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Formation of Ruthenium Nitrosyl Complexes: Reactions of $Ru(bpy)(CO)_2Cl_2$ and Its Methyl-Substituted Analogues $Ru(4,4'\text{-}dmbpy)(CO)_2Cl_2$ and $Ru(6,6'\text{-}dmbpy)(CO)_2Cl_2$ in Oxidizing Acidic Solutions

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Introduction

The chemistry of ruthenium-bipyridine complexes has been widely studied during the last few years for several reasons. Monomeric and dimeric mono(2,2′-bipyridine)ruthenium complexes have been shown to be useful reagents in electrochemistry as well as in some catalytic processes.[1−6] Tris- and bis(2,2′-bipyridine) complexes have unusual photoredox properties, and much of the recent studies in converting solar energy involve the use of ruthenium bis(bipyridine) complexes.[7−11] Recently there has been a growing interest in modifying the properties of Ru−bpy complexes by ligand substitution reactions or by altering the steric and electronic properties of the whole complexes by using differently substituted polypyridine ligands.[12−16] The main goals of these studies have been the investigation of the reactivity of these compounds under various conditions as well as identifying the possible intermediates in different chemical processes, such as the water-gas shift reaction.[17]

In the present study, we have investigated the reactions of monomeric ruthenium(II) bipyridine carbonyl complexes in oxidizing acidic solutions and solved the crystal structure of the resulting compounds. Furthermore, we have studied the effect of the sterically hindered bipyridine ligands 4,4′-dimethyl-2,2′-bipyridine and 6,6′-dimethyl-2,2′-bipyridine on the formation of ruthenium nitrosyl complexes. The ligand substitution reactions may be accompanied by simultaneous oxidation of the polypyridine ligands, a case which strongly depends on the acidity of the reaction mixture. On the basis of these observations, we also report an alternative synthesis for preparing dicarboxy-substituted 2,2′-bipyridine ligands.

Experimental Section

Materials. $[Ru(CO)_3Cl_2]_2$ was purchased from Johnson & Matthey, and 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine from were purchased Aldrich Chemicals. 6,6′-Dimethyl-2,2′-bipyridine was obtained from the University of Oulu, where it was synthesized according to the literature method.[16] $Ru(bpy)(CO)_2Cl_2$ and its dimethyl-substituted analogues were synthesized from $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine reagents by refluxing in THF as described earlier.[17,18] HNO_3 (65%, J. T. Baker) and HCl (37%, Merck) were of analytical grade and were used as received. Ligand substitution reactions were carried out in a Berghof 60 mL digestive pressure bomb with a PTFE liner.[19] All manipulations were performed in air.

Characterization of the Products. Infrared spectra were measured with a Nicolet Magna FTIR spectrometer 750. X-ray diffraction data were collected with a Nicolet R3m or Syntex P21 diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). Cell parameters were obtained from 25 automatically centered reflections. Intensities were corrected for background, polarization, and Lorentz effects. Data collection, data reduction, and cell refinement were carried out with the P3/P4-Diffractometer Program V 4.27.[20] The structures were solved by direct methods. The structure solution was carried out with the SHELXS 86 program and the structure refinement with the SHELXL 93 program.[21,22] All non-hydrogen atoms, except one of the NO_3^- oxygens in **3**, were refined anisotropically. The NO_3^- oxygen was disordered in two positions with an equal occupation factor (0.5) and refined isotropically. All hydrogens in **1**, **2**, and **4** were located from the difference Fourier map and refined isotropically with a fixed isotropic displacement parameter ($U = 0.08$ Å^2 for uncoordinated H_2O hydrogens in **2** and $U = 0.05$ Å^2 for all other hydrogens). The hydrogens of the H_2O ligand in **3** and those of the H_3O^+ ions in $(H_3O)_2[Ru(NO)Cl_5]$ could not be located from the difference Fourier map and were therefore omitted. Both oxygens of the H_3O^+ ions in $(H_3O)_2[Ru(NO)Cl_5]$ were surrounded by nine chlorines of the $[RuCl_5(NO)]2-$ anions in the range 3.32−3.65 Å, allowing weak interactions and several orientations of the H_3O^+ ions. The crystallographic data are collected in Table 1.

