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Reactions of $[Ru(bpy)(CO)_2Cl_2]$ in Acidic Media: Formation and Structural Characterization of $[Ru(bpy)Cl_3(NO)]$, $[Ru_2N(bpy)_2Cl_5(H_2O)]$, and $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$

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Reactions of $[Ru(bpy)(CO)_2Cl_2]$ in concentrated HCl/HNO_3 solutions at high temperatures were studied. In acidic solutions carbonyl groups are lost and replaced by chlorine and nitrosyl, nitrido or water ligands. Formation of $[Ru(bpy)Cl_3(NO)]$ and $[Ru_2N(bpy)_2Cl_5(H_2O)]$ was time-dependent; with shorter reaction times (<6 h, 240 °C) solid crystalline *fac*(Cl)-$[Ru(bpy)Cl_3(NO)]$ (**1a**) and *mer*(Cl)- $[Ru(bpy)Cl_3(NO)]$ (**1b**) were formed, and with longer reaction times a new crystalline nitrido-bridged complex $[Ru_2N(bpy)_2Cl_5(H_2O)]$ (**2**) was produced, most probably via a nitrosyl intermediate. Both **1** and **2** are practically insoluble and highly stable. However, the reaction of $[Ru(bpy)(CO)_2Cl_2]$ in HCl/HNO_3 solution with small amounts of $[Ru(bpy)Cl_3(NO)]$ added gave in low yield another nitrido-bridged product, $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$ (**3**). The role of added $[Ru(bpy)Cl_3(NO)]$ in this reaction is unclear, and it is possible that (**3**) may also form directly from pure $[Ru(bpy)(CO)_2Cl_2]$. Crystal structures of *fac*(Cl)-$[Ru(bpy)Cl_3(NO)]$, *mer*(Cl)- $[Ru(bpy)Cl_3(NO)]$, $[Ru_2N(bpy)_2Cl_5(H_2O)]$, and $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$ showed that the ruthenium atoms are octahedrally coordinated in all complexes. Crystal data: **1a**, monoclinic, space group $P2_1/c$, $a = 6.798(3)$ Å, $b = 11.993(4)$ Å, $c=16.760(8)$ Å, $\beta = 98.89(3)°$, $Z = 4$; **1b**, monoclinic, space group Pn, $a = 8.175(2)$ Å, $b = 6.733(2)$ Å, $c = 12.594(5)$ Å, $\beta = 105.06(3)°$, $Z = 2$; **2**, monoclinic, space group $P2_1/n$, $a = 10.133(5)$ Å, $b = 15.042(6)$ Å, $c = 16.506(8)$ Å, $\beta = 104.86(4)°$, $Z = 4$; **3**, triclinic, space group $P\bar{1}$, $a = 10.281(3)$ Å, $b = 10.776(3)$ Å, $c = 12.527(5)$ Å, $\alpha = 90.78(3)°$, $\beta = 98.31(3)°$, $\gamma = 100.91(2)°$, $Z = 2$.

Introduction

Ruthenium easily forms nitrosyl compounds when brought into contact with a suitable nitrosyl source such as HNO_3.[1] The Ru−(NO) bond is typically highly stable and can resist relatively drastic conditions. Even though nitrosyl ligands usually are difficult to remove or substitute, nitrosyl complexes may react further to produce nitrido compounds. Several ruthenium nitrido clusters have been prepared via nitrosyl compounds.[2] Binuclear nitrido-bridged $[Ru_2NX_8(H_2O)_2]^{3-}$ (X = Cl, Br) complexes have also been synthesized from the nitrosyl compound in the reaction between $[RuX_5(NO)]^{2-}$ and formaldehyde or $SnCl_2$ in HCl.[3,4]

We investigated the reactions of $[Ru(bpy)(CO)_2Cl_2]$ under drastic conditions in HCl/HNO_3 solutions at 240 °C. The substitution of the carbonyl ligands by chlorine, nitrosyl, nitrido, and water ligands and the formation of $[Ru(bpy)Cl_3(NO)]$, $[Ru_2N(bpy)_2Cl_5(H_2O)]$ and $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$ were verified by single-crystal X-ray studies. Although several Ru_2N type nitrido complexes have been reported in the literature (Table 1), only a few crystal structures are known.[5,6]

Table 1. Characterization of Ru_2N Compounds[a]

	ν(Ru−N−Ru)/ cm^{-1}	characterization	ref
$[Ru_2NCl_8(H_2O)_2]^{3-}$	1080−1078	XRD, spectrosc	3−5
$[Ru_2N(en)_5]^{5+}$	1048	XRD, spectrosc	6
$[Ru_2NX_8(H_2O)_2]^{3-}$	1037	spectrosc	4
$[Ru_2N(OH)_2(NO_2)_6(H_2O)_2]^{3-}$	1029	spectrosc	4
$[Ru_2N(NH_3)_8Y_2]^{3+}$	1039−1055	spectrosc	4
$[Ru_2N(NH_3)_6Z_3(H_2O)]^{3-}$	1013−1056	spectrosc	4
$[Ru_2NX_8(CO)_2]^{3-}$	(1016)	spectrosc	27
$[Ru_2N(CN)_{10}]^{5-}$	(1017)	spectrosc	27
$[Ru_2N(en)_4Cl_2]^{3+}$	1052	spectrosc	27
$[Ru_2N(bpy)_4Cl_2]^{3+}$	1054	spectrosc	27
$([Ru_2N(S_2CNEt_2)_4Cl])^{b}$	1031	spectrosc	27

[a] XRD = single-crystal X-ray diffraction measurement; en = 1,2-diaminoethane; X = Br^-, NCS^-; Y = Cl^-, Br^-, NO_3^-; Z = Cl^-, NCS^-, N_3^-. [b] Probably polymer in the solid state with ...Ru−N−Ru−Cl... chain.

