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Reactions of Ruthenium Bipyridine Catalyst Precursors: Synthetic, Structural, and Theoretical Studies on Ruthenium Mono(bipyridine) Carbonyls in Ethylene Glycol Solutions

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Carbonyl-containing ruthenium mono(bipyridines) are effective catalysts or catalyst precursors in processes such as the water-gas shift reaction. Ethylene glycol solutions provide versatile solvent systems for synthesizing the mono(bipyridines) from $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine. These starting compounds were used here in the preparation of three primary products, $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$, $Ru(bpy)(CO)_2ClH$, and $[Ru(bpy)(CO)_2Cl]_2$, which were formed consecutively and isolated by adjusting the reaction conditions. Reactions were studied by analyzing the solid products and monitoring the evolution of gases in each reaction step. Computational nonlocal density functional methods were applied to estimate the total reaction energies and to study isomerism of the compounds. Ethylene glycol solvent plays an active role in the synthesis reactions. It provides a reactive alkoxy group, $^-OCH_2CH_2OH$, which is able to act as a nucleophile attacking the carbon of a Ru−CO group. The first product, $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$, is formed under mild conditions at room temperature. The alkoxy carbonyl complex reacts further to $Ru(bpy)(CO)_2ClH$ and CO_2 when heated. Formation of the hydride complex requires the presence of water. $Ru(bpy)(CO)_2ClH$ can be further converted to dimeric $[Ru(bpy)(CO)_2Cl]_2$. $Ru(bpy)(CO)_2Cl_2$ is a side product which is also obtained from $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine. Crystal data: $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)\cdot{}^1/_4(HOCH_2CH_2OH)$ (**1**), space group $C2/c$, cell constants $a = 27.889(3)$ Å, $b = 10.270(2)$ Å, $c = 26.563(2)$ Å, $\beta = 112.01(3)°$, $V = 7053.7(17)$ Å^3, $Z = 16$; $Ru(bpy)(CO)_2ClH$ (**2**), $P\bar{1}$, $a = 6.3871(10)$ Å, $b = 8.132(2)$ Å, $c = 12.693(3)$ Å, $\alpha = 89.20(3)°$, $\beta = 81.37(3)°$, $\gamma = 81.20(3)°$, $V = 644.2(2)$ Å^3, $Z = 2$; $[Ru(bpy)(CO)_3Cl][Cl]\cdot(H_5O_2)(Cl)$ (**3**), $Pbcn$, $a = 20.856(4)$ Å, $b = 13.523(3)$ Å, $c = 13.203(3)$ Å, $V = 3723.7(14)$ Å^3, $Z = 8$.

Introduction

Ruthenium bipyridine compounds have been widely studied because of their versatile catalytic and photo- and electrochemical properties. Research has mainly been focused on ruthenium tris- and bis(bipyridine) compounds. Ruthenium mono(bipyridines) have been much less studied, despite proven effectiveness in catalysis. Carbonyl-containing ruthenium mono(bipyridines) provide excellent catalysts or catalyst precursors for processes such as the water-gas shift reaction (WGSR) and reduction of CO_2.[1−5] For example, in WGSR the mono(bipyridine) based catalysts are 5−20 times as active as the corresponding ruthenium bis(bipyridines).[1,6] Although most of the ruthenium mono(bipyridine) compounds are simple octahedral monomers or dimers, the detailed structures play an important role in their catalytic activity, or more generally in their chemical reactivity.

Ruthenium mono(bipyridine) carbonyls are typically prepared from ruthenium chloride in alcohol solutions, with CO or HCOOH supplying the carbonyl source,[7−11] or directly from a carbonyl-containing reagent such as $[Ru(CO)_3Cl_2]_2$.[12] In both methods there have been difficulties in explaining the detailed reaction route and selectively synthesizing target isomers. The method employing $RuCl_3$ and CO or HCOOH has mainly been used to prepare $Ru(bpy)(CO)_2Cl_2$. It has recently been proposed that, in this method, the isomer selectivity can be controlled by modifying the properties of the solvent, in this case pH.[13] Carbonyl-containing $[Ru(CO)_3Cl_2]_2$ has been used in the preparation of several ruthenium mono(bipyridine) carbonyls, including $Ru(bpy)(CO)_2Cl(C(O)OCH_3)$, $Ru(bpy)(CO)_2ClH$, $[Ru(bpy)(CO)_2Cl]_2$, and $Ru(bpy)(CO)_2Cl_2$.[12] Again the properties of the solvent play an important role in the reactions. In nonalcoholic solutions such as THF, reaction of $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine produces a mixture of *cis*(CO), *cis*(Cl) and *cis*(CO), *trans*(Cl) isomers of $Ru(bpy)(CO)_2Cl_2$ as the main product, while reaction in methanol leads to $Ru(bpy)(CO)_2Cl(C(O)OCH_3)$ via nucleophilic attack of a methoxy group. Diolic ethylene glycol has proved to be an especially useful solvent.

