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Synthesis and dynamic NMR studies of fluxionality in palladium(II) and platinum(II) 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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Abstract

Complexes of general formulae cis-[M(C₀F₄CF₃)₂L] (M = Pd^{II}, Pt^{II}; L = 2,4,6-tris(2-pyridyl)-1.3,5-triazine (TPT) and 2,4,6-tris(2-pyridyl)-pyrimidine (TPP)) were isolated as air-stable solids. In all cases cis square-planar complexes were formed with the nitrogen ligands acting as bidentate chelates towards each metal moiety. The complexes exhibited various modes of fluxionality in solution, namely 1,4metallotropic shifts, a new 'metal hurdling' fluxion and, at below-ambient temperatures, restricted rotation of the pendant pyridyl ring adjacent to the metal chelate ring. Dynamic NMR experiments (one-dimensional bandshape analysis and two-dimensional EXSY experiments) provided activation energy data for these processes. Gibbs free energy values (ΔG^* (298.15 K)) were in the ranges 74–113 (metal hurdling). 69–118 (metal 1,4-shifts) and 37–43 (pendant pyridyl rotations) kJ mol⁻¹. Energies of any of these fluxions were considerably higher in the Pt^{II} complexes than in the Pd^{II} complexes.

To aid understanding of the low temperature fluxionality of the TPT complexes, the complex $[Pd(C_F_2CF_1)_1(mstd)]$ (mstd=mesostilbenediamine) was synthesised. At low temperatures, $C_6F_4CF_7$, ring rotations and five-membered ring puckering in this complex were arrested, ΔG^* (208 K) for the latter process being 42.8 kJ mol⁻¹. © 1997 Elsevier Science S.A.

Keywords: Platinum(II) complexes; Palladium(II) complexes; Pyridyl-based ligand complexes; Fluxional processes; Dynamic NMR

1. Introduction

2,4,6-Tris(2-pyridyl)-1,3,5-triazine (TPT) has been employed for many years as a strong binding agent to metals [1-3]. Its normal single-metal binding mode is terdentate [4,5], but it can form dimetallic complexes where it acts simultaneously as a bidentate and terdentate ligand [6]. In such cases the stereochemistry of the ligand is effectively locked by the two metal moieties. Our interest in this ligand centres on its potential fluxionality when only two of its six nitrogen donors are involved in chelation with a single metal. We have shown that in 2,4,6-tris(pyrazol-1-yl)-1,3,5-triazines [7] fluxionality occurs readily in the form of 1,4metallotropic shifts (tick-tock twists). An analogous fluxion occurs when the central ligand ring is pyrimidine rather than 1,3,5-triazine, but now there is strong preference for one of the two possible chemically distinct coordination complexes [8].

The aim of this present study is to understand more fully the solution fluxional properties of bidentate chelate complexes of TPT and its pyrimidyl analogue TPP (2,4,6-tris(2pyridyl)-pyrimidine) by examining solution NMR properties, over a wide temperature range, of four-coordinate square-planar complexes of Pd(C₆F₄CF₃)₂ and Pt(C₆F₄-CF₃)₂. The perfluoro-p-tolyl groups were chosen as suitable 'spectator' ligands for following any fluxionality via ¹⁹F NMR. This paper describes the solution properties of 1:1 metal:ligand complexes. 2:1 Metal:ligand complexes will be described elsewhere.

2. Experimental

2.1. Materials

2.4,6-Tris(2-pyridyl)-1,3,5-triazine (TPT) was purchased from Aldrich and recrystallised before use from 1:1 dichloromethane/hexane. 2,4,6-Tris(2-pyridyl)-pyrimidine (TPP) was prepared according to a literature method [9]

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and characterised by NMR spectroscopy. The metal precursors trans- $[Pd(C_6F_4CF_3)_2(1.4-dioxane)_2]$ [10] and trans- $[Pt(C_6F_4CF_3)_2(Et_2S)_2)$] [11] were prepared by previously published procedures.

2.2. Synthesis of complexes

All manipulations were performed under an atmosphere of dry, oxygen-free nitrogen by standard Schlenk techniques [12], using freshly distilled, dried and degassed solvents.

2.2.1. Cis-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)(2,4,6-tris(2-pyridyl)-1,3,5-triazine)palladium(II) [Pd(C₆F₄CF₃)₂(TPT)]

The complex trans-[Pd($C_6F_4CF_3$)₂(1,4-dioxane)₂] (0.1 g, 0.14 mmol) was dissolved in a mixture of diethyl ether and dichloromethane (1:1, 20 cm³) and added to a dichloromethane solution (10 cm³) of TPT (0.08 g, 0.26 mmol). A cloudy pale yellow solution was immediately formed. The reaction mixture was stirred for 30 nin, filtered and concentrated under vacuum at roorn temperature to half volume, giving a clear yellow solution. The crude material crystallised upon cooling to -20° C and was filtered off, washed with hexane (2×10 cm³) and recrystallised from dichloromethane:hexane (1:1). The pure material was obtained as a yellow crystalline solid. Yield 0.12 g (71%).

