A Deuterium Exchange Reaction of the Tris-(2,2′-bipyridine)ruthenium(II) Cation: Evidence for the Acidity of the 3,3′-Protons

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The first observation of deuterium exchange upon 2,2′-bipyridine (bipy) co-ordinated to ruthenium(II) is reported; the reaction of $[Ru(bipy)_3]^{2+}$ in $(CD_3)_2SO$ with $Na[OCD_3]$ in CD_3OD to yield $[Ru([3,3'\text{-}^2H_2]\text{-}bipy)_3]^{2+}$ is demonstrated to involve deprotonation of the co-ordinated bipy ligand at the slightly acidic 3,3′-positions, an acidity promoted by steric strain.

Although there have been many claims[1] to have observed 'covalent hydration,' or 'pseudo-base' formation, for 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and pyridine (py) complexes of the transition metals, there is no conclusive evidence to support the existence of such intermediates. Indeed, the evidence proferred to support the 'pseudo-base' mechanism for the attack of nucleophiles (*e.g.* $[OH]^-$ or $[CN]^-$) upon such complexes as $[Pt(bipy)_2]^{2+}$ [2] and $[Pt(bipy)(CN)_2]$[3] is said by Nord and her co-workers[4,5] to be due to nucleophilic attack at the metal and *not* at the ligand, and the results upon which Nord's arguments are based have been independently verified in our own laboratory.[6,7] However, these results do not demonstrate that 'pseudo-bases' do not exist, merely that the evidence quoted to support their existence, in these particular instances, can be interpreted in other ways. In a search for meaningful evidence, we discounted an examination of square-planar complexes, as vacant co-ordination sites upon the metal were considered to preclude nucleophilic attack upon the heterocyclic ligand. We thus turned our attention to six-co-ordinate complexes. The only claim of 'covalent hydration' for a six-co-ordinate platinum complex is for $[Pt(py)_4Cl_2]^{2+}$,[8] a claim which has been challenged by Nord.[9] Our own investigation of this system[10] gave experimental results contrary to those in ref. 8; we found that the pK_a of $[Pt(py)_4Cl_2]^{2+}$ in water is not 3.4, but 7.2 (as originally reported by Grinberg in 1966).[11] As this acidity had originally been ascribed[11] to hydrolysis of the labile chloride ligand, we selected for study $[Ru(bipy)_3]^{2+}$, a molecule which (under non-photochemical conditions) has shown no evidence for metal–ligand dissociation in any solvent at ambient temperatures. This molecule would appear to be an ideal substrate for studying the postulated nucleophilic attack upon co-ordinated 2,2′-bipyridine, the ligand being the only available site for facile attack.

There has been one claim for covalent hydration of a ruthenium(II) complex, for the species $[Ru(bipy)_2(py)_2]^{2+}$. Gillard[12] reported reversible changes in the ^1H n.m.r. spectra of solutions of $[Ru(bipy)_2(py)_2]^{2+}$, upon the addition of $[OH]^-$, $[OR]^-$ or $[CN]^-$, and attributed them to 'covalent hydration' of the bipy ligand. The 300 MHz ^1H n.m.r. spectrum of a