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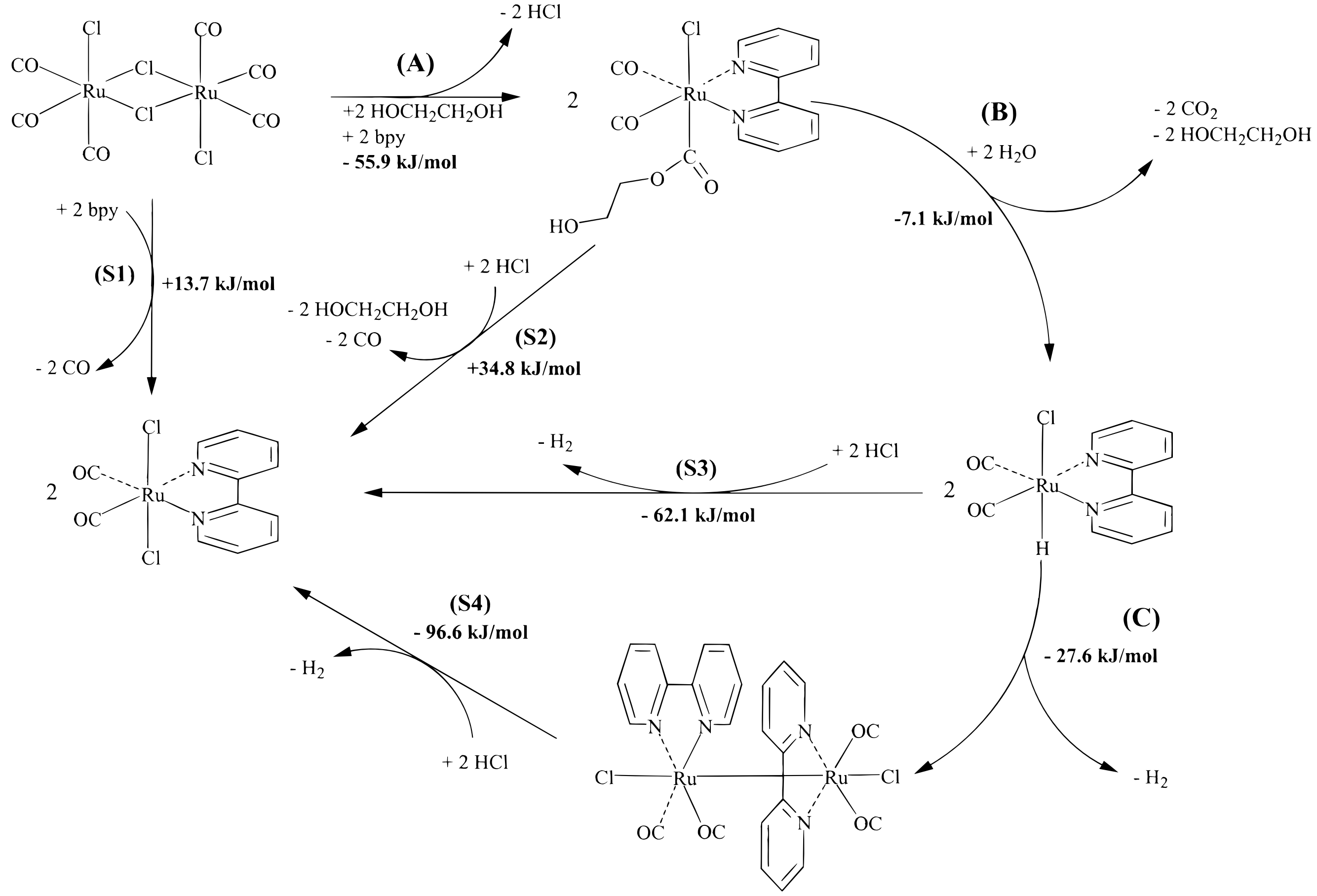
Scheme 1



Proper control of the reaction time and temperature has allowed both monomeric Ru(bpy)(CO)$_2$ClH and dimeric [Ru(bpy)(CO)$_2$Cl]$_2$ to be synthesized and isolated.[12] Also Ru(bpy)(CO)$_2$Cl$_2$ has been obtained in ethylene glycol reaction, though in this case it is more like a side product.

We have studied the reactions and possible reaction routes of [Ru(CO)$_3$Cl$_2$]$_2$ and 2,2′-bipyridine in ethylene glycol solutions. The complete reaction route consists of consecutive steps, which proceed via monomeric intermediates to dimeric [Ru(bpy)(CO)$_2$Cl]$_2$ principal product or to monomeric side product Ru(bpy)(CO)$_2$Cl$_2$. Reactions were studied experimentally by isolating and characterizing the intermediates and monitoring the evolution of gases during each step. The reactions were modeled by applying a computational, nonlocal density functional method. The main goal of the theoretical studies was to estimate thermodynamic factors of the reactions by investigating the total reaction energies. In the case of Ru(bpy)(CO)$_2$Cl$_2$ and [Ru(bpy)(CO)$_2$Cl]$_2$, the computational approach was also used to study the isomerism of the complex.

Experimental Section

Syntheses involving ethylene glycol were carried out in a closed 100-mL glass reaction vessel under a nitrogen atmosphere. After introduction of the reagents and solvent, the pressure of the vessel was reduced to slightly under normal pressure. [Ru(bpy)(CO)$_3$Cl]$^+$ was synthesized in HCl under normal atmosphere in air. Spectroscopic analysis of the solid reaction products was carried out with a Nicolet Magna 750 FTIR spectrometer and Bruker AMX-400 NMR spectrometer. Gaseous reaction products H$_2$, CO$_2$, and CO were analyzed with a Carlo Erba 4200 GC using a TC detector. Results were calculated as moles of gas per mole of ruthenium in the solid product. The expected amount of gases refers to the reactions in Scheme 1. After the solid products had been isolated, the reaction solutions were analyzed by an HP 5890 Series II gas chromatograph with a 5971 Series mass selective detector. Chlorides were detected by adding Ag(NO$_3$) to the reaction solution, which precipitated ammonia-soluble AgCl. The presence of chlorides was confirmed by qualitative GC/MS analysis.