Formation of $Ru(dcbpy)Cl_3(NO)$ (1) (dcbpy = 4,4′-Dicarboxy-2,2′-bipyridine). A 50 mg sample of $Ru(4,4'\text{-}dmbpy)(CO)_2Cl_2$, 4 mL of hydrochloric acid (37%), and 50 μL of nitric acid (65%) were introduced into a 60 mL Berghof pressure vessel. The reaction mixture was heated to 240 °C (temperature was maintained at 240 °C for 2.5 h) and cooled slowly to room temperature (cooling rate about 16 °C/h). Dark red crystals (15.4 mg) formed during the cooling period were separated from the red solution by filtration and dried in air. The solid product was analyzed by X-ray diffraction and IR spectroscopic measurements as well as by elemental analysis. Anal. Calcd for **1**: C, 29.95; N, 8.74; H, 1.68. Found: C, 30.05; N, 8.46; H, 1.59. IR (in KBr): ν(NO) 1912 (vs), 1895 (s, sh) cm^{-1}; ν(COO) 1731 (vs), 1708 (s) cm^{-1}. The poor solubility of the nitrosyl complexes studied in this paper prevented NMR studies.

Formation of $[Ru(bpy)Cl_2(NO)H_2O]NO_3{\cdot}H_2O$ (2) (bpy = 2,2′-Bipyridine). A 102 mg (0.27 mmol) sample of $Ru(bpy)(CO)_2Cl_2$, 3.5 mL of H_2O, and 50 μL of HNO_3 were placed in a 60 mL pressure vessel, and the reaction mixture was heated to 200 °C. The temperature

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Table 1. Crystallographic Data for Ru(dcbpy)Cl_3(NO) (**1**), [Ru(bpy)Cl_2(NO)(H_2O)](NO_3)·H_2O (**2**), [Ru(4,4′-dmbpy)Cl_2(NO)(H_2O)](NO_3) (**3**), and 6,6′-Dicarboxy-2,2′-bipyridine Hydrochloride (**4**·HCl)

	1	**2**	**3**	**4**·HCl
empirical formula	$C_{12}H_8N_3O_5Cl_3Ru$	$C_{10}H_{12}N_4O_6Cl_2Ru$	$C_{12}H_{14}N_4O_5Cl_2Ru$	$C_{12}H_9N_2O_4Cl$
fw	481.63	456.21	466.24	280.66
space group	$P2_1/_n$	$P2_1/_c$	$P2_1/_c$	$P2_1/_c$
a, Å	8.359(2)	10.570(2)	17.221(6)	12.062(5)
b, Å	19.625(8)	11.226(1)	11.560(4)	7.982(3)
c, Å	10.339(4)	13.976(2)	8.940(4)	13.382(4)
β, deg	110.50(2)	101.89(1)	102.71(3)	107.78(3)
V, Å^3	1588.7(10)	1622.8(4)	1736.1(12)	1226.9(8)
Z	4	4	4	4
T, °C	20	20	20	20
ρ_{calc}, g/cm^3	2.014	1.867	1.784	1.519
μ, mm^{-1}	1.52	1.33	1.24	0.32
R1	0.0466	0.0393	0.0481	0.0340
wR2^a	0.0923	0.0963	0.1237	0.0645

^{a} $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; $P = (F_o^2 + 2F_c^2)/3$.

was maintained at 200 °C for 6 h, after which the reaction vessel was cooled slowly to room temperature (cooling rate about 4 °C/h). The red crystalline product (yield ca. 25 mg) was separated from the orange solution by filtration and dried in air. The product was analyzed by X-ray diffraction and IR spectroscopic measurements and by elemental analysis. Anal. Calcd for **2**: C, 26.33; N, 12.28; H, 2.65. Found: C, 27.08; N, 12.58; H, 2.62. IR (in KBr): ν(NO) 1891 (vs), 1878 (s, sh) cm^{-1}.

