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Reactions of $[Ru(bipy)(CO)_2Cl_2]$ in aqueous HX and $HX–HNO_3$ solutions (X = F, Br or I; bipy = 2,2′-bipyridine)

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Aqueous halogen acids HBr and HI have been used to direct exchange of the chlorides in $[Ru(bipy)(CO)_2Cl_2]$ (bipy = 2,2′-bipyridine) at elevated temperatures (160–200 °C). Reaction of *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$ with HBr and HI produced the corresponding *cis*(CO),*trans*(Br)-$[Ru(bipy)(CO)_2Br_2]$ **1** and *cis*(CO),*trans*(I)-$[Ru(bipy)(CO)_2I_2]$ **2**. A similar reaction was not observed with the weaker (aqueous) acid HF. Addition of HNO_3 as a nitrosyl source in the acid solution led to formation of nitrosyl complexes $[Ru(bipy)(NO)X_3]$ (X = F, Cl, Br or I). In the case of $HBr–HNO_3$ or $HI–HNO_3$ addition of nitrosyl was most probably accompanied by complete exchange of chlorides giving $[Ru(bipy)(NO)X_3]$ (X = Br or I), while in $HF–HNO_3$ no exchange was observed. In the latter case a mixed-halide complex $[Ru(bipy)(NO)Cl_2F]$ **3** was obtained. By using $HBr–HNO_3$ solutions and extended reaction times, nitrido-bridged $[(H_2O)Br_2(bipy)Ru–N–Ru(bipy)Br_3]$ **4** was formed at 240 °C probably *via* a nitrosyl intermediate. The complexes were characterised by IR, NMR spectroscopy and single-crystal X-ray crystallography.

Mononuclear ruthenium tris- and bis-bipyridine complexes have been extensively studied because of their electrochemical, photochemical and catalytic properties. Among the most studied catalytic processes are electrochemical[1] or photochemical reduction[2] of CO_2 and the water-gas shift reaction.[3] The synthesis, reactions and characterisation of mononuclear ruthenium monobipyridine complexes have been studied less intensively. Catalytically one of the most interesting is $[Ru(bipy)(CO)_2Cl_2]$ (bipy = 2,2′-bipyridine) which has been found to be active in both photochemical and electrochemical reduction of CO_2.[1f,g] It has been proposed that in the electrochemical reduction it is converted into an active polymer $[\{Ru(bipy)(CO)_2\}_2]$.[1f,g] Another catalytically interesting system is $[Ru_3(CO)_{12}]$–bipy,[4] where the active catalyst most probably consist also of mono(bipyridine)ruthenium units.[5] The synthesis, chemical behaviour and structural characterisation of ruthenium monobipyridines provides not only potential new catalysts or catalyst precursors but also useful information in understanding the catalytic properties of related systems.

We have reported earlier reactions of $[Ru(bipy)(CO)_2Cl_2]$ in aqueous $HCl–HNO_3$ solutions at high temperatures (240 °C).[6] Under such harsh conditions $[Ru(bipy)(CO)_2Cl_2]$ can be converted into nitrosyl or nitrido derivatives $[Ru(bipy)(NO)Cl_3]$, $[(H_2O)Cl_2(bipy)Ru–N–Ru(bipy)Cl_3]$ or $[Cl_3(bipy)Ru–N–Ru(bipy)Cl_3]^-$. In the present work we have investigated halide-exchange reactions of $[Ru(bipy)(CO)_2Cl_2]$ in aqueous HX and the formation of nitrosyl and nitrido complexes in $HX–HNO_3$ solutions (X = F, Br or I).

Experimental

All reagents were analytical grade. The complex $[Ru(bipy)(CO)_2Cl_2]$ was prepared from $[\{Ru(CO)_3Cl_2\}_2]$ (Johnson Matthey) and 2,2′-bipyridine (Aldrich) according to the literature method.[7] The compounds HBr (48%) and HI (67%) were obtained from Merck, HNO_3 (67%) from J. T. Baker and HF (40%) from Riedel de Haën. All acid reactions were carried out in a stainless-steel autoclave (Berghof, 100 cm^3) with a Teflon liner. The Fourier-transform IR measurements were carried out with a Nicolet Magna-IR 750 spectrometer and NMR measurements with a Bruker AMX-400, 400 MHz spectrometer.

Reaction of $[Ru(bipy)(CO)_2Cl_2]$ with HX (X = F, Br or I) and formation of $[Ru(bipy)(CO)_2Br_2]$ 1 and $[Ru(bipy)(CO)_2I_2]$ 2

Reaction A. A 100 mg sample of *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$, HBr (48%, 2 cm^3) and water (2 cm^3) were transferred to an autoclave. The autoclave was closed tightly and heated at 160 °C for 4 h, after which it was cooled slowly (7 °C h^{-1}) to room temperature. A greenish yellow crystalline product was filtered from the acid solution, washed with water, and dried in air. The primary yield was 106 mg (86%) of *cis*(CO),*trans*(Br)-$[Ru(bipy)(CO)_2Br_2]$ **1**. The product was recrystallised from CH_2Cl_2 (Found: C, 30.60; H, 1.60; N, 5.85. Calc.: C, 30.45; H, 1.70; N, 5.90%). IR (in CH_2Cl_2): ν(CO) 2062 and 2004 cm^{-1}. NMR ($CDCl_3$): $^{13}C-\{^1H\}$, δ 197.2 (CO); 155.7, 154.2, 140.0, 128.0 and 123.8 (bipy); ^1H, δ 9.2 (d), 8.3 (d), 8.1 (t) and 7.7 (t) (bipy). λ_{max}(in CH_2Cl_2): 373, 315, 291 and 232 nm.

