

# Metal hurdling in transition-metal complexes of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) and 2,4,6-tris-(2-pyridyl)pyrimidine (tpp)

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**<sup>1</sup>H NMR two-dimensional exchange spectroscopy (EXSY) reveals that in palladium(II) and platinum(II) complexes of the ligands 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) and 2,4,6-tris(2-pyridyl)pyrimidine (tpp), a highly novel type of fluxion occurs in which the metal moiety hurdles a C–C bond and moves from one edge of the central ligand ring to an adjacent edge; this process is accompanied by 1,4 metallotropic shifts analogous to those found in complexes of 2,2':6',2''-terpyridine.**

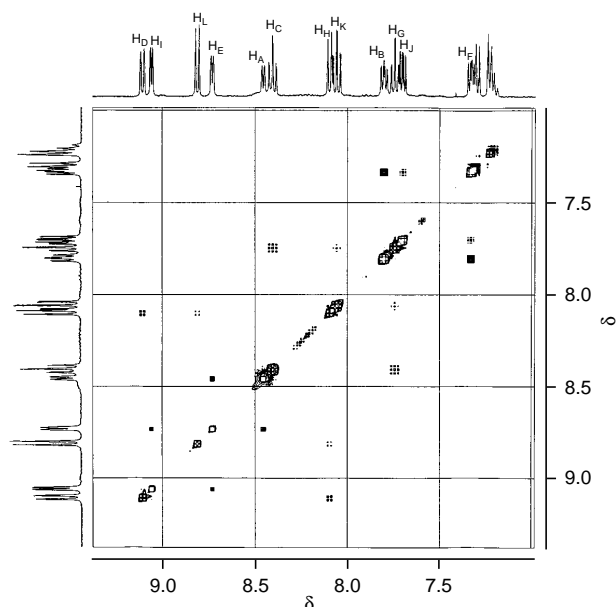
Since our discovery that 2,2':6',2''-terpyridine (terpy) acts as a fluxional bidentate ligand to certain metals<sup>1–4</sup> we have revealed analogous 1,4 metallotropic shifts in a range of rhenium(I) or platinum(IV)<sup>5–7</sup> complexes of N,N,N-ligands based on combinations of pyridine, pyrazole, pyrimidine and 1,3,5-triazine rings. Recently we have presented NMR evidence that the metallotropic shift in 2,2':6',2''-terpyridine complexes occurs through a purely associative process.<sup>8</sup> We have now turned our attention to transition-metal complexes of the related trigonal planar ligands 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) and 2,4,6-tris(2-pyridyl)pyrimidine (tpp).

The presence of more than one N heteroatom in the central ring in these ligands allows for much greater variety of fluxionality compared to terpy complexes. In the <sup>1</sup>H two-dimensional EXSY spectrum of the complex [Pt(C<sub>6</sub>F<sub>4</sub>CF<sub>3</sub>-*p*)<sub>2</sub>(tpt)] at 393 K, in addition to the exchanges of H<sub>A</sub>–H<sub>D</sub> (ring 1) with H<sub>E</sub>–H<sub>H</sub> (ring 2) associated with the 1,4 metallotropic shift, exchange of H<sub>E</sub>–H<sub>H</sub> (ring 2) with H<sub>I</sub>–H<sub>L</sub> (ring 3) was also observed (Fig. 1 and Scheme 1). This second exchange between uncoordinated pyridyls can only be rationalised by a movement of the metal moiety from one side of the pyridyl–triazine C–C bond of the chelate ring to the other. Such 'hurdling' of the C–C bond by the metal moiety can be achieved in two ways, either by full dissociation of the metal centre from the ligand followed by recombination, or, by partial dissociation, by the breaking of a single metal–nitrogen bond (that to the triazine), followed by 180° rotation of the metal-bound pyridyl about the pyridyl–triazine bond, followed by recombination of the metal to the new triazine nitrogen. The first process would lead to an equal probability of the metal recombining at nitrogens on any pair of adjacent rings, and hence exchange between hydrogens of all pyridine rings would occur with equal rates. As this is not seen, in fact no exchange between the hydrogens of rings 1 and 3 (Scheme 1 and Fig. 1) is observed, we conclude that the second partially dissociative process occurs with the metal effectively hurdling the pyridyl–triazine bond and recombining to the triazine.