Formation of [Ru(4,4′-dmbpy)Cl_2(NO)H_2O]NO_3 (3) (4,4′-dmbpy = 4,4′-Dimethyl-2,2′-bipyridine). The synthesis of complex **3** is similar to that of complex **2**, except that 95.4 mg (0.23 mmol) of Ru(4,4′-dmbpy)$(CO)_2Cl_2$ was weighed into the pressure vessel. After cooling of the reaction mixture, the reddish-brown solution was separated from the brown precipitate which had formed. During the evaporation of the aqueous solvent, orange crystals suitable for X-ray diffraction analysis were formed (yield of the crystalline product ca. 20 mg). Anal. Calcd. for **3**: C, 30.91; N, 12.02; H, 3.03. Found: C, 30.50; N, 12.17; H, 2.96. IR (in KBr): ν(NO) 1902 (vs), 1890 (s, sh) cm^{-1}.

Synthesis of 6,6′-Dicarboxy-2,2′-bipyridine (4). A 50 mg sample of 6,6′-dimethyl-2,2′-bipyridine was dissolved in 4 mL of HCl, and 50 μL HNO_3 was added. The solution was heated at 200 °C in a pressure vessel for 2.5 h, after which the reaction mixture was allowed to cool to room temperature. The colorless acidic solution was poured into 10 mL of cool water, and the resultant solution was allowed to stand overnight in a refrigerator. The resulting white fine precipitate was collected by filtration, washed with water, and dried in air. Anal. Calcd for **4**: C, 59.02; N, 11.47; H, 3.30. Found: C, 58.90; N, 11.17; H, 3.40. The yield of product was about 34%.

Results and Discussion

Although the monomeric Ru−bpy complexes are relatively stable, several studies have been published on the ligand substitution reactions of Ru(bpy)$(CO)_2Cl_2$ and its derivatives. The carbonyl ligands can be replaced by chlorine, nitrosyl, nitrido, and water ligands.[23] Ru(bpy)$(CO)_2Cl_2$ can also be either chlorinated or dechlorinated, the reactions being dependent on the reaction conditions. Electrochemical dechlorination has been suggested to yield the polymeric Ru−bpy complex, whereas in acidic solutions with a suitable nitrosyl source the products are either nitrosyl or nitrido complexes.[23] The chlorine ligands can also be substituted by other halogen or pseudohalogen ligands.[16,24] In the present study, we have investigated the reactivity of Ru(bpy)$(CO)_2Cl_2$ and its methyl-substituted derivatives in oxidizing acidic solutions. The reactions are summarized in Scheme 1.

Reactions of Ru(4,4′-dmbpy)$(CO)_2Cl_2$ and Ru(6,6′-dmbpy)$(CO)_2Cl_2$ in HCl/HNO_3 Solutions. On the basis of earlier studies, we investigated the formation of ruthenium nitrosyl complexes from dimethyl-substituted derivatives of Ru(bpy)$(CO)_2Cl_2$. 4,4′-Dimethyl substitution of the polypyridine ligand does not interfere with the formation of the nitrosyl complex. The dark red crystals formed from Ru(4,4′-dmbpy)$(CO)_2Cl_2$ after heating at 240 °C in HCl/HNO_3 solution could be identified as Ru(dcbpy)Cl_3(NO) (**1**) (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) by X-ray diffraction analysis. The IR spectrum of **1** showed two peaks at 1731 (vs) and 1708 (s) cm^{-1} (in KBr), which indicated the formation of carboxy groups in the complex. As compared with those of the corresponding 2,2′-bipyridine nitrosyl complex Ru(bpy)Cl_3(NO), the ν(NO) stretching bands were shifted to higher energy (1912 and 1895 cm^{-1} for **1** vs 1891 and 1878 cm^{-1} for Ru(bpy)Cl_3(NO)[23]), due to the attachment of the electron-withdrawing carboxy groups to the bipyridine rings.