Synthesis of Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH). [Ru(CO)$_3$Cl$_2$]$_2$ (500 mg) (Alfa) and 625 mg of 2,2′-bipyridine (Aldrich, 99%) were dissolved separately in 5 mL of deoxygenated ethylene glycol (Fluka Chemika, 99.5%). Solutions were gently heated until reagents were completely dissolved. Solutions were combined and stirred for 1−2 h at room temperature. Pale yellow, nearly white Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH) started to precipitate almost immediately after combining of the solutions. Gaseous products were analyzed by GC before filtering of the product. No significant formation of H$_2$, CO$_2$, or CO was observed. After the reaction solution was filtered, it was analyzed by GC/MS. The solid product was washed with 2-propanol or with 1-octanol and hexane and dried under vacuum. The primary yield of Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH) was 435 mg (51%). Anal. Calcd: C, 41.15; H, 2.99; N, 6.40. Found: C, 41.24; H, 3.22; N, 6.20. IR (in CH$_2$Cl$_2$): ν(CO) 2058 (s), 1995 (s) cm^{-1}; ν(CO) in alkoxy carbonyl group 1636 (w, br). $\{^1H\}^{13}C$ NMR aromatic carbons 155.8, 153.5, 139.9, 127.6, 123.7 ppm; CO 198.3, 194.6 ppm; CH$_2$ carbons 66.0, 64.4 ppm.

Gas analysis expected: CO$_2$, 0 mol/mol of Ru; H$_2$, 0 mol/mol of Ru; CO, 0 mol/mol of Ru. Found: CO$_2$, <0.14 mol/mol of Ru; H$_2$, 0 mol/mol of Ru; CO, <0.015 mol/mol of Ru.

Synthesis of Ru(bpy)(CO)$_2$ClH. [Ru(CO)$_3$Cl$_2$]$_2$ (500 mg) and 625 mg of 2,2′-bipyridine were separately dissolved in 3.5 mL of deoxygenated ethylene glycol/water (5−10 drops, or 115−230 mg, of water per 7 mL of ethylene glycol). Solutions were gently heated until reagents were completely dissolved. Solutions were combined and stirred at room temperature until precipitation of Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH) was complete (1−2 h). The reaction vessel was evacuated and filled with nitrogen to remove possible gaseous products formed during the precipitation of Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH). The nitrogen pressure was reduced to slightly under normal, and the reaction solution was heated at 65 °C for 30 min. During heating, the originally red solution darkened to almost black and the orange brown product started to precipitate. At this stage, gaseous products were analyzed by GC, and the solution was filtered and transferred to another glass vessel. Filtering was required to remove possible side products, such as $[Ru(bpy)(CO)_2Cl]_2$. Both filtering and transfer of the solution were done under a nitrogen atmosphere. The dark filtrate solution was allowed to stand under a nitrogen atmosphere at room temperature for 1−3 days. During this period, orange brown $Ru(bpy)(CO)_2ClH$ precipitated. Again gaseous products were analyzed and the solid product was separated by filtering, washed with 2-propanol, and dried under vacuum. Analysis of the gaseous products showed the main product to be CO_2. The synthesis was repeated several times, and only small amounts of CO and H_2 were occasionally observed. The primary yield of $Ru(bpy)(CO)_2ClH$ was 524 mg (77%). Anal. Calcd: C, 41.21; H, 2.59; N, 8.01. Found: C, 41.40; H, 2.52; N, 8.03. IR and NMR spectra were in agreement with the previous results.[12] Gas analysis expected: CO_2, 1 mol/mol of Ru; H_2, 0 mol/mol of Ru; CO, 0 mol/mol of Ru. Found: CO_2, 1.1−1.35 mol/mol of Ru; H_2, <0.04 mol/mol of Ru; CO, <0.23 mol/mol of Ru.

Synthesis of $[Ru(bpy)(CO)_2Cl]_2$. $Ru(bpy)(CO)_2ClH$ (350 mg) was dissolved in 3.5 mL of deoxygenated ethylene glycol. The solution was heated overnight under nitrogen at 80−90 °C. Gaseous products were analyzed by GC. The main gaseous product was H_2. The synthesis was repeated several times, and only small amounts of CO_2 or CO were occasionally observed. An orange or orange red precipitate of $[Ru(bpy)(CO)_2Cl]_2$ was filtered out under air, washed with 2-propanol, and dried under vacuum. The yield of $[Ru(bpy)(CO)_2Cl]_2$ was 259 mg (74%). Anal. Calcd: C, 41.33; H, 2.31; N, 8.03. Found: C, 41.27; H, 2.43; N, 7.97. IR (in KBr): ν(CO) 2020, 2004, 1970, 1937 cm^{-1}.

Gas analysis expected: CO_2, 0 mol/mol of Ru; H_2, 0.5 mol/mol of Ru; CO, 0 mol/mol of Ru. Found: CO_2, 0 mol/mol of Ru; H_2, 0.3−0.34 mol/mol of Ru; CO, <0.02 mol/mol of Ru.