Experimental Section

Materials. All reagents were p.a. grade. HNO_3 (J. T. Baker) was 65% and HCl (Merck) 37%. $[\{Ru(CO)_3Cl_2\}_2]$ was obtained from Johnson & Matthey and 2,2′-bipyridine from Aldrich Chemicals. All acid reactions were carried out in a Berghofs 60 mL pressure vessel with PTFE liner. FTIR spectra were measured with a Nicolet Magna-IR Spectrometer 750.

Reactions of $[Ru(bpy)Cl_2(CO)_2]$ in HCl/HNO_3 Solution. Formation of *fac*(Cl)-$[Ru(bpy)Cl_3(NO)]$ (1a) and *mer*(Cl)-$[Ru(bpy)Cl_3(NO)]$ (1b). A 50-mg sample of $[Ru(bpy)(CO)_2Cl_2]$, prepared according to a literature procedure,[7] 4.0 mL of HCl (37%), and 50 μL of HNO_3 (65%) were transferred into a pressure vessel. The vessel was closed tightly and heated at 240 °C for 2−5 h, after which it was cooled slowly to room temperature. A solid product was filtered from the reddish solution, washed with water, and dried in air. The major advantage of this procedure was that the poorly soluble products were

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Table 2. Crystallographic Data for *fac*(Cl)-[Ru(bpy)Cl_3(NO)] (**1a**), *mer*(Cl)-[Ru(bpy)Cl_3(NO)] (**1b**), [$Ru_2N(bpy)_2Cl_5(H_2O)$] (**2**), and (H_5O_2)[$Ru_2N(bpy)_2Cl_6N$] (**3**)

	1a	**1b**	**2**	**3**
fw	393.62	393.62	723.80	778.28
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	Pn	$P2_1/n$	$P\bar{1}$
a, Å	6.798(3)	8.175(2)	10.133(5)	10.281(3)
b, Å	11.993(4)	6.733(2)	15.042(6)	10.776(3)
c, Å	16.760(8)	12.594(5)	16.506(8)	12.527(5)
α, deg	90	90	90	90.78(3)
β, deg	98.89(3)	105.06(3)	104.86(4)	98.31(3)
γ, deg	90	90	90	100.91(2)
V, Å^3	1350(1)	669.3(4)	2432(2)	1347.3(7)
Z	4	2	8	2
D_{calc}, g/cm^3	1.937	1.953	3.954	1.918
cryst source	HCl/HNO_3	HCl/HNO_3	HCl/HNO_3	HCl/HNO_3
cryst size, mm	0.4 × 0.4 × 0.4	0.1 × 0.2 × 0.3	0.3 × 0.4 × 0.4	0.1 × 0.2 × 0.2
color	red	reddish black	red	red
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ mm^{-1}	1.729	1.743	3.597	1.730
2θ limits, deg	5−50	4−55	5−60	5−55
h range	0 to 8	0 to 10	0 to 14	0 to 13
k range	0 to 15	0 to 8	0 to 21	−14 to 13
l range	−21 to 21	−16 to 15	−23 to 22	−16 to 16
no. of unique rflns	3096	1644	7120	6071
no. of obsd. data	2297[a]	1484[b]	5959[b]	4413[b]
no. of params	163	161	298	331
R^c	0.0283	0.0290	0.0265	0.0329
$R_w{}^d$	0.0337	0.0337	0.0359	0.0362
goodness of fit	1.01	1.01	1.14	0.98

[a] $I \geq 3\sigma(I)$. [b] $I \geq 2\sigma(I)$. [c] $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)2/\Sigma w|F_o|2]1/2$, $w = 1/(\sigma^2F + 0.0005F^2)$.

obtained directly in crystalline form. The product consisted of red crystals, **1a**, and greenish black or reddish black crystal-like particles, **1b**. Primary yield of the mixture varied from 20 to 40 mg. Both products were insoluble, and they were separated mechanically. Anal. Calcd for red $C_{10}H_8N_3OCl_3Ru$ (mol wt 393.62): C, 30.51; H, 2.05; N, 10.68; O, 4.06. Found: C, 29.95; H, 1.89; N, 10.51; O, 4.19. IR (KBr): ν(NO) 1891 (vs), 1878 (s, sh) cm^{-1}. Anal. Calcd for **1b**: C, 30.15; H, 1.90; N, 10.62; O, 4.13. IR (KBr): ν(NO) 1865 (vs) cm^{-1}.

Similar reaction products were obtained by using a diluted acid solution [2 mL HCl (37%), 2 mL of H_2O, and 50 μL of HNO_3 (65%)] and longer reaction times.

Extended Reactions of [Ru(bpy)$Cl_2(CO)_2$] in Concentrated HCl/ HNO_3 Solutions. Formation of [$Ru_2(bpy)_2Cl_5N(H_2O)$] (2). A 50-mg sample of [Ru(bpy)$(CO)_2Cl_2$], 4 mL of HCl (37%), and 50 μL of HNO_3 (65%) were heated in the pressure vessel at 240 °C for 12 h and cooled slowly to room temperature. Red crystalline [$Ru_2(bpy)_2Cl_5N(H_2O)$] (**2**) was filtered from yellow or colorless solution. The solid product was washed with water and dried in air. The yield was ca. 20 mg (38%). Anal. Calcd for $C_{20}H_{18}N_5OCl_5Ru_2$ (mol wt 723.80): C, 33.19; H, 2.51; N, 9.68; O, 2.21. Found: C, 32.86; H, 2.45; N, 9.39; O, 2.46. IR (KBr): ν(Ru−N−Ru) 1071 (s), 1033 (m) cm^{-1}.