2.2.2. Cis-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)(2,4,6-tris(2-pyridyl)-1,3,5-triazine)platinum(II) [Pt(C₆F₄CF₃)₂(TPT)]

The complex trans- [Pt(C₆F₄CF₃)₂(Et₂S)₂] (0.20 g, 0.25 mmol) was dissolved in toluene (10 cm³) and added to a dichloromethane:hexane solution (1:2, 15 cm³) of TPT (0.08 g, 0.26 mmol). The reaction mixture was refluxed for 20 h, giving a clear orange solution, which was evaporated to dryness under reduced pressure. The resulting yellow solid was washed with diethyl ether (5 cm³) and dried under vacuum. Yield 0.15 g (63%).

2.2.3. Cis-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)(2,4,6-tris(2-pyridyl)pyrimidine)palladium(II) [Pd(C₆F₄CF₃)₂(TPP)]

The complex trans $[Pd(C_cF_4CF_3)_2(1,4-dioxane)_2]$ (0.10 g, 0.14 mmol) was dassolved in dichloromethane (40 cm³) and added to a dichloromethane solution (20 cm³) of TPP (0.05 g, 0.14 mmol). The clear yellow solution immediately turned cloudy. The reaction mixture was stirred for 1 h at room temperature and then filtered. The solution was concentrated under vacuum and addition of hexane (50 cm³) yielded a yellow solid. The product was washed with hexane (2×20 cm³), dried under vacuum and recrystallised from dichloromethane:hexane (1:1). The pure material was obtained as a yellow microcrystalline solid. Yield 0.06 g (53%).

2.2.4. Cis-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)(2,4,6-tris(2-pyridyl)pyrimidine)platinum(II) [Pt(C₆F₄CF₃)₂(TPP)]

The complex trans- $[Pt(C_6F_4CF_3)_2(Et_2S)_2]$ (0.20 g, 0.25 mmol) was dissolved in benzene (15 cm³) and added to a benzene solution (15 cm³) of TPP (0.08 g, 0.25 mmol). The reaction mixture was refluxed for 30 h, giving a clear golden solution. The solution was concentrated under vacuum and addition of hexane (50 cm³) yielded a yellow solid. The product was washed with hexane (2×20 cm³), dried under vacuum and recrystallised from dichloromethane:hexane (1:1). The pure material was obtained as a yellow micro-crystalline solid. Yield 0.16 g (69%).

2.2.5. Cis-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)(meso-stilbenediamine)palladium(II) [Pd(C₆F₄CF₃)₂(mstd)]

The complex $[Pd(C_6F_4CF_3)_2(1.4-dioxane)_2]$ (0.10 g, 0.14 mmol) was dissolved in a mixture of diethyl ether and dichloromethane (1:1, 40 cm³), and added to a dichloromethane solution (5 cm³) of *meso*-stillenediamine (0.03 g, 0.14 mmol). The reaction mixture was stirred at room temperature for 1 h and then filtered, to give a clear yellow solution. Concentration under vacuum and addition of hexane (20 cm³) yielded the desired pure product as a white precipitate. Yield 0.06 g (60%).

2.3. Physical methods

Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex, UK. Melting points were recorded open to air on a digital Gallenkamp melting point apparatus and are uncorrected.

IR spectra were recorded as CsI discs on a Nicolet Magna 550 FT-IR spectrometer. 'H NMR spectra were recorded on either a Bruker AC300 FT spectrometer operating at 300.13 MHz or on a Bruker DRX-400 FT spectrometer operating at 400.13 MHz. 19F spectra were recorded on either of the above instruments, at 283.34 and 376.46 MHz, respectively. 'H NMR chemical shifts are quoted relative to Me₄Si ($\delta = 0$) and ¹⁹F shifts relative to C_6F_6 ($\delta=0$) as internal standards. Variable temperature NMR spectra were obtained using the Bruker variable temperature units B-VT 100 (AC300) and B-VT 2000 (DRX-400). Two-dimensional exchange (EXSY) spectra and homonuclear correlated (COSY) spectra were obtained using the standard Bruker programs NOESYPH.AU and COSY.AU, respectively. The relaxation delay was typically 2 s and the evolution time had an initial value of 3×10⁻⁶ s. Mixing times in the EXSY experiments were chosen in the range 0.5-1.5 s according to the nature of the complex and its temperature of measurement. Rate data were derived from bandshape analysis of the 'H or 19F NMR spectra using a version [13] of the DNMR3 program [14], or from 2D-EXSY spectra using volume integration data in the authors' D2DNMR program [15]. Activation parameters based on experimental rate data were calculated using the THERMO program [13].

3. Results

3.1. Complexes cis- $[M(C_6F_4CF_3)_2(TPT)]$ ($M = Pd^{II}$ or Pt^{II})

These complexes were prepared from the reaction of the ligand TPT with trans-[Pd(C₆F₄CF₃)₂(1,4-dioxane)₂] or trans-[Pt(C₆F₄CF₃)₂(Et₂S)₂]. They were air-stable, yellow crystalline solids, soluble in most chlorinated solvents but insoluble in hexane. IR spectra (Table 1) exhibited two metal-carbon stretching vibrations [16,17] indicative of a *cis* relationship of the two C₆F₄CF₃ groups in a square-planar complex. Elemental analysis data for these, and the other complexes, are given in Table 1.