Formation of $[Ru(bpy)(CO)_3Cl]^+$ in HCl. $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ (8.6 mg) was dissolved in two drops (ca. 46 mg) of concentrated (37%) HCl (Merck) under air. After a few minutes, nearly colorless $[Ru(bpy)(CO)_3Cl]^+[Cl]^-\cdot(H_5O_2)^+Cl^-$ started to crystallize. The crystals contained two cations, $[Ru(bpy)(CO)_3Cl]^+$ and $(H_5O_2)^+$, with a Cl^- counteranion. The solution was allowed to evaporate to dryness at room temperature. The yield of crystalline $[Ru(bpy)(CO)_3Cl]^+[Cl]^-\cdot(H_5O_2)^+Cl^-$ was 8.9 mg (93%). Anal. Calcd: C, 32.22; H, 2.70; N, 5.78. Found: C, 32.30; H, 2.68; N, 5.68. IR (in KBr): ν(CO) 2140, 2086, 2068 cm^{-1}.

^1H NMR (in CD_3OD): aromatic hydrogens 9.1 (d), 8.8 (d), 8.4 (t), 7.9 (t) ppm. $\{^1H\}^{13}C$ NMR: aromatic carbons 157.1, 156.0, 143.5, 130.0, 126.6; CO 188.0, 184.1 ppm.

Conversion of Monomeric $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$, $Ru(bpy)(CO)_2ClH$, and Dimeric $[Ru(bpy)(CO)_2Cl]_2$ to $Ru(bpy)(CO)_2Cl_2$. All of these reactions were carried out in a closed 100 mL reaction vessel under a nitrogen atmosphere. $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ (115 mg) was dissolved in ethylene glycol/HCl solution (1.5 mL of ethylene glycol, 5 drops or about 115 mg of 37% HCl). The solution was heated at 100 °C for 3 days. The initially pink solution turned yellow during reaction, and 22 mg of solid, pale yellow, $Ru(bpy)(CO)_2Cl_2$ was precipitated. A considerable amount of $Ru(bpy)(CO)_2Cl_2$ was dissolved in acidic ethylene glycol. The yield was improved by removal of the ethylene glycol by distillation. This secondary yield was 19.7 mg, giving a total yield of 42 mg (32%). The solid product was almost pure *cis*(CO), *trans*(Cl) isomer of $Ru(bpy)(CO)_2Cl_2$. The main gaseous product was CO. Only traces of H_2 and CO_2 were observed. The solid product was washed with 2-propanol and dried under vacuum. IR (in CH_2Cl_2): ν(CO) 2065 (s), 2004 (s) cm^{-1}. ^1H NMR (in $CDCl_3$): aromatic hydrogens 9.8 (d, weak, cis), 9.2 (d, strong, trans), 8.9 (d, weak, cis), 8.4−8.1 several overlapping peaks (bands from both isomers) 7.8 (t, weak, cis), 7.7 (t, strong, trans), 7.6 (t, weak, cis). $\{^1H\}^{13}C$ NMR (in $CDCl_3$): aromatic carbons 155.8, 154.0, 140.2, 128.1, 123.9 ppm; CO 196.6 ppm (only peaks from the trans isomer were clearly found, peaks from the cis isomer were very weak). Here c*is* refers to *cis*(CO), *cis*(Cl) isomer and trans to *cis*(CO), *trans*(Cl) isomer.

Gas analysis expected: CO_2, 0 mol/mol of Ru; H_2, 0 mol/mol of Ru; CO, 1 mol/mol of Ru. Found: CO_2, traces; H_2, traces; CO, 1.18 mol/mol of Ru.

$Ru(bpy)(CO)_2ClH$ (118 mg) was dissolved in ethylene glycol/HCl solution (1.5 mL of ethylene glycol, 5 drops, or 115 mg, of 37% HCl). The solution was heated at 100 °C for 2 days. The pale yellow solid of $Ru(bpy)(CO)_2Cl_2$ (total yield 95 mg, 94%) was filtered out under air, washed with 2-propanol, and dried under vacuum. The product was almost pure *cis*(CO), *cis*(Cl) isomer of $Ru(bpy)(CO)_2Cl_2$. The main gaseous product was H_2. Only traces of CO_2 or CO were observed. The solid product was washed with 2-propanol and dried under vacuum. IR (in CH_2Cl_2): ν(CO) 2068 (s), 2005 (s) cm^{-1}. ^1H NMR (in $CDCl_3$): aromatic hydrogens 9.8 (d, strong, cis), 9.2 (d, weak, trans), 8.9 (d, strong, cis), 8.4−8.1 several overlapping peaks (bands from both isomers), 7.8 (t, strong, cis), 7.7 (t, weak, trans), 7.6 (t, strong, cis). Gas analysis expected: CO_2, 0 mol/mol of Ru; H_2, 1 mol/mol of Ru; CO, 0 mol/mol of Ru. Found: CO_2, traces, H_2, 1.15 mol/mol of Ru; CO, <0.02 mol/mol of Ru.