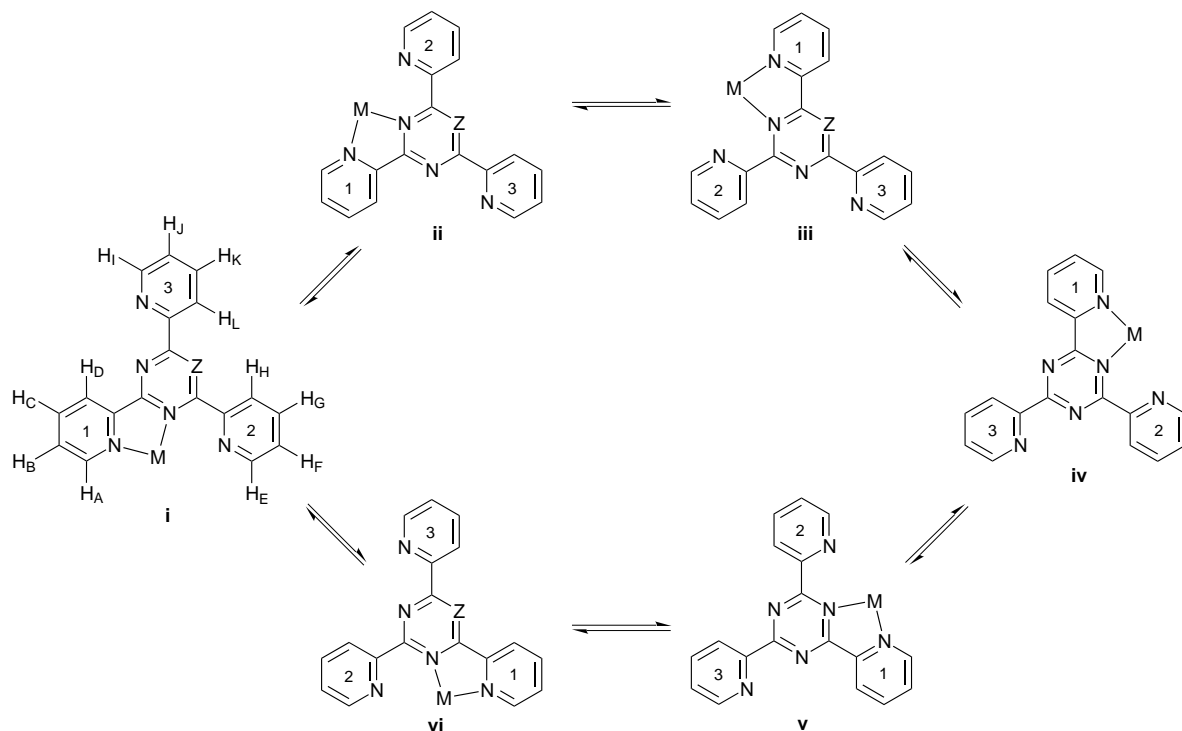
Rates of the metallotropic shift and rotational hurdling processes were found, by high-temperature quantitative <sup>1</sup>H two-dimensional EXSY experiments, to be comparable. A combination of the two processes enables the metal moiety to move completely round the outside of the triazine ring passing through structures **i**–**vi** (Scheme 1). The rate of the metallotropic shift relative to that of the rotation was found to increase more rapidly with temperature leading to a slightly higher activation energy ( $\Delta G^\ddagger$ ) than for the hurdling process (Table 1).

In the complex [Pd(C<sub>6</sub>F<sub>4</sub>CF<sub>3</sub>-*p*)<sub>2</sub>(tpt)] metallotropic shifts and metal hurdling processes occur at measurable rates at ambient temperatures. Consequently, <sup>19</sup>F one-dimensional bandshape analysis (of CF<sub>3</sub> signals) over a temperature range 293–403 K enabled the metallotropic shift to be monitored, and a <sup>1</sup>H two-dimensional EXSY experiment at room temperature provided an estimate of the activation energy for the hurdling process (Table 1).

Metal complexes of the pyrimidine-based ligand tpp differ in two fundamental ways from those of tpt. Firstly, while all tpt chelate complexes are degenerate with equal populations of coordination species, in tpp complexes the two coordination species are chemically different and so differing populations are expected. Surprisingly, there was a very great imbalance in populations, namely 99 : 1. It is known that in the X-ray crystal structure of terpyridine the nitrogens adopt a *trans,trans* configuration,<sup>9</sup> and, by analogy, this will be the preferred configuration in tpp. This can be achieved by rotation of the pyridyls attached to the 4- and 6-positions of the pyrimidine ring. However, when the 2-position pyridyl ring is coplanar with the other rings, its nitrogen donor is inevitably *cis* to one of the pyrimidine nitrogens and thus ideally placed to effect metal chelation. Thus, in Scheme 1, complexes **i** and **ii** are strongly preferred over **iii** and **vi**. The second major difference from the tpt complexes is that no combination of metallotropic shifts and rotational hurdling will allow the metal to move completely round the ligand. Only one rotation and two 1,4 shifts are



