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Inorganica Chimica Acta 300-302 (2000) 525-530

Inorganica Chimica Acta

### Redox properties of two new ruthenium(III) isocyanide complexes, trans-[NBu<sub>4</sub>][RuX<sub>4</sub>(CNTM)<sub>2</sub>](X = Cl or Br, CNTM = p-tolylsulfonylmethylisocyanide)

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Received 15 November 1999; accepted 28 November 1999

#### Abstract

New ruthenium(III) complexes *trans*-[NBu<sub>4</sub>][RuX<sub>4</sub>(CNTM)<sub>2</sub>] (X = Cl or Br, CNTM = *p*-tolylsulfonylmethylisocyanide) have been prepared by treating [NBu<sub>4</sub>]<sub>2</sub>[RuX<sub>6</sub>] with the isocyanide ligand CNTM in EtOH–CH<sub>2</sub>Cl<sub>2</sub> solution. In situ IR and UV–Vis spectroelectrochemical studies have shown that reduction of *trans*-[RuX<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> in acetonitrile and subsequent oxidation yields *mer*,*trans*-[RuX<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)]. Similar studies have shown, interestingly, that oxidation of *trans*-[RuX<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> and subsequent reduction also yields the same product. Differences between the redox behaviour of *trans*-[RuX<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> and *trans*-[RuX<sub>4</sub>(CN<sup>t</sup>Bu)<sub>2</sub>]<sup>-</sup> (X = Cl or Br, CN<sup>t</sup>Bu = *tert*-butylisocyanide) in the presence of free isocyanide ligand have also been identified. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Redox properties; Ruthenium(III) complexes; Isocyanide complexes; Spectroelectrochemical studies; IRRAS and OTTLE cell measurements

#### 1. Introduction

Isocyanide ligands are isoelectronic with carbon monoxide and form transition metal complexes analogous to metal carbonyls [1]. However, in general, they are better  $\sigma$ -donors than CO but poorer  $\pi$ -acceptors [2] and consequently isocyanide cations are wellknown, but homoleptic isocyanide anions [3] are rare. Furthermore, isocyanide ligands can stabilise metal ions in relatively high oxidation states, for example as in [Cr(CNR)<sub>6</sub>]<sup>3+</sup> [4] and [Mo(CNR)<sub>7</sub>]<sup>2+</sup> [5], for which the carbonyl analogues are unknown. This means that a wider range of oxidation states is usually accessible for isocyanide than carbonyl systems.

Recently, the redox properties of the complexes trans-[NBu<sub>4</sub>][RuX<sub>4</sub>(CN<sup>t</sup>Bu)<sub>2</sub>] (X = Cl or Br) [6–8] were reported. These complexes readily undergo halide substitution upon reduction with neutral donor ligands such as acetonitrile or pyridine. In addition, spectro-

electrochemical (IR and UV–Vis) studies have shown that these complexes can also undergo halide substitution upon oxidation [7,8]. This unexpected result means that reduction followed by oxidation or oxidation followed by reduction, of *trans*-[RuX<sub>4</sub>(CN<sup>-</sup>Bu)<sub>2</sub>]<sup>-</sup> in the presence of certain ligands may ultimately lead to the formation of the same substituted product.

In this publication, the isocyanide ligand *p*-tolylsulfonylmethylisocyanide,  $CH_3(C_6H_4)\cdot SO_2CH_2NC$ , has been investigated since it is a poorer  $\sigma$ -donor than *tert*-butylisocyanide and thus its ruthenium(III) complexes may be expected to display different redox properties from those of *tert*-butylisocyanide. Two new ruthenium(III) complexes of *p*-tolylsulfonylmethylisocyanide have been prepared and their redox behaviour investigated by means of infrared reflection-absorption spectroscopy (IRRAS) [9] and, in an optically transparent thin-layer electrochemical (OTTLE) cell [10], by electronic spectroscopy. The results of these spectroelectrochemical (IR and UV–Vis) studies are presented and discussed herein.

