The mechanism of 1,4-metallotropic shifts in transition-metal complexes of bidentate 2,2′ : 6′,2″-terpyridine ligands

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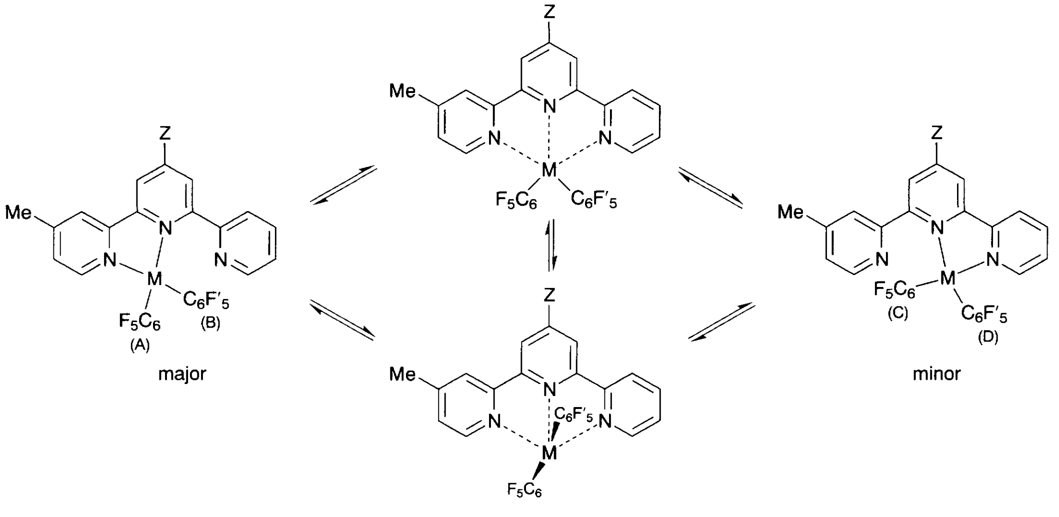
^{1}H/^{19}F NMR two-dimensional exchange spectroscopy (EXSY) reveals that the 1,4-metallotropic shifts in bidentate chelate complexes of a substituted 2,2′ : 6′,2″-terpyridine ligand occur by an associative mechanism involving five-coordinate intermediates for Pd^{II} and Pt^{II} complexes, and seven-coordinate intermediates for Pt^{IV} and, by analogy, Re^I complexes.

Following our original discovery of 2,2′ : 6′,2″-terpyridine (terpy) acting as a fluxional bidentate ligand in octahedral complexes of Re^I, Ru^{II} and Pt^{IV},[1–4] we have subsequently shown that this type of 1,4-metallotropic shift occurs widely in complexes of other N,N,N-ligands based on combinations of pyridyl, pyrazolyl, pyrimidine and 1,3,5-triazine rings.[5,6] It further occurs in *cis*-square-planar complexes of Pd^{II} and Pt^{II}.[7] The process is always accompanied by an interchange of the chemical environments of the two spectator groups attached to the metal in positions *trans* to the M–N bonds. We have proposed an associative mechanism for the fluxion involving a quasi-terdentate ligand intermediate formed by a twisting of the metal moiety through an angle equal to half that of the N–M–N angle at the metal centre. This mechanism has recently been questioned in the case of the square-planar complexes *cis*-[M(C$_6$F$_5$)$_2$(terpy)] (M = Pd^{II}, Pt^{II}) and an alternative dissociative process, based on a T-shaped 14-electron three-coordinate species, proposed.[8] We now present conclusive NMR evidence in support of an associative mechanism for these terpyridine fluxions in both square-planar and octahedral complexes of transition metals.

Our studies rely on the syntheses of metal complexes of unsymmetrically substituted 2,2′ : 6′,2″-terpyridine proligands. Accordingly, we developed a synthetic route to the ligand 4-methyl-4′-(4-chlorophenyl)-2,2′ : 6′,2″-terpyridine (L) according to the original method of Krohnke[9] and latterly of Constable *et al.*[10].