Formation of [$Ru_2(bpy)_2Cl_6N$](H_5O_2) (3). A 100 mg-sample of [Ru(bpy)$(CO)_2Cl_2$], 5 mg of a a mixture of **1a** and **1b**, 4 mL of HCl (37%) and 2 μL of HNO_3 (65%) were heated in the pressure vessel at 240 °C for 12 h and cooled slowly to room temperature. An orange solid with a very few red [$Ru_2(bpy)_2Cl_6N$](H_5O_2) crystals was filtered from the yellow solution, washed with water, and dried under air. Anal. Calcd for $C_{20}H_{21}N_5O_2Cl_6Ru_2$ (mol wt 778.28): C, 30.87; H, 2.72; N, 9.00. Found: C, 31.27; H, 2.64; N, 8.64.

X-ray Data Collection and Structure Solution for [Ru(bpy)Cl_3(NO)] (1), [$Ru_2N(bpy)_2Cl_5(H_2O)$] (2) and (H_5O_2)[$Ru_2N(bpy)_2Cl_6$] (3). Data were collected at 20 °C on a Nicolet R3m diffractometer using an ω-scan data collection mode and graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Accurate cell parameters were obtained from 25 automatically centered reflections. Intensities were corrected for background, polarization, and Lorentz factors. Structures were solved by direct methods and subsequent Fourier synthesis using the SHELXTL program package.[8] All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were placed in idealized positions (C−H = 0.96 Å, U = 0.08 Å^2) and not refined. Hydrogens attached to oxygen atoms were located from difference Fouries maps but not refined in **2**. In structure **1b**, there appeared to be some disorder after refinement in the space group Pn. However, disorder models in *P2/n* did not succeed at all. Crystallographic data are summarized in Table 2.

Table 3. Atomic Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for *fac*(Cl)-[Ru(bpy)Cl_3(NO)] (**1a**)

atom	x	y	z	U^a
Ru(1)	3519(1)	3001(1)	2730(1)	27(1)
Cl(12)	1504(2)	2286(1)	1546(1)	41(1)
Cl(11)	4094(2)	4626(1)	1982(1)	45(1)
Cl(1)	744(1)	3875(1)	3143(1)	40(1)
O(1)	7037(5)	2012(3)	2265(2)	63(1)
N(11)	2897(4)	1730(2)	3497(2)	30(1)
N(12)	5133(4)	3537(2)	3821(2)	31(1)
N(1)	5641(5)	2372(3)	2452(2)	34(1)
C(10)	1683(6)	862(3)	3280(2)	38(1)
C(11)	1282(6)	71(3)	3839(3)	45(1)
C(12)	2146(7)	198(4)	4631(3)	49(1)
C(13)	3354(6)	1105(3)	4861(2)	42(1)
C(14)	3747(5)	1856(3)	4285(2)	34(1)
C(15)	5053(6)	2842(3)	4452(2)	35(1)
C(16)	6167(6)	3060(4)	5205(2)	47(1)
C(17)	7330(6)	4022(4)	5306(2)	48(1)
C(18)	7370(6)	4733(3)	4663(3)	45(1)
C(19)	6262(5)	4463(3)	3926(2)	38(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Several studies on [Ru(bpy)$(CO)_2Cl_2$] have been published because of its electrochemical and photochemical properties.[9] [Ru(bpy)$(CO)_2Cl_2$] is relatively stable. It dechlorinates under H_2/CO pressure at 150 °C, yielding dimeric [Ru(bpy)$(CO)_2$-$Cl]_2$ only poorly.[7] Dechlorination can be completed by elec-

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Table 4. Atomic Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for *mer*(Cl)-[Ru(bpy)Cl$_3$(NO)] (**1b**)

atom	*x*	*y*	*z*	*U*[a]
Ru(1)	2500	2919(1)	2500	30(1)
Cl(1)	3958(3)	4642(3)	4094(2)	47(1)
Cl(3)	925(3)	1017(3)	1038(2)	56(1)
Cl(11)	4831(3)	788(3)	2677(2)	53(1)
N(11)	340(7)	4543(7)	2506(4)	33(2)
N(12)	1428(7)	1212(8)	3542(4)	33(2)
C(10)	−135(10)	6239(10)	1939(6)	45(2)
C(11)	−1565(11)	7233(12)	1975(7)	56(3)
C(12)	−2546(17)	6510(11)	2630(12)	63(4)
C(13)	−2092(9)	4753(11)	3196(7)	51(3)
C(14)	−630(8)	3807(10)	3117(5)	36(2)
C(15)	−31(8)	1931(9)	3700(5)	35(2)
C(16)	−870(10)	940(11)	4374(6)	47(3)
C(17)	−170(10)	−795(11)	4893(6)	52(3)
C(18)	1326(11)	−1512(11)	4721(6)	48(2)
C(19)	2074(9)	−475(10)	4028(5)	39(2)
N(2)	3315(15)	4683(14)	1534(8)	55(3)
O(2)	3531(15)	5377(17)	1140(9)	84(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Atomic Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for [Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)](**2**)

