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Adducts Formed by Attack of Nitromethane Anion on Ru(II) Complexes of 5-Nitro-1,10-phenanthroline

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We have previously reported the reactions of nucleophiles such as OH^-, CN^- and OMe^- at the ligand in transition metal complexes of diimine ligands such as 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy), [1–4]. Variations in the site of attack have been observed. Hydroxide reacts at carbon atoms *para*- to coordinated nitrogen and also at the uncoordinated ring in 5-nitro-1,10-phenanthroline (5-NO_2phen) complexes [1]. We have extended our studies of this class of reactions to carbanions. Here we report the first such reaction involving adduct formation of nitromethane anion ($CH_2NO_2^-$) with Ru(II) complexes of 5-NO_2phen and bipy.

Experimental

All complexes were prepared as previously described [1, 2]. ^{1}H nmr spectra were recorded at 35 °C using a 90 MHz Perkin Elmer R32 spectrometer. CD_3NO_2 and d^5-pyridine were used as solvents and spectra measured relative to TMS as internal standard Throughout this communication chemical shifts are given in ppm and coupling constants in Hz.

Results and Discussion

No reaction of the complexes was observed in CD_3NO_2 or in d^5-pyridine alone during several weeks. However, when d^5-pyridine is added to solutions in CD_3NO_2 thus generating some $CD_2NO_2^-$, addition of the anion to the ligand occurs. Spectra recorded during the reaction of Ru(5-NO_2phen)$_3^{2+}$ are shown in Fig. 1. The original spectrum (δ: H^2 8.35, H^3 7.83, H^4 8.87, H^6 9.18, H^7 9.16, H^8 7.86, H^9 8.41 ppm; $J_{2,3}$ = 4.5, $J_{3,4}$ = 8.5, $J_{7,8}$ = 8.0, $J_{8,9}$ = 5.0 Hz) changes with the H^6 singlet being quantitatively replaced by a new upfield singlet at δ 6.33. H^4 and

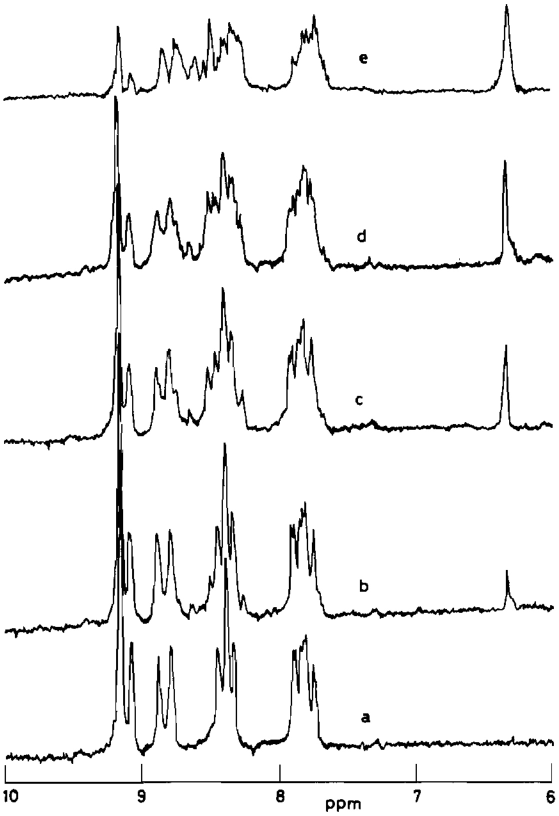

Fig. 1. 90 MHz ^{1}H nmr spectra of the reaction of Ru(5-NO_2-phen)$_3^{2+}$ in CD_3NO_2/d^5-pyridine (5:1, v/v); a: t = 0, b: t = 20 mins, c: t = 55 mins; d: t = 115 mins, e: t = 400 mins; T = 35 °C. For e, spectral intensity is halved.