The fluxional shifts of the four complexes, namely *fac*-[PtIMe$_3$L], *fac*-[ReBr(CO)$_3$L], *cis*-[Pd(C$_6$F$_5$)$_2$L] and *cis*-[Pt(C$_6$F$_5$)$_2$L], interconvert *chemically distinct* species and the mechanism of the fluxion can be monitored by observing its effect on the NMR signals of the spectator groups attached to the metal in the *trans* N positions (*i.e.* ^{1}H equatorial Pt–methyl signals, ^{13}C equatorial carbonyl signals and ^{19}F signals of C$_6$F$_5$ rings). If the process is purely associative a selective pairwise exchange of the four signals will occur, whereas a dissociative process will lead to an exchange of all four NMR signals. Scheme 1 depicts the associative mechanism for the square-planar complexes *cis*-[M(C$_6$F$_5$)$_2$L].

Rates of the metallotropic shifts varied considerably according to the metal moiety, being in the order Pt^{IV} > Re^I ≈ Pd^{II} > Pt^{II} (Table 1). Rates were slow on the ^{1}H or ^{19}F NMR timescale at room temperature (or slightly below for Pt^{IV}), and relative populations of the two complex species were measured, with the more abundant form being identified as involving coordination to the 4-methylpyridyl ring. On warming solutions of these complexes the metallotropic shift was detected by the exchange of the appropriate pairs of pyridyl ring hydrogens (and methyl substituents), and by the exchange of the metal-bonded spectator groups [*viz.* PtMe (equatorial) groups or C$_6$F$_5$ groups] (Table 1). In the case of the square-planar complexes, two-dimensional (2D) exchange NMR spectroscopy (EXSY) experiments carried out at appropriate temperatures showed *double pairwise exchanges* between the four spectator groups. The case of [Pt(C$_6$F$_5$)$_2$L] is shown in Fig. 1. The ^{19}F NMR 2D-EXSY spectrum of this complex at 413 K shows pairs of cross peaks between the *p*-F signals, assigned A–D (Scheme 1). Signals A/B are associated with the more populous complex and



Scheme 1 The 1,4-metallotropic shift occurring *via* an associative mechanism in the complexes *cis*-[M(C$_6$F$_5$)$_2$L] (L = 4-methyl-4′-Z-2,2′ : 6′,2″-terpyridine) (Z = 4-chlorophenyl). The C$_6$F$_5$ rings exchange selectively according to A $\rightleftharpoons$ C and B $\rightleftharpoons$ D. Possible distortion from a planar intermediate towards a trigonal-bipyramidal geometry is shown, but this must be totally reversible to be consistent with these double pairwise exchanges. Any dissociative mechanism will lead to full exchange of all four ring environments.

Table 1 Selected $^1H/^{19}F$ NMR data for transition metal complexes of 4-methyl-4′-(4-chlorophenyl)-2,2′ : 6′,2″-terpyridine (L)

Complex	Relative populations (%)	T/K	δ^a	$T_c{}^b$/K	$k_c{}^c$/s^{-1}	$\Delta G_c{}^{\ddagger d}$/ kJ mol^{-1}
[PtIMe$_3$L]	63	263	1.606(A), 0.296(B)^e	353	1153	66.3
	37		1.635(C), 0.350(D)^e			
[ReBr(CO)$_3$L]	66	303	2.648^f	353	98	73.5
	34		2.538^f			
[Pd(C$_6$F$_5$)$_2$L]	53	303	48.97(A), 48.18(B)^g	383	*ca.* 725	*ca.* 74
	47		48.30(C), 49.25(D)^g			
[Pt(C$_6$F$_5$)$_2$L]	64.5	303	2.308(A), 0.095(B)^h	>413^i	—^{j}	—^{j}
	35.5		0.214(C), 2.473(D)^h			

[a] Chemical shifts relative to SiMe$_4$ (^1H) or C_6F_6 (^{19}F). Solvent $(CDCl_2)_2$ for all experiments. [b] Coalescence temperature. [c] First-order rate constant for the major → minor exchange pathway. [d] Gibbs activation energy change for the major → minor complex exchange. [e] Equatorial Pt–Me signals. ^1H 2D-EXSY experiment at 273 K showed $A \rightleftharpoons C$, $B \rightleftharpoons D$ exchanges only. [f] 4-Methyl signals. No ^{13}C 2D-EXSY experiment possible. [g] *Ortho*-ring fluorines. ^{19}F 2D-EXSY experiment at 323 K showed $A \rightleftharpoons C$, $B \rightleftharpoons D$ exchanges only. [h] *Para*-ring fluorines. ^{19}F 2D-EXSY experiment at 413 K showed $A \rightleftharpoons C$, $B \rightleftharpoons D$ exchanges only. [i] High temperature limit of solvent $(CDCl_2)_2$. [j] Not calculated.