3.1.1. Ambient temperature 'H NMR spectra

The room temperature spectra of both complexes showed 12 well resolved multiplet signals which were unambiguously assigned with the aid of COSY spectra (and EXSY spectra,

Table 1

Synthetic and analytical data for the complexes

3.1.2. Ambient temperature ¹⁹F NMR spectra

These spectra were also consistent with *cis*-square-planar complexes of Pt^{II} or Pd^{II} (Fig. 1). Six distinct fluorine environments were detected, these being attributed to the *ortho*and *theta*-ring fluorines, and the *para*-CF₃ fluorines of the two non-equivalent C₆F₄CF₃ rings. Chemical shifts are listed in Table 3 and the main three- and four-bond F-F scalar coupling constants in Table 4. Ortho- and *meta*-fluorine signals showed further partially resolved splittings due to crossring couplings but these are not listed. The spectrum of the Pt^{II} complex also exhibited ³J(¹⁹⁵Pt-¹⁹F) coupling to the ortho-ring fluorine nuclei.

Complex	Colour	M.p. * (°C)	Yield *	VM-C	Analysis ^a (%)		
			(%)	(cm ⁻)	с	н	N
$[Pd(C_6F_4CF_3)_2(TPT)]$	yellow	216-217	71	778(m), 733(w)	44.50 (45.07)	1.90 (1.42)	9.30 (9.85)
$[Pt(C_6F_4CF_3)_2(TPT)]$	yellow	244-248	63	808(m), 768(s)	40.47	1.32	8.50 (8.93)
$[Pd(C_6F_4CF_3)_2(TPP)]$	yellow	227-232	53	790(m), 711(w)	46.92	1.59	8.40 (8.22)
$[Pt(C_6F_4CF_3)_2(TPP)]$	yellow	253-257	69	800(m), 7 5 4(w)	41.34 (42.14)	1.48	7.44 (7.45)
$[Pd(C_6F_4CF_3)_2(mstd)]$	white	252-256	60	788(w), 710(s)	44.10 (44.55)	2.80 (2.40)	3.40 (3.72)

" With decomposition.

h Yield quoted relative to metal containing reagent.

^c Recorded as CsI discs; s = strong, v = very, m = medium, w = weak, sh = shoulder.

d Calculated values in parentheses.



Fig. 1. Interconverting structures of the complexes $\{M(C_6F_4CF_3)_2(TPT)\}$ (M = Pd or Pt) due to the 1,4-metallotropic shift.



Fig. 2. 400 MHz ¹H NMR spectrum of [Pt(C₆F₄CF₃)₂(TPT)] at 30°C in (CDCl₂)₂. Signal labelling refers to Fig. 1.

Table 2 'H NMR chemical shift data * for TPT and the complexes cis-[M(C₆F₄CF₃)₂(TPT)] (M = Pd^h, Pt^e)

Compound	Solvent	Temp. (°C)	δ _{AEt} ^u	δ _{BFJ}	δ_{CGK}	δ _{юні.} ^d
 TPT	CDCl ₃	30	8.94	7.52	7.94	8.80
$[Pd(C_6F_4CF_3)_2(TPT)]$	(CDCl ₂) ₂	30	8.11(A)	7.78(B)	8.31(C)	9.12(D)
			8.72(E)	7.31(F)	7.70(G)	8.05(H)
			9.03(1)	8.09(J)	7.73(K)	8.88(L)
$[Pt(C_{0}F_{4}CF_{3})_{2}(TPT)]$	$(CDCl_2)_2$	30	8.41(A)	7.81(B)	8.43(C)	9.09(D)
			8.70(E)	7.32(F)	7.75(G)	8.11(H)
			9.02(1)	7.73(J)	8.08(K)	8.85(L)

" Relative to SiMe₄ ($\delta = 0$).

h Recorded at 300 MHz.

^d All signals were multiplets due to three-bond and four-bond scalar couplings within each ring. Magnitudes of three-bond couplings were in the order $J_{CD} > J_{BC} > J_{AB}$ for ring 1 (Scheme 1). This relative order applied to each ring.

Table 3

¹⁹F chemical shift data " for the complexes cis- $\{M(C_hF_4CF_3)_2(TPT)\}$ (M = Pd or Pt) at ambient and limiting low temperatures

Complex	Temp. (°C)	¹⁹ F (δ)				
		CF ₁	o-F	<i>m</i> -F		
[Pd(C ₆ F ₂ CF ₃) ₂ (TPT)]	30 ^h	105.88, 104.80	47.20, 46.70	19.33, 18.02		
	- 100 °	107.91, 107.86	46.23, 44.81	19.97, 18.49		
			45.31, 44.24	18.92, 17.99		
$Pt(C_6F_4CF_3)_2(TPT)$	30 ^h	106.49, 10%.11	44.38, 43.80	18.54, 17.38		
	- 90 °	106.86, 106.52	44.70, 43.49-42.70 d	19.20, 17.80		
				18.40, 17.00		

^a Relative to C_6F_6 ($\delta = 0$).

h Recorded in (CDCl₂)₂.

' Recorded in CD₂Cl₂,

^d Broad overlapping signals.

