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Oxidative and reductive activation of tetra-*n*-butylammonium *trans*-tetrabromobis(*tert*-butylisocyanide)ruthenium(III): a spectroelectrochemical study

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Electrochemical and spectroelectrochemical studies have shown that oxidation of *trans*-$[RuBr_4(CNBu^t)_2]^-$ in acetonitrile produces tervalent *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]$, whilst reduction leads to the formation of a divalent complex of the same stoichiometry, *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]^-$, which can be oxidised reversibly to *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]$.

The tendency of monomeric halide or mixed halide (X)–neutral donor ligand (L) complexes $[MX_nL_{6-n}]^z$ ($n = 1$–6) to expel halide upon reduction is well documented and has been used with great effect to prepare a variety of novel species.[1–7] A voltammetric study has indicated that such a process may accompany the reduction of the tervalent mixed halide–isocyanide complex *trans*-$[NBu_4][RuBr_4(CNBu^t)_2]$.[8] It was suggested that, following one-electron reduction at room temperature, substitution of halide by solvent (acetonitrile) occurs to form $[RuBr_3(CNBu^t)_2(NCMe)]^-$. *In situ* spectroelectrochemical studies (IR and UV/VIS), discussed herein, have confirmed the formation of *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]^-$ under the conditions just described and enabled the one-electron oxidised form, *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]$, to be characterised. The ligand combination of halide and isocyanide in *trans*-$[RuBr_4(CNBu^t)_2]^-$ also facilitates oxidation of tervalent Ru^{III} to quadrivalent Ru^{IV}, although this process is electrochemically (and chemically) irreversible. Through the use of spectroelectrochemical techniques, it has been discovered that oxidation of *trans*-$[RuBr_4(CNBu^t)_2]^-$ in acetonitrile leads to the direct formation of *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]$. The formation of the latter species *via oxidation* of the parent complex is quite unexpected, and provides a new method of activation of complexes of this type.

The cyclic voltammogram of *trans*-$[NBu_4][RuBr_4(CNBu^t)_2]$, recorded in 0.25 mol dm^{-3} $[NBu_4][PF_6]$ in acetonitrile–dichloromethane (1:1),‡ displays a partially reversible one-electron reduction ($E_{pc} = -0.18$ V) to $[RuBr_4(CNBu^t)_2]^{2-}$ [Fig. 1(*a*)], which reacts rapidly to form an electroactive species detected on the return scan ($E_{\frac{1}{2}} = +0.41$ V). The species detected at $E_{\frac{1}{2}} = +0.41$ V is not observed if the cathodic scan is switched prior to the *trans*-$[RuBr_4(CNBu^t)_2]^{-/2-}$ reduction wave, nor if the solution is cooled ($T < 253$ K), whereupon the *trans*-$[RuBr_4(CNBu^t)_2]^{-/2-}$ reduction becomes quasi-reversible. These observations are indicative of EC-type behaviour, where electron transfer (E) is followed by a homogeneous chemical reaction (C) which gives rise to a new species in solution. The shift in $E_{\frac{1}{2}}$ ($Ru^{III/II}$) between $[RuBr_4(CNBu^t)_2]^-$ and the newly formed species (*ca.* 0.6 V) is consistent with the loss of bromide and the co-ordination of acetonitrile,[10] as stated previously.[8] If, after cycling over the *trans*-$[RuBr_4(CNBu^t)_2]^{-/2-}$ reduction, the return scan is extended to more anodic potentials, two irreversible waves are observed at ≈+0.9 and ≈+1.2 V, which correspond to the oxidation of free Br^- under similar conditions.

For the present complex, the changes in the IR and UV/VIS spectra accompanying reduction (and subsequent re-oxidation) are particularly informative. The ν_{CN} band of the co-ordinated isocyanide in *trans*-$[RuBr_4(CNBu^t)_2]^-$ occurs at 2170 cm^{-1} and, upon reduction ($E_{app} = -0.4$ V), this band collapses with the growth of bands at 2109 and 2275 cm^{-1} [Fig. 2(*a*)]. The former can be assigned to ν_{CN} from the isocyanide, whilst the latter is due to ν_{NC} of newly co-ordinated acetonitrile,[11] indicating the exchange of Br^- for MeCN. Returning the potential of the working electrode of 0.0 V does not result in any flow of current in the cell nor any spectral changes, hence confirming that the reduction of *trans*-$[RuBr_4(CNBu^t)_2]^-$ results in a chemical transformation. Oxidation of the newly formed species is observed at $E_{app} = +0.6$ V, whereupon ν_{CN} moves to 2192 cm^{-1} and ν_{NC} to 2326 cm^{-1}, the latter band being very weak [Fig. 2(*b*)]. The retention of a single ν_{CN} band throughout the sequence of redox and chemical reactions (ECE) implies that the co-ordinated $CNBu^t$ ligands remain in the *trans* configuration,§ and therefore that the product has a meridional arrangement of bromides, *i.e.* the product of reduction is *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]^-$, which can be reversibly oxidised to *mer,trans*-$[RuBr_3(CNBu^t)_2(NCMe)]$. The halide geometry can be confirmed by UV/VIS spectroscopy, since certain d^5 metal–halide chromophores give rise to diagnostic halide-to-metal charge-transfer spectra.[5] Reduction of *trans*-$[RuBr_4(CNBu^t)_2]^-$ ($E_{app} = -0.4$ V) followed by re-oxidation