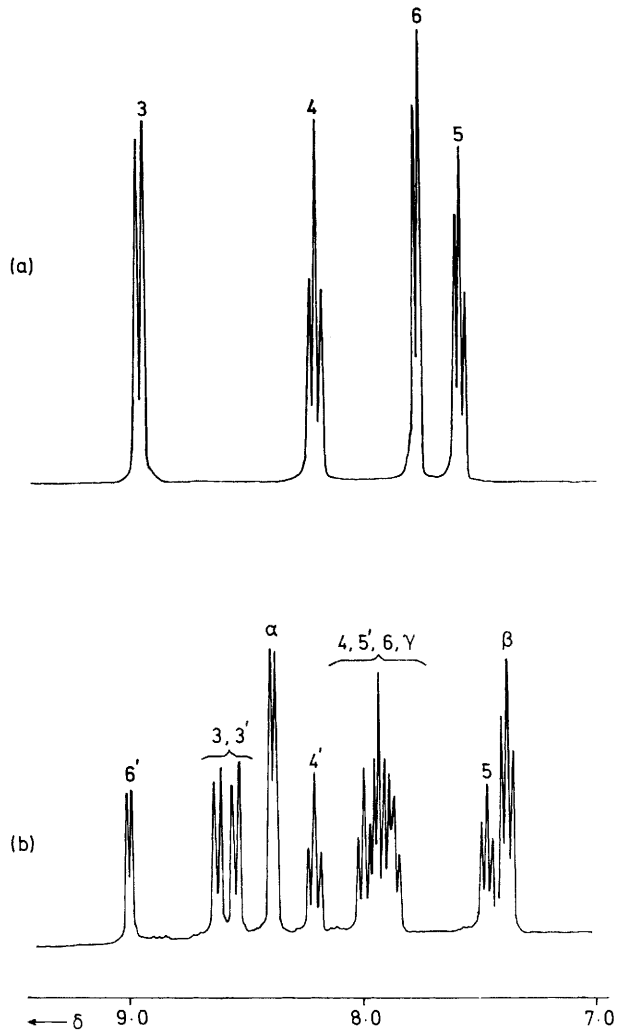

Figure 1. The 300 MHz ^1H n.m.r. spectra of (a) $[Ru(bipy)_3]^{2+}$ and (b) $[Ru(bipy)_2(py)_2]^{2+}$ in $(CD_3)_2SO$. The numbering system for bipy is given in Figure 2; in (b) the primed ring is *trans* to bipy, whilst the unprimed ring is *trans* to py. The α, β, and γ signals are due to 2,6-H, 3,5-H, and 4-H protons on py, respectively.

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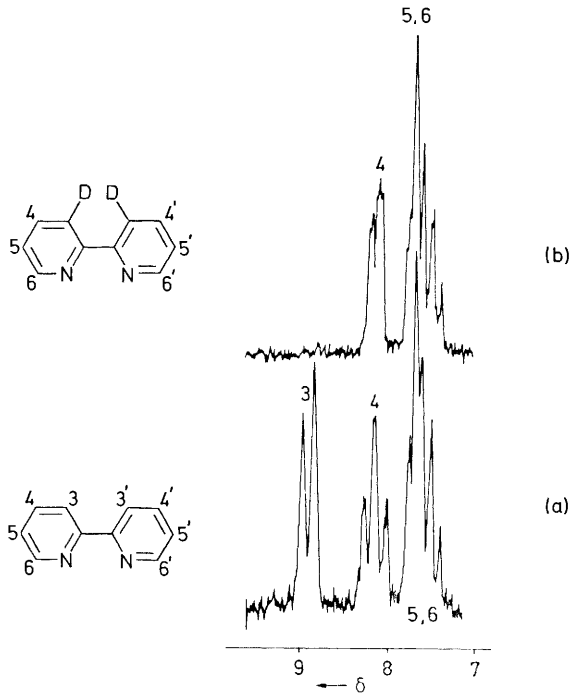

Figure 2. The 60 MHz ^{1}H n.m.r. spectra of $[Ru(bipy)_3]^{2+}$ in $(CD_3)_2SO$ (a) immediately after the addition of $Na[OCD_3]$ in CD_3OD and (b) 24 h later. The reaction mixture was maintained at 35 °C.

solution of $[Ru(bipy)_2(py)_2]^{2+}$ in $(CD_3)_2SO$ is shown in Figure 1, and the features attributable to the bipy and py ligands are readily identified by comparison with the spectrum of $[Ru(bipy)_3]^{2+}$ in the same solvent. Upon the addition of Na[OD] in D_2O to the $(CD_3)_2SO$ solution of $[Ru(bipy)_2(py)_2]^{2+}$, no significant changes were observed in the ^{1}H n.m.r. spectrum, and a brown solid slowly separated from solution. It was concluded that any changes which may have been originally observed could only be attributed to the facile reaction (1), which is well documented for $[Ru(phen)_2(py)_2]^{2+}$.[13] As such a displacement reaction is unknown for

$$[Ru(bipy)_2(py)_2]^{2+} + L \rightleftharpoons [Ru(bipy)_2(py)L]^{2+} + py \quad (1)$$

$[Ru(bipy)_3]^{2+}$, and $[Ru(bipy)_2(py)_2]^{2+}$ is electronically similar (it has the same redox potential) to $[Ru(bipy)_3]^{2+}$, studies were concentrated upon this latter, stable molecule.