3.1.3. One-dimensional DNMR studies

On raising the temperature of a $(\text{CDCl}_{2})_{2}$ solution of the Pd^{II} complex to ~ 140°C (the upper temperature limit of the solvent), its ¹H spectrum underwent extensive changes affecting 8 of the 12 signals. These exchanged according to the dynamic spin case ABCD = EFGH. Signals due to the hydrogens I. J. K and L on the third pyridyl ring were unaffected by temperature and remained sharp. At 140°C, a much simplified spectrum of eight chemically shifted signals was obtained. These spectral changes were consistent with the occurrence of the 1.4-metallotropic shift as depicted in Fig. 1. Such shifts have been studied extensively by us in

Table 4			
"F NMR coupling constants "	for [M(C ₀ F ₄	CF ₁) ₂ (TPT) { (M = Pd, Pt

Complex	⁴ J(m, CF ₃)	³ J(o, m)
$Pd(C_6F_4CF_3)_2(TPT)$	21.3, 21.2	28.2. 33.9
$Pt(C_6F_4CF_3)_2(TPT)$	21.4, 21.3	25.0 °, 25.0 °

" In Hz.

 $^{3}J(^{195}\text{Pt}-^{19}\text{F}) = 417 \text{ Hz}.$

 195 Pt- 19 F) = 456 Hz.

a range of closely related nitrogen-ligand complexes [7,8,18,19]. They have been shown to involve an associative

[&]quot; Recorded at 400 MHz.



Fig. 3. 282 MHz ¹⁹F spectra (CF, region only) of [Pd(C₄F₄CF₁)₂(TPT)] in (CDCl₃)₂ in the temperature range 20-140°C. Computer sinulated spectra are shown alongside with 'best-fit' rate constants for the 1,4-metal shift process.

twisting of the metal moiety through an angle equivalent to the NMN angle of the chelate ring. The process always exchanges the environments of the groups attached *trans* to the two M–N bonds.

Variable temperature ¹H spectra of the Pt^{II} complex in the same temperature range as above showed little change with temperature suggesting that any fluxional metallotropic shift is very much slower than in the Pd^{II} case, and cannot be detected by 1D dynamic NMR.

It was decided to measure the dynamics of the fluxional process in the Pd^{II} complex from changes in lineshape of the CF₃ signals with temperature. These signals act as sensitive probes to the dynamic process. A set of ¹⁹F spectra was therefore obtained (Fig. 3), which were fitted theoretically using standard DNMR bandshape analysis and rate constants obtained.

3.1.4. 2D-EXSY studies

Since it appeared that 1,4-metallotropic shifts in the Pt^{II} complex were occurring too slowly to produce any significant line broadening in 1D NMR spectra it was felt that the 2D-EXSY methods, being sensitive to much slower exchange rates, might provide evidence for their occurrence. Accordingly, 2D-EXSY spectra were recorded at various high temperatures; the spectrum at 393 K is shown in Fig. 4. This reveals clear cross peaks associated with the exchanges shift, but most unexpectedly, a second set of cross peaks visible. This set involves exchanges between corresponding hydrogens of the two uncoordinated pyridyl rings and is clearly the result of a second mode of fluxion. It can 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. The effective 'hurdling' of this C-C bond by the metal moiety can be achieved in two ways; one involves full dissociation of the metal centre from the TPT ligand followed by recombination, the other mechanism involves partial dissociation, by cleavage of a single metal-nitrogen bond (that to the triazine) followed by 180° rotation of the metal-bound pyridyl abcut the pyridyl-triazine C-C bond followed by recombination of the metal to the new triazine nitrogen. The first process would lead to an equal probability of the metal recoordinating at nitrogens on any pair of adjacent rings, and hence exchange between hydrogens on all pyridyl rings would occur at equal rate. As this is not seen, indeed no direct ABCD ⇒ IJKL exchange is observed, it would appear that the second partial dissociative process occurs with the metal passing over (or under) the pyridyl-triazine bond and recoordinating to the triazine. A preliminary report of this very novel fluxion has been already given [20].

Quantitative estimates of the rates of the two fluxional processes from this 2D-EXSY spectrum at 393 K were made using the authors' D2DNMR program [15]. Rates were of comparable magnitude. Similar measurements were made from 2D-EXSY spectra at 363, 373, 403 and 413 K, in order that activation energies for the two processes could be estimated (see later).

An intriguing consequence of these observations is that a combination of the 1,4-metallotropic shift and the metal hurdling process enables the metal moiety to move completely round the outside of the triazine ring passing through structures (i)-(vi) (Scheme 1). In this scheme it should be noted that the three pyridyl rings are labelled 1-3 according to their chemical environments. Thus, the 1,4-shift always exchanges rings 1 and 2, while the hurdling process exchanges rings 2 and 3; no direct exchange of rings 1 and 3 occurs.

Since 2D-EXSY spectra provided much greater insight into the fluxionality of the Pt^{II} complex than 1D spectra, it seemed appropriate to examine the Pd^{II} complex by this 2D technique. Accordingly, a 2D-EXSY ¹H spectrum of [Pd(C₆F₄CF₃)₂-(TPT)] was recorded at 303 K. Cross peaks due to both fluxional processes were again detected. Quantitative measurements showed that the two processes were again occurring at relatively similar rates, the magnitude of these rates being comparable to those seen in the Pt^{II} complex at temperatures over a hundred degrees higher.