Reaction B. A 100 mg sample of *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$, HI (67%, 1.25 cm^3) and water (3.25 cm^3) were transferred to an autoclave and heated at 200 °C for 24 h. After reaction the autoclave was cooled slowly (7.5 °C h^{-1}) to room temperature. The brownish yellow precipitate was filtered from the acid solution, washed with water, and dried in air. The primary yield was *ca.* 120 mg ($\approx$81%) of *cis*(CO),*trans*(I)-$[Ru(bipy)(CO)_2I_2]$ **2**, *M* 567.09. The product was recrystallised from CH_2Cl_2 (Found: C, 25.40; H, 1.35; N, 5.00. Calc.: C, 25.40; H, 1.40; N, 4.95%). IR (in CH_2Cl_2): ν(CO) 2056 and 2000 cm^{-1}. NMR (in $CDCl_3$): $^{13}C-\{^1H\}$, δ 198.5 (CO); 155.6, 154.6, 139.7, 127.8 and 123.9 (bipy); ^1H, δ 9.2 (d), 8.2 (d), 8.1 (t) and 7.6 (t) (bipy). λ_{max}(in CH_2Cl_2): 397, 307 and 239 nm.

Reaction C. The reactivity of $[Ru(bipy)(CO)_2Cl_2]$ with aqueous HX (X = F, Br or I) was tested under various conditions. In a typical experiment 50–100 mg of $[Ru(bipy)(CO)_2Cl_2]$ were placed in an autoclave with aqueous HX (3–5 cm^3). The HX concentrations varied from 10 to 30%, reaction temperatures from 160 to 200 °C, reaction times from 2 to 24 h, and cooling rates from 5 to 20 °C h^{-1}. Solid products were filtered off, washed with water, dried in air, and analysed spectroscopically and by single-crystal X-ray crystallography.

Reaction of $[Ru(bipy)(CO)_2Cl_2]$ with $HX-HNO_3$ (X = F, Br or I) and formation of $[Ru(bipy)(NO)Cl_2F]$ 3 and $[(H_2O)Br_2(bipy)Ru-N-Ru(bipy)Br_3]$ 4

Reaction D. A 100 mg sample of *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$ was transferred to an autoclave (100 cm^3) with HF(aq) (40%, 2 cm^3), HNO_3 (50 μl) and water (2 cm^3). The mixture was heated to 240 °C for 3 h and cooled slowly (7.3 °C h^{-1}) to room temperature. The brownish yellow crystalline product was filtered from the acid solution, washed with water, and dried under air. The primary yield of the solid $[Ru(bipy)(NO)Cl_2F]$ **3** was *ca.* 10 mg (≈10%), *M* 377.17 (Found: C, 31.60; H, 2.00; N, 11.15. Calc.: C, 31.85; H, 2.15; N, 11.15%).

Reaction E. A 50 mg sample of *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$, (48%, 2 cm^3), HNO_3 (50 μl), and water (2 cm^3) were placed in an autoclave (100 cm^3). The mixture was heated to 200 °C for 19 h and cooled slowly (20 °C h^{-1}) to room temperature. The crystalline product consisted of black crystalline particles {product **5**, mixture of *mer*(Br)-$[Ru(bipy)(NO)Br_3]$ and *cis*(CO),*trans*(I)-$[Ru(bipy)(CO)_2Br_2]$, see Results and Discussion} and red crystals of $[(H_2O)Br_2(bipy)Ru-N-Ru(bipy)Br_3]$ **4**. The solid product was filtered off, washed with water, and dried in air. The primary yield of the mixture was *ca.* 50 mg. The poorly soluble crystalline products were separated manually (Found: C, 25.40; H, 1.70; N, 7.45. Calc. for **4**: C, 25.40; H, 1.90; N, 7.40%). Complexes **3** and **4** were also characterised by single-crystal X-ray crystallography.

Reaction F. The reactivity of $[Ru(bipy)(CO)_2Cl_2]$ with aqueous $HX-HNO_3$ (X = F, Br or I) was tested under various conditions. In a typical experiment 50–100 mg of $[Ru(bipy)(CO)_2Cl_2]$ were placed in an autoclave with aqueous $HX-HNO_3$ (3.05–4.05 cm^3). The HX concentrations varied from 13 to 40%, HNO_3 concentrations from 0.8 to 1.1%, reaction temperatures from 200 to 240 °C, reaction times from 3 to 19 h, and cooling rates from 7.3 to 20 °C h^{-1}. Solid products were filtered off, washed with water, dried in air, and analysed spectroscopically and by single-crystal X-ray crystallography. In the reaction of $[Ru(bipy)(CO)_2Cl_2]$ with $HBr-HNO_3$ a dark brown solid product **5** was obtained with or without **4** (for identification see text). In the case of $HI-HNO_3$ reactions dark red crystals covered by a black layer were formed (**6**). After washing the product **6** with dichloromethane, dark red crystalline particles were obtained (for identification see text).

Crystallography

Data were collected at 20 °C on a Nicolet R3m diffractometer using an ω-scan data-collection mode and graphite-monochromatised Mo-Kα radiation (λ = 0.710 73 Å). Accurate cell parameters were obtained from 25 automatically centred reflections. Intensities were corrected for background, and Lorentz-polarisation factors. Structures were solved by direct methods and subsequent Fourier synthesis. An experimental absorption correction was measured for all complexes (maximum, minimum transmission factors 0.139, 0.102; 0.108, 0.056; 0.137, 0.104; and 0.246, 0.177 for **1**, **2**, **3** and **4** respectively). Data collection, data reduction and cell refinement (on F^2) were carried out by the SHELXTL PLUS program package.[8a] Structure solution was carried out using the SHELXS 86 program[8b] and structure refinement by using the SHELXL 93 program.[8c] Weighting schemes of the form $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ $(P = F_o^2 + 2F_c^2/3)$ were used. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were placed in idealised positions (C–H 0.93 Å) and not refined. Hydrogens attached to oxygen atoms in **4** were located from Fourier-difference maps but not refined. Bond lengths and angles are summarized in Tables 1–3. Crystallographic data are summarised in Table 4 and atomic coordinates are given in Tables 5–8.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Halogen exchange in $[Ru(bipy)(CO)_2Cl_2]$

