Is the fluxional motion of bidentate 2,2′:6′,2″-terpyridine in *cis*-[M(C_6F_5)$_2$(terpy)] (M = Pd^{II} or Pt^{II}) a dissociative process?

Abel *et al.*[1] have recently described the oscillatory fluxional motion of 2,2′:6′,2″-terpyridine (terpy) between equivalent bonding modes in octahedral complexes. About 1 year ago we decided to extend their study to square-planar complexes, which had apparently been neglected. For this purpose we synthesized the compounds [M(C_6F_5)$_2$(terpy)] (M = Pd^{II} **1** or Pt^{II} **2**) by treating terpy with *cis*-[M(C_6F_5)$_2$(tht)$_2$] (M = Pd^{II} or Pt^{II}, tht = tetrahydrothiophene)[2] and were about to submit a paper when Abel *et al.*[3] published their results concerning the same complexes. Even though our paper would not have added significant information to their data, it pointed to a mechanism which in our opinion is worthy of mention.

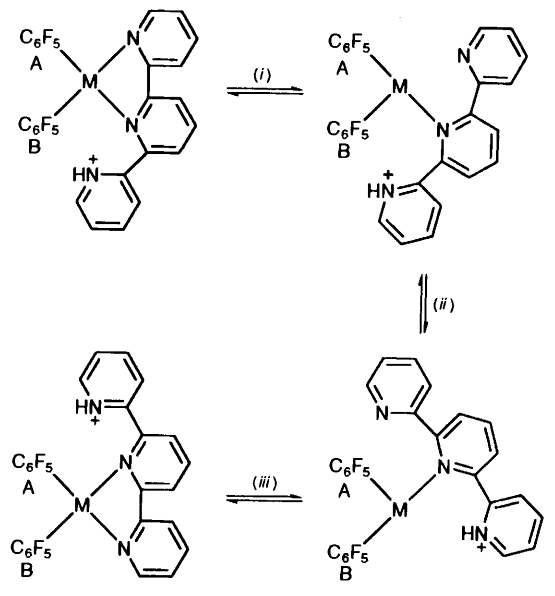
To explain the fluxional motion Abel *et al.* proposed an associative path which proceeds *via* a five-co-ordinate intermediate in which the three heterocyclic nitrogens of terpy are associated with the metal. The alternative which we propose is dissociative, the rate-determining process being rupture of the outer metal–nitrogen bond and formation of a highly unsaturated T-shaped 14-electron three-co-ordinated species. Rotation of terpy around the central pyridine nitrogen acting as a pivot and rapid ring closure would exchange the outer pyridines without affecting the pentafluorophenyl groups. Abel *et al.*[3] demonstrated the simultaneous scrambling of both the pentafluorophenyls and pyridines; thus the dissociative mechanism also requires rapid isomerization of the T-shaped fragments. Molecular orbital calculations provide a theoretical background to the configurational stability of T-shaped three-co-ordinated species and to the relatively low activation energy for their interconversion.[4]

Evidence in support of dissociative twisting is provided by the influence of some acids on the rate of scrambling. The addition of HCl to solutions of complexes **1** and **2** (5 : 1 mol ratio) results in high-frequency ^1H NMR shifts for the pendant pyridine protons in the range 0.1–0.25 ppm. No significant variations are observed for the remaining protons and for the pentafluorophenyls in the ^{19}F NMR spectra at acid concentrations up to $\approx 8 \times 10^{-3}$ mol dm^{-3}. This suggests that, at these concentrations, the only effect of the acid on both complexes is an extensive protonation of the pendant pyridine. Under these conditions the rates of exchange are equal or somewhat faster than in the absence of acid (Table 1). These experiments suggest that the rate-determining step of the fluxional motion is rupture rather than formation of a metal–nitrogen bond (Scheme 1); protonation should dramatically depress the co-ordination ability of the pendant pyridine and the ensuing rate of exchange in an associative framework. The rates of the fluxional motion are only slightly affected by the solvent. This rules out mechanisms involving nucleophilic substitution of the pyridine by the solvent. Different acids (CF_3CO_2H, $HClO_4$), at concentrations up to 8×10^{-3} mol dm^{-3}, show similar effects on the rate of exchange.