atom	*x*	*y*	*z*	*U*[a]
Ru(2)	2114(1)	3807(1)	2925(1)	22(1)
Ru(1)	−425(1)	5396(1)	2299(1)	20(1)
Cl(22)	3682(1)	4697(1)	3903(1)	34(1)
Cl(21)	1257(1)	3212(1)	4023(1)	39(1)
Cl(11)	794(1)	6580(1)	3161(1)	33(1)
Cl(12)	485(1)	5853(1)	1140(1)	34(1)
Cl(1)	−2395(1)	6372(1)	1791(1)	37(1)
O(2)	3699(2)	2785(1)	3215(1)	40(1)
N(1)	888(2)	4628(1)	2645(1)	21(1)
N(21)	2915(2)	4109(2)	1924(1)	29(1)
N(22)	1042(2)	2913(1)	2029(1)	29(1)
N(12)	−1399(2)	4960(1)	3186(1)	24(1)
N(11)	−1652(2)	4397(1)	1636(1)	25(1)
C(20)	3829(3)	4751(2)	1919(2)	39(1)
C(21)	4280(3)	4946(3)	1214(2)	50(1)
C(22)	3730(4)	4454(3)	490(2)	53(1)
C(23)	2783(3)	3805(2)	483(2)	45(1)
C(24)	2365(3)	3635(2)	1211(2)	32(1)
C(25)	1345(3)	2960(2)	1272(2)	32(1)
C(26)	709(3)	2392(2)	622(2)	43(1)
C(27)	−212(4)	1768(2)	749(2)	51(1)
C(28)	−504(4)	1718(2)	1516(2)	48(1)
C(29)	131(3)	2304(2)	2147(2)	38(1)
C(19)	−1209(3)	5291(2)	3967(2)	32(1)
C(18)	−1881(3)	4954(2)	4527(2)	38(1)
C(17)	−2762(4)	4246(2)	4284(2)	46(1)
C(16)	−2958(3)	3889(2)	3487(2)	43(1)
C(15)	−2265(3)	4262(2)	2941(2)	29(1)
C(14)	−2417(3)	3957(2)	2072(2)	28(1)
C(13)	−3283(3)	3267(2)	1702(2)	38(1)
C(12)	−3371(3)	3042(2)	883(2)	43(1)
C(11)	−2592(3)	3496(2)	441(2)	40(1)
C(10)	−1736(3)	4172(2)	840(2)	34(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Atomic Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for (H$_5$O$_2$)[Ru$_2$N(bpy)$_2$Cl$_6$] (**3**)

atom	*x*	*y*	*z*	*U*[a]
Ru(1)	1721(1)	3844(1)	2841(1)	22(1)
Ru(2)	3411(1)	1452(1)	2331(1)	24(1)
Cl(11)	3295(1)	4633(1)	4409(1)	40(1)
Cl(12)	3103(1)	5198(1)	1770(1)	37(1)
Cl(1)	561(1)	5609(1)	3092(1)	40(1)
Cl(22)	4051(1)	1042(1)	4179(1)	43(1)
Cl(21)	1475(1)	−214(1)	2281(1)	38(1)
Cl(2)	4712(1)	−93(1)	1840(1)	41(1)
N(1)	2532(3)	2613(3)	2619(3)	25(1)
O(3)	4773(5)	2875(4)	6222(4)	57(2)
O(4)	6928(5)	2231(4)	6515(4)	64(2)
N(12)	358(4)	2705(3)	3656(3)	30(1)
N(11)	192(4)	3171(3)	1581(3)	29(1)
N(21)	5101(3)	2815(3)	2214(3)	27(1)
N(22)	3117(3)	1769(3)	685(3)	27(1)
C(19)	542(6)	2515(5)	4720(4)	46(2)
C(18)	−405(7)	1685(6)	5193(5)	61(2)
C(17)	−1535(7)	1057(6)	4563(6)	67(3)
C(16)	−1735(6)	1240(5)	3464(5)	53(2)
C(15)	−762(5)	2082(4)	3024(4)	34(2)
C(14)	−865(4)	2335(4)	1871(4)	35(1)
C(13)	−1938(5)	1803(5)	1078(5)	48(2)
C(12)	−1919(6)	2120(5)	22(5)	58(2)
C(11)	−856(6)	2964(5)	−264(4)	49(2)
C(10)	189(5)	3474(4)	543(4)	38(2)
C(20)	5991(5)	3371(4)	3052(4)	35(1)
C(21)	7069(5)	4314(5)	2897(4)	40(2)
C(22)	7216(5)	4680(4)	1862(4)	41(2)
C(23)	6287(5)	4123(4)	1004(4)	35(2)
C(24)	5221(4)	3180(4)	1190(3)	27(1)
C(25)	4154(4)	2554(4)	332(3)	27(1)
C(26)	4157(5)	2736(4)	−762(4)	38(2)
C(27)	3070(5)	2154(5)	−1496(4)	44(2)
C(28)	1987(5)	1405(5)	−1128(4)	40(2)
C(29)	2052(5)	1229(4)	−34(4)	33(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 7. Selected Bond Lengths (Å) for *fac*(Cl)-[Ru(bpy)Cl$_3$(NO)] (**1a**), *mer*(Cl)-[Ru(bpy)Cl$_3$(NO)] (**1b**), [Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)] (**2**), and (H$_5$O$_2$)[Ru$_2$N(bpy)$_2$Cl$_6$] (**3**)

	1a	**1b**	**2**	**3**
Ru(1)−Cl(1)	2.354 (2)	2.356 (2)	2.447 (1)	2.468 (2)
Ru(1)−Cl(11)	2.383 (2)	2.349 (2)	2.413 (1)	2.390 (1)
Ru(1)−Cl(12)	2.390 (1)		2.425 (1)	2.402 (2)
Ru(1)−N(11)	2.079 (3)	2.079 (6)	2.074 (2)	2.075 (3)
Ru(1)−N(12)	2.083 (3)	2.100 (6)	2.072 (3)	2.076 (4)
Ru(1)−N(1)	1.754 (3)		1.744 (2)	1.734 (4)
N(1)−O(1)	1.131 (5)			
Ru(1)−Cl(3)		2.336 (2)		
Ru(1)−N(2)		1.938 (11)[a]		
N(2)−O(2)		0.735 (16)[a]		
Ru(2)−Cl(2)				2.448 (2)
Ru(2)−O(2)			2.186 (2)	
Ru(2)−Cl(21)			2.375 (1)	2.408 (1)
Ru(2)−Cl(22)			2.368 (1)	2.385 (2)
Ru(2)−N(21)			2.070 (3)	2.076 (3)
Ru(2)−N(22)			2.087 (2)	2.083 (4)
Ru(2)−N(1)			1.728 (2)	1.738 (4)