Reactions of aqueous HBr and HI with *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$ were limited to halogen exchange even though they were carried out at elevated temperatures (160–200 °C, see Experimental section). Both HBr and HI led to complete halogen exchange producing corresponding bromide and iodide complexes $[Ru(bipy)(CO)_2Br_2]$ **1** and $[Ru(bipy)(CO)_2I_2]$ **2**. No evidence of formation of either $[Ru(bipy)(CO)X_3]^-$ or $[Ru(bipy)X_4]^-$ was obtained although these type of (X = Cl) complexes are known.[9] Furthermore, no significant decomposition of $[Ru(bipy)(CO)_2Cl_2]$ was observed.

Replacement of chloride ligands in $[Ru(bipy)(CO)_2Cl_2]$ with Br or I caused a slight shift in ν(CO) frequencies towards lower wavenumbers in the order Cl > Br > I in CH_2Cl_2. Deacon and co-workers[10a,b] have also reported a weak halogen effect in dichloromethane, while in Nujol mulls the Cl > Br trend is more emphasised. A weak shift has also been found in *trans*-(halide)-$[Ru(terpy)(CO)_2X_2]$ (X = Cl, Br or I) where the 2,2′:6′,2″-terpyridine (terpy) acts as a bidentate ligand.[10a,11] Systematic behaviour was also found in the chemical shift of the CO carbon in the ^{13}C NMR spectra. A slight shift towards lower field can be found in the order Cl > Br > I. Unlike in the case of the carbonyl ligand, the effect of the halide ligand on the chemical shift of the bipy carbons or hydrogens was negligible.

Fluorination of $[Ru(bipy)(CO)_2Cl_2]$ with aqueous HF was also tested using similar reaction conditions to those with HBr and HI, but no evidence of exchange of chlorides to fluorides was found. This is probably due to the different nature of HF compared to other aqueous halogen acids. In aqueous solutions HF is a weaker acid than HBr or HI because of the weaker basic character of F^- ion.

Two ν(CO) bands found in the IR spectrum of both $[Ru(bipy)(CO)_2Br_2]$ and $[Ru(bipy)(CO)_2I_2]$ resembled closely those of *cis*(CO)-$[Ru(bipy)(CO)_2Cl_2]$. However, characterisation of the $[Ru(bipy)(CO)_2X_2]$ complexes only by using IR spectroscopy could be insufficient and even lead to wrong conclusions.[7] Four aromatic signals in ^1H NMR and five in the $^{13}C-\{^1H\}$ NMR spectra of $[Ru(bipy)(CO)_2Br_2]$ and $[Ru(bipy)(CO)_2I_2]$ indicated that both halves of the bipy rings were equivalent. Such equivalency is an indication of similar ligands positioned *trans* to nitrogens of the bipy rings. Combined with IR data, the NMR results suggested a *cis*(CO),*trans*(X) structure for both $[Ru(bipy)(CO)_2Br_2]$ and $[Ru(bipy)(CO)_2I_2]$, in agreement with the earlier reports for $[Ru(bipy)(CO)_2X_2]$ (X = Cl or Br).[7,10] The structures of $[Ru(bipy)(CO)_2Br_2]$ **1** and $[Ru(bipy)(CO)_2I_2]$ **2** were confirmed by single-crystal X-ray measurements (Fig. 1). Both complexes were crystallised from dichloromethane.

As expected, the crystal structures of complexes **1** and **2** are very similar to that of *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$[7]. Change of the halide ligands in the axial positions has very little effect on the bond lengths of the equatorial ligands. The Ru–CO bonds in **1** and **2** (Table 1) are slightly longer than the corresponding bond lengths of 1.835(17) and 1.841(16) Å in *cis*(CO),*trans*(Cl)-$[Ru(bipy)(CO)_2Cl_2]$, but both the C–Ru–C and the 'bite angle' of bipyridine are similar to those of $[Ru(bipy)(CO)_2Cl_2]$ [90.2(7) and 77.2(4)° respectively]. The Ru–I bond lengths of 2.716(2) and 2.695(2) Å and the Ru–Br

Table 1 Selected bond lengths (Å) for [Ru(bipy)$(CO)_2Br_2$] **1**, [Ru(bipy)$(CO)_2I_2$] **2**, [Ru(bipy)(NO)Cl_2F] **3** and [$Ru_2N$$(bipy)_2$$Br_5$$(H_2O)$] **4**

	1	**2**	**3**	**4**
Ru(1)–X(11)	2.523(2)	2.716(2)	1.942(5)	2.583(2)
Ru(1)–X(12)	2.520(2)	2.695(2)		
Ru(1)–X(13)			2.378(2)	2.538(2)
Ru(1)–X(14)			2.357(2)	2.557(2)
Ru(1)–N(11)	2.114(9)	2.109(12)	2.082(6)	2.077(9)
Ru(1)–N(12)	2.119(9)	2.118(12)	2.076(6)	2.065(10)
Ru(1)–C(1)	1.882(13)	1.866(18)		
Ru(1)–C(2)	1.870(13)	1.855(16)		
C(1)–O(1)	1.078(14)	1.130(20)		
C(2)–O(2)	1.117(14)	1.128(19)		
Ru(1)–N(3)			1.706(7)	1.736(10)
N(3)–O(3)			1.140(9)	
Ru(2)–Br(23)				2.509(2)
Ru(2)–Br(24)				2.494(2)
Ru(2)–O(4)				2.189(9)
Ru(2)–N(3)				1.729(10)
Ru(2)–N(21)				2.064(10)
Ru(2)–N(22)				2.086(10)

X = Cl, Br, I or F.