Table 1 First-order rate constants for the fluxional motion of terpy in complexes **1** and **2** ($\approx 1.2 \times 10^{-3}$ mol dm^{-3}) calculated in different solvents by magnetization transfer in the presence or absence of added hydrochloric acid

Complex	[HCl]/mol dm^{-3}	T/K	k_{obs}/s^{-1}
1	0	298	3.0,^{a} 4.0,^{b} 2.6,^{c} 3.3^d
	6×10^{-3}	298	3.5,^{a} 4.6,^{b} 2.6,^{c} 3.7^d
2	0	383	1.3^a
	6×10^{-3}	383	1.5^a

[a] In 1,1,2,2-tetrachloroethane. [b] In chloroform. [c] In acetone. [d] In dimethylformamide.



Scheme 1 M = Pd^{II} or Pt^{II}. (*i*) M–N rupture; (*ii*) rapid isomerization of the T-shaped fragment; (*iii*) rapid proton exchange and ring closure

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Abel *et al.* reply. We question the alternative mechanism on the following grounds.

(1) The ligand co-ordination properties of Hterpy$^+$ are likely to be quite different from those of terpy itself and thus the rate of fluxionality of its metal complexes is likely to vary with the addition of acid *irrespective of the mechanism of the fluxion.*

(2) The changes in magnitude of the fluxional rate constants on protonating the ligand are actually very small (probably within the error limits of these values, which the authors do not give), and are significantly smaller than those associated with changing the organic solvent itself, so evidence for a M–N bond rupture mechanism following protonation of the pendant pyridyl ring is unconvincing.

(3) If a T-shaped intermediate is proposed surely protonation of *both* unco-ordinated nitrogens in the two three-co-ordinate intermediate species (shown in Scheme 1) must be considered.

(4) A dissociative mechanism of the type proposed is likely to involve a significantly large, positive entropy of activation, $\Delta S^{\ddagger}$.[5] We have shown[3] from our dynamic NMR measurements that this is *not* the case.

(5) Perhaps the strongest argument against a dissociative process, which involves initial rupture of the M–N bond with the 'outer' pyridyl ring, comes from the crystal structure of

$[Pd(C_6F_5)_2(terpy)]$. This particular Pd–N bond is shown[3] to be shorter (2.064 Å) than the other Pd–N bond (2.131 Å), and therefore if anything *less* prone to fission than the other bond.

We therefore see no evidence in support of a dissociative mechanism for 1,4-fluxional shifts of bidentate chelate terpy complexes, and maintain that all structural, kinetic and spectroscopic data point towards an associative process, involving five-co-ordinate intermediates[3] in the case of complexes of Pd^{II} and Pt^{II} and seven-co-ordinate ones[1,6,7] in the case of complexes of Re^{I}, Pt^{IV}, Ru^{II} and W^{0}.

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References

1 E. W. Abel, K. G. Orrell, A. G. Osborne, H. M. Pain and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1994, 111 and refs. therein.
2 D. Minniti, *Inorg. Chem.*, 1994, **33**, 2631.
3 E. W. Abel, K. G. Orrell, A. G. Osborne, H. M. Pain, V. Šik, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1994, 3441.
4 K. Tatsumi, R. Hoffmann, A. Yamamoto and J. K. Still, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1857.
5 J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.
6 E. W. Abel, V. S. Dimitrov, N. J. Long, K. G. Orrell, A. G. Osborne, V. Šik, M. B. Hursthouse and M. A. Mazid, *J. Chem. Soc., Dalton Trans.*, 1993, 291.
7 E. W. Abel, V. S. Dimitrov, N. J. Long, K. G. Orrell, A. G. Osborne, H. M. Pain, V. Šik, M. B. Hursthouse and M. A. Mazid, *J. Chem. Soc., Dalton Trans.*, 1993, 597.

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