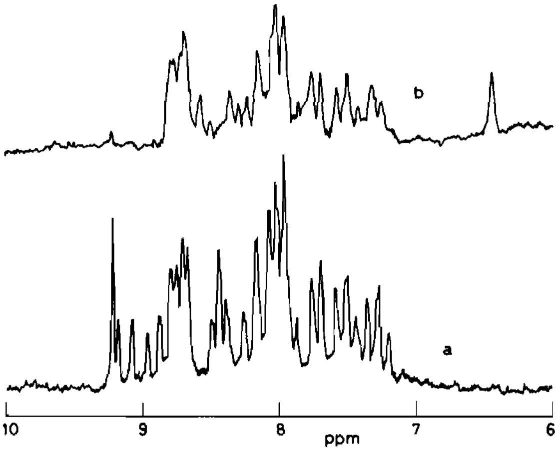

Fig. 2. 90 MHz$_2^2$ ^{1}H nmr spectra of a: Ru(5-NO_2phen)-(bipy)$_2^{2+}$ in CD_3NO_2, and, b: in CD_3NO_2/d^5-pyridine (5:1, v/v) 10 mins after mixing. T = 35 °C. For b, spectral intensity is 0.75 that of a.

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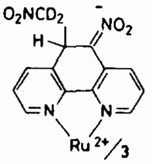
H^7 diminish and new signals for these protons are observed at δ 8.55 and 8.80 ppm respectively with $J_{3,4}$ = 9.0, $J_{7,8}$ = 8.5 Hz. These unambiguous spectral changes are entirely consistent with the formation of the adduct 1 with a nitromethane anion added to each of the 5-NO_2phen ligands. During the reaction, adduct formation at only the one site is observed. This is analogous to the reaction of $CD_2NO_2^-$ with pyridinium ions [5]. No migration from sites which are kinetically favoured to the thermodynamically favoured ones is seen as was the case in related reactions of OH^- with Ru(5-NO_2phen)$(bipy)_2^{2+}$ [1] and in the reaction of OMe^- to form pseudo-base adducts with certain nitro-aromatics [6, 7].



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Reaction of $CH_2NO_2^-$ with Ru(5-NO_2phen)-$(bipy)_2^{2+}$ (Fig. 2) follows a course analogous to that above. The bipy ligands are unaffected (parent complex, δ: H^3 8.74, $H^{3'}$ 9.71, H^4 8.18, $H^{4'}$ 8.27, H^5 7.28, $H^{5'}$ 7.51, H^6 7.72, $H^{6'}$ 8.00 ppm; $J_{3,4}$ = 8.0, $J_{4,5}$ = 8.0, $J_{5,6}$ = 6.5, $J_{3',4'}$ = 8.0, $J_{4',5'}$ = 7.5, $J_{5',6'}$ = 5.5 Hz; mono-adduct, δ: H^3 $H^{3'}$ 8.76, H^4 8.07, $H^{4'}$ 8.15, H^5 7.32, $H^{5'}$ 7.61, H^6 7.77, $H^{6'}$ 8.00 ppm). The 5-NO_2phen ligand undergoes the same addition as was found in Ru(5-NO_2phen$)_3^{2+}$. The new H^6 singlet is found at δ 6.45. Signals from the newly formed adduct of 5-NO_2phen of H^4 and H^7 are located at δ 8.60 and beneath the H^3 and $H^{3'}$ signals of bipy respectively.

The spectral changes observed during the corresponding reaction of Ru(5-NO_2phen$)_2$(bipy$)^{2+}$ are more difficult to interpret than the above due to complexity arising from the magnetically non-equivalent halves of the 5-NO_2phen ligands. However, in this case C^6 of the coordinated 5-NO_2phen also undergoes reaction, the upfield signal of H^6 appearing at δ 6.40. In all of these reactions, the site of attack is the same carbon atom as is found in the addition of OH^- [8] and OMe^- [9] to the free, uncoordinated 5-NO_2phen molecule.

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