Scheme 1. Reactions of Ru(bpy)$(CO)_2Cl_2$, Ru(4,4′-dmbpy)$(CO)_2Cl_2$, and Ru(6,6′-dmbpy)$(CO)_2Cl_2$ in Oxidizing Acidic Solutions

H_2O/HNO_3 Solutions

$$[\mathrm{Ru(bpy)(CO)_2Cl_2}] \xrightarrow{200\ ^\circ\mathrm{C}} [\mathrm{Ru(bpy)Cl_2(NO)(H_2O)](NO_3)]\cdot H_2O}$$

$$[\mathrm{Ru(4,4'\text{-}dmbpy)(CO)_2Cl_2}] \xrightarrow{200\ ^\circ\mathrm{C}} [\mathrm{Ru(4,4'\text{-}dmbpy)Cl_2(NO)(H_2O)](NO_3)}$$

HCl/HNO_3 Solutions

$$[\mathrm{Ru(4,4'\text{-}dmbpy)(CO)_2Cl_2}] \xrightarrow{240\ ^\circ\mathrm{C}} [\mathrm{Ru(4,4'\text{-}dcbpy)Cl_3(NO)}]$$

$$[\mathrm{Ru(6,6'\text{-}dmbpy)(CO)_2Cl_2}] \xrightarrow{240\ ^\circ\mathrm{C}} \mathrm{(H_3O)_2[RuCl_5(NO)]} + \text{6,6}'\text{-dicarboxy-2,2}'\text{-bipyridine hydrochloride}$$

To the best of our knowledge, ruthenium(II) complexes containing 4,4′-dicarboxy-2,2′-bipyridine ligands have not been characterized by single-crystal X-ray diffraction measurements, although such complexes have been synthesized, for instance, for solar cell applications.[7−10] As a free ligand, dcbpy is practically insoluble in common organic solvents, alcohols, and water, which makes it advantageous to use a more soluble dimethyl derivative of 2,2′-bipyridine as the starting material. The dmbpy ligand may be oxidized by strong oxidizing agents, such as $KMnO_4$ or $K_2Cr_2O_7$,[25] which, unfortunately, tend to decompose Ru−bpy−carbonyl complexes. In this case, simultaneous oxidation of the dmbpy ligand and the formation of the nitrosyl complex are best achieved by using HCl/HNO_3 solution as a solvent.

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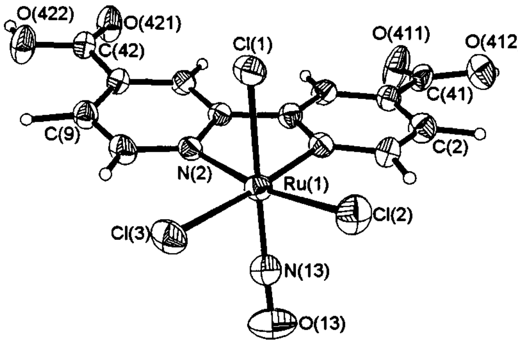

Figure 1. Structure of Ru(dcbpy)Cl_3(NO) (**1**).

Table 2. Selected Bond Lengths (Å) for Ru(dcbpy)$(Cl)_3$(NO) (**1**), [Ru(bpy)Cl_2(NO)(H_2O)](NO_3)·H_2O (**2**), and [Ru(4,4′-dmbpy)Cl_2(NO)(H_2O)](NO_3) (**3**)

	1	2	3
Ru(1)−Cl(1)[a]	2.364(2)	2.044(3)	2.045(6)
Ru(1)−Cl(2)	2.360(2)	2.341(1)	2.354(3)
Ru(1)−Cl(3)	2.392(2)	2.365(1)	2.363(3)
Ru(1)−N(1)	2.071(4)	2.078(3)	2.062(6)
Ru(1)−N(2)	2.076(4)	2.064(2)	2.071(6)
Ru(1)−N(13)	1.750(5)	1.729(3)	1.712(9)
N(13)−O(13)	1.123(5)	1.135(4)	1.134(9)
C(3)−C(41)	1.501(7)		1.480(12)
C(8)−C(42)	1.503(7)		1.496(12)
C(41)−O(411)	1.191(6)		
C(41)−O(412)	1.313(6)		
C(42)−O(421)	1.193(6)		
C(42)−O(422)	1.323(6)		

[a] Cl(1) = O(1) for **2** and **3**.