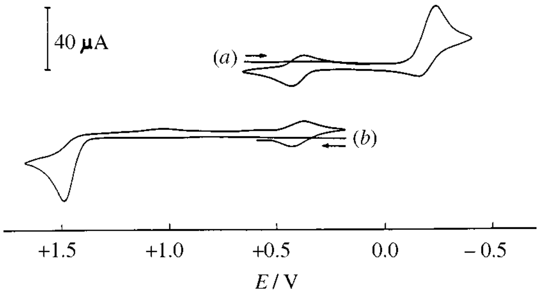

Fig. 1 Cyclic voltammetry of *trans*-$[NBu_4][RuBr_4(CNBu^t)_2]$ in 0.25 mol dm^{-3} $[NBu_4][PF_6]$ in acetonitrile–dichloromethane (1:1) at room temperature, *vs.* Ag–AgCl, scan rate = 100 mV s^{-1}. Arrow indicates commencement of scan (potential and direction)

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‡ Electrochemical and spectroelectrochemical experiments were performed as described previously.[9] All potentials are quoted *vs.* the Ag–AgCl reference electrode, against which the ferrocenium–ferrocene couple was measured to be +0.55 V; E_{app} refers to the potential at which the electrolysis was performed in the infrared reflection-absorption spectroscopic (IRRAS) cell or optically transparent thin-layer electrochemical (OTTLE) cell.

§ The shoulder at ≈2070 cm^{-1} may arise through the symmetry of the complex being lowered by bending of the Ru–CN–C axis, as a result of back bonding from $Ru^{II}(d\pi)$ to $CNBu^t(\pi^*)$.

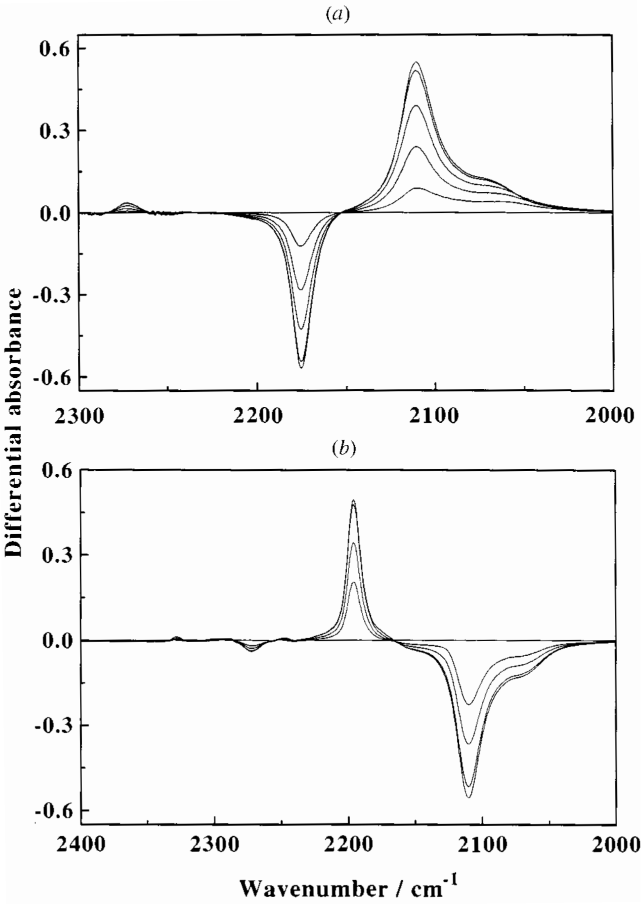

Fig. 2 Changes in IR difference absorption spectra accompanying (*a*) reduction of *trans*-$[\mathrm{RuBr_4(CNBu^t)_2}]^-$ in 0.25 mol dm^{-3} $[\mathrm{NBu_4}][\mathrm{PF_6}]$ in acetonitrile–dichloromethane (1 : 1) in an IRRAS cell at room temperature. The horizontal line at zero absorbance corresponds to the initial spectrum, *i.e.* that of *trans*-$[\mathrm{RuBr_4(CNBu^t)_2}]^-$, prior to electrolysis. The potential of the working electrode is stepped to $E_{\mathrm{app}} = -0.4$ V, and single-scan IR spectra collected as a function of time. Consumption of *trans*-$[\mathrm{RuBr_4(CNBu^t)_2}]^-$, upon reduction, is indicated by increasing negative absorbance at 2170 cm^{-1}, whilst increasing positive absorbance at 2272 and 2109 cm^{-1} corresponds to the formation of *mer,trans*-$[\mathrm{RuBr_3(CNBu^t)_2(NCMe)}]^-$; (*b*) oxidation of *mer,trans*-$[\mathrm{RuBr_3(CNBu^t)_2(NCMe)}]^-$ to *mer,trans*-$[\mathrm{RuBr_3(CNBu^t)_2(NCMe)}]$ at $E_{\mathrm{app}} = +0.6$ V

($E_{\mathrm{app}} = +0.6$ V) produces a spectrum typical of a complex with a meridional arrangement of bromide ions (Fig. 3)[12,13] thus confirming that the product formed is *mer,trans*-$[\mathrm{RuBr_3(CNBu^t)_2(NCMe)}]$.