Fig. 4. 'H 2D-EXSY NMR spectrum of [Pt(C₆F₂CF₁)₂(TPT)] in (CD₂Cl₂)₂ at 393 K with mixing time 0.8 s. The cross peaks result from 1.4-metallotropic shifts (H₆-H₆ \Rightarrow H₆-H₄) and the rotational hurdling process (H₆-H₄ \Rightarrow H₆-H₄). 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 $[M(C_6F_4(CF_4)_2L]$ 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.

3.1.5. Below-ambient temperature ¹⁹F NMR spectra

A third type of internal dynamic process is possible in these complexes, namely restricted rotation of the pendant pyridyl ring adjacent to the metal moiety and restricted rotations of the perfluoro-p-tolyl rings. These rotations were investigated by low temperature ¹⁹F NMR studies of both complexes in CD₂Cl₂ solutions. On cooling to $\sim -100^{\circ}$ C, the pairs of ortho- and meta-ring fluorine signals broadened and eventually split into equal intensity pairs of signals, whilst the CF₃ signals were unaffected by these temperature changes. The spectra for the meta-ring fluorine signals of the Pt^{II} complex are shown in Fig. 5. These spectral changes are characteristic



Fig. 5. 282 MHz ¹⁰F NMR spectra (*meta*-F region only) of [Pt($C_sF_s(F_s)$ -(TPT)] in CD₂Cl₂ in the temperature range -90 to -30°C. Computer simulated spectra are shown alongside with the best-fit rate constants for the pyridyl ring rotation process.

of restricted rotation of either both C6F4CF3 rings or of the pendant pyridyl ring or of all three rings. The fact that the ortho- and meta-ring fluorine signals split into equal intensity pairs, whilst the CF₃ groups, lying on the axes of rotation remain unaffected, implies that at low temperatures these complexes exist in two chemically indistinguishable rotamer forms. The most likely structures are those where the planes of the C₆F₄CF₃ rings and the adjacent pendant pyridyl ring are mutually parallel and orthogonal to the plane of the coordinated portion of the ligand. The rate constants associated with these low temperature spectral changes were deduced by bandshape analysis of the meta fluorine signals. Computer generated bandshapes (Fig. 5) allowed for the major threebond ortho-meta fluorine couplings but weaker cross-ring couplings were not fully resolved and were compensated for in the bandshape calculations by the magnitude of the effective transverse relaxation time, T_2^* , used in the calculations. Fig. 5 shows the rate constants for the 'best-fit' band shapes obtained. Spectra at any temperature could be fitted to a single magnitude of rate constant, implying either that both fluorinated rings are rotating at identical rates (which is highly unlikely) or that the spectral changes are due solely to the effects of the pyridyl ring, with the C₆F₄CF₃ ring rotation always being slow compared to the pyridyl ring rotation. This second explanation was preferred in the case of the complexes $[MC_{0}F_{5})_{2}terpy]$ (M = Pd^{II}, Pt^{II}; terpy = 2.2':6',2''-terpyridine) [18] and it appears to be the more plausible rationalisation of the present observations as well.

In order to provide support for the assumption that rotation of the $C_6F_4C\Gamma_3$ ring was arrested at low temperatures, the complex [Pd($C_6F_4CF_3$)_(mtsd)] (mstd = meso-stilbenediamine) was synthesised (see Section 2). The air-stable, white crystalline solid was characterised by elemental analysis (Table 1) and ¹H/¹⁹F NMR spectra (below).

The complex was expected to possess the structure shown in Fig. 6. If the perfluoroaromatic rings were not rotating then the ortho- and meta-ring fluorines would consist of nonequivalent pairs A/B and C/D depending on whether the fluorines were above or below the plane containing the Pd and N atoms. The room temperature 19F spectrum consists of three signals at δ 100.14 (CF₃), 44.04 (ortho-F) and 17.11 (meta-F) implying that the rings were rotating at this temperature. However, on cooling the complex, the ring fluorine signals soon split as a result of the arresting of the ring rotation, so confirming the assumption made earlier for the TPT and terpy [18] complexes. The signal splittings, however, were more extensive than expected, the ortho-F signal splitting into four signals (δ =43.51, 44.25, 44.81 and 44.91) suggesting inequivalence of the two C6F4CF3 rings themselves. This inequivalence was also detected in the CF3 signals ($\delta = 100.55$, 100.56) and the meta-F signals ($\delta = 17.75$ -18.45, complex multiplet).

The changes were explained in terms of a combination of a 'freezing' of the $C_6F_1CF_3$ ring rotations and of the fivemembered ring puckering process (Fig. 7). Five-membered diamine chelate rings are known to rapidly interconvert between pairs of half-chair conformers, usually via an envelope form [21–23]. In the present case, when this process becomes slow on the 'H NMR timescale it will lead to nonequivalences of the two $C_6F_4CF_3$ rings, the NH₂ geminal hydrogens and the backbone methine hydrogens. This was clearly seen in the variable temperature 'H spectra where signals changed as follows: 30° C, $\delta 3.07$ (AA'), 3.39 (BB'), 4.63 (CC'), 7.32 (phenyl); -100° C, $\delta 3.15$ (A or A'), 2.97 (A or A'), 3.15 (B), 3.64 (B'), 4.58 (C'), 4.75 (C) and 6.55–8.18 (phenyl). The signals of the hydrogen pairs B/B' and C/C' were differentiated by a selective decoupling exper-



Fig. 6. Proposed structure of cis-[Pd($C_6F_4CF_3$)₂(mstd)] (mstd=mesostilbenediamine).