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#### 2. Experimental

Commercial  $RuCl_3 xH_2O$  was obtained from Johnson-Matthey. The isocyanide ligand *p*-tolylsulfonylmethylisocyanide (CNTM) was purchased from Avocado. The complexes  $[NBu_4]_2[RuCl_6]$  [11] and  $[NBu_4]_2[RuBr_6]$  [12] were prepared by published methods. Both ruthenium(III) isocyanide complexes were prepared under a nitrogen atmosphere using standard Schlenk-line techniques.

#### 2.1. Preparation of trans-[NBu<sub>4</sub>][RuCl<sub>4</sub>(CNTM)<sub>2</sub>]

[NBu<sub>4</sub>]<sub>2</sub>[RuCl<sub>6</sub>] (0.10 g, 0.13 mmol) and CNTM (0.10 g, 0.50 mmol) were dissolved in a degassed 1:20 ethanol-dichloromethane (30 cm<sup>3</sup>) solution. The mixture was stirred for 24 h at room temperature whereupon it changed from dark brown to dark yellow. Then the insoluble by-products were filtered off under gravity and the filtrate volume was reduced to approximately 5 cm<sup>3</sup>. A dark yellow solid was precipitated on adding diethyl 1:1 ether-hexane solution to the filtrate. The product was recrystallised twice from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether solution. Yield: 51%. Anal. Calc. for C<sub>34</sub>H<sub>54</sub>N<sub>3</sub>S<sub>2</sub>O<sub>4</sub>Cl<sub>4</sub>Ru: C, 46.6; H, 6.2; N, 4.8; Cl, 16.2; S, 7.3. Found: C, 46.3; H, 6.0; N, 4.7; Cl, 16.9; S, 7.5%. IR spectrum (KBr disc):  $v_{\rm NC} = 2168$  cm<sup>-1</sup>. Electronic absorption spectrum (CH<sub>2</sub>Cl<sub>2</sub> solvent):  $v_{max}$  ( $\varepsilon$  (dm<sup>3</sup>  $mol^{-1} cm^{-1}$ )) 19 300 (500), 22 700 (6700), 32 000 (2500), 38 000 (15 000), 42 000 (20 000) cm  $^{-1}$ . Negative-ion FAB mass spectrum: major m/z peaks at 634 (A<sup>-</sup>); 599 (A<sup>-</sup>-Cl); 439 (A<sup>-</sup>-CNTM); 244 (A<sup>-</sup>-2 CNTM) amu. A- refers to the ion fragment trans- $[RuCl_4(CNTM)_2]^-$  (assignments are based on <sup>102</sup>Ru and <sup>35</sup>Cl).

#### 2.2. Preparation of trans-[NBu<sub>4</sub>][RuBr<sub>4</sub>(CNTM)<sub>2</sub>]

[NBu<sub>4</sub>]<sub>2</sub>[RuBr<sub>6</sub>] (0.10 g, 0.09 mmol) and CNTM (0.07 g, 0.36 mmol) were dissolved in a degassed 1:20 ethanol-dichloromethane (30 cm<sup>3</sup>) solution. The mixture was stirred for 7 h at room temperature whereupon it changed from dark blue to violet. Then the insoluble by-products were filtered off under gravity and the filtrate volume was reduced to approximately 5 cm<sup>3</sup>. A violet solid was precipitated on adding diethyl ether to the filtrate. The product was recrystallised twice from CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether. Yield: 78%. Anal. Calc. for C<sub>34</sub>H<sub>54</sub>N<sub>3</sub>S<sub>2</sub>O<sub>4</sub>Br<sub>4</sub>Ru: C, 38.8; H, 5.2; N, 4.0; Br, 30.3; S, 6.1. Found: C, 38.9; H, 5.0; N, 4.0; Br, 30.2; S, 6.2%. IR spectrum (KBr disc):  $v_{\rm NC} = 2161$  cm<sup>-1</sup>. Electronic absorption spectrum (CH<sub>2</sub>Cl<sub>2</sub> solvent):  $v_{max}$  ( $\varepsilon$  (dm<sup>3</sup>  $mol^{-1} cm^{-1}$ )) 14 000 (500), 16 500 (6700), 18 000 (4800), 19 700 (1300), 21 400 (1700), 26 000sh (1800), 30 500 (7500), 38 500 (17 000), 42 000 (24 000). Negative-ion FAB mass spectrum: major m/z peaks at 812

(A<sup>-</sup>); 733 (A<sup>-</sup>-Br); 617 (A<sup>-</sup>-CNTM); 538 (A<sup>-</sup>-Br-CNTM); 422 (A<sup>-</sup>-2CNTM) amu. A<sup>-</sup> refers to the ion fragment *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> (assignments are based on  $^{102}$ Ru and  $^{79}$ Br).

