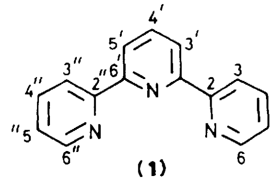
Ligand Reactivity in Polypyridine Complexes; the Deuteriation of the Bis(2,2′:6′,2″-terpyridine)ruthenium(II) Cation

Edwin C. Constable
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The complex $[Ru(terpy)_2][PF_6]_2$ (terpy = 2,2′:6′,2″-terpyridine) undergoes a specific deuterium-exchange reaction involving $H^{3,3',5',3''}$ upon treatment with $NaOCD_3$ in CD_3SOCD_3–CD_3OD, analogous to that observed with $[Ru(bipy)_3][PF_6]_2$ (bipy = 2,2′-bipyridine). The exchange of $H^{3',5'}$ is most rapid, an observation which enables cyclometallation pathways to be eliminated.

Transition-metal complexes of 2,2′-bipyridine (bipy) have recently been shown to exhibit a hitherto unsuspected chelating *C,N* cyclometallated bonding mode.[1] To date, this bonding mode has only been unequivocally established for mononuclear complexes of iridium(III), which have been fully characterised structurally and spectroscopically.[2] A cyclometallated 2,2′-bipyridine ligand has also been observed to bridge two metal centres in triosmium clusters.[3] In view of the well documented anomalies in the reactivity of transition-metal complexes of 2,2′-bipyridine, cyclometallated species have been suggested as possible reaction intermediates.[4]

It has been shown that $[Ru(bipy)_3]^{2+}$ salts undergo specific deuteriation at the 3 and 3′ positions of the ligand upon treatment with CD_3SOCD_3 solutions of $NaOCD_3$.[5] The kinetics of this reaction have been studied, and it has been shown that at elevated temperatures other protons also exchange, but at a rate considerably slower than those at the 3 and 3′ positions.[6] This paper reports the analogous deuteriation reaction of $[Ru(terpy)_2]^{2+}$ complexes [terpy = 2,2′:6′,2″-terpyridine, (**1**)] and discusses possible mechanisms for the exchange process in the light of the new observations.



(**1**)

Experimental

Proton n.m.r. spectra were recorded on a Bruker WM 250 spectrometer, operating at a frequency of 250.13 MHz. The deuterium resonance of the deuteriated solvent was used as internal lock. A pulse angle of *ca.* 45° and a relaxation delay of 0.2 s were used as routine acquisition parameters. Spectra were recorded at 25 °C.

