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Acid–base responsive switching between "3+1" and "2+2" platinum complexes†

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We report that the acid–base induced changes to a cyclometallated platinum complex can be used to drive the exchange of accompanying ligands with different denticities.

Central to the development of synthetic molecular machines is the discovery of new externally addressable, switchable molecular or supramolecular elements.[1] Bistable rotaxanes and catenanes which utilise transition metal–ligand interactions are particularly attractive,[2–5] not least because their inherent strength can be used for purposes such as ratcheting.[6] Another desirable feature of switchable systems is that they should exhibit a large thermodynamic bias in both states. In this regard, the benchmark for systems where the metal ion remains integrated during operation[4] is still Sauvage's exploitation of the preferred coordination differences of Cu(I) and Cu(II), which was first described nearly twenty years ago.[2a] Herein, we describe cyclometallated platinum motifs which are able to exchange monodentate and bidentate ligands with excellent selectivity in response to acid–base stimuli.

We recently reported that 2,6-diphenylpyridine ($H_2\mathbf{L^1}$) can coordinate to platinum(II) either as a doubly anionic tridentate or monoanionic bidentate ligand, and that this can be exploited to assemble–disassemble metallosupramolecular architectures based on *cis*-coordinating multitopic pyridyl ligands.[7] As well as accepting two monodentate ligands, we envisaged that a platinum complex where $H\mathbf{L^1}$ coordinates in a η^2 C^N fashion would be able to accommodate a neutral bidentate ligand. Thus, when [$\mathbf{L^1}$Pt(DMSO)] was treated with a mixture of *para*-toluene sulfonic acid (TsOH) and 5,5′-dimethyl-2,2′-bipyridine (dmbipy) in CH_2Cl_2, a compound was isolated which spectroscopic data indicated was the "2+2" complex, [$H\mathbf{L^1}$Pt(dmbipy)]OTs. For instance, the ^{1}H NMR spectrum (see ESI†) showed that the two pyridyl "halves" of the dmbipy ligand resonate quite differently, fully consistent with the occupation of the *trans*-to-nitrogen and *trans*-to-phenylato coordination sites, the latter which experiences pronounced shielding from the non-coordinating phenyl group of $H\mathbf{L^1}$. The structure of [$H\mathbf{L^1}$Pt(dmbipy)]OTs, confirmed by X-ray crystallography (Fig. 1a) using crystals grown from diisopropyl ether and chloroform, shows that while platinum adopts a near planar geometry (the Pt ion sits just 0.078 Å above the mean N_3C coordination plane) there is significant distortion and twisting of the ligands to alleviate steric clash between the non-coordinating phenyl group and the adjacent dmbipy ligand such that the complex adopts an overall helical twist.[8] In the solid state, both *P* and *M* enantiomers are observed, although in solution at room temperature the interconversion appears to be rapid.[9]

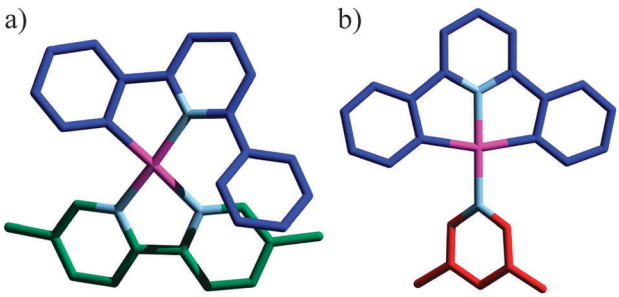

Fig. 1 X-ray crystal structures of (a) [$H\mathbf{L^1}$Pt(dmbipy)]OTs and (b) [$\mathbf{L^1}$Pt(3,5-lut)]. Colour code: C($\mathbf{L^1}$/$H\mathbf{L^1}$), blue; C(3,5-lut), red; C(dmbipy), green; N, light blue; Pt, magenta. Counter anion and solvent molecules have been removed for clarity.