Table 3. Selected Bond Angles (deg) for Ru(dcbpy)$(Cl)_3$(NO) (**1**), [Ru(bpy)Cl_2(NO)(H_2O)](NO_3)·H_2O (**2**), and [Ru(4,4′-dmbpy)Cl_2(NO)(H_2O)](NO_3) (**3**)

	1	2	3
Cl(1)−Ru(1)−N(13)[a]	178.5(2)	178.2(1)	176.6(3)
Cl(1)−Ru(1)−Cl(2)[a]	88.2(1)	86.0(1)	88.6(2)
Cl(1)−Ru(1)−Cl(3)[a]	91.6(1)	88.2(1)	86.7(2)
Cl(1)−Ru(1)−N(1)[a]	86.9(1)	86.2(1)	86.3(3)
Cl(1)−Ru(1)−N(2)[a]	83.2(1)	84.7(1)	83.9(2)
N(1)−Ru(1)−N(2)	78.9(2)	79.2(1)	79.3(3)
Cl(2)−Ru(1)−Cl(3)	90.3(1)	88.3(0)	89.5(1)
Ru(1)−N(13)−O(13)	173.5(4)	176.0(3)	172.3(8)
N(1)−Ru(1)−Cl(3)	175.0(1)	173.1(1)	171.4(2)
N(2)−Ru(1)−Cl(2)	169.3(1)	169.5(1)	171.0(2)
C(2)−C(3)−C(41)	120.4(5)		
C(7)−C(8)−C(42)	117.9(4)		
O(421)−C(42)−O(422)	125.2(5)		
O(411)−C(41)−O(412)	123.5(5)		

[a] Cl(1) = O(1) for **2** and **3**.

The structure for **1** is given in Figure 1. The linear nitrosyl ligand lies *trans* to the axial chlorine with Ru−N(13) and N(13)−O(13) bond lengths of 1.750(5) and 1.123(5) Å, respectively. These values appear to be normal for other nitrosyl complexes having nitrosyl groups *trans* to chlorine ligands.[23] The arrangement of the dicarboxybipyridine ligand in **1** is nearly planar, the angle between the py planes being 7.2° with equal Ru−N bond lengths of 2.071(4) and 2.076(4) Å. The selected bond lengths and angles for complexes **1**−**3** are given in Tables 2 and 3.

The formation of Ru−nitrosyl complex was greatly altered when 6,6′-dimethyl-substituted bipyridine (6,6′-dmbpy) was used instead of 4,4′-dmbpy. Ru(6,6′-dmbpy)$(CO)_2Cl_2$ formed a dark red solution after heating at 240 °C in the HCl/HNO_3 mixture. Evaporation of the solvent mixture yielded both red and colorless crystalline compounds which could be identified as $(H_3O)_2$[Ru(NO)Cl_5] and 6,6′-dicarboxy-2,2′-bipyridine hydrochloride (**4**·HCl) by single-crystal X-ray crystallography. According to earlier X-ray crystallographic studies, ruthenium is able to coordinate sterically hindering 6,6′-dmbpy, even though the bipyridine ring system is considerably bent in Ru−6,6′-dmbpy complexes.[16] The Ru−2,2′-bipyridine bonds are reasonably stable; e.g., formation of the Ru−bpy nitrido complex[23] required heating of Ru(bpy)$(CO)_2Cl_2$ at 240 °C in the HCl/HNO_3 mixture for 12 h, under which conditions no severe fragmentation of the parent complex was observed. However, when the methyl groups in 6,6′-dmbpy were converted to carboxy groups, coordination to Ru was no longer possible owing to the enhanced steric hindrance, which resulted in the breaking of the Ru−N bonds. During the evaporation of the acidic solvent, the 6,6′-dicarboxy-2,2′-bipyridine fragment trapped HCl, which is a common feature for pyridine-type compounds. The electronegative nitrogens in bipyridine are able to donate the unshared electron pairs to hydrogen, which may lead to the formation of bipyridium chloride in HCl solutions. The structure for compound **4**·HCl is given in Figure 4.