$[Ru(bpy)(CO)_2Cl]_2$ (200 mg) and 2.5 mL of ethylene glycol/HCl solution (2.5 mL of ethylene glycol, 5 drops, or 115 mg, of 37% HCl) were introduced to a 100-mL glass vessel, and the solution was heated at 80 °C for 6 days. The pale yellow solid of $Ru(bpy)(CO)_2Cl_2$ (total yield 163 mg, 74%) was filtered out under air, washed with 2-propanol, and dried under vacuum. The product was a ca. 1:1 mixture of *cis*(CO), *trans*(Cl) and *cis*(CO), *cis*(Cl) isomers of $Ru(bpy)(CO)_2Cl_2$. The main gaseous product was H_2. The solid product was washed with 2-propanol and dried under vacuum. IR (in CH_2Cl_2): ν(CO) 2068 (s), 2003 (s) cm^{-1}. ^1H NMR (in $CDCl_3$) aromatic hydrogens 9.8 (d, cis), 9.2 (d, trans), 8.9 (d, cis), 8.4−8.1 several overlapping peaks (bands from both isomers), 7.8 (t, cis), 7.7 (t, trans), 7.6 (t, cis). $\{^1H\}^{13}C$ NMR: aromatic carbons 156.5, 154.0, 151.8, 140.5, 140.2, 139.8, 128.2, 127.8, 124.2, 123.4.

Gas analysis expected: CO_2, 0 mol/mol of Ru; H_2, 0.5 mol/mol of Ru; CO, 0 mol/mol of Ru. Found: CO_2, traces; H_2, 0.59 mol/mol of Ru; CO, <0.015 mol/mol of Ru.

X-ray Data Collection and Structure Solution for $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)\cdot{}^1/_4(HOCH_2CH_2OH)$ (1), $Ru(bpy)(CO)_2ClH$ (2), and $[Ru(bpy)(CO)_3Cl]^+[Cl]^-\cdot(H_5O_2)^+(Cl)^-$ (3). All data were collected at 20 °C on an Nonius KappaCCD diffractometer with a kcd program (Nonius) using a ϕ or a combined $\phi-\omega$ scan and Mo Kα radiation ($\lambda = 0.710\,73$ Å). Cell refinement and data reduction were done with Denzo and Scalepack programs.[14] The structures were solved by direct methods and successive difference Fourier synthesis using the Shelxs-97 program.[15] The structure refinement was carried out with the Shelxl-97 program.[16] Crystals of **1** and **2** were obtained directly from ethylene glycol solution. Compound **3** was crystallized from concentrated HCl. Although the crystal structure of compound **2** has been published earlier,[12] it was redetermined to locate the position of the hydride ligand. All non-hydrogen atoms in **2** and **3** were refined anisotropically. Crystals of compound **1** contained ethylene glycol solvent. C and O atoms of the solvent were refined only isotropically because of disorder. Atoms of ethylene glycol were disordered in two positions with equal population parameters. Because of the disorder, hydrogens of the solvent were omitted. All other hydrogens in **1** were placed in idealized positions (aromatic H, C−H = 0.93 Å, $U_{iso} = 1.2U_{iso}$ of the parent carbon; CH_2 hydrogens in alkoxy carbonyl group, C−H = 0.97 Å, $U_{iso} = 1.2U_{iso}$ of the parent carbon; OH hydrogens in alkoxy carbonyl group, O−H = 0.82 Å, $U_{iso} = 1.5U_{iso}$ of the parent oxygen). All hydrogens in **2** and **3** were refined isotropically. Crystallographic data are summarized in Table 1 and selected bond lengths and angles in Table 2.

Computational Methods. Computational methods are an important predictive tool in many applications, including the calculation of full

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Table 1. Crystallographic Data for $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)\cdot{}^1/_4(HOCH_2CH_2OH)$ (**1**), $[Ru(bpy)(CO)_2ClH]$ (**2**), and $[Ru(bpy)(CO)_3Cl][Cl]\cdot(H_5O_2)(Cl)$ (**3**)

	1	**2**	**3**
empirical formula	$C_{15.5}H_{14.5}ClN_2O_{5.5}Ru$	$C_{12}H_9ClN_2O_2Ru$	$C_{13}H_{13}Cl_3N_2O_5Ru$
fw	453.31	349.73	484.67
cryst syst	monoclinic	triclinic	orthorhombic
space group	*C*2/*c*	$P\bar{1}$	*Pbcn*
λ, Å	0.710 73	0.710 73	0.710 73
a, Å	27.889(3)	6.3871(10)	20.856(4)
b, Å	10.270(2)	8.132(2)	13.523(3)
c, Å	26.563(2)	12.693(3)	13.203(3)
α, deg		89.20(3)	
β, deg	112.01(3)	81.37(3)	
γ, deg		81.20(3)	
V, $Å^3$	7053.7(17)	644.2(2)	3723.7(14)
Z	16	2	8
D_{calc}, g/cm^3	1.707	1.803	1.729
μ, mm^{-1}	1.071	1.418	1.296
T, °C	20	20	20
R1	0.0275	0.0257	0.0203
wR2	0.0464	0.0556	0.0498
x	0.0059	0.0222	0.0308
y	0.0000	0.2687	0.0000

$|F_o| > 4\sigma(F_o)$, $R1 = \sum||F_o| - |F_c||/|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$.

catalysis cycles.[17,18] Quantum chemical methods have found a particular role in chemistry as a support to experimental work. There are, nevertheless, many limitations regarding transition metal complexes. The size of the calculations increases when heavy transition metal atoms are present in the molecules. Also the variety of electronic structures and bonding types in these complexes makes the theoretical methods more complicated. Although, in many cases, even low-level quantum chemical methods have performed well in optimization of the geometry of transition metal complexes,[19] careful testing is still needed for complicated systems with large ligands like bipyridines. An example of a theoretical study for a tris(2,2′-bipyridine)ruthenium complex has been reported by Buchs et al.[20]

All computational work in this paper was carried out by nonlocal hybrid density functionals B3PW91, as incorporated in the Gaussian 94 program package.[21] A standard double-ζ basis set 6-31G* was used for all other elements except ruthenium. For ruthenium, Huzinaga's extra basis (433321/4331/421)[22] was used. All calculations refer to the complexes in the gas phase. In the present experimental conditions they are either in solution or in the solid state. The effect of solvent was anticipated to be small on the geometries of the complexes, but will cause uncertainty to the energies of the reaction cycle. Simulation of the solvent by reaction field methods was not feasible in this study.