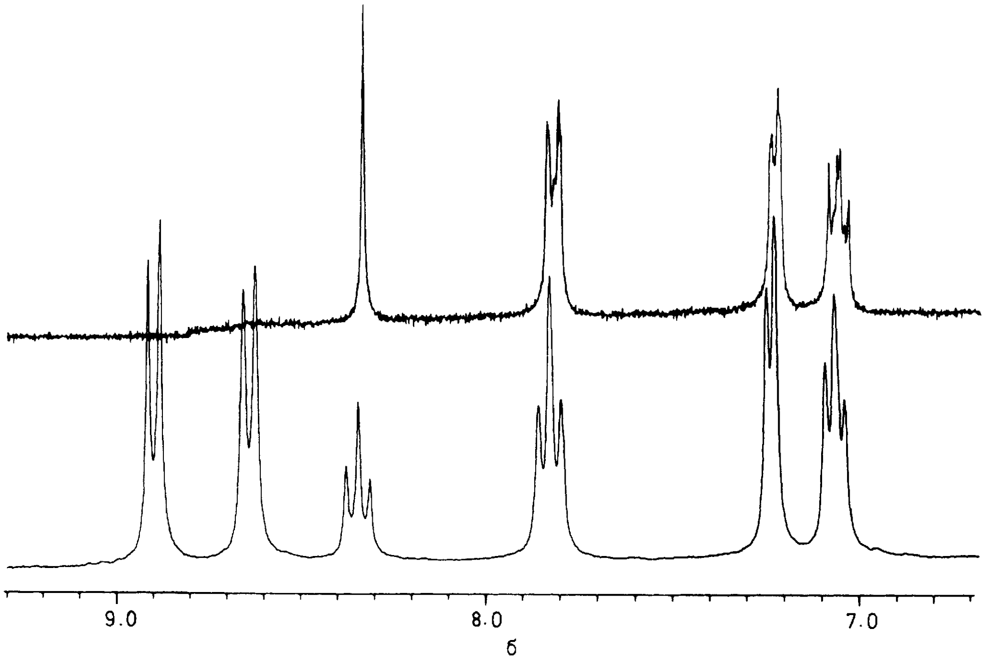
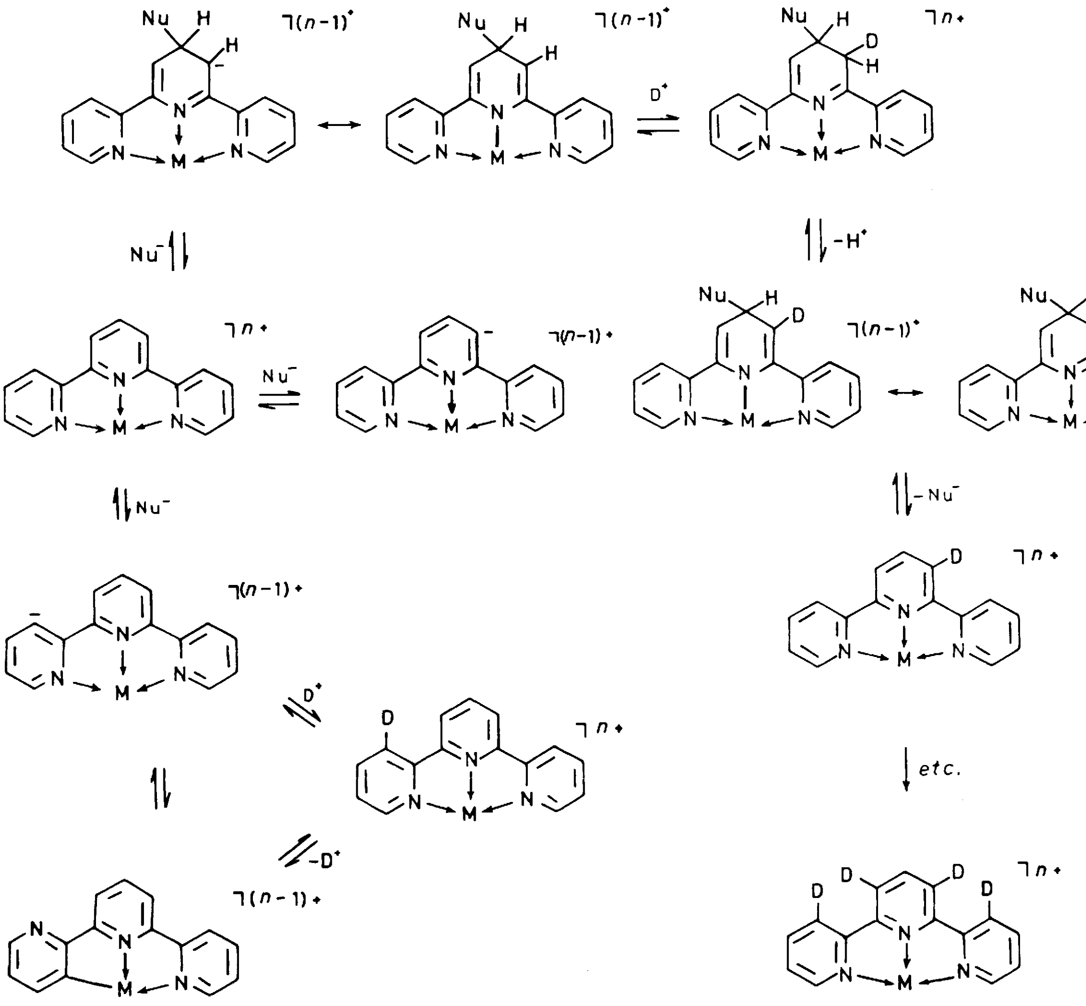


Figure. The 250-MHz ^1H n.m.r. spectrum of $[Ru(terpy)_2][PF_6]_2$ [6 mmol dm^{-3}, CD_3SOCD_3–CD_3OD (1 : 1), 0.5 mol dm^{-3} $NaOCD_3$] before (lower) and after (upper) exchange was complete



Scheme. Nu = Nucleophile

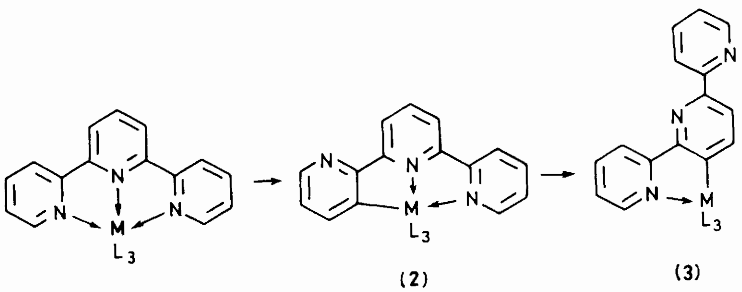
Bis(2,2′:6′,2″-*terpyridine*)*ruthenium*(II) *Hexafluorophosphate*.—The salt $RuCl_3\cdot3H_2O$ (0.261 g, 1 mmol) was dissolved in ethanol (40 cm^3) and the resulting solution heated to reflux for 1 h, after which a green colour had developed. 2,2′:6′,2″-Terpyridine (48 g, 2 mmol) was added, and the solution heated to reflux for 2 h, after which it was filtered to remove a dark solid {presumably [Ru(terpy)Cl_3]}. The red filtrate was treated with a solution of ammonium hexafluorophosphate (0.89 g) in water (2 cm^3) and allowed to crystallise, when red plates of the complex $[Ru(terpy)_2][PF_6]_2$ separated (0.200 g, 23%). No attempt was made to optimise the yield in this preparation.