Cyclic voltammetric experiments utilised a PAR 174A polarographic analyzer and a PAR 175 waveform generator in conjunction with a Bryans Instruments 60000 Series X-Y/t chart recorder. The experiments were performed using a cell comprising a platinum working electrode, a platinum counter-electrode, and an Ag/AgCl reference electrode [13] calibrated against the ferrocenium–ferrocene couple (+0.55 V) [14]. The voltammetric data were not corrected for the IR drop across the working and reference electrodes. The solvents dichloromethane [13] and acetonitrile [15] were dried and distilled from CaH<sub>2</sub> prior to use; the supporting electrolyte, tetra-n-butylammonium hexafluorophosphate, was prepared as described previously [13].

Infrared (IR) spectroelectrochemical experiments were performed using an IRRAS cell [9] mounted on a modified Specac specular reflectance attachment located in the sample compartment of a Nicolet Magna 750 FTIR spectrometer. The electrode arrangement consisted of a highly polished platinum disc electrode (5 mm diameter), a platinum gauze counter-electrode, and a platinum wire pseudo-reference electrode. All spectroelectrochemical experiments were performed by first stepping to a potential of approximately 0.2 V past the appropriate  $E_{1/2}$  and then collecting single-scan IR spectra (resolution = 1 cm<sup>-1</sup>) as a function of time.

Ultraviolet–visible (UV–Vis) spectroelectrochemical experiments were performed using a cryostated OTTLE cell [10] positioned in the sample compartment of a Perkin–Elmer Lambda 16 spectrophotometer. The cell contained a platinum gauze working electrode (ca. 75% transmission), a platinum wire counter-electrode, and a platinum pseudo-reference electrode.

Negative-ion FAB mass spectra were recorded on a VG ZAB 2SE mass spectrometer.

#### 3. Results and discussion

## 3.1. Reductive chemistry of trans-[NBu<sub>4</sub>][RuBr<sub>4</sub>(CNTM)<sub>2</sub>] in acetonitrile

The cyclic voltammogram of *trans*-[NBu<sub>4</sub>][RuBr<sub>4</sub>-(CNTM)<sub>2</sub>] recorded in 1:1 acetonitrile-dichloromethane solution displays a one-electron reduction  $(E_{1/2} = -0.01 \text{ V})$  to *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>2-</sup> (Fig. 1(a)). The *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-/2-</sup> couple is quasireversible since it displays  $\Delta E_p$  values which increase with increasing scan rates. The reduced species reacts rapidly with acetonitrile to form an electroactive species which



Fig. 1. Cyclic voltammograms showing (a) reductive cycle, (b) oxidative cycle of *trans*- $[NBu_4][RuBr_4(CNTM)_2]$  in 1:1 acetonitriledichloromethane containing 0.25 mol dm<sup>-3</sup>  $[NBu_4][PF_6]$  at r.t. vs. Ag–AgCl, scan rate = 100 mV s<sup>-1</sup>. Arrows indicate commencement of scan direction.

can be detected on the return scan ( $E_{pa} = +0.54$  V). The latter is not observed if the cathodic scan is switched prior to the detection of the trans-[RuBr<sub>4</sub>- $(CNTM)_2]^{-/2-}$  reduction wave nor if the solution is held throughout the redox cycle below 273 K. These observations indicate that *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> displays EC-type [16] behaviour whereby electron transfer(E) is followed by a homogeneous chemical reaction(C) which gives rise to a new species ( $E_{na} =$ +0.54 V) in solution. The shift in  $E_{1/2}(\text{Ru(III/II)})$  (ca. +0.6 V) between trans-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>2-</sup> and the newly formed species indicates that the latter is [RuBr<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)] [17]. Two irreversible waves are detected at  $\approx +0.9$  and +1.2 V, observations which relate to the oxidation of bromide expelled from trans-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>2-</sup>.