[a] Incorrect due to disorder (see text).

trochemical reduction in aqueous MeCN, giving polymeric [{Ru(bpy)(CO)$_2$}$_n$].[9c,9d] Further chlorination of [Ru(bpy)(CO)$_2$Cl$_2$] should also be possible since both [Ru(bpy)(CO)Cl$_3$]$^-$ [10] and [Ru(bpy)Cl$_4$]$^-$ [11] are known. In the present work we studied the reactions of [Ru(bpy)(CO)$_2$Cl$_2$] in acidic media and the possibility of preparing ruthenium bipyridine nitrosyl and nitrido complexes directly from [Ru(bpy)(CO)$_2$Cl$_2$]. Reactions are summarized in Scheme 1.

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Table 8. Selected Bond Angles (deg) for *fac*(Cl)-[Ru(bpy)Cl$_3$(NO)] (**1a**), *mer*(Cl)-[Ru(bpy)Cl$_3$(NO)] (**1b**), [Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)] (**2**), and (H$_5$O$_2$)[Ru$_2$N(bpy)$_2$Cl$_6$] (**3**)

	1a	**1b**	**2**	**3**
N(1)−Ru(1)−Cl(1)	177.9 (1)		175.4 (1)	178.1 (1)
N(1)−Ru(1)−Cl(11)	90.2 (1)		93.6 (1)	92.5 (1)
N(1)−Ru(1)−Cl(12)	90.8 (1)		91.9 (1)	90.7 (1)
N(1)−Ru(1)−N(11)	95.9 (1)		89.8 (1)	91.5 (1)
N(1)−Ru(1)−N(12)	91.3 (1)		91.2 (1)	92.4 (2)
N(11)−Ru(1)−N(12)	79.3 (1)	78.0 (2)	79.3 (1)	79.0 (1)
Cl(11)−Ru(1)−Cl(12)	88.6 (1)		90.9 (1)	88.8 (1)
Ru(1)−N(1)−O(1)	177.0 (3)			
Cl(3)−Ru(1)−Cl(1)		174.1 (1)		
Cl(3)−Ru(1)−Cl(11)		90.4 (1)		
Cl(3)−Ru(1)−N(11)		89.8 (1)		
Cl(3)−Ru(1)−N(12)		87.6 (1)		
Cl(3)−Ru(1)−N(2)		92.9 (3)[a]		
Cl(11)−Ru(1)−N(2)		91.8 (3)[a]		
Ru(1)−N(2)−O(2)		174.1 (15)[a]		
N(1)−Ru(2)−Cl(2)				176.3 (1)
N(1)−Ru(2)−O(2)			176.7 (1)	
N(1)−Ru(2)−Cl(21)			95.5 (1)	92.8 (1)
N(1)−Ru(2)−Cl(22)			95.1 (1)	94.3 (1)
N(1)−Ru(2)−N(21)			91.8 (1)	90.9 (2)
N(1)−Ru(2)−N(22)			93.6 (1)	92.1 (2)
N(21)−Ru(2)−N(22)			79. 3 (1)	79.3 (1)
Cl(21)−Ru(2)−Cl(22)			90.3 (1)	88.8 (1)

[a] Incorrect due to disorder (see text).

Formation of Neutral [Ru(bpy)Cl$_3$(NO)] in Acidic Solution. Reactivity of [Ru(bpy)(CO)$_2$Cl$_2$] with HCl or gaseous Cl$_2$ was poor. When [Ru(bpy)(CO)$_2$Cl$_2$] was treated with concentrated HCl (37%) at 180 °C for 3 h, only the original complex was observed and no chlorination occured. With extended reaction times and at elevated reaction temperatures (24 h at 240 °C and 24 h at 200 °C) some chlorination might occur, but even in such drastic conditions it is more probable that [Ru(bpy)(CO)$_2$Cl$_2$] was simply decomposed or solvated. Similarly, no chlorination of [Ru(bpy)(CO)$_2$Cl$_2$] with gaseous Cl$_2$ was observed. However, by adding HNO$_3$ as a nitrosyl source in HCl solution, chlorination took place along with addition of a nitrosyl ligand.

The structure of red crystalline *fac*(Cl)-[Ru(bpy)Cl$_3$(NO)] (**1a**) was characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction studies (Figure 1a). The coordination geometry of the ruthenium nitrosyl complex is octahedral with a linear Ru−(NO) group (177.0(3)°) *trans* to chlorine (*fac*-chloro isomer). Nitrosyl bond lengths, Ru−N of 1.754(3) Å and N−O of 1.131(5) Å, are comparable with other linear nitrosyls positioned *trans* to Cl.[12,13,15] The Ru−Cl(1) bond *trans* to N−O is the shortest Ru−Cl bond. This can be explained by noting that NO is a very strong π-acceptor but a much weaker σ-donor than Cl$^-$.[16,17] In the IR spectrum of **1a**, sharp ν(NO) peaks were resolved at 1891 (vs) and 1878 (s, sh) cm^{-1}. This is in agreement with the results (1886 and 1879 cm^{-1}) reported by Fairy and Irwing.[18]