**Fig. 1** <sup>1</sup>H NMR two-dimensional EXSY spectrum (at 393 K, mixing time 0.8 s) of [Pt(C<sub>6</sub>F<sub>4</sub>CF<sub>3</sub>-*p*)<sub>2</sub>(tpt)] in CDCl<sub>2</sub>, CDCl<sub>2</sub> showing exchanges due to both the 1,4 metallotropic shift (H<sub>A</sub>–H<sub>D</sub> ⇌ H<sub>E</sub>–H<sub>H</sub>) and the rotational hurdling process (H<sub>E</sub>–H<sub>H</sub> ⇌ H<sub>I</sub>–H<sub>L</sub>). The unlabelled signals at δ 7.2–7.3 are due to an unknown impurity.



**Scheme 1** The exchange pathways for both the 1,4-metallotropic shift and rotational hurdling processes in  $[M(C_6F_4CF_3-p)_2L]$  complexes [ $M = Pt$  or  $Pd$ ;  $L = tpt$  ( $Z = N$ ) or  $tpp$  ( $Z = CH$ )]. Individual rings are numbered to show how exchange affects their chemical environments. In the case of  $L = tpt$  the metal can travel completely round the ligand exchanging all six structures **i–vi** while in the  $L = tpp$  complexes this motion is restricted to only four of them **i–iii** and **vi** as coordination to  $Z = CH$  is impossible.

**Table 1** Activation energy data for both the 1,4-metallotropic shift and hurdling rotation

Complex	$\Delta G^\ddagger$ (1,4 shift) <sup>a/</sup> kJ mol <sup>-1</sup>	$\Delta G^\ddagger$ (hurdling)/ kJ mol <sup>-1</sup>
$[Pt(C_6F_4CF_3-p)_2(tpt)]$	$102.7 \pm 0.4^b$	$92.5^c$
$[Pd(C_6F_4CF_3-p)_2(tpt)]$	$72.0 \pm 0.2^d$	$73.7^e$
$[Pt(C_6F_4CF_3-p)_2(tpp)]$	$117.7^{f,g}$	$113.0^g$
$[Pd(C_6F_4CF_3-p)_2(tpp)]$	$69.0^{f,h}$	— <sup>i</sup>

<sup>a</sup> At 298 K unless otherwise stated. <sup>b</sup> Based on results of two-dimensional EXSY experiments. <sup>c</sup> Calculated at 298 K from high-temperature two-dimensional EXSY experiments. <sup>d</sup> Based on bandshape analysis of one-dimensional <sup>19</sup>F spectra (*p*-CF<sub>3</sub> groups). <sup>e</sup> Based on two-dimensional EXSY at 303 K. <sup>f</sup> For major → minor exchange pathway. <sup>g</sup> Based on two-dimensional EXSY at 413 K. <sup>h</sup> Based on bandshape analysis of one-dimensional <sup>1</sup>H spectra (pyrimidyl hydrogens). <sup>i</sup> Not measured.

possible, since complexes of type **iv** and **v** in Scheme 1 do not exist for *tpp* complexes.

The <sup>1</sup>H two-dimensional EXSY spectrum of the complex  $[Pt(C_6F_4CF_3-p)_2(tpp)]$  at 413 K shows exchange of the signals H<sub>E</sub>–H<sub>H</sub> (ring 2) with H<sub>I</sub>–H<sub>L</sub> (ring 3); such an exchange between signals of major solution species can only be due to the presence of the rotational hurdling process as the 1,4-metallotropic shift would exchange signals of major and minor species. Despite the very low populations of the minor species and the fact that not all their signals could be unambiguously detected in the one-dimensional spectrum, all exchange cross peaks due to the 1,4-metallotropic shift could be observed in the two-dimensional EXSY spectrum leading to the identification of the chemical shifts of all hydrogens in the minor species. Rates of metallotropic shift and rotational hurdling are again of comparable magnitude, although the calculated activation energies are slightly higher than for the *tpt* complexes (Table 1), presumably reflecting the differing basicities of the pyrimidine and triazine centres.

Both metal hurdling and 1,4-shifting processes were also detected in  $[Pd(C_6F_4CF_3-p)_2(tpp)]$ , this time at room temperature as in the case of the Pd<sup>II</sup>–*tpt* complex. In contrast, no evidence of the metal hurdling process was found for the octahedral complex  $[ReBr(CO)_3(tpt)]$ ; only the 1,4-shift process occurs. This implies that axial ligands on the metal sterically prevent the metal moiety from rotating over (or under) the pyridyl–triazine C–C bond. Presumably the same negative result would be found for the isoelectronic metal moiety PtBrMe<sub>3</sub>.

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