To explore whether other neutral monodentate ligands would be similarly displaced, experiments starting with [$\mathbf{L^1}$Pt(py)], [$\mathbf{L^1}$Pt(3,5-lut)] and [$\mathbf{L^1}$Pt(DMAP)] (py = pyridine; 3,5-lut = 3,5-lutidine; DMAP = 4-dimethylaminopyridine) have been undertaken (Scheme 1). In the absence of TsOH, ^{1}H NMR spectroscopy shows that, in all cases, dmbipy does not displace the monodentate ligand and remains uncoordinated (see the ESI,† Fig. S1–S3). For [$\mathbf{L^1}$Pt(py)], the addition of a slight excess (1.3 eq.) of TsOH to the charge neutral complex and dmbipy results in the rapid displacement of the monodentate ligand and concomitant generation of [$H\mathbf{L^1}$Pt(dmbipy)]OTs (Scheme 1 and Fig. S1, ESI†). When similar ligand exchange experiments were carried out with [$\mathbf{L^1}$Pt(3,5-lut)] and [$\mathbf{L^1}$Pt(DMAP)], it was found that the addition of over two equivalents of TsOH was required in order to

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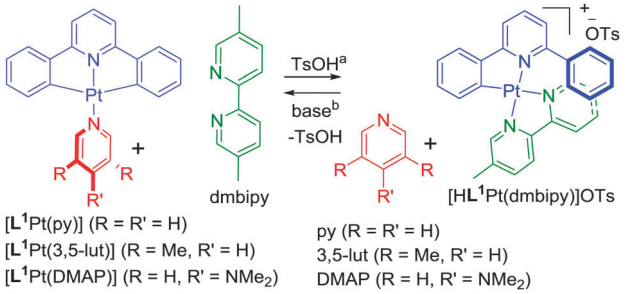


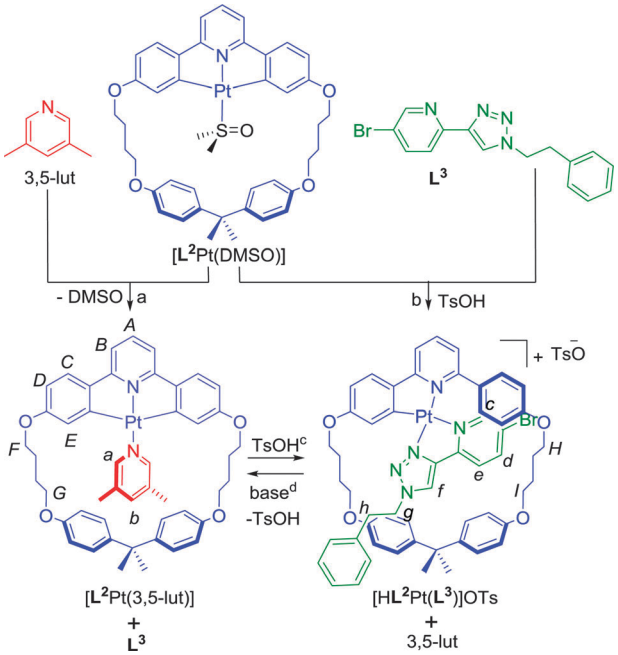
Scheme 1 Acid–base interconversion between ''3+1'' and ''2+2'' cyclometallated Pt complexes. Conditions: [a] 1.3–2.7 eq. TsOH, CD_2Cl_2, 298 K, 5 min; [b] P_1-^{t}Bu, CD_2Cl_2, 298 K, 1.5–2 h.

generate the "2+2" complex (Fig. S2 and S3, ESI†). We attribute this difference to two main factors – (i) the increased basicity of the liberated 3,5-lut and DMAP heterocycles, which leads to partial re-cyclometallation and (ii) the formation of more stable "2+1+1" intermediates (*e.g.* [HL^{1}Pt(DMAP)OTs] and [HL^{1}Pt(3,5-lut)OTs]), from which the chelate-driven displacement of DMAP/3-5-lut and tosylate ligands by dmbipy requires additional proton-assistance (for further discussion of these processes, see the ESI†).

As the pyridyl-based ligands are not replaced in the absence of acid, we predicted that simply adding base to a mixture of [HL^{1}Pt(dmbipy)]-OTs and monodentate moiety would reverse the coordinative bias. We have previously used the phosphazene base, P_1-^{t}Bu, to affect (re)cyclometallation.[7] Thus, when P_1-^{t}Bu was added to the mixture of [HL^{1}Pt(dmbipy)]OTs and monodentate pyridyl ligand (py, 3,5-lut or DMAP), the gradual disappearance of signals due to [HL^{1}Pt(dmbipy)]-OTs and re-appearance of [L^{1}Pt(py)], [L^{1}Pt(3,5-lut)] and [L^{1}Pt(DMAP)] followed 1.5–2 h at room temperature (Scheme 1 and Fig. S1–S3, ESI†).