Together with **1a**, a crystal-like precipitate, **1b** (*mer*(Cl)-[Ru(bpy)Cl$_3$(NO)], Figure 1b), varying in color from greenish black to reddish black was formed. In the IR spectrum of **1b** only a single strong ν(NO) at 1865 cm^{-1} was observed. Although the elemental analysis of **1b** was not totally reproducible it was typically very close to that of *fac*(Cl)-[Ru(bpy)Cl$_3$(NO)]. There appeared to be some disorder in the (NO) group of complex **1b**. The N(12)−O(12) bond length of 0.76(2) Å is too short and the Ru(1)−N(12) bond length of 1.910(11) Å too long for a typical nitrosyl group. Overestimation of the Ru(1)−O(12) bond and underestimation of the N(12)−O(12) bond is presumably due to the co-existence of another complex, one probably containing a water ligand in the position of the nitrosyl group. Both N(12) and O(12) are displaced along the Ru(1)−N(12)−O(12) bond (Figure 1b), supporting the model of an alternative ligand at the nitrosyl position. In fact, a third maximum was observed in the difference Fourier map along the Ru(1)−N(2)−O(2) bond axis after isotropic refinement. The distance from Ru to this maximum was about 1.7 Å, which is close to a typical Ru−N bond length in the nitrosyl group. During anisotropic refinement the third maximum was lost.

Differing from those in **1a**, the ruthenium−2,2′-bipyridine bonds in **1b** are unequal. Owing to the strong *trans* effect of the nitrosyl group, the Ru(1)−N(12) bond of 2.103(6) Å *trans* to NO is clearly longer than the Ru(1)−N(11) bond of 2.078(5) Å *trans* to Cl(11).

In addition to the solid products, also the reddish acid solution produced in the reaction was analyzed. The solution was evaporated to dryness under vacuum and the precipitate was analyzed by IR (in KBr). One strong peak was found at 1868 cm^{-1}, with shoulders at 1913, 1903, and 1845 cm^{-1}, strongly suggesting **1b**. Crystallization directly from acid solution yielded reddish crystals which were identified as **1a** by single-crystal X-ray studies. Both IR and X-ray results thus indicate that the nitrosyl complexes are probably the dominating compounds also in acid solution. The HNO$_3$ content of the acid solution seemed not to be critical in the formation of nitrosyl products as long as the nitrosyl source was available. The nitrosyl products (mainly **1a**) were found in the acid solution with various HCl/HNO$_3$ ratio (0.03−0.16% HNO$_3$). The formation of *mer*(Cl)-[Ru(bpy)Cl$_3$(NO)] in HCl/HNO$_3$ solution was also detected by using complexes such as [Ru(bpy)(CO)$_2$ClH], [Ru(bpy)(CO)$_2$Cl(C(O)OCH$_3$)], and supported [Ru$_3$(CO)$_{12}$/2,2′-bipyridine/SiO$_2$] catalyst as a reactant or by using KNO$_3$ as a nitrosyl source.

Formation and Crystal Structure of [Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)]. When [Ru(bpy)(CO)$_2$Cl$_2$] was treated with concentrated HCl/HNO$_3$ (0.8% HNO$_3$) at 240 °C for about 12 h (see Experimental Section), the acid solution turned yellow or colorless, and new dark red crystals were formed. No peaks were observed in the nitrosyl stretching region of the IR spectrum of this solid component. An elemental analysis gave a reasonably good fit with [Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)] (**2**). Evidently the formation of this nitrido complex depends on reaction time. The optimum reaction time at 240 °C was found to be 12 h. With shorter reaction times (<6 h), only nitrosyl compounds (**1a** and **1b**) were produced, and with longer reaction times (>48 h) no solid products were observed.

Several binuclear Ru$_2$(μ-N)-type compounds are known (Table 1), but to our knowledge only two crystal structures have been published, [Ru$_2$NCl$_8$(H$_2$O)$_2$]$^{3-}$ [5] and [Ru$_2$N(en)$_5$]$^{5+}$.[6] In these complexes the (L$_5$Ru) units are connected by linear and symmetric nitrido bridges. Typically, the Ru−N bond is relatively short (1.718(3), 1.725(5), and 1.728(9) Å in [Ru$_2$NCl$_8$(H$_2$O)$_2$]$^{3-}$ with countercations K$^+$, NH$_4^+$, and Rb$^+$, respectively, and 1.742(1) Å in [Ru$_2$N(en)$_5$]$^{5+}$). In the IR spectrum of the Ru$_2$N compounds the Ru−N−Ru stretching frequency is typically in the range 1020−1080 cm^{-1} (see Table

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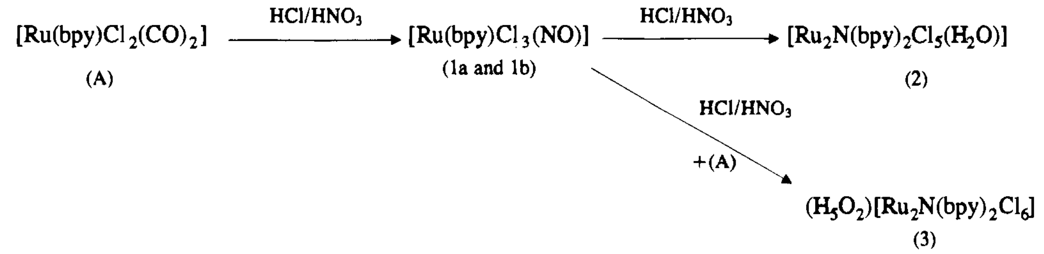
Scheme 1