Fig. 7. Interconverting structures of [M(C₆F₄CF₃)₂(mstd)] due to the ring puckering process, showing how the process affects the amino and methine hydrogen environments.

iment. By measuring the coalescence of the signals due to hydrogens C and C', an approximate value of the activation energy (ΔG^* , 208 K) of 42.8 kJ mol⁻¹ was calculated for the chelate ring conformational process.

3.2. Complexes cis- $[M(C_6F_4CF_3)_2(TPP)]$ $(M = Pd^{II} \text{ or } Pt^{II})$

Bispyridyl pyrimidines have been known for almost 30 years, yet the only mention of their coordination chemistry is in their first reported preparation [24] where both bidentate and terdentate ligand potentialities towards iron were recognised. Trispyridyl pyrimidines are equally scarce, and the coordination chemistry of 2,4,6-tris(2-pyridyl)-pyrimidine (TPP) appears to be totally unexplored.

The TPP ligand was chosen in this work to examine how the lowering of symmetry of the central ligand ring (from three-fold symmetry in TPP) might affect the coordination properties of the ligands. The complexes *cis*-[M(C₆F₄CF₃)₂(TPP)] (M=Pd or Pt) were readily synthesised from the reaction of TPP with *trans*-[Pd(C₆F₄CF₃)₂(1.4-discane)₂] and *trans*-[P(C₆F₄CF₃)₂. (Et₂S)₂], respectively, and isolated as air-stat⁻¹; yellow microcrystalline solids. These were characterised by elemental analysis. IR spectroscopy (Table 1) and ¹H/¹⁰F NMR (see below).

3.2.1. Ambient temperature NMR spectra

The two-fold symmetry of the uncoordinated TPP ligand causes chemical equivalence of the pyridyl rings attached to the 4- and 6-positions of the pyrimidine ring. Bidentate chelate coordination to a metal removes this symmetry and renders all hydrogen environments non-equivalent (Fig. 8). Furthermore, two chemically distinct bidentate chelate complexes may now be formed, each of which consists of 13 nonequivalent hydrogen environments.

An initial examination of the room temperature ¹H spectra of both the Pd and Pt complexes revealed 13 signals only, indicating apparent exclusive formation of only one coordination complex. However, 2D-EXSY spectra at 30°C (Pd complex) and at 140°C (Pt complex) revealed cross peaks which enabled identification of a minor intensity set of signals due to the less favoured coordination complex. Full ¹H chemical shift assignments are given in Table 5.

The major coordination complex was attributed to the complex involving coordination to the pyridyl ring attached to the 2-position of the pyrimidine ring. The argument for this is analogous to that used for the complexes of 2,4,6tris(pyrazol-1-yl)pyrimidines [8] where a similarly large imbalance of coordination species was detected. The preferred conformation of the TPP free ligand will be one where the N heteroatoms of the pyridyls are *trans* with respect to the pyrimidyl nitrogens. However, the N atom of the 2-position pyridyl ring is necessarily *cis* to one of the pyrimidyl nitrogens and thus ideally placed to form a bidentate chelate complex. In contrast, the other two pyridyl rings need to rotate through 180° from their preferred free ligand *trans* conformations in order to be suitably placed for metal chelation. This, therefore, accounts for coordination involving the 2-



Fig. 8. Interconverting isomers of the complexes $[M(C_nF_4CF_3)_2(TPP)]$ (M = Pd or Pt) showing the hydrogen labelling.

Table 5	
¹ H NMR chemical shift data ^a for TPP and the complexes cis -[M(C ₆ F ₄ CF ₃) ₂ (TPP)] (M=Pd or F	4)

Compound	Solvent	Temp. (°C)	$\delta_{ m AEI}$	$\delta_{\rm BFJ}$	бсак	δ _{DHL}	δ_{Y}
ТРР	CDCl ₃	30	8.80 (A) 8.75 (E) 8.75 (1)	7.45 (B) 7.43 (F) 7.43 (J)	7.92 (C) 7.91 (G) 7.91 (K)	8.74 (D) 8.75 (H) 8.75 (L)	9.44
$[Pd(C_6F_4CF_3)_2(TPP)]^{b}$	(CDCl ₂) ₂	30	7.96 (A) 8.60 (E) 8.85 (1)	7.65 (B) 7.26 (F) 7.62 (J)	8.26 (C) 7.72 (G) 8.06 (K)	8.96 (D) 7.86 (H) 8.76 (L)	8.88
			δ _{MQU}	$\delta_{ m NRV}$	δ_{nsw}	$\delta_{ m PTX}$	δz
			8.07 (M) 8.71 (Q) ° (U)	7.64 (N) 8.27 (R) ° (V)	8.24 (O) 7.67 (S) ° (W)	8.58 (P) 7.92 (T) ° (X)	9.27
			δ_{AEI}	$\delta_{ m BFJ}$	δ_{CGK}	δ_{DHL}	δ_{Y}
$ Pt(C_6F_4CF_1)_2(TPP) ^{h}$	(CDCl ₂) ₂	140	8.37 (A) 8.63 (E) 8.91 (1)	7.68 (B) 7.26 (F) 7.62 (J)	8.34 (C) 7.74 (G) 8.06 (K)	8.93 (D) 8.01 (H) 8.73 (L)	9.01
			δ_{MQU}	δ _{NRV}	$\delta_{ m OSW}$	$\delta_{\rm PTX}$	ôz
			8.47 (M) 8.72 (Q) ° (U)	7.67 (N) 7.26 (R) ° (V)	8.32 (O) 7.63 (S) ° (W)	8.55 (P) 7.95 (T) ° (X)	9,38

All signals are multiplets due to three-bond and four-bond scalar couplings within each ring.