Table 2 Selected bond angles (°) for [Ru(bipy)$(CO)_2Br_2$] **1** and [Ru(bipy)$(CO)_2I_2$] **2**

	1	**2**
X(11)–Ru–X(12)	176.97(6)	179.01(6)
X(11)–Ru–C(1)	90.6(4)	90.4(5)
X(11)–Ru–C(2)	92.4(4)	89.2(6)
X(11)–Ru–N(11)	89.7(2)	88.3(3)
X(11)–Ru–N(12)	88.1(3)	91.2(3)
X(12)–Ru–C(1)	90.4(4)	89.6(5)
X(12)–Ru–C(2)	90.5(4)	89.8(6)
X(12)–Ru–N(11)	89.1(2)	88.3(3)
X(12)–Ru–N(12)	88.9(3)	91.2(3)
N(11)–Ru–N(12)	77.2(3)	76.3(5)
N(11)–Ru–C(1)	174.1(5)	173.4(6)
N(11)–Ru–C(2)	96.4(4)	97.2(6)
N(12)–Ru–C(1)	96.9(4)	97.6(6)
N(12)–Ru–C(2)	173.6(5)	173.4(6)
C(1)–Ru–C(2)	89.5(5)	89.0(7)
Ru–C(1)–O(1)	179.1(11)	174.6(16)
Ru–C(2)–O(2)	179.5(12)	175.7(17)

X = Br or I.

bond lengths of 2.523(2) and 2.520(2) Å are comparable with typical Ru–Br and Ru–I bond lengths found in the literature.[10,12]

Reaction of [Ru(bipy)$(CO)_2Cl_2$] with HX–HNO_3 (X = F, Br or I)

When nitric acid was added to HBr solution as a nitrosyl source (reaction F, see Experimental section) [Ru(bipy)$(CO)_2Cl_2$] was converted into the corresponding, poorly soluble nitrosyl [Ru(bipy)(NO)Br_3] at elevated temperatures (200–240 °C). The IR (in KBr) spectrum of this dark brown or black crystalline product (**5**) showed either a single nitrosyl stretching band at 1861 cm^{-1} or two bands at 1878 and 1861 cm^{-1}. In the former case the single band closely resembles that of *mer*(Cl)-[Ru(bipy)(NO)Cl_3], [ν(NO) 1865 cm^{-1}][6] indicating the presence of *mer*(Br)-[Ru(bipy)(NO)Br_3]. Single-crystal X-ray measurements supported this. Bipyridine, ruthenium and axial *trans*-bromides were well defined in the Fourier-difference map, but the equatorial ligands *trans* to bipy nitrogens were heavily disordered. Although several measurements were carried out the disorder prevented complete characterisation of this product. However, the partial results showed clearly the presence of the *trans*(Br) ligands, which is a strong argument for *mer*(Br)-[Ru(bipy)(NO)Br_3]. The disorder arises possibly from a mixture of *mer*(Br)-[Ru(bipy)(NO)Br_3] and *cis*(CO), *trans*(Br)-[Ru(bipy)$(CO)_2Br_2$]. However, the co-presence of water in the equatorial (*trans* to bipy nitrogen) position, as suggested for *mer*(Cl)-[Ru(bipy)(NO)Cl_3],[6] cannot be completely excluded. The appearance of a second ν(NO) band at 1878 cm^{-1} in the IR spectrum of some samples indicated that the formation of *fac*(Br)-[Ru(bipy)(NO)Br_3] in addition to the dominant *mer*(Br) isomer is also possible. Although it seems likely that the product **5** contains mainly [Ru(bipy)(NO)Br_3], two weak and broad ν(CO) bands corresponding to *cis*(CO),*trans*(Br)-[Ru(bipy)$(CO)_2Br_2$] were found in the carbonyl stretching region indicating the possible co-presence of *cis*(CO),*trans*(Br)-[Ru(bipy)$(CO)_2Br_2$] in agreement with the X-ray results. The elemental composition of the product **5** was relatively close to [Ru(bipy)(NO)Br_3] but varied from lot to lot. This also is most probably due to formation of a mixture of products.

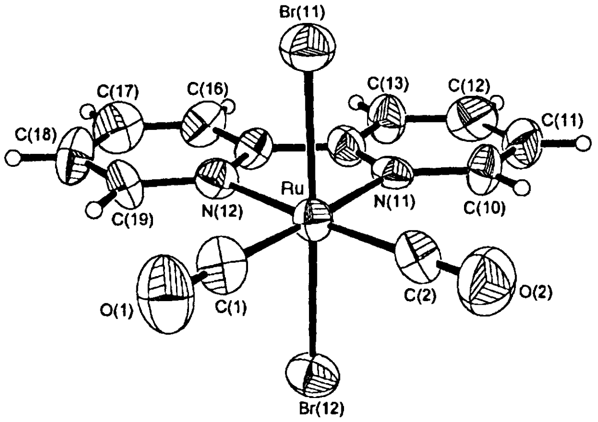


Fig. 1 Crystal structure of *cis*(CO),*trans*(Br)-[Ru(bipy)$(CO)_2Br_2$] **1** and the numbering scheme for *cis*(CO),*trans*(X)-[Ru(bipy)$(CO)_2X_2$] (X = Br or I)

Use of nitric acid in the reaction of [Ru(bipy)$(CO)_2Cl_2$] and HI (reaction F, see Experimental section) at 200–220 °C gave dark red crystals (**6**) with one (1851 cm^{-1}) or two (1851, 1864 cm^{-1}) ν(NO) bands (in KBr). The crystalline product **6** was characterised by single-crystal X-ray crystallography, but again the equatorial ligands *trans* to bipy nitrogens were heavily disordered. However, both bipy rings and the two axial iodine ligands were located from the Fourier-difference map. As for product **5**, a pair of ν(CO) bands, corresponding to *cis*(CO),*trans*(I)-[Ru(bipy)$(CO)_2I_2$] were found in the IR spectrum. The product **6** most probably thus consists of a mixture of *mer*(I)- and *fac*(I)-[Ru(bipy)(NO)I_3] and *cis*(CO),*trans*(I)-[Ru(bipy)$(CO)_2I_2$], the *mer* isomer being the dominant nitrosyl species similarly to product **5**. However, in the case of **6** the carbonyl bands typically dominated the IR spectrum suggesting that the formation of nitrosyl complexes was less important than for the corresponding HBr product **5**.