Results and Discussion

The 250-MHz ^1H n.m.r. spectrum of a 6 mmol dm^{-3} solution of $[Ru(terpy)_2][PF_6]_2$ in CD_3SOCD_3–CD_3OD (1:1) exhibits the six resonances expected from a chelating, terdentate 2,2′:6′,2″-terpyridine ligand (Figure). The lowest-field resonance, a doublet centred at δ 8.93 (J = 8.1 Hz), was shown by homonuclear decoupling experiments to be coupled to the triplet centred at δ 8.33. These two resonances may thus be assigned to the protons $H^{3'}$, $H^{5'}$, and $H^{4'}$ respectively of the central ring. Similar decoupling experiments established the assignment of the remaining resonances; the doublet at δ 8.67 (J = 8.0 Hz) to $H^{3,3''}$, the apparent triplet at δ 7.93 to $H^{4,4''}$, the doublet at δ 7.36 (J = 5.1 Hz) to $H^{6,6''}$, and the apparent triplet at δ 7.19 to $H^{5,5''}$. The assignment of the lowest-field protons to $H^{3,3''}$ and $H^{3',5'}$ is contrary to that expected from the spectrum of the free ligand, but is fully in accord with the van der Waals interactions of $H^{3,3''}$ with $H^{3',5'}$ in the *cis* chelated form, resulting in a deshielding. The assignment of the lowest-field resonances in the spectrum of $[Ru(bipy)_2]^{2+}$ has previously been made on the basis of relaxation measurements and the study of substituted derivatives.[7] The spectrum of $[Ru(terpy)_2]^{2+}$ provides independent support for this, since the assignment of the resonance for $H^{3',5'}$ is entirely unambiguous.

Upon treatment with $NaOCD_3$, solutions of $[Ru(terpy)_2][PF_6]_2$ darken, but no other changes are apparent. The upper trace in the Figure shows the 250-MHz ^1H n.m.r. spectrum of such a solution of 6 mmol dm^{-3} $[Ru(terpy)_2][PF_6]_2$ and 0.5 mol dm^{-3} $NaOCD_3$ in CD_3SOCD_3–CD_3OD (1:1). Immediately on addition of the $NaOCD_3$, a series of low intensity resonances appear [δ 9.28 (d), 8.52 (d), 8.08 (t), and 7.47 (t)]. These peaks are not observed when an equivalent amount of methanol is added, and we believe them to represent an intermediate in the reaction. They disappear as the reaction proceeds to completion. Further studies are underway in an attempt to characterise this transient species.

After prolonged periods at room temperature, or shorter periods (*ca.* 15 min) at 80 °C, marked changes occur in the spectrum. The signals at δ 8.93 and 8.67 disappear, whilst the triplets at δ 8.33 and 7.93 collapse to a singlet and doublet respectively. This is fully consistent with deuteriation occurring at positions 3,3′,5′, and 3″ exclusively. Spectra obtained at



(2) (3)

intermediate stages in the exchange process indicate that the rate of exchange of the lowest-field protons ($H^{3',5'}$) is faster than that of the protons on the terminal rings, H^3 and $H^{3''}$. Preliminary kinetic studies under pseudo-first-order conditions suggest that the rate of exchange of $H^{3',5'}$ is almost twice as fast as that of $H^{3,3''}$.

A number of possible schemes may be proposed to account for this deuteriation behaviour. The recent characterisation of a cyclometallated bonding mode in $[Ir(bipy\text{-}NN')_2(bipy\text{-}C^3N)]^{2+}$ strongly suggested that such species might occur at sufficiently low energy to act as reactive intermediates. In the case of a 2,2′:6′,2″-terpyridine complex it is easy to see how exchange at positions 3 and 3″ may occur *via* a cyclometallation process to give (**2**); however, exchange at positions 3′ and 5′ involves the intermediacy of a bidentate cyclometallated 2,2′:6′,2″-terpyridine (**3**). This intermediate is expected to be higher in energy than the terdentate *C,N,N′* bonding mode leading to exchange at the 3 and 3″ positions. The observation that the 3′ and 5′ positions exchange more rapidly than those of the terminal rings indicates that the cyclometallation pathway is not the dominant mechanism for the deuteriation reaction. It seems reasonable to discount the cyclometallation pathway in the 2,2′-bipyridine complex also.

On the basis of the experimental results presented hitherto, it is not possible to distinguish between the remaining mechanistic possibilities (Scheme); *i.e.* nucleophilic attack by methoxide to give a 3,4-dihydropyridyl anion, or deprotonation to form a 3-pyridyl anion. However, one of the mechanistic possibilities has been eliminated, enabling experiments to distinguish between the remaining two to be devised.

Acknowledgements

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