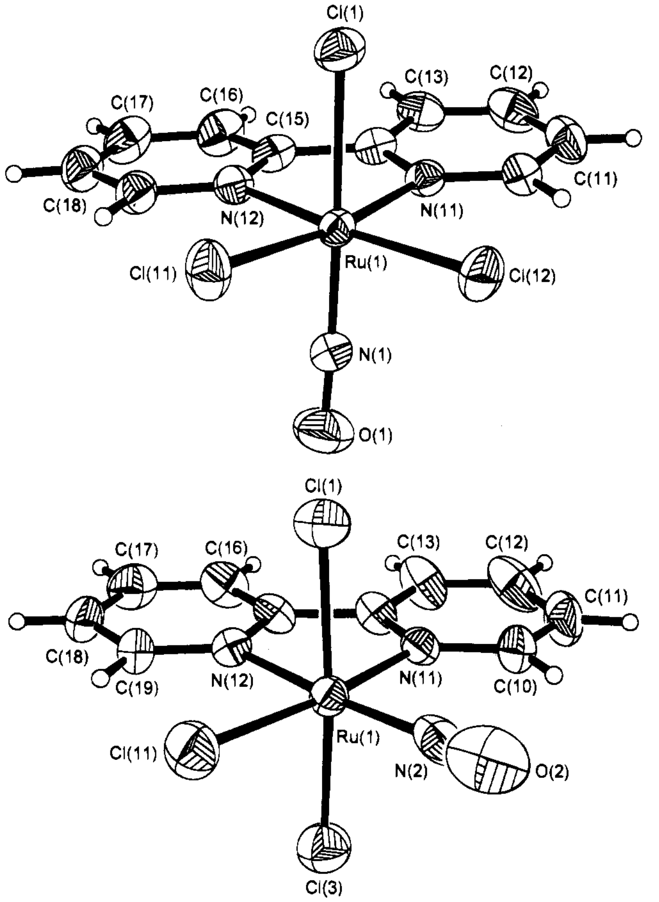


Figure 1. (a) Crystal structure of *fac*-(Cl)-[Ru(bpy)Cl$_3$(NO)]. (b) Crystal structure of *mer*-(Cl)-[Ru(bpy)Cl$_3$(NO)].

1). Compound **2** gave two bands in that region, at 1071 and 1033 cm^{-1}.

[Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)] consists of two slightly distorted octahedral (L$_5$RuN) units, with no center of symmetry (Figure 2). The Ru(2)–[μ-N(1)] bond of 1.728 (2) Å opposite H$_2$O(2) is slightly shorter than the Ru(1)–(μ-N(1)) bond of 1.744 (2) Å *trans* to Cl(1). Similarly, the Ru–(μ-N) bond lengths *trans* to H$_2$O in [Ru$_2$NCl$_8$(H$_2$O)$_2$]$^{3-}$ are somewhat shorter (1.718–1.728 Å) than in [Ru$_2$N(en)$_5$]$^{5+}$ (1.742(1) Å). Generally, the Ru–(μ-N) bond lengths in the nitrido bridge are clearly shorter than the Ru–O bond length of 1.869 (1) Å in a similar oxygen-bridged complex, [Ru$_2$O(bpy)$_4$(H$_2$O)$_2$]$^{4+}$.[19] The ruthenium–water bond length of 2.186(2) Å is relatively long compared with the corresponding bond lengths in the mononuclear Cs$_2$-[RuCl$_5$(H$_2$O)] (2.10 Å)[5c,20] and Ph$_4$As[RuCl$_5$(H$_2$O)] (2.12 Å)[5c,21] but very close to the ruthenium–water bonds of 2.180–2.248 Å found in M$_3$[Ru$_2$NCl$_8$(H$_2$O)$_2$] (M = K$^+$, NH$_4^+$, or Rb$^+$).[5] The Ru–Cl bonds perpendicular to the Ru–N–Ru axis are shorter than the axial Ru(1)–Cl(1) bond. Both Ru–O and Ru–Cl bond lengths show the *trans* effect of the bridging nitrido group.[6] In Rb$_3$[Ru$_2$NCl$_8$(H$_2$O)$_2$] the (μ-N)–Ru–Cl angles are distorted from the ideal 90° and vary from 94.8(3) to 95.2(3)°. The distortion is probably due to the short Ru–(μ-N) bond and to the increased repulsion between the equatorial chlorines and the nitrogen bridge.[5c] In **2** the (μ-N)–Ru(1)–Cl angles of the equatorial chlorines at the "chlorine end" of the dimeric unit are closer to the ideal of 90° (91.9(1), 93.6(1)°) than those at the "water end" (95.1(1), 95.5(1)°). The (μ-N)–Ru–Cl angles and the lengthening of the axial Ru–Cl(1) bond indicate repulsion between the axial and equatorial chlorines. The intermolecular hydrogen bonding occurs between the apical water ligand and the equatorial chlorines of the neighboring molecule.[21]

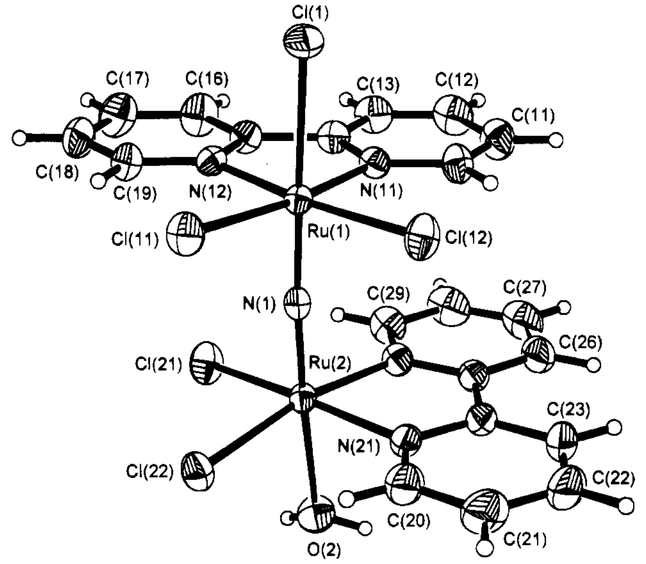


Figure 2. Crystal structure of [Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)].