We find no evidence at all for reaction of either free bipy or $[Ru(bipy)_3]^{2+}$ with either sodium hydroxide or sodium methoxide in methanol, water, or dimethyl sulphoxide, under a wide variety of reaction conditions. However, when $[Ru(bipy)_3]^{2+}$ is allowed to react with $Na[OCD_3]$ in $(CD_3)_2SO$–CD_3OD solution, pronounced changes in the ^{1}H n.m.r. spectrum of the complex are observed. (*N.b.* Under similar reaction conditions, free bipy is unreactive.) The spectrum of $[Ru(bipy)_3]^{2+}$ shows a low-field doublet due to the 3,3′-protons. After 24 h at 35 °C, this low-field doublet completely vanishes (Figure 2), and the signals due to the 4,4′-protons collapse from a triplet to a doublet (showing fine structure due to H–D coupling). The signals due to the 5,5′- and 6,6′-protons remain essentially unchanged. The integrated ratios, and the values of J and δ for this novel reaction product are entirely in accord with complete exchange of the 3,3′-protons for deuterium having occurred. The product was isolated as a hexafluorophosphate salt, and analysis was consistent with the formulation $[Ru([3,3'-^2H_2]bipy)_3][PF_6]_2$, hence eliminating the possibility of the formation of $[Ru\{bipy\text{-}3,3'\text{-}(OCD_3)_2\}_3][PF_6]_2$. Treatment of this complex with Na[OMe] in $(CH_3)_2SO$–CH_3OH resulted in the reappearance of the signals close to those of 3- and 3′-H in the ^{1}H n.m.r. spectrum. Moreover, $[Ru([3,3'-^2H_2]bipy)_3][PF_6]_2$ shows a signal corresponding to the 3,3′-deuterons in its ^{2}H n.m.r. spectrum.

Both the ^{1}H n.m.r. spectrum and the crystal structure[14] of $[Ru(bipy)_3]^{2+}$ point to the high steric strain upon the 3,3′-protons, and we interpret the lability of these protons towards H–D exchange in terms of a decreased pK_a generated as a result of that strain. It is significant that when that strain is released {in the formation of, say, $[Ru(bipy)_2(py)_2]^{2+}$, in which the pyridine rings are free to rotate and twist}, the position of the 3,3′-protons (now inequivalent) moves upfield to an extent that they are no longer the lowest-field resonance of the complex. It is also significant that, once exchange at the 3,3′-positions is complete, *no further exchange at any other position is observed.* We consider this observation as strong evidence in favour of a mechanism involving an initial deprotonation of the complex, rather than the alternative mechanism involving nucleophilic attack at the C-4 or C-4′ positions (*i.e.* 'pseudo-base' formation), which would also lead to complete exchange of 5,5′-protons. Thus, nucleophilic attack of the co-ordinated bipy has occurred, but at an acidic proton in a conventional acid-base reaction, and *not* by 'pseudo-base' formation.‡ Attempts to obtain similar reactions with $[CHMe_2O]^-$ or $[CMe_3O]^-$ in $(CD_3)_2SO$ (*i.e.* with species which are more basic, but less nucleophilic) led to complete decomposition of the complex, owing to the generation of the highly reactive $[CD_2SOCD_3]^-$ anion under these highly basic conditions.[15] Thus, $[OCH_3]^-$ occupies a special position in $(CH_3)_2SO$, being sufficiently basic to deprotonate the co-ordinated ligand, but not basic enough to generate significant amounts of $[CH_2SOCH_3]^-$. Finally, these observations lead to a rationalisation of the structure observed recently for $[Ir(bipy)_3][ClO_4]_3.2H_2O$,§[16] in which a water molecule is bound in the plane of one of the bipy ligands, the O atom being about 2.9 Å from the 3- and 3′-skeletal atoms. This can be clearly understood in terms of hydrogen-bonding of the water to the acidic protonic positions of the ligand.

In conclusion, we find that even in a complex which is optimally arranged for nucleophilic attack upon the carbon atoms of the co-ordinated heterocyclic ligand (according to the 'pseudo-base' theory), no evidence for 'covalent hydration' could be observed. However, the observation of a previously unsuspected acidity of the co-ordinated 2,2′-bipyridine ligand suggests that much of the kinetic data previously reported to support the 'pseudo-base' mechanism may now be open to an alternative interpretation, in terms of a conjugate base mechanism.

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‡ Studies upon $[Ru(phen)_3]^{2+}$ (which possesses no positions of steric strain) or upon $[Ru(4,4'\text{-}Me_2bipy)_3]^{2+}$ (in which the 3,3′-position is shielded to nucleophilic attack by the 4,4′-methyl groups) revealed no reaction under the conditions in which $[Ru(bipy)_3]^{2+}$ underwent H–D exchange.

§ We have just completed a ^{1}H and ^{13}C n.m.r. study of the hydrated isomers of $[Ir(bipy)_3]^{3+}$, and these results will be published shortly. It is pertinent to note, however, that no evidence for loss of aromatic character of the ligand (as claimed in ref. 17) has been observed (K. R. Seddon and J. E. Turp, unpublished observations).

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