Formation of [Ru(bipy)(NO)Cl_2F]

Addition of nitric acid to HF solution (reaction D, see Experimental section) led to the formation of a mixed-halide compound [Ru(bipy)(NO)Cl_2F] at 240 °C. As in the reaction of [Ru(bipy)$(CO)_2Cl_2$] with pure aqueous HF (reaction C), no exchange of chlorides was observed despite slightly more oxidising conditions. Brownish yellow or orange [Ru(bipy)(NO)Cl_2F] **3** was crystallised directly from the acid solution and its structure characterised by single-crystal X-ray crystallography (Fig. 2). In [Ru(bipy)(NO)Cl_2F] the fluorine and nitrosyl ligands are located in the axial positions. The formation of such a complex requires not only the replacement of carbonyls in *cis*(CO),*trans*(Cl)-[Ru(bipy)(CO)$_2$Cl$_2$] by fluorine and nitrosyl, but also rearrangement of the ligands, since both the original chloride ligands are located in *cis* positions in the equatorial plane in **3**. The general structure of **3** is similar to that of [Ru(bipy)(NO)Cl$_3$].[6] However, in **3** the bipyridine ring is slightly bent away from the nitrosyl towards fluorine, N(bipy)–Ru–NO angles being 95.7(3) and 98.8(3)°. Furthermore, the Ru–NO bond length of 1.706(7) Å is clearly shorter than that in *fac*(Cl)-[Ru(bipy)(NO)Cl$_3$]. The Ru–F bond length of 1.942(5) Å is in accord with the typical Ru–F bond lengths found in the literature.[13]

Owing to the low primary yield of solid [Ru(bipy)(NO)Cl$_2$F] the acid solution was allowed to evaporate slowly to dryness at room temperature. During evaporation brownish yellow crystals were formed. These were characterised as [Ru(bipy)(NO)Cl$_2$F] by X-ray crystallography. This suggests that [Ru(bipy)(NO)Cl$_2$F] is the dominant nitrosyl species also in the acid solution.

Two partially overlapping ν(NO) bands were found at 1880 and 1868 cm^{-1} in the IR spectrum of [Ru(bipy)(NO)Cl$_2$F] (in KBr). However, no evidence of the presence of another isomer or a bent nitrosyl group was found in the crystal structure. Similar spectral behaviour has been found for *fac*(Cl)-[Ru(bipy)(NO)Cl$_3$] which gives two ν(NO) bands at 1891 and 1878 cm^{-1}.[6] Since isomerism seems not very likely, the split ν(NO) band probably originates from coupling in the crystal lattice.

According to electronegativity it would be expected that replacement of chlorine with fluorine in a position *trans* to the axial nitrosyl group in [Ru(bipy)(NO)XCl$_2$] would shift the NO stretching to higher frequency. However, the ν(NO) bands in [Ru(bipy)(NO)Cl$_2$F] are shifted downwards compared to *fac*(Cl)-[Ru(bipy)(NO)Cl$_3$] indicating increased electron donation in the case of the fluoride ligand. Similar 'reversed' effects of halides on the stretching frequencies of strong π-acid ligands NO or CO have been observed for example for [Re(η-C$_5$H$_5$)(PR$_3$)(NO)X],[14] [RuH(X)(CO)(PBu$^t_2$Me)$_2$] or [RuH(X)(CO)(py)(PBu$^t_2$Me)$_2$] (py = pyridine).[15] Hall and Fenske[16] have suggested that, in octahedral 18-electron complexes, F may be a better π donor than Cl. Such behaviour could also explain the shift of the ν(CO) bands of [Ru(bipy)(NO)XCl$_2$] (X = F or Cl) complexes. However, a more subtle explanation based on the ionicity of the Ru–X bond and σ/π interactions has also been proposed.[15]

Formation of [(H$_2$O)Br$_2$(bipy)Ru–N–Ru(bipy)Br$_3$]

Extended reaction (17 h) of [Ru(bipy)(CO)$_2$Cl$_2$] with HBr–HNO$_3$ at 200 °C (reaction E, see Experimental section) gave a mixture of the black crystalline product **5** {which is mainly *mer*(Br)-[Ru(bipy)(NO)Br$_3$]} and red crystals. The latter