The changes in the IR spectra accompanying the reduction and subsequent oxidation of *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> in 1:1 acetonitrile-dichloromethane solution in an IRRAS cell are also informative. The  $v_{\rm NC}$  band of the coordinated isocyanide ligand in *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> occurs at 2170 cm<sup>-1</sup> and, upon reduction at  $E_{\rm app} = -0.20$  V<sup>1</sup>, it collapses with the growth of bands at 2282, 2109 and 2038 cm<sup>-1</sup> (Fig. 2, Table 1). The bands at 2109 and 2038 cm<sup>-1</sup> can be assigned to  $v_{\rm NC}$  of the isocyanide in the reduced species whilst the band at 2282 cm<sup>-1</sup> is due to  $v_{\rm CN}$  of newly coordinated acetonitrile. Oxidation of the reduced species occurs at  $E_{\rm app} = +0.75$  V, whereupon  $v_{\rm NC}$  is

shifted to 2194 cm<sup>-1</sup> and  $v_{\rm CN}$  to 2335 cm<sup>-1</sup>. The changes in the  $v_{\rm NC}$  throughout this redox sequence imply that the coordinated CNTM ligands remain in the *trans* configuration, i.e. that the ultimate product of reduction is *mer*,*trans*-[RuBr<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)]<sup>-</sup>, which can be reversibly oxidised to *mer*,*trans*-[RuBr<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)] (Table 1)<sup>2</sup>. The halide



Fig. 2. Changes in the IR differential absorbance spectra accompanying the reduction of *trans*- $[NBu_4][RuBr_4(CNTM)_2]$  (ca. 10 mmol dm<sup>-3</sup>) in 1:1 acetonitrile–dichloromethane (2 cm<sup>3</sup>) containing 0.25 mol dm<sup>-3</sup>  $[NBu_4][PF_6]$  at 298 K.

 $<sup>^1</sup>E_{\rm app}$  refers to the potential at which the electrolysis was performed in the IRRAS or OTTLE cell.

<sup>&</sup>lt;sup>2</sup> The complex *mer*,*trans*-[RuBr<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)] has skeletal  $C_{2v}$  symmetry and therefore should display two  $v_{NC}$  ( $a_1 + b_1$ ) bands in its IR spectrum. However, the dipole moment change for the  $a_1$  mode is nearly zero and usually only the strong  $b_1$  band is detected. The reduced species has lower symmetry on account of back-bonding (Ru(II) to CN( $\pi^*$ )) along its Ru–CN–C axes and consequently its  $a_1$  mode becomes detectably IR active.

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Complex ( $z = charge$ )	Band maxima (cm <sup>-1</sup> ) <sup>a</sup> Ru(II)		Band maxima (cm <sup>-1</sup> ) <sup>a</sup> Ru(III)	
	v <sub>NC</sub>	v <sub>CN</sub>	v <sub>NC</sub>	v <sub>CN</sub>
[RuCl <sub>3</sub> (CNTM) <sub>2</sub> (NCMe)] <sup>z b</sup>	2110 (s) 2043 (m)	2275 (w)	2202 (s)	2332(w)
[RuBr <sub>3</sub> (CNTM) <sub>2</sub> (NCMe)] <sup>z b</sup>	2109 (s) 2038 (m)	2282 (w)	2194 (s)	2335(w)
[RuCl <sub>3</sub> (CNTM) <sub>3</sub> ] <sup>z c</sup>	2141 (w) 2086 (m) 2034 (m)		2242 (w) 2208 (m) 2178 (s)	
[RuBr <sub>3</sub> (CNTM) <sub>3</sub> ] <sup>z c</sup>	2144 (m) 2088 (m) 2035 (m)		2235 (w) 2199 (m) 2169 (s)	

<sup>a</sup> Recorded in an IRRAS cell under conditions stated in the text. Relative band intensities: s = strong, m = medium and w = weak. <sup>b</sup> *mer.trans*-isomer.