To develop the system further, and with a stimuli-responsive molecular shuttle in mind, the macrocyclic C^N^C Pt complex, [L^{2}Pt(DMSO)], has been prepared. The free macrocycle, H_2L^2, was obtained in an excellent 80% from 2,6-di-(4-hydoxyphenyl)pyridine[10] and a bisphenol A derived dialkylbromide,[11] while insertion of platinum also occurs in an highly respectable 80% yield (see ESI†). From [L^{2}Pt(DMSO)], [L^{2}Pt(3,5-lut)] was prepared by exchange of the coordinated DMSO for 3,5-lut (Scheme 2, step a). The structure of [L^{2}Pt(3,5-lut)] has been confirmed by X-ray crystallography using single crystals grown from slow diffusion of diethyl ether into a saturated dichloromethane solution (Fig. 2). In solution, the ^{1}H NMR spectrum of [L^{2}Pt(3,5-lut)] (Fig. 3a) exhibits coordinated *ortho* lutidine signals (H_a) with characteristic ^{195}Pt satellites, while the *para* site (H_b) is significantly upfield shifted with respect to the free heterocycle, most likely due to shielding by the bisphenol A unit.

The TsOH induced formation of a "2+2" complex from [L^{2}Pt(DMSO)], this time using the unsymmetrical bidentate 2-(1-ethyl-phenyl-1*H*-1,2,3-triazol-4-yl)-5-bromopyridine (L^3) was also carried out (Scheme 2, step b). The ^{1}H NMR spectrum of the product revealed several interesting features (Fig. 3e). Firstly, when it could be reasonably expected that a mixture of both geometric isomers would result, only one – *trans*-[HL^{2}Pt(L^3)]OTs (see the ESI† for details of assignment using NOESY) – is produced. As the NMR of this product did not change over time, we would suggest that this product is both the kinetically and thermodynamically favoured isomer, as it has been previously observed that platinum isomers which feature cyclometallated ligands undergo sluggish rearrangement.[12] The second thing to note from the ^{1}H NMR



Scheme 2 Synthesis of, and acid–base responsive interconversion between, ''3+1'' and ''2+2'' macrocyclic cyclometallated Pt complexes. Conditions: [a] CH_2Cl_2, 313 K, 16 h, 37%; [b] CH_2Cl_2, 298 K, 1 h, 34%; [c] 1.7 eq. TsOH, CD_2Cl_2, 298 K, 5 min; [d] 5 eq. P_1-^{t}Bu, CD_2Cl_2, 298 K, 48 h.

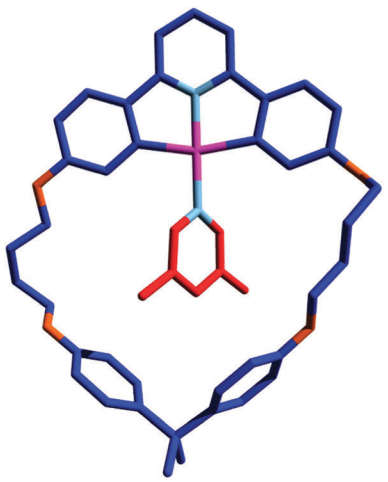


Fig. 2 X-ray crystal structure of [L^{2}Pt(3,5-lut)]. Colour code: C(L^2), blue; C(3,5-lut), red; N, light blue; O, orange; Pt, magenta. Solvent molecules have been removed for clarity.

spectrum of [HL^{2}Pt(L^3)]OTs (Fig. 3e) is the sterically congested nature of the complex, as the four triplets that arise from the H_F, H_G, H_g and H_h environments in the [L^{2}Pt(3,5-lut)] and L^3 precursors have been replaced by a complex diastereotopic pattern of signals.

Finally, the "3+1" to "2+2" interconversion between [L^{2}Pt(3,5-lut)] and [HL^{2}Pt(L^3)]OTs was examined using ^{1}H NMR spectroscopy (Scheme 2 and Fig. 3b–d). When L^3 was mixed with [L^{2}Pt(3,5-lut)] in CD_2Cl_2, only signals which are attributable to those two species were apparent (Fig. 3b). Upon the addition of 1.7 eq. of TsOH, the NMR spectrum changed to give a set of signals that were virtually indistinguishable from those of *trans*-[HL^{2}Pt(L^3)]OTs (Fig. 3c). As with the acyclic system, this change occurred within the time taken to record a subsequent spectrum. This rapid generation coupled to