Results and Discussion

Alcoholic solvents, such as methanol, play an active role in the reaction between $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine. For example, a methoxy group acts as a nucleophile attacking the carbon of the CO ligand and giving rise to a methoxy carbonyl group.[12] Unlike methanol, which typically leads to the single product $Ru(bpy)(CO)_2Cl(C(O)OCH_3)$, diolic ethylene glycol is a more versatile solvent. We reported previously that reaction in ethylene glycol leads to two principal products: monomeric $Ru(bpy)(CO)_2ClH$ and dimeric $[Ru(bpy)(CO)_2Cl]_2$.[12] Formation of these products is proposed to be in succession and dependent on the reaction conditions. The monomer, which is the first to appear, is converted to the dimer when the reaction time is extended or the reaction temperature raised. In addition to the principal products, formation of the side product $Ru(bpy)(CO)_2Cl_2$ was also reported.[12] In the current work we studied the reaction of $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine in ethylene glycol and ethylene glycol/water solutions step by step. Reactions are summarized in Scheme 1.

Reactions of $[Ru(CO)_3Cl_2]_2$ and 2,2′-Bipyridine in Ethylene Glycol Solutions: Step A, Formation of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$. $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine react easily in ethylene glycol solution at room temperature to produce white (or pale yellow) $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ (Figure 1).

Step A in Scheme 1 requires breaking of the Ru−Cl−Ru bridges of $(Ru(CO)_3Cl_2)_2$, addition of 2,2′-bipyridine on a ruthenium center, and nucleophilic attack of a solvent molecule on a carbonyl group. Formation of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ as a primary product and liberation of chloride also suggests that a single Cl ligand is replaced by a bond to bipyridine nitrogen. Ethylene glycol is most probably behaving as an acid, deprotonating during step A. The alkoxy group, $-OCH_2CH_2OH$, then attacks the carbon of the carbonyl ligand forming the alkoxy carbonyl ligand. Bipyridine is a Lewis base which probably enhances the deprotonation of ethylene glycol. When bipyridine is coordinated to the ruthenium center, the proton forms HCl with the leaving chloride ligand. Experimentally no significant amounts of gaseous products were observed during step A. Only traces of CO_2 and H_2 were occasionally observed. Lack of CO shows that no decarbonylation occurred during the reaction, while traces of CO_2 and H_2 may indicate that, in some cases, a small portion of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ had already reacted further according to Scheme 1. The water content of ethylene glycol did not have a notable effect on the reaction as long as it remained low. The reaction of step A occurred readily both in dry, freshly distilled ethylene glycol and in ethylene glycol/water solution.

Step B, Formation of $Ru(bpy)(CO)_2ClH$. $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ was easily converted to $Ru(bpy)(CO)_2ClH$ (Figure 2) in the presence of water.

Conversion occurred when the reaction of $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine was continued, after precipitation of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$, by gentle heating at 65 °C. Reactivity of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ is probably the main reason this compound was not observed in earlier studies.[12] Unlike in step A, the presence of water strongly affected the hydride formation in step B. If the reaction was carried out in freshly distilled dry ethylene glycol, the $Ru(bpy)(CO)_2ClH$ complex was not obtained at all or the yield of the complex remained extremely low.

Gas phase analysis showed that, during hydride formation, only CO_2 gas was liberated in a considerable amount. Evolution of carbon dioxide suggests that the replacement of alkoxy carbonyl ligand with hydride proceeds via decomposition of $-C(O)OCH_2CH_2OH$. This type of reaction has been proposed for Ru−C(O)OH complexes during the water-gas shift reaction, where cleavage of CO_2 from Ru−C(O)OH leads to formation

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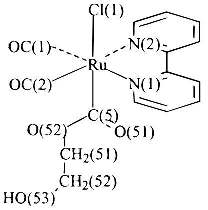
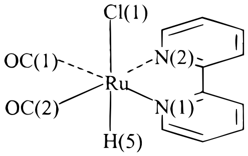
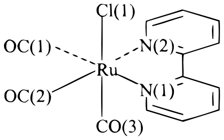
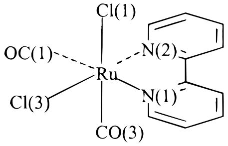
Table 2. Calculated and Experimental Geometry of Ru(bpy)$(CO)_2$Cl(CO(O)CH_2CH_2OH), Ru(bpy)$(CO)_2$ClH, [Ru(bpy)$(CO)_3$Cl]$^+$, and *cis*(CO),*cis*(Cl)-Ru(bpy)$(CO)_2Cl_2$