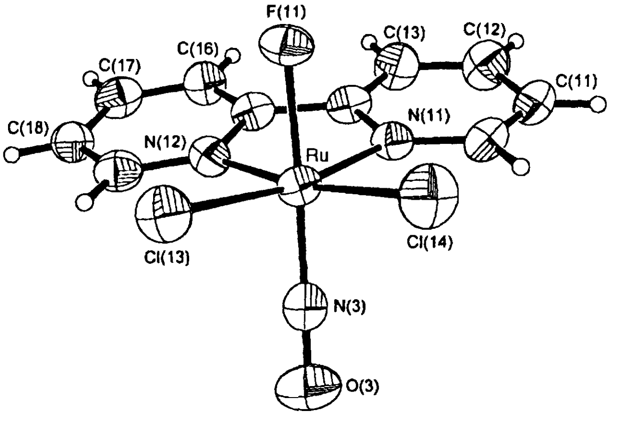


Fig. 2 Crystal structure of [Ru(bipy)(NO)Cl$_2$F] **3**

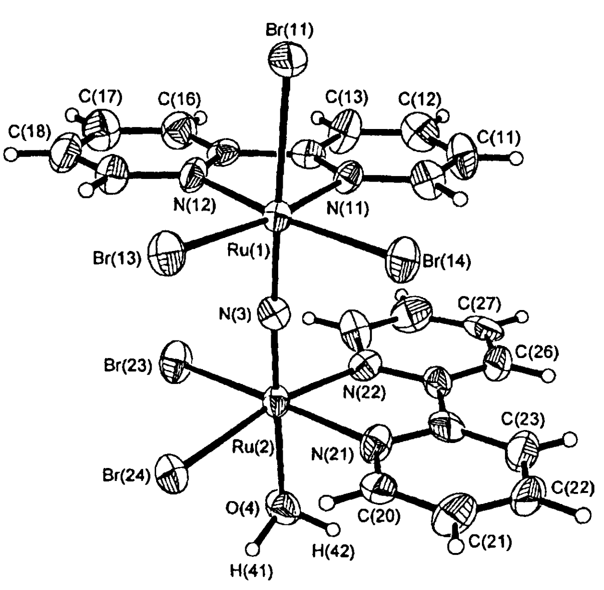


Fig. 3 Crystal structure of [Ru$_2$N(bipy)$_2$Br$_5$(H$_2$O)] **4**

Table 3 Selected bond angles (°) for [Ru(bipy)(NO)Cl$_2$F] **3** and [Ru$_2$N(bipy)$_2$Br$_5$(H$_2$O)] **4**

	3	**4**		**4**
X(11)–Ru(1)–N(3)	177.2(3)	175.9(3)	Br(23)–Ru(2)–N(3)	94.4(4)
X(11)–Ru(1)–X(13)	86.8(2)	90.87(6)	Br(23)–Ru(2)–Br(24)	89.70(6)
X(11)–Ru(1)–X(14)	88.3(2)	90.18(6)	Br(23)–Ru(2)–O(4)	87.3(3)
X(11)–Ru(1)–N(11)	83.9(2)	85.1(3)	Br(23)–Ru(2)–N(21)	170.8(3)
X(11)–Ru(1)–N(12)	84.0(2)	86.7(3)	Br(23)–Ru(2)–N(22)	95.0(3)
X(13)–Ru(1)–X(14)	90.18(8)	90.37(5)	Br(24)–Ru(2)–N(3)	95.1(3)
X(13)–Ru(1)–N(3)	90.4(2)	93.0(3)	Br(24)–Ru(2)–O(4)	85.6(2)
X(13)–Ru(1)–N(11)	169.7(2)	172.8(3)	Br(24)–Ru(2)–N(21)	95.6(3)
X(13)–Ru(1)–N(12)	95.1(2)	94.7(3)	Br(24)–Ru(2)–N(22)	169.3(3)
X(14)–Ru(1)–N(3)	92.2(2)	91.0(3)	O(4)–Ru(2)–N(3)	178.7(4)
X(14)–Ru(1)–N(11)	94.1(2)	95.7(3)	O(4)–Ru(2)–N(21)	86.2(4)
X(14)–Ru(1)–N(12)	170.4(2)	174.1(3)	O(4)–Ru(2)–N(22)	85.0(3)
N(11)–Ru(1)–N(12)	79.4(2)	79.0(4)	N(21)–Ru(2)–N(22)	78.5(4)
N(11)–Ru(1)–N(3)	98.8(3)	90.9(4)	N(21)–Ru(2)–N(3)	92.6(4)
N(12)–Ru(1)–N(3)	95.7(3)	91.8(4)	N(22)–Ru(2)–N(3)	94.1(4)
Ru(1)–N(3)–O(3)	172.8(6)			
Ru(1)–N(3)–Ru(2)		175.3(6)		

X = F, Cl or Br.

Table 4 Crystallographic data for complexes **1**–**4**

	1	**2**	**3**	**4**
M	473.09	567.09	377.17	946.08
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pn*	$Pca2_1$	$P2_1$	$P2_1/n$
a/Å	8.397(3)	24.856(5)	6.514(2)	10.181(2)
b/Å	6.941(1)	6.953(1)	11.319(3)	15.422(3)
c/Å	12.824(3)	8.867(2)	8.808(2)	16.740(2)
β/°	103.72(2)		105.13(2)	104.81(2)
U/Å^3	726.1(3)	1532.4(5)	627.0(3)	2541.1(8)
Z	2	2	2	4
D_c/g cm^{-3}	2.164	2.458	1.998	2.473
Crystal source	Dichloromethane	Dichloromethane	HF–HNO_3	HCl–HNO_3
Crystal size/mm	0.2 × 0.2 × 0.3	0.2 × 0.4 × 0.5	0.1 × 0.1 × 0.2	0.2 × 0.2 × 0.4
Colour	Greenish yellow	Brownish yellow	Brownish yellow	Red
μ/mm^{-1}	6.580	5.050	1.678	9.075
θ limits/°	2.64–25.05	2.82–27.56	2.40–25.05	2.13–25.04
h,k,l Ranges	0–10, 0–8, −15 to 14	0–32, 0–9, 0–11	0–7, 0–13, −10 to 10	0–12, 0–18, −19 to 19
F(000)	448	1040	368	1776
No. unique reflections	1373	1889	1176	4489
No. observed reflections [$I > 2\sigma(I)$]	1204	1425	1090	2866
No. parameters	173	173	163	299
Terms *a,b* in weighting scheme	0.0342, 0.0504	0.0580, 0.9254	0.0453, 0	0.0529, 5.6387
*R*1	0.0344	0.0441	0.0293	0.0581
*wR*2	0.0691	0.1026	0.0710	0.1096
Goodness of fit	1.059	1.106	1.045	1.016