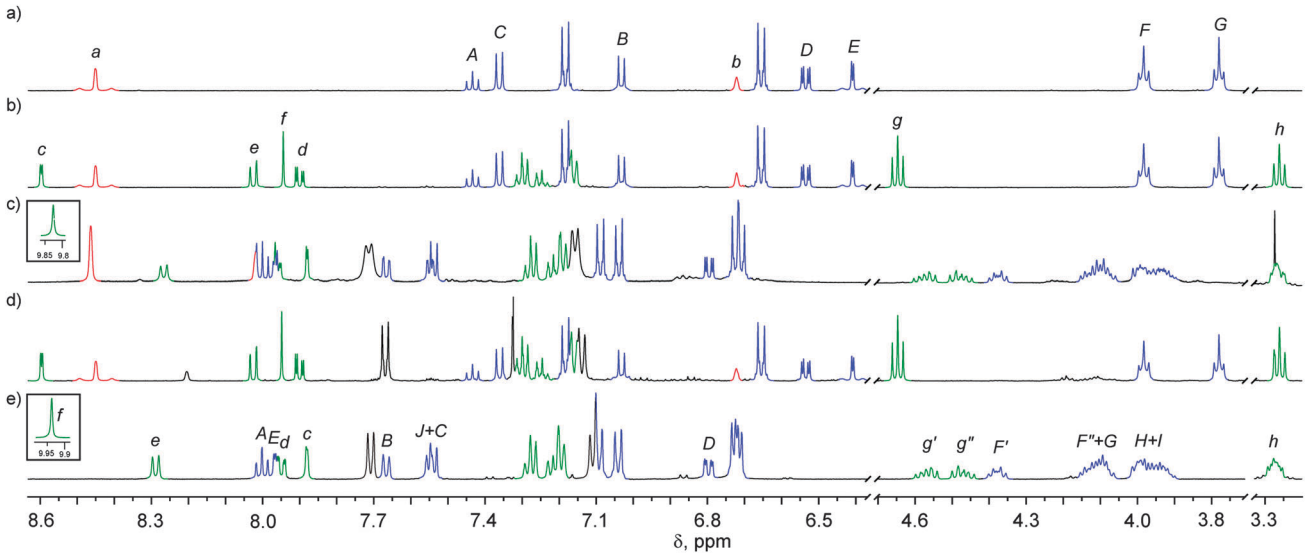


Fig. 3 Partial ^{1}H NMR spectra (CD_2Cl_2, 500 MHz, 300 K) showing interconversion between "3+1" and "2+2" macrocyclic cyclometallated Pt complexes. (a) [$\mathbf{L}^2$Pt(3,5-lut)]; (b) a 1 : 1 mixture of [$\mathbf{L}^2$Pt(3,5-lut)] and $\mathbf{L}^3$; (c) a 1 : 1 mixture of [$\mathbf{L}^2$Pt(3,5-lut)] and $\mathbf{L}^3$, 5 minutes after the addition of TsOH (1.7 eq.); (d) 48 h after the addition of P_1-^{t}Bu (5 eq.) to a solution of [H$\mathbf{L}^2$Pt($\mathbf{L}^3$)]OTs and 3,5-lut; (e) [H$\mathbf{L}^2$Pt($\mathbf{L}^3$)]OTs. Macrocycle signals are shown in blue, 3,5-lut in red and $\mathbf{L}^3$ in green. The assignments correspond to the lettering shown in Scheme 2.

the lack of observation of another isomer further supports that *trans*-[H$\mathbf{L}^2$Pt($\mathbf{L}^3$)]OTs is the kinetic (and thermodynamic) product, irrespective of the neutral monodentate ligand in the starting "3+1" complex. When five eq. of P_1-^{t}Bu was added to the NMR sample containing [H$\mathbf{L}^2$Pt($\mathbf{L}^3$)]OTs and free lutidine, the signals due to the "2+2" complex and monodentate ligand started to disappear, accompanied by the appearance of signals due to [$\mathbf{L}^2$Pt(3,5-lut)] and free $\mathbf{L}^3$. After 48 h, only signals due to [$\mathbf{L}^2$Pt(3,5-lut)] and free $\mathbf{L}^3$ could be observed (Fig. 3d). The sluggishness of this reaction in comparison to the same process for the acyclic complexes is almost certainly due to an increased steric barrier. We are currently investigating methods of lowering this by employing different bases/anions and/or using light to accelerate ligand exchange.[12a]

In summary, a rare example of a metallosupramolecular switch which can be alternated with excellent selectivity between different states using acid–base inputs has been described. We envisage that these types of externally addressable coordination complexes will continue to play a significant role in the development of molecular machines.

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