<sup>c</sup> mer-isomer.

configuration of the latter is confirmed by UV–Vis spectroscopy since such ruthenium(III)-halide species display diagnostic halide-to-metal charge-transfer spectra [11]. The reduction of *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> ( $E_{app} = -0.20$  V) and its subsequent oxidation ( $E_{app} = +0.75$  V) in an OTTLE cell produces a spectrum characteristic of a complex with a meridional arrangement of bromide ions (Fig. 3, Table 2).

#### 3.2. Oxidative chemistry of trans-[NBu<sub>4</sub>][RuBr<sub>4</sub>(CNTM)<sub>2</sub>] in acetonitrile

The species trans-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> in 1:1 acetonitrile-dichloromethane solution undergoes irreversible oxidation ( $E_{pa} = +1.58$  V) and ultimately forms an electroactive species detected at  $E_{\rm pc} = +0.54$  V on the return scan (Fig. 1(b)). Both IR and UV-Vis spectroelectrochemical experiments show that the product oxidation followed by reduction of transof mer, trans-[RuBr<sub>3</sub>(CNTM)<sub>2</sub>- $[RuBr_4(CNTM)_2]^$ is (NCMe)] since the final spectra thus formed are identical to those obtained following reduction and subseoxidation quent of trans-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> in acetonitrile.

## 3.3. Redox chemistry of trans-[NBu<sub>4</sub>][RuCl<sub>4</sub>(CNTM)<sub>2</sub>] in acetonitrile

The redox behaviour of the analogous chloride is qualitatively very similar. Cyclic voltammetric experi-



Fig. 3. The UV–Vis spectra of *trans*-[NBu<sub>4</sub>][RuBr<sub>4</sub>(CNTM)<sub>2</sub>] (—) and *mer*,*trans*-[RuBr<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)] (---). The initial complex (ca. 1.6 mmol) was dissolved in 1:1 acetonitrile–dichloromethane (1.4 cm<sup>3</sup>) containing 0.25 mol dm<sup>-3</sup> [NBu<sub>4</sub>][PF<sub>6</sub>] at 298 K.

Table 2		
UV-Vis	spectroelectrochemical	data

Complex $(z = charge)$	Band maxima (cm <sup>-1</sup> ) <sup>a</sup> Ru(II)	Band maxima (cm <sup>-1</sup> ) <sup>a</sup> Ru(III)
$[RuCl_{3}(CNTM)_{2}(NCMe)]^{z b}$ $[RuBr_{3}(CNTM)_{2}(NCMe)]^{z b}$ $[RuCl_{3}(CNTM)_{3}]^{z c}$ $[RuCl_{4}(CNTM)_{3}]^{z d}$	35700 (s), 41000 (vs) 38000 (m), 43000 (vs) 33000 sh, 38000 (vs), 42000 (vs) 25000 sh, 33000 (w), 37000 (vs)	18800 (m), 22400 (s), 39000 sh 14300 (m), 16800 (s), 29000 sh, 32800 (s) 17200 (m), 19700 (s), 33000 sh, 38000 (vs) 18900 (s) 24100 (w) 36000 (vs) 40000 (vs)
$[RuBr_2(CNTM)_4]^{z d}$	23500 (w), 31000 sh, 38000 (vs), 42000 (vs)	12400 (s), 17900 (w), 37500 (vs), 40500 (vs)

<sup>a</sup> Recorded in an OTTLE cell under conditions stated in the text. Relative band intensities: vs = very strong, s = strong, m = medium and w = weak.

<sup>b</sup> mer,trans-isomer.

<sup>c</sup> mer-isomer.

<sup>d</sup> trans-isomer.



Fig. 4. The electrogeneration of *mer*-[RuCl<sub>3</sub>(CNTM)<sub>3</sub>]<sup>-</sup> from *trans*-[NBu<sub>4</sub>][RuCl<sub>4</sub>(CNTM)<sub>2</sub>] in an IRRAS cell. The initial complex (ca. 10 mmol dm<sup>-3</sup>) and CNTM ligand (ca. 15 mmol dm<sup>-3</sup>) were dissolved in dichloromethane (2 cm<sup>3</sup>) containing 0.5 mol dm<sup>-3</sup> [NBu<sub>4</sub>][PF<sub>6</sub>] at 243 K.