Table 5 Atomic coordinates (× 10^4) for $[Ru(bipy)(CO)_2Br_2]$ **1**

Atom	*x*	*y*	*z*
Ru	53(1)	2234(1)	50(1)
Br(11)	1659(1)	4202(2)	1600(1)
Br(12)	−1463(1)	347(2)	−1560(1)
C(1)	−1800(16)	3802(18)	−29(9)
O(1)	−2871(13)	4682(14)	−69(8)
C(2)	−711(15)	559(18)	965(10)
O(2)	−1178(12)	−439(14)	1508(8)
N(11)	2199(11)	664(12)	19(7)
N(12)	1132(11)	3908(13)	−982(7)
C(10)	2687(14)	−991(15)	570(9)
C(11)	4059(15)	−1939(16)	486(11)
C(12)	5017(14)	−1215(18)	−159(10)
C(13)	4561(15)	479(16)	−705(10)
C(14)	3129(12)	1394(16)	−608(8)
C(15)	2552(12)	3191(14)	−1155(8)
C(16)	3373(17)	4150(17)	−1821(10)
C(17)	2750(16)	5833(19)	−2290(9)
C(18)	1327(16)	6569(17)	−2123(9)
C(19)	523(14)	5553(16)	−1492(9)

Table 6 Atomic coordinates (× 10^4) for $[Ru(bipy)(CO)_2I_2]$ **2**

Atom	*x*	*y*	*z*
Ru	3565(1)	−3304(2)	2006(1)
I(11)	4490(1)	−5044(2)	2895(2)
I(12)	2637(1)	−1620(2)	1154(1)
C(1)	3614(7)	−1586(24)	3616(20)
O(1)	3684(6)	−513(19)	4553(16)
C(2)	3181(7)	−4968(26)	3238(18)
O(2)	2964(6)	−6072(20)	3944(17)
N(11)	3529(5)	−4976(18)	24(14)
N(12)	4004(4)	−1665(16)	413(15)
C(10)	3277(6)	−6691(22)	−163(21)
C(11)	3249(7)	−7587(26)	−1508(23)
C(12)	3512(8)	−6914(27)	−2704(22)
C(13)	3779(9)	−5198(25)	−2573(18)
C(14)	3769(6)	−4286(24)	−1193(17)
C(15)	4069(7)	−2391(24)	−992(17)
C(16)	4350(6)	−1489(23)	−2084(20)
C(17)	4600(7)	235(26)	−1758(23)
C(18)	4557(7)	1014(26)	−330(24)
C(19)	4243(6)	63(22)	715(18)

insoluble crystals did not show bands in the nitrosyl stretching region. The red product (**4**) was characterised by single-crystal X-ray crystallography as the nitrido-bridged $[(H_2O)Br_2(bipy)$-Ru–N–$Ru(bipy)Br_3]$ (Fig. 3). Similarly to **4**, the corresponding chlorine complex $[(H_2O)Cl_2(bipy)Ru$–N–$Ru(bipy)Cl_3]$ has been obtained by extended (12 h) reaction of $[Ru(bipy)$-$(CO)_2Cl_2]$ in HCl–HNO_3 at 240 °C.[6] These complexes are most probably formed *via* nitrosyl intermediates. For example $[(H_2O)Cl_4Ru$–N–$RuCl_4(H_2O)]$ can be prepared from $[RuCl_5(NO)]^{2-}$ by using tin(II) halides and formaldehyde as a reduction agent for the NO group.[17] However, the formation of $[(H_2O)X_2(bipy)Ru$–N–$Ru(bipy)X_3]$ (X = Cl or Br) occurs under oxidising conditions without any special reductant for the NO group. A possible reductant in these reactions is coordinated carbonyl of $[Ru(bipy)(CO)_2Cl_2]$ or an unidentified carbonyl-containing derivative. The reaction may thus be an intermolecular one between M–CO and M–NO according to equation (1). A corresponding route has been proposed for metal clusters, where a nitrosyl ligand reacts with a neighbouring carbonyl group.[18]

$$\text{M–NO} + \text{OC–M} \xrightarrow{-CO_2} \text{M–N–M} \qquad (1)$$

Although several dinuclear Ru–N–Ru type complexes have been reported, few crystal structures are known.[6,19] In $[(H_2O)Br_2(bipy)Ru$–N–$Ru(bipy)Br_3]$ Ru–N–Ru is practically symmetrical the Ru(1)–N(3) and Ru(2)–N(3) bond lengths being 1.736(10) Å and 1.729(10) Å, respectively, while in $[(H_2O)Cl_2(bipy)Ru$–N–$Ru(bipy)Cl_3]$ Ru–N–Ru is slightly unsymmetrical [Ru–N 1.728(2) and 1.744(2) Å].[6] The axial Ru(1)–Br(11) bond length is slightly longer than the equatorial Ru–Br bonds due to the *trans* effect of the nitrido bridge.[6,19] The elongated ruthenium water [Ru(2)–O(4)] bond of 2.189(9) Å is also affected by the *trans* effect.[6]

In principle, formation of other $[(H_2O)X_2(bipy)Ru$–N–Ru-$(bipy)X_3]$ (X = I or F) or $[X_3(bipy)Ru$–N–$Ru(bipy)X_3]^-$ (X = Cl, I or F) should also be possible under acidic conditions, but so far these complexes have not been obtained. Other reagents such as $[Ru(bipy)(CO)_2Cl(H)]$, $[Ru(bipy)(CO)_2Cl$-$\{C(O)OMe\}]$ or $[\{Ru(bipy)(CO)_2Cl\}_2]$ or $[Ru(bipy)(CO)_2X_2]$ (X = I or Br) with halogen acids could also offer a