" Relative to SiMe₄ ($\delta = 0$); see Fig. 8 for labelling.

^b Assignment of minor signals H_M-H_x by 2D-EXSY.

" Undetected and assumed to be unchanged from the major species.

Table 6

¹⁹F chemical shift data ^a for the complexes $cis_{1}[M(C_{s}F_{4}CF_{3})_{2}(TPP)]$ (M = Pd or Pt) at ambient and limiting low temperatures

Complex	Temp.	¹⁹ F (δ)				
	()	CF ₃	<i>o</i> -F	<i>m</i> -F		
[Pd(C ₄ F ₄ CF ₄) ₂ (TPP)]	30 ^h	108.56, 107.98	49.70, 49.09	21.69, 20.39		
	- 80 %	107.84, 107.43	49.08, 47.56	20.48, 19.39		
			48.03, 47.49	20.43, 18.57		
Pt(C ₆ F ₄ CF ₃) ₂ (TPP)	30 ^h	108.63, 108.11	46.57, 45.96	20.90, 19.54		

" Relative to C_6F_6 ($\delta = 0$).

^b Recorded in (CDCl₂)₂,

" Recorded in CD₃Cl₃.

position pyridyl ring being much more strongly preferred to that involving the 4- and 6-position pyridyls.

Further support for the identification of the major coordination species was provided by ¹H NOE difference experiments. These showed relatively weak NOE effects between hydrogens H_v and H_H implying that H_H was part of a pendant pyridyl ring which was undergoing rotation about the C–C bond attaching this ring to the pyrimidyl ring. The other coordination complex would have given rise to a very strong H_z/H_P NOE effect due to the fixed proximities of these two H atoms.

The 19 F 1D spectra of these complexes (Tables 6 and 7) revealed the expected numbers of signals for a single type of

bidentate, chelate complex and there was no clear evidence of the minor species.

Table 7

¹⁰F NMR coupling constants ⁴ for the complexes cis-[M(C₆F₄CF₃)₂(TPP)] (M = Pd or Pt)

Complex	$^{4}J(m, \operatorname{CF}_{3})$	`J(o,m)
Pd(C ₆ F ₄ CF ₃) ₂ (TPP)]	21.1, 21.1	29.3, 28.5
$Pt(C_6F_4CF_3)_2(TPP)$	21.1, 21.2	21.1 *, 22.6 *

" In Hz.

 b $^{3}J(^{195}Pt-^{19}F) = 433$ Hz.

 $J(^{195}Pt-^{19}F) = 457$ Hz.

3.2.2. Above-ambient temperature ¹H NMR spectra

On raising the temperature of a $(\text{CDCl}_{2})_2$ solution of the complex $[\text{Pd}(C_6F_3CF_3)_2(\text{TPP})]$ very slight broadening effects were detected consistent with the onset of the 1.4-metallotropic shift. Signals H_1-H_1 (and H_U-H_X) remained sharp until ~ 120°C whereas the other signals particularly the major and minor pyrimidyl signals H_Y and H_Z showed dynamic broadening. The $H_Y \rightleftharpoons H_Z$ dynamic exchange was carefully studied in the range 10-40°C. At 10°C, two 'static' signals were detected in an intensity ratio 98.1%/1.9%. On warming, the minor signal broadened rapidly and then collapsed into the baseline. The major signal showed slight line broadening and then sharpened. Approximate bandshape analysis was carried out on this system.

Similar variable temperature studies on $[Pt(C_6F_4CF_5)_2-(TPP)]$ did not reveal any significant changes up to 140°C. Populations of the two coordination species at 30°C were 98.8%/1.2%.

3.2.3. 2D-EXSY spectra

This 2D-NMR technique provided further insight into the fluxionality of both TPP complexes. A ¹H spectrum of the Pd^{II} complex at 30°C proved to be most informative, Fig. 9. It revealed exchange cross peaks between major and minor signals, namely ABCD ⇒ QRST and EFGH ⇒ MNOP (see Fig. 8 for labelling), providing clear evidence for the 1.4metallotropic shift, and allowing identification of many of the minor signals which are not visible in the 1D spectrum. Additional cross peaks were also clearly detected as arising from exchanges between pairs of major signals, namely EFGH=1IKL. (i.e. exchanges between corresponding hydrogens of pyridyl rings 2 and 3, Scheme 1). As in the TPT complexes this is most reasonably rationalised as arising from the metal moiety hurdling the C-C bond attaching the pyridyl ring to the 2-position of the pyrimidyl ring. The rate of this process was computed using the D2DNMR program [15]. Its magnitude was comparable to that of the 1.4-shift process as measured by bandshape analysis (Section 3.2.2 above).

A similar 2D-EXSY NMR study of the Pt^{II} complex at 140°C revealed both the 1,4-shift and metal hurdling processes, again with both proceeding at comparable rates.