											
Bonds (Å)	Expt.1 (A)	Expt. 1(B)	DFT	Ref. 1	Expt. 2	DFT	Expt. 3	DFT	Ref. 1	Ref. 1	DFT
Ru-Cl(1)	2.5081(10)	2.5118(10)	2.5045	2.524(2)	2.5219(11)	2.5172	2.3872(7)	2.399	2.439 (3)	2.417 (3)	2.431
Ru-H(5)					1.67(3)	1.6262					
Ru-Cl(3)									2.411 (4)	2.396 (3)	2.42
Ru-C(5)	2.045(3)	2.045(3)	2.0584								
Ru-C(1)	1.875(4)	1.866(4)	1.8817	1.874(6)	1.859(4)	1.8651	1.937(2)	1.9356	1.899 (11)	1.874 (12)	1.8867
Ru-C(2)	1.870(4)	1.865(4)	1.8775	1.860(8)	1.854(4)	1.8651	1.9317(19)	1.9369			
Ru-C(3)							1.918(2)	1.9306	1.938 (10)	1.859 (12)	1.8821
Ru-N(1)	2.117(3)	2.101(3)	2.155	2.118(4)	2.117(3)	2.1579	2.1015(14)	2.1393	2.117 (8)	2.100 (8)	2.1497
Ru-N(2)	2.119(3)	2.109(2)	2.1555	2.120(5)	2.121(3)	2.1579	2.1062(14)	2.1388	2.090 (8)	2.072 (8)	2.1082
C(1)-O(1)	1.132(4)	1.146(4)	1.1499	1.142(8)	1.148(4)	1.1535	1.121(2)	1.1382	1.115 (14)	1.155 (15)	1.1471
C(2)-O(2)	1.138(3)	1.147(3)	1.1512	1.130(10)	1.140(4)	1.1535	1.122(2)	1.1381			
C(3)-O(3)							1.126(2)	1.141	1.012 (15)	1.137 (15)	1.1506
C(5)-O(51)	1.174(3)	1.202(4)	1.2158								
C(5)-O(52)	1.366(3)	1.362(4)	1.3624								
O(52)-C(51)	1.463(3)	1.461(3)	1.4349								
C(51)-C(52)	1.501(4)	1.475(5)	1.5094								
C(52)-O(53)	1.408(4)	1.424(4)	1.4141								
Angles (°)											
N(1)-Ru-N(2)	77.57(12)	77.26(10)	76.64	77.02(2)	76.96(10)	76.20	77.87(5)	77.36	77.6(3)	77.6(3)	77.24
Cl(1)-Ru-H(5)					174.0(11)	173.09					
Cl1(1)-Ru-C(5)	174.00(9)	172.47(11)	171.81								
Cl1(1)-Ru-C(3)							177.52(5)	177.04	178.8(3)	178.4(3)	178.77
N(1)-Ru-C(1)	176.04(14)	176.11(13)	173.61	172.5(2)	172.44(13)	172.85	170.67(7)	171.27	174.1(4)	175.5(4)	173.14
N(2)-Ru-C(2)	172.81(14)	171.68(12)	173.47	171.9(2)	172.17(13)	172.83	173.41(7)	170.89			
N(2)-Ru-Cl(3)									173.4(2)	171.3(3)	170.36
Ru-C(1)-O(1)	178.2(3)	176.9(4)	177.64	176.7(7)	177.2(3)	177.40	174.72(17)	177.70	174.5(10)	177.3(10)	178.52
Ru-C(2)-O(2)	179.0(3)	176.9(3)	177.96	176.7(7)	177.2(4)	177.38	176.17(17)	177.48			
Ru-C(3)-O(3)							175.07(16)	178.65	171.1(11)	177.7(11)	179.55
Ru-C(5)-O(51)	127.1(2)	126.2(3)	124.47								
Ru-C(5)-O(52)	112.5(2)	113.6(3)	114.66								
O(51)-C(5)-O(52)	120.4(3)	120.2(3)	120.87								

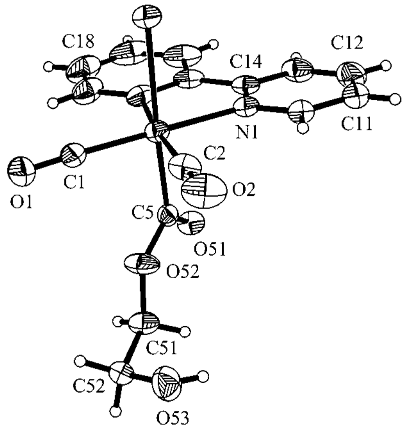


Figure 1. Crystal structure of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$.

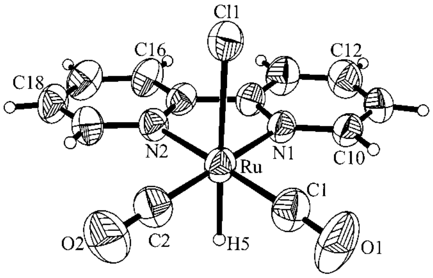


Figure 2. Crystal structure of $Ru(bpy)(CO)_2ClH$.

of the Ru−H group.[6,23,24] The identical procedure in the case of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ would lead to $Ru(bpy)(CO)_2Cl(CH_2CH_2OH)$, which has not been observed. More probably, the alkoxy carbonyl in $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ is decomposed to $HOCH_2CH_2OH$ and CO_2. The aqueous solvent thus provides the hydride source for Ru−H and the OH^- for recovering $-CH_2CH_2OH$ to ethylene glycol. Earlier we suggested that the hydride ligand in $Ru(bpy)(CO)_2ClH$ might originate solely from the ethylene glycol.[12] However, the observation that $Ru(bpy)(CO)_2ClH$ was not formed at all or was formed only with extremely low yield in dry ethylene glycol indicates that water is the main source of hydride ligand and has an essential role in the formation of the hydride complex.