Fig. 5. Electrogeneration of *mer*-[RuCl<sub>3</sub>(CNTM)<sub>3</sub>] from *mer*-[RuCl<sub>3</sub>(CNTM)<sub>3</sub>]<sup>-</sup> in an IRRAS cell under the conditions indicated in the caption for Fig. 4.



Fig. 6. The UV–Vis spectra of *trans*- $[NBu_4][RuCl_4(CNTM)_2]$  (—) and *mer*- $[RuCl_3(CNTM)_3]$  (---). The initial complex (ca. 1.6 mmol) and CNTM ligand (ca. 5 mmol) were dissolved in dichloromethane (2 cm<sup>3</sup>) containing 0.5 mol dm<sup>-3</sup> [NBu\_4][PF\_6] at 298 K.

ments show that reduction of *trans*-[RuCl<sub>4</sub>(CNTM)<sub>2</sub>] in 1:1 acetonitrile-dichloromethane solution at -0.10V leads to the formation of an electroactive species detected at  $E_{1/2} = +0.51$  V on the return scan. Oxidation of the same complex at +1.70 V also leads to the formation of an electroactive species detected at the same potential ( $E_{1/2} = +0.51$  V). Both IR and UV–Vis spectroelectrochemical studies indicate that the species formed upon either reduction followed by oxidation or followed reduction oxidation by of trans- $[RuCl_4(CNTM)_2]^-$  in the presence of acetonitrile is mer, trans-[RuCl<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)] (Table 1). The visible spectrum of mer, trans-[RuCl<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)] shows bands at 22400 and 18800 cm<sup>-1</sup> arising from transitions of the type  $Cl(p\pi) \rightarrow Ru(d\pi)$  [11] (Table 2). It that complexes is proposed the mer, trans-[RuX<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)] are formed by the same free radical mechanism as that discussed for the formation of mer, trans-[RuBr<sub>3</sub>(CN<sup>t</sup>Bu)<sub>2</sub>(NCMe)] [7].

#### 3.4. Redox chemistry of trans- $[NBu_4][RuX_4(CNTM)_2]$ in the presence of uncoordinated CNTM

Both complex ions *trans*- $[RuX_4(CNTM)_2]^-$  (X = Cl or Br) also undergo reduction-induced halide substitution with neutral donor ligands other than acetonitrile. For example, in dichloromethane solution, the  $v_{\rm NC}$ band of the coordinated isocyanide in trans- $[RuCl_4(CNTM)_2]^-$  occurs at 2176  $cm^{-1}$  and, upon reduction at  $E_{app} = -0.30$  V in the presence of free CNTM, it collapses with the growth of bands at 2141, 2086 and 2034 cm<sup>-1</sup> arising from the formation of mer-[RuCl<sub>3</sub>(CNTM)<sub>3</sub>]<sup>-</sup> (Fig. 4, Table 1). Oxidation at  $E_{\rm app} = +1.30$  V leads to the collapse of these bands and the growth of new ones at 2242, 2208 and 2178 cm<sup>-1</sup> corresponding to the formation of mer-[RuCl<sub>3</sub>(CNTM)<sub>3</sub>] (Fig. 5, Table 1). Under the same conditions trans-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> can be reduced to mer-[RuBr<sub>3</sub>(CNTM)<sub>3</sub>]<sup>-</sup> which in turn can be oxidised to mer-[RuBr<sub>3</sub>(CNTM)<sub>3</sub>] (Table 1). These results differ from those established for the analogous complexes of tert-butylisocyanide, viz. trans-[NBu<sub>4</sub>][RuX<sub>4</sub>(CN<sup>t</sup>Bu)<sub>2</sub>] in dichloromethane, since the reduction and subsequent oxidation of the latter in the presence of free CN<sup>t</sup>Bu yields the disubstituted species  $trans - [RuX_2(CN^tBu)_4]^+$ [9]. This implies that CN<sup>t</sup>Bu is capable of exerting a stronger trans-influence than CNTM when present in complexes of the type *trans*- $[NBu_4][RuX_4(CNR)_2]$ . Oxidation and subsequent reduction of trans- $[RuX_4(CNTM)_2]^-$  in dichloromethane in the presence of free CNTM also leads to the formation of mer-[RuX<sub>3</sub>(CNTM)<sub>3</sub>]. The shorter timescale of an IRRAS experiment compared to one performed using an OT-TLE cell favours the detection of monosubstituted species such as mer-[RuX<sub>3</sub>(CNTM)<sub>3</sub>] which may be short-lived.