It follows, therefore, that a combination of both fluxions causes the metal moiety to move over appreciable distances around the TPP ligand as depicted in Scheme 1. Whereas the metal moiety in the TPT complexes could move completely round the ligand passing through all the chemically equivalent structures (i)–(vi), in the TPP complexes structures (ii) and (ii) are strongly preferred over structures (iii) and (vi), and no combination of metallotropic shifts and rotational hurdling will allow the metal to move completely round the TPP ligand. Thus, the fluxionality involves an oscillatory eachange of type $(vi) \Rightarrow (i) \Rightarrow (ii) \Rightarrow (iii)$, with the life



Fig. 9. ¹H 2D-EXSY spectrum of $[Pd(C_bF_b(CF_b)_2(TPP)]$ at 30°C in (CDCl₂)₂ showing the cross peaks associated with the 1.4-metallotropic shift exchanges (ABCD \Rightarrow QRST, EFGH \Rightarrow MNOP and Y \Rightarrow Z) and the metal hurdling exchanges (EFGH \Rightarrow UKL). The broad, unlabelled signals are impurities.

Table 8 Activation parameters for fluxions in $[M(C_6F_4CF_3)_3L]$ (M = Pd, Pt; L = TPT, TPP) complexes

Complex	Temp. range (°C)	Fluxion	<i>E</i> " (kJ mol ^{~1})	$\log_{10} A$	∆ <i>H*</i> (kJ mol ^{−1})	Δ <i>S*</i> (J K ⁻¹ mol ⁻¹)	ΔG* * (kJ mol ⁻¹)
[Pd(C ₆ F ₄ CF ₃) ₂ TFT]	30–130 30	1.4-shift hurdling	82.5 ± 1.1	14.6±0.2	79.6±1.1	25.4±3.2	72.0±0.2 73.0 ^h
	-90 to -20	pyr rotation	49.6 ± 1.2	15.0 ± 0.3	47.8 ± 1.1	37.4 ± 5.5	36.7 ± 0.5
{Pd(C ₆ F ₅) ₂ (terpy)} ^c	30-140	1,4-shift	75.7 ± 1.1	13.6 ± 0.2	72.8 ± 1.2	5.8 ± 3.3	71.0 ± 0.2
$[Pt(C_6F_4CF_3)_2(TPT)]$	30140 90140	l ,4-shift hurdling					102.7±0.4
	- 80 to - 30	pyr rotation	46.9 ± 2.0	13.6 ± 0.5	45.1 ± 2.0	9.2 ± 9.3	42.3 ± 0.7
$[Pt(C_6F_5)_2(terpy)]^{\circ}$ $[Pd(C_6F_4CF_3)_2(TPP)]$	100–140 10–40	1,4-shift 1,4-shift	96.2 ± 2.9	13.2 ± 0.4	93.0±2.9	-3.2 ± 7.3	93.9±0.7 69.0 ^a
	- 60 to - 10	pyr rotation	57.2 ± 0.4	15.2 ± 0.1	55.2 ± 0.4	40.4 ± 1.8	43.2 ± 0.1
[Pt(C,F,CF,),(TPP)]	140	1,4-shift					117.7 4.0
	140	hurdling					113.0 °

* At 298.15 K unless otherwise stated.

^d Major → minor isomer exchange.

° At 413 K.

times and populations of structures (i) and (ii) being considerably greater than those of structures (iii) and (vi).

3.2.4. Below-ambient temperature NMR spectra

A low temperature ¹⁹F NMR study was carried out on the Pd^{II} complex in CD₂Cl₂ solution. This revealed the 'freezing out' of the rotation of the pendant pyridyl ring 2 (Scheme 1), as evidenced by the splitting of the *ortho-* and *meta-*ring fluorine signals into equal intensity pairs, while the CF₃ signals of the two rings were unaffected. Bandshape analysis of the *ortho-*ring fluorine signals was carried out and an activation energy for the pyridyl ring rotation process was calculated.

3.3. Activation energies

Activation energies for the 1,4-metallotropic shifts, the metal hurdling process and pyridyl ring rotations, based on the ¹H/¹⁹F 1D-bandshape analyses and quantitative 2D-EXSY studies of the TPT and TPP complexes are collected in Table 8. The energies of the 1,4-shifts and the metal hurdling processes are very similar. This implies that there is little energetic preference in the metal loosening *both* its M–N bonds and undergoing a localised 'tick-tock' twist process, as opposed to the M–N bond (to the central ring) breaking, the metal moiety then rotating with its attached pyridyl ring and then re-making its bond with the other N atom of the central ring, having hurdled over (or under) the C–C bond linking the two rings.

The energies of the 1,4-shifts are of a similar magnitude to those calculated for the analogous complexes $[M(C_6F_5)_2(terpy)]$ (M=Pd, Pt) [18]. They also reflect the same metal dependence of the fluxion, namely $\Delta G^*(Pt^{II}) - \Delta G^*(Pt^{II}) \geq 20 \text{ kJ mol}^{-1}$. The energies of the restricted rotations of the pendant pyridyl ring (adjacent to the metal moiety) are considerably lower in magnitude, 36–43 kJ mol⁻¹, and are less metal dependent. These values are approximately 10 kJ mol⁻¹ lower than the values for the corresponding terpy complexes [18].

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