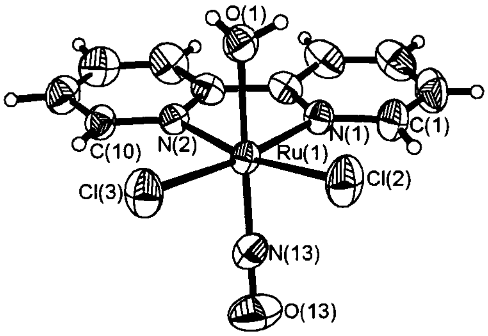

Figure 2. Structure of [Ru(bpy)Cl_2(NO)(H_2O)]$^+$ (**2**).

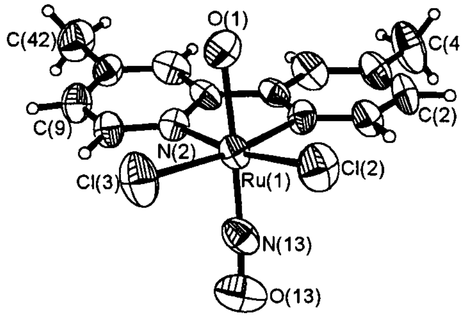

Figure 3. Structure of [Ru(dmbpy)Cl_2(NO)(H_2O)]$^+$ (**3**).

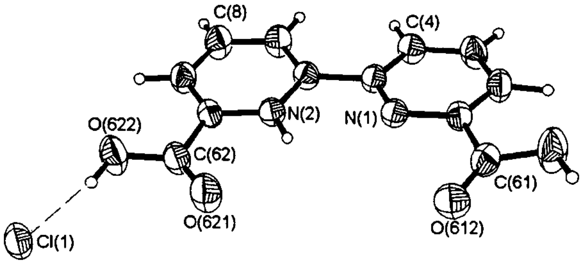

Figure 4. The structure of 6,6′-dicarboxy-2,2′-bipyridine hydrochloride (**4**·HCl). Cl(1)−O(622) = 2.066 Å.

The crystal structure of the [Ru(NO)Cl_5]$^{2-}$ anion closely resembles the structure reported earlier for the corresponding potassium salt,[26] with no significant structural effects due to different cations. Therefore the structural data are provided only as Supporting Information, as well as the complete structural data for compound **4**·HCl.

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On the basis of these studies, the reaction conditions described above were tested for synthesizing dicarboxy-substituted 2,2′-bipyridine from 6,6′-dmbpy (see Experimental Section). A simple and fast two-stage procedure was developed, the first stage including the oxidation of the methyl groups and the second the precipitation of the final product. (The same procedure can be applied for synthesizing other carboxy-substituted polypyridines as well.) The trapping of hydrochloride was not observed when the ligand was precipitated from the HCl/HNO_3 solution with cold water, differing from the procedure where the solvent was slowly evaporated. Without further purification, the product turned out to be sufficiently pure for synthetic applications. Using the permanganate- or dichromate-based oxidations, the raw product usually contains partially oxidized products which may be removed by refluxing in nitric acid (50%) for several hours.[25]

Reactions of $Ru(bpy)(CO)_2Cl_2$ and $Ru(4,4'\text{-dmbpy})(CO)_2Cl_2$ in H_2O/HNO_3 Solutions. Ruthenium(II) carbonyl bipyridine complexes exchange carbonyl ligands in the HCl/HNO_3 mixture to yield chlorinated nitrosyl complexes. We tested the reactions of $Ru(bpy)(CO)_2Cl_2$ and $Ru(4,4'\text{-dmbpy})(CO)_2Cl_2$ in H_2O/HNO_3 solutions to determine the effect of the reduced acidity and the lack of the chlorine ligands on the formation of ruthenium nitrosyl complexes. In both cases, the carbonyl ligands were lost, followed by the coordination of the nitrosyl groups to the parent complexes. In order to complete the full octahedral coordination symmetry, both complexes coordinated a water molecule. The products could be identified as $[Ru(bpy)Cl_2(NO)(H_2O)](NO_3)\cdot H_2O$ (**2**) and $[Ru(4,4'\text{-dmbpy})Cl_2(NO)(H_2O)](NO_3)$ (**3**) by single-crystal X-ray crystallography.

