited a direct measure of the *cis:trans* complex ratio. Instead, an indirect measure was obtained by treating the samples, after irradiative equilibration was complete (6.5 h for R = H, 5 h for R = CF₃), with the base P₁-^tBu to affect cyclometallation, from

which ratios of 26:74 ($R = H$) and 20:80 ($R = CF_3$) [$LPt(PyR)$]:[$LPt(PyNMe_2)$] could be obtained.¹⁵ For comparison, the non-irradiative reactions produced ratios of 49:51 ($R = H$) and 30:70 ($R = CF_3$) after 11 days at 313 K and a further 11 days at 333 K. In both cases, the thermal reactions were halted prior to equilibrium due to small amounts of decomposition.

To reverse the coordinative bias of the heterocycles, it was anticipated that a second equivalent of acid could be used. Promisingly, the addition of 1 equiv. of TsOH to [*trans*- $HLPt(PyNMe_2)(PyR)$]OTs ($R = CF_3$ or H) in 1:1 [D_7]DMF: CD_2Cl_2 resulted in liberation of $PyR.TsOH$ along with formation of a complex we presume to be the solvato complex [*cis*- $HLPt(PyNMe_2)(S)$]OTs, where $S = [D_7]DMF$. Irradiation of these solutions resulted in the emergence of $PyNMe_2.TsOH$ and the concomitant reduction of $PyR.TsOH$ ($R = CF_3$ or H) (Scheme 1c). However, the complexity of these NMR spectra, again, prohibited a direct measure of the equilibrium position, so the samples were treated with P_1-^tBu after 5.2 h ($R = H$) and 5.5 h ($R = CF_3$) irradiation, from which ratios of [$LPt(PyR)$]:[$LPt(PyNMe_2)$] of 70:30 ($R = H$) and 85:15 ($R = CF_3$) were obtained. Again, for comparison, the thermal reactions produced ratios of 41:59 ($R = H$) and 63:37 ($R = CF_3$) after 13 days at 313 K and a further 11 days at 333 K. Both thermal reactions were again stopped prior to equilibrium due to small amounts of decomposition.

A likely mechanism for the pronounced rate enhancements upon irradiation is through excitation into a metal centred (MC) state with σ antibonding $d_{x^2-y^2}$ character.^{11a,b} Due to the heavy atom effect, it is probable that this proceeds *via* a ³MLCT (metal-ligand charge transfer) state, from which the ³MC state is thermally accessible.¹² However, strong field cyclometallated ligands are known to raise the energy of the MC state, which is why many similar Pt complexes are luminescent, rather than photochemically active, at room temperature.¹⁶ In this current investigation, it could be anticipated that the MC states of [$LPt(PyR)$] would be less accessible than the corresponding states for either [*cis*- $HLPt(PyR)(PyNMe_2)$]OTs or [*cis*- $HLPt(PyNMe_2)(S)$]OTs. This appears to be supported, experimentally, as the $C^{\wedge}N$ complexes exhibit greater irradiative rate enhancements in comparison to the thermal reactions (in effect, protonation photochemically activates the $C^{\wedge}N^{\wedge}C$ complexes).¹⁷ Interestingly, it is known that the related $C^{\wedge}N^{\wedge}C$ complex [$LPt(CNPh)$] is not luminescent at room temperature and a recent theoretical analysis has shown that a likely reason for this is due to significant distortion of the triplet ground state, which reduces the ligand field and brings the MC state into thermal range.¹⁸

In conclusion, we have described the orthogonal, dual stimuli-responsive behaviour of heteroleptic cyclometallated platinum complexes, in which protons are used to switch the thermodynamic bias, and in which light functions as a true kinetic stimulus by lowering the activation barrier to ligand exchange. We envisage that switchable complexes such as these, where both the thermodynamic and kinetic components of switching can be independently manipulated, will play a pivotal role in the development of future devices and smart materials.

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