Table 7 Atomic coordinates (× 10^4) for [Ru(bipy)(NO)Cl_2F] **3**

Atom	*x*	*y*	*z*
Ru	1492(1)	−9(1)	745(1)
Cl(13)	604(3)	1232(2)	2658(2)
Cl(14)	4848(3)	−386(2)	2482(2)
F(11)	2706(7)	1385(4)	29(5)
N(3)	372(10)	−1190(7)	1428(7)
O(3)	−272(11)	−1937(6)	2040(8)
N(11)	2241(10)	−817(6)	−1165(7)
N(12)	−1178(9)	419(6)	−1043(7)
C(10)	3945(12)	−1486(7)	−1108(9)
C(11)	4429(15)	−1878(8)	−2440(11)
C(12)	3161(15)	−1537(8)	−3870(10)
C(13)	1408(13)	−847(9)	−3941(10)
C(14)	932(12)	−509(7)	−2568(8)
C(15)	−920(11)	190(8)	−2500(8)
C(16)	−2491(13)	551(8)	−3826(10)
C(17)	−4262(12)	1125(8)	−3671(9)
C(18)	−4511(12)	1336(8)	−2188(9)
C(19)	−2903(12)	991(8)	−884(10)

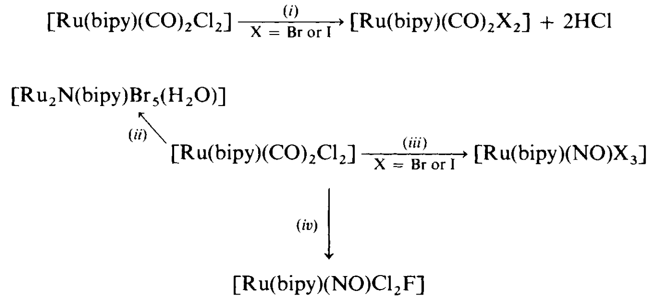
Table 8 Atomic coordinates (× 10^4) for [Ru_2N(bipy)$_2$$Br_5$($H_2O$)] **4**

Atom	*x*	*y*	*z*
Ru(1)	442(1)	5371(1)	7681(1)
Ru(2)	−2091(1)	3826(1)	7101(1)
Br(11)	2499(2)	6389(1)	8200(1)
Br(14)	−536(2)	5859(1)	8870(1)
Br(23)	−1192(2)	3218(1)	5955(1)
Br(24)	−3736(2)	4729(1)	6075(1)
Br(13)	−860(2)	6565(1)	6770(1)
O(4)	−3644(9)	2812(6)	6804(5)
N(3)	−864(10)	4625(6)	7359(6)
N(12)	1409(11)	4936(6)	6813(6)
N(11)	1697(10)	4417(6)	8348(6)
N(22)	−1038(10)	2959(6)	7993(6)
N(21)	−2877(11)	4121(6)	8088(6)
C(19)	1233(13)	5242(8)	6039(8)
C(18)	1865(15)	4871(9)	5486(8)
C(17)	2736(15)	4184(9)	5736(9)
C(16)	2943(15)	3846(9)	6521(8)
C(15)	2255(12)	4258(7)	7047(8)
C(14)	2406(12)	3969(7)	7921(8)
C(13)	3281(14)	3284(8)	8284(8)
C(12)	3399(15)	3091(9)	9097(9)
C(11)	2630(15)	3543(8)	9515(8)
C(10)	1796(13)	4185(8)	9145(8)
C(29)	−123(15)	2378(8)	7888(8)
C(28)	507(16)	1785(10)	8493(10)
C(27)	218(13)	1851(9)	9270(9)
C(26)	−723(15)	2471(9)	9371(8)
C(25)	−1332(13)	3019(8)	8734(7)
C(24)	−2372(14)	3663(8)	8787(8)
C(23)	−2797(14)	3816(9)	9491(8)
C(22)	−3746(15)	4450(11)	9483(9)
C(21)	−4250(15)	4937(10)	8795(9)
C(20)	−3812(13)	4730(9)	8110(8)

useful route for halide-exchange reactions and addition of nitrosyl or nitride ligands in ruthenium monobipyridine systems.

Conclusion

The reactions of [Ru(bipy)$(CO)_2$$Cl_2$] in acid solution are summarised in Scheme 1. At elevated temperatures (160–200 °C) aqueous HBr or HI leads to complete halide exchange giving corresponding bromo and iodo complexes [Ru(bipy)$(CO)_2$$Br_2$] and [Ru(bipy)$(CO)_2$$I_2$]. Direct fluorination of [Ru(bipy)$(CO)_2$$Cl_2$] with aqueous HF has not been observed. By using a suitable nitrosyl source, such as HNO_3, with halogen acids [Ru(bipy)$(CO)_2$$Cl_2$] can be converted into nitrosyl complexes [Ru(bipy)(NO)X_3] (X = F, Cl, Br or I) at elevated temperatures (160–240 °C). Even use of the more oxidising HF–HNO_3 acid mixture did not lead to exchange of the chlorides in [Ru(bipy)$(CO)_2$$Cl_2$], but to the formation of a mixed-halide nitrosyl complex [Ru(bipy)(NO)Cl_2F]. With extended reaction times (12–16 h) [Ru(bipy)$(CO)_2$$Cl_2$] can be directly converted into nitrido-bridged [(H_2O)X_2(bipy)Ru–N–Ru(bipy)X_3] (X = Cl or Br) or [Cl_3(bipy)Ru–N–Ru(bipy)Cl_3]$^-$ by using HX–HNO_3 (X = Cl or Br). Nitrido complexes are most probably formed *via* intermolecular reaction of a nitrosyl intermediate with either [Ru(bipy)$(CO)_2$$Cl_2$] or an unidentified carbonyl-containing derivative. Although nitrido-bridged complexes with iodine ligands or mixed-halide ligands (for example Cl and F) have not yet been obtained, they could possibly be produced by acid reactions.



Scheme 1 (*i*) HX; (*ii*) HBr–HNO_3; (*iii*) HX–HNO_3; (*iv*) HF–HNO_3

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