The methyl groups in the methyl-substituted complex remained intact due to the diminished oxidizing power of the solvent mixture. The attack of HCl/HNO_3 solutions containing free chlorine and ClNO on various compounds is more effective than that of HNO_3 mainly because of the complexing function of the chloride ion.

Contrary to expectations, the ν(NO) bands in the IR spectrum of **3** were shifted to higher energy in comparison to those of **2**; $\nu(NO) = 1891$ and 1878 cm^{-1} for **2** and 1902 and 1890 cm^{-1} for **3**, in KBr. The carboxy substituents discussed above seem to have effects on the nitrosyl stretching bands similar to those of the electron-donating methyl substituents in the bpy rings in this case. It may be noted that although N−O stretching bands in IR spectra are useful in terms of preliminary qualitative analysis, these frequencies are not necessarily sensitive to electronic alterations in the metal center of nitrosyl complexes or to changes in N−O bond order or bond distance.[27,28] Furthermore, it has been noted that distortions in Ru−bpy bonds may affect the π-acid strength of the polypyridine ligands.[14] In this case, the arrangement of the polypyridine ligand is more planar in complex **2** than in the methyl-substituted analogue **3,** whereas the N−O bond lengths are almost identical (*vide infra*).

Both complexes **2** and **3** exhibit octahedral coordination geometry, with a water molecule coordinated *trans* to the linear nitrosyl ligand, the Ru−N−O bond angles being 176.0(3) and 172.3(8)° for **2** and **3**, respectively. The Ru−water bond distances of 2.044(3) and 2.045(6) Å for **2** and **3** are relatively short as compared with those of other water-coordinated Ru complexes ranging from 2.10 to 2.25 Å,[23] which may be explained by the poor σ-bonding ability of the opposing nitrosyl ligand. The N−O bond distances in both complexes are identical (1.135(4) and 1.134(9) Å for **2** and **3**) but somewhat longer than that in complex **1**, with chlorine lying trans to the nitrosyl ligand. The coordination of the polypyridine ligands in these complexes is rather typical for those already mentioned. In $[Ru(bpy)Cl_2(NO)(H_2O)](NO_3)H_2O$, the arrangement of the polypyridine ligand is nearly planar whereas, in $[Ru(4,4'\text{-dmbpy})Cl_2(NO)(H_2O)](NO_3)$, the deviations from planarity are greater, most probably owing to the bulky methyl substituents in the dmbpy rings. The angles between the pyridine ring halves are about 1.5° for **2** and 7.4° for **3**.

Conclusions. The carbonyl ligands in $Ru(bpy)(CO)_2Cl_2$ and its methyl-substituted derivatives can be replaced by NO and Cl ligands in HCl/HNO_3 solution using elevated temperature (240 °C). The ligand-substituting reactions lead to stable nitrosyl compounds via rearrangement of the coordination sphere of the metal center. Under these conditions, the ligand exchange reactions are accompanied by simultaneous oxidation of the methyl-substituted polypyridine ligands. $Ru(4,4'\text{-dmbpy})(CO)_2Cl_2$ forms the dicarboxy-substituted bipyridine nitrosyl complex $Ru(dcbpy)Cl_3(NO)$, whereas 6,6′-dimethyl substitution of the 2,2′-bipyridine ligand leads to the splitting of the parent complex $Ru(6,6'\text{-dmbpy})(CO)_2Cl_2$ to the fragments $(H_3O)_2[Ru(NO)Cl_5]$ and 6,6′-dicarboxy-2,2′-bipyridine hydrochloride. The attachment of the nitrosyl ligand to the parent complex is crucial to the formation of the ligand-substituted compounds; without the added nitrosyl source, the parent complexes are not further chlorinated using the same reaction conditions. On the other hand, if nitrosyl ligands are available without a suitable chlorine source (H_2O/HNO_3 solutions), the metal center is able to coordinate the water molecule to gain a full octahedral coordination sphere. In this case, the oxidizing power of the solvent mixture is so reduced that the methyl groups in the 2,2′-bipyridine rings remain intact.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**, **2**, **3**, **4**$\cdot$HCl, and $(H_3O)_2[RuCl_5(NO)]$ are available on the Internet only. Access information is given on any current masthead page.

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