In an OTTLE cell, reduction of trans- $[RuCl_4(CNTM)_2]^-$  in dichloromethane in the presence of free CNTM at  $E_{app} = -0.30$  V leads to the formation of a ruthenium(II) species which upon oxidation at  $E_{\text{app}} = +1.70 \text{ V}$  yields trans-[RuCl<sub>2</sub>(CNTM)<sub>4</sub>]<sup>+</sup>. The visible spectrum of the latter is typical of a complex with a trans arrangement of chloride ions [11], showing a single band at 18 900 cm<sup>-1</sup> arising from a halide-tometal charge transfer (XMCT) (Table 2). However, under the same conditions, oxidation of trans- $[RuCl_4(CNTM)_2]^-$  at  $E_{app} = +1.90$  V followed by reduction yields mer-[RuCl<sub>3</sub>(CNTM)<sub>3</sub>], which shows XMCT bands at 19 700 and 17 200 cm<sup>-1</sup> in its visible spectrum (Fig. 6, Table 2).

In an OTTLE cell, reduction of the analogous bromo species, *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup>, in dichloromethane in the presence of CNTM at  $E_{app} = -0.20$  V followed by oxidation at  $E_{app} = +1.70$  V yields *trans*-[RuBr<sub>2</sub>(CNTM)<sub>4</sub>]<sup>+</sup> (Table 2). However, *trans*-[RuBr<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup>, differs from *trans*-[RuCl<sub>4</sub>(CN-TM)<sub>2</sub>]<sup>-</sup> in that, under the same conditions, its oxidative cycle leads to the formation of the same species, viz. *trans*-[RuBr<sub>2</sub>(CNTM)<sub>4</sub>]<sup>+</sup>, as obtained in the reductive cycle described above. Limiting the amount of free ligand present in solution does not yield *mer*-[RuBr<sub>3</sub>(CNTM)<sub>3</sub>] but only a decrease in the amount of disubstituted species formed.

#### 4. Conclusion

Spectroelectrochemical (IR and UV–Vis) studies have shown that reduction of trans-[RuX<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> in acetonitrile yields *mer*,*trans*-[RuX<sub>3</sub>(CNTM)<sub>2</sub>-(NCMe)]<sup>-</sup> which can be reversibly oxidised to *mer*,*trans*-[RuX<sub>3</sub>(CNTM)<sub>2</sub>(NCMe)];



# The oxidation and subsequent reduction of *trans*- $[RuX_4(CNTM)_2]^-$ in acetonitrile also ultimately yields *mer,trans*- $[RuX_3(CNTM)_2(NCMe)]$ via the formation of *trans*- $[RuX_4(CNTM)_2]$ . The Ru(IV/III) reduction step is assumed to involve the mechanism proposed for

the analogous reaction of *trans*-[ $RuX_4(CN^tBu)_2$ ] [7].



In general, the complexes *trans*-[NBu<sub>4</sub>][RuX<sub>4</sub>-(CNTM)<sub>2</sub>] have similar redox properties to the analogous ones formed by *tert*-butylisocyanide. However, there is one significant difference; the reduction and subsequent oxidation of *trans*-[RuX<sub>4</sub>(CNTM)<sub>2</sub>]<sup>-</sup> in an IRRAS cell and in the presence of free CNTM yields *mer*-[RuX<sub>3</sub>(CNTM)<sub>3</sub>], whereas the reduction and subsequent oxidation of *trans*-[RuX<sub>4</sub>(CN'Bu)<sub>2</sub>]<sup>-</sup> in the presence of free CN'Bu yields *trans*-[RuX<sub>2</sub>(CN'Bu)<sub>4</sub>]<sup>+</sup>.

#### Acknowledgements

J.P.A. thanks the EPSRC for a postgraduate award. M.A.S. is indebted to the Commonwealth Scholarship Commission for an award of a Commonwealth Fellowship. M.S.S. thanks CONICYT for funding her research at University College London.

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