Along with [Ru$_2$N(bpy)$_2$Cl$_5$(H$_2$O)] also a small amount of [Ru(bpy)$_2$Cl$_2$]·3.5H$_2$O was formed, indicating partial decomposition of Ru-bpy units. The formation of [Ru(bpy)$_2$Cl$_2$]·3.5H$_2$O was verified by single-crystal X-ray measurements.

[Ru(bpy)Cl$_3$(NO)] acts most probably as an intermediate in the formation of **2**. It is known that the nitrosyl compounds can be used in the preparation of Ru$_2$N-type compounds. For example, [Ru$_2$NCl$_8$(H$_2$O)$_2$]$^{3-}$ has been prepared from [RuCl$_5$-(NO)]$^{2-}$ by using stannous halides or formaldehyde[3,4] as a reduction agent for NO. Nitrido clusters have also been

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(22) The intermolecular hydrogen bonding occurs between the apical water ligand and the equatorial chlorines of the neighboring molecule at the equivalent position 0.5 − *x*, −0.5 − *y*, 0.5 − *z*. The H(1)··Cl(11), H(2)··Cl(12), O(2)··Cl(11), and O(2)··Cl(12) distances are 2.155, 2.524, 3.051, and 3.132 Å, respectively.

prepared from nitrosyls via cleavage of the N−O bond.[2] In these synthesis the nitrosyl ligand is reduced by neighboring CO group liberating CO_2. In the case of $[Ru_2N(bpy)_2Cl_5(H_2O)]$, the reduction of NO may proceed *via* an intermolecular reaction between the nitrosyl complex and the coordinated CO ligand of $[Ru(bpy)(CO)_2Cl_2]$ or its derivative. Attempts to prepare the nitrido complex from pure **1a** failed, which also support the role of carbonyl as a possible reduction agent.

Formation and Crystal Structure of $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$ (3). Insoluble dark red crystals (**3**) were obtained when a mixture of $[Ru(bpy)(CO)_2Cl_2]$, **1a**, and **1b** was treated with HCl/HNO_3 (0.3% HNO_3) (see Experimental Section). Like $[Ru_2N(bpy)_2Cl_5(H_2O)]$, formation of **3** was observed only with extended reaction times (ca. 12 h, at 240 °C). Yields of **3** in these reactions were low; only a few crystals per reaction were obtained, with some unreacted $[Ru(bpy)(CO)_2Cl_2]$.

The coordination geometry in (L_5RuN) units of $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$ is again octahedral (Figure 3). Unlike in **2** the Ru−N−Ru unit is symmetrical, with Ru−N(1) bond lengths of 1.734(4) and 1.738(4) Å. Both axial Ru−Cl bonds are somewhat longer than the equatorial Ru−Cl bonds due to the *trans* effect of the nitrido bridge. The counter cation $(H_5O_2)^+$ is slightly bent (O(3)−H(3)−O(4) 165(6)°). The very short O(3)−O(4) distance of 2.425 Å is comparable with the distances reported in the literature.[23-25] Both intra- and intermolecular hydrogen bond interaction occur between $(H_5O_2)^+$ and equatorial chlorine ligands of $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$.[26]

The role of the added nitrosyl complexes **1a** and **1b** in the formation of **3** is not yet clear, and it is possible that small amounts of **3** could be obtained directly from pure $[Ru(bpy)(CO)_2Cl_2]$, although this was not observed. However, the formation of complex **3** proceeds most probably *via* nitrosyl intermediates similarly to $[Ru_2N(bpy)_2Cl_5(H_2O)]$.

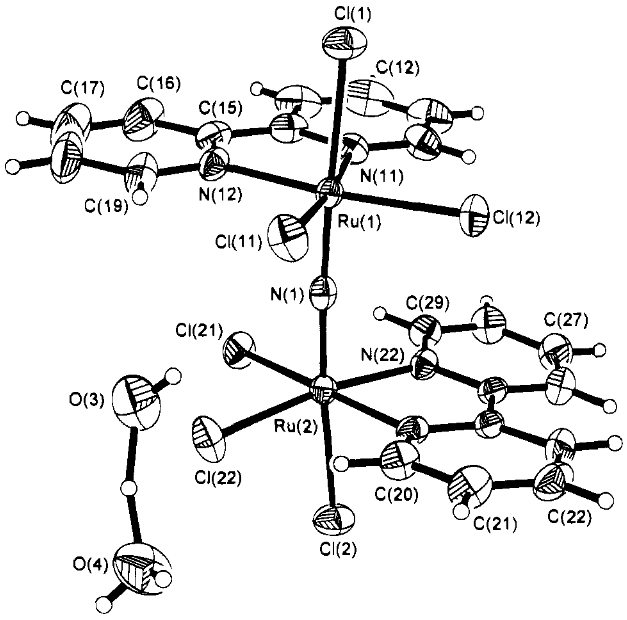

Figure 3. Crystal structure of $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$.

Supplementary Material Available: Tables of all positional parameters, anisotropic thermal parameters, complete bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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(26) A weak hydrogen bond interaction occurs between $(H_5O_2)^+$ and equatorial chlorine ligand, H(2)···Cl(22) and O(3)···Cl(22), distances being 2.392 and 3.124 Å, respectively. $(H_5O_2)^+$ also interacts with the axial and equatorial chlorines of two neighboring $[Ru_2N(bpy)_2Cl_6]^-$ anions in the equivalent positions ($i = 1 - x, 1 - y, 1 - z$, and $ii = 1 - x, 0 - y, 1 - z$). The H(5)···Cl(1)^i, O(4)···Cl(1)^i, H(4)···Cl(21)^{ii}, and O(4)···Cl(21)^{ii} distances are 2.318, 3.107, 2.477, and 3.227 Å, respectively.

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