Although addition of a small amount of water to the reaction solution improves the yield of hydride complex, an excess of water directs the reaction along a completely different route. Heating of ruthenium mono(bipyridine) carbonyls such as $Ru(bpy)(CO)_2ClH$, $Ru(bpy)(CO)_2Cl_2$, $Ru(bpy)(CO)_2Cl(C(O)OCH_3)$, and $[Ru(bpy)(CO)_2Cl]_2$ in water tends to yield an insoluble bluish black product. This reaction is strongly enhanced in dilute NaOH solution.[1,25] It has been proposed that the role of NaOH in this reaction is to act as a dechlorination agent. Besides ruthenium bipyridines, NaOH has been used for dechlorination in the synthesis of $[Ru(CO)_2Cl(OH)]_n$ and $[Ru(CO)_2(OH)_2]_n$ from $[Ru(CO)_3Cl_2]_2$.[26] This type of reaction might also occur in ethylene glycol/water solutions if the water content is too high.

Step C, Formation of Dimeric $[Ru(bpy)(CO)_2Cl]_2$. The third solid product obtained from the reaction between $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine was dimeric $[Ru(bpy)(CO)_2Cl]_2$. When $Ru(bpy)(CO)_2ClH$ was heated at 80−90 °C in ethylene glycol solution, it dissolved, and after few hours the orange or orange red $[Ru(bpy)(CO)_2Cl]_2$ started to precipitate. Formation of $[Ru(bpy)(CO)_2Cl]_2$ was accompanied by liberation of gaseous H_2. Although the detailed reaction mechanism is not known, such results indicate that, during the dimer formation, two $Ru(bpy)(CO)_2Cl$ units, formed from $Ru(bpy)(CO)_2ClH$, react to produce Ru−Ru bonded $[Ru(bpy)(CO)_2Cl]_2$, while the hydride hydrogens are liberated as gaseous H_2. Only traces of other gases, CO and CO_2, were observed during dimer formation. The appearance of CO_2 is probably due to residues of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ converting first to $Ru(bpy)(CO)_2ClH$. Traces of CO could be a sign of minor decarbonylation or an alternative reaction route.

When the synthesis of $[Ru(bpy)(CO)_2Cl]_2$ was carried out in dry ethylene glycol at 80 °C using $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ as a starting compound, no $Ru(bpy)(CO)_2ClH$ intermediate was observed. In this case the main gaseous product was CO, and only traces of H_2 and CO_2 were liberated. This indicates that at least in nonaqueous solution an alternative reaction route for dimer formation is possible. In this mechanism the decomposition of the glycoxy carbonyl group follows a different path from reactions B and C in Scheme 1.

Side Reactions involving $Ru(bpy)(CO)_2Cl_2$. All three primary products in Scheme 1 may contain $Ru(bpy)(CO)_2Cl_2$ as an impurity. In principle, $Ru(bpy)(CO)_2Cl_2$ may be formed from any other ruthenium mono(bipyridine) ($Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$, $Ru(bpy)(CO)_2ClH$, $[Ru(bpy)(CO)_2Cl]_2$) or directly from the reagents $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine. In the former case, reaction would require the presence of a suitable chlorine source such as HCl, which is liberated during the formation of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ (step A in Scheme 1). All the side reactions involving $Ru(bpy)(CO)_2Cl_2$ were enhanced by higher temperatures (typically ≥80−100 °C). It was thus possible to avoid these reactions by controlling the temperature or by removing the chlorine source. The direct formation of $Ru(bpy)(CO)_2Cl_2$ from $[Ru(CO)_3Cl_2]_2$ and 2,2′-bipyridine (S1 in Scheme 1) was usually not observed at all at low reaction temperatures.

Conversion of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ to $Ru(bpy)(CO)_2Cl_2$ (S2). In conversion of $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ to $Ru(bpy)(CO)_2Cl_2$ (S2), the key issue is how does the glycoxy carbonyl group react when it is replaced by chloride? Reactions of $Ru-C(O)OCH_2CH_2OH$ with hydrogen chloride were studied experimentally by dissolving $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ in ethylene glycol containing a small amount of HCl. When the reaction solution was heated at 100 °C, a light yellow isomer mixture (mainly *cis*(CO), *trans*(Cl) isomer) of $Ru(bpy)(CO)_2Cl_2$ was precipitated. Gas phase analysis showed that only CO was liberated during the reaction, indicating that in acidic conditions the glycoxy carbonyl group decomposes by a different route from reaction B. GC/MS analysis of the reaction solution revealed that also $HOCH_2CH_2OCH_2CH_2OH$ was formed during the reaction. However, since ether formation was observed even when pure ethylene glycol/HCl solution with no ruthenium complex was heated, it probably was just a product of a side reaction with no significant role in the reaction of the ruthenium complexes.

The reaction of glycoxy carbonyl with hydrogen chloride was studied further by adding a small amount of concentrated HCl directly to solid $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$ without ethylene glycol solvent. The ruthenium compound dissolved instantaneously