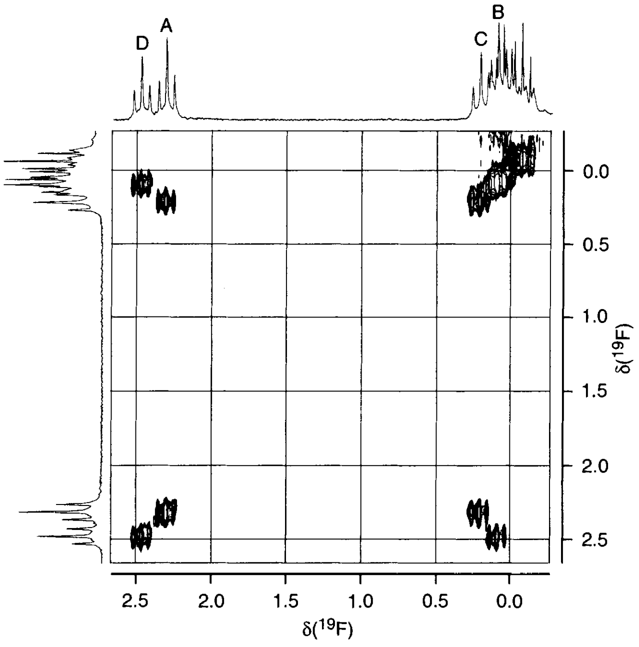


Fig. 1 ^{19}F NMR 2D-EXSY spectrum (413 K) of [Pt(C$_6$F$_5$)$_2$L] in $CDCl_2CDCl_2$ showing the *para* ring fluorine signals A–D, and showing cross-peaks for the $A \rightleftharpoons C$ and $B \rightleftharpoons D$ exchanges. Triplet splittings are due to $^3J_{FF}$ couplings (*ca.* 19.3 Hz). Additional multiplet near δ = 0 due to some of the *meta* ring fluorines. Mixing time for spectrum was 800 ms.

C/D to the other complex. The pairs of cross-peaks are due to the specific exchanges $A \rightleftharpoons C$ and $B \rightleftharpoons D$. Very analogous results were obtained from the ^{19}F 2D-EXSY spectrum of the *o*-F signals of [Pd(C$_6$F$_5$)$_2$L] at 323 K, and from the ^1H 2D-EXSY spectrum of the equatorial Pt-methyl signals of [PtIMe$_3$L] at 273 K. The double pairwise exchange detected between the M-bonded spectator ligands in the complexes of Pd^{II}, Pt^{II} and Pt^{IV} complexes provide definitive evidence for an associative fluxional movement which proceeds *via* a quasi-terdentate ligand intermediate. A dissociative process would probably involve a three-coordinate T-shaped intermediate in the case of the square-planar complexes or a five-coordinate trigonal-bipyramidal intermediate in the case of the octahedral complexes. Both these species would be expected to be highly fluxional, and involve isomerisation and rotation about the M–N bond on the central pyridyl ring, leading to total exchange of all four equatorial spectator ligands. This clearly does *not* occur. The process actually occurring may therefore be depicted as an associative, oscillatory, 'tick-tock' or 'windscreen wiper' motion of the metal moiety through an angle equal to the N–M–N angle at the metal centre.

The geometry and bonding of the intermediates raises interesting theoretical speculation. In the square planar Pd^{II}/Pt^{II} complexes the intermediate can be envisaged as a planar quasi-five-coordinate structure (Scheme 1). Any distortion from planarity, *e.g.* *via* Berry pseudorotations, towards trigonal-bipyramidal or square-pyramidal structures must be *totally reversible*, otherwise exchange of all spectator equatorial ligands will occur. We realise that a five-coordinate planar geometry is highly unusual and feel it befits some theoretical examination. In the octahedral complexes of Pt^{IV} and Re^{I}, a likely intermediate would be a seven-coordinate pentagonal bipyramid. Such a geometry is normally highly non-rigid. However, in the present Pt^{IV} complexes the 'tick-tock' twist does not produce any exchange of equatorial and axial Pt–methyl environments, so the seven-coordinate intermediate does appear to exhibit some considerable degree of stereochemical rigidity, a result which again calls for theoretical study.

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