The oxidation of *trans*-$[\mathrm{RuBr_4(CNBu^t)_2}]^-$ is irreversible ($E_{\mathrm{pa}} = +1.50$ V) and leads to the formation of a redox active species with $E_{\frac{1}{2}} = +0.41$ V [Fig. 1(*b*)]. Both IR and UV/VIS spectroelectrochemical experiments have shown, unequivocally, that the ultimate product of *oxidation* of *trans*-$[\mathrm{RuBr_4(CNBu^t)_2}]^-$ is, paradoxically the Ru$^{\mathrm{III}}$ complex *mer,trans*-$[\mathrm{RuBr_3(CNBu^t)_2(NCMe)}]$, since the spectra thus formed are identical to those obtained following reduction of *trans*-$[\mathrm{RuBr_4(CNBu^t)_2}]^-$ and subsequent re-oxidation (see above). The replacement of a bromide ion by acetonitrile under these circumstances is quite unexpected, since oxidation may have been anticipated to strengthen the Ru–Br bonds. The tendency of halide ions to stabilise higher valent complexes more commonly results in the scavenging of halide upon oxidation, often at the expense of neutral donor ligands.[3,14,15] In the present case there is no evidence to suggest expulsion of isocyanide, since free isocyanide would be readily detected in the IR spectroelectrochemical experiments on account of the very strong ν_{CN} band for free CNBu^t, which occurs at 2139 cm^{-1}.

The mechanism by which this transformation occurs may involve metal-based oxidation followed by homolytic fission of the Ru$^{\mathrm{IV}}$–Br bond, producing a tervalent species with a vacant co-ordination site and Br$^{\bullet}$. The co-ordinatively unsaturated complex is likely to bind solvent rapidly to form the product *mer,trans*-$[\mathrm{RuBr_3(CNBu^t)_2(NCMe)}]$. The fate of the Br$^{\bullet}$ radical is uncertain but, at the potentials required to oxidise the complex ($E_{\mathrm{pa}} = +1.50$ V), Br$^{\bullet}$ could be oxidised to Br$_2$, or alternatively, Br$^{\bullet}$ could react with solvent or adventitious water to form HBr. This type of redox-induced substitution reaction, previously termed *oxidatively induced reductive elimination*, has been proposed for other transition-metal complexes.[16] Further studies are in progress to explore the generality of this reaction as a means of introducing other neutral ligands. The analogous chloride complex, *trans*-$[\mathrm{NBu_4}][\mathrm{RuCl_4(CNBu^t)_2}]$, is also under investigation.

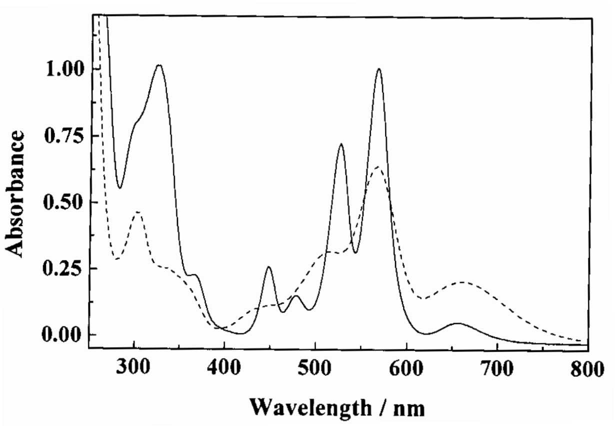

Fig. 3 The UV/VIS spectra of *trans*-$[\mathrm{RuBr_4(CNBu^t)_2}]^-$ (——) and *mer,trans*-$[\mathrm{RuBr_3(CNBu^t)_2(NCMe)}]$ (– – –), recorded in an OTTLE cell at 243 K, in 0.25 mol dm^{-3} $[\mathrm{NBu_4}][\mathrm{PF_6}]$ in acetonitrile–dichloromethane (1 : 1)

Acknowledgements

The authors thank Johnson Matthey for the loan of hydrated ruthenium trichloride and the Central Research Fund of the University of London for financial assistance. D. G. H. acknowledges the Royal Society for an Endeavour Fellowship and the Ramsay Memorial Fellowships Trust for a British Ramsay Memorial Fellowship. J. P. A. thanks the EPSRC for a postgraduate award.

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Received 12*th May* 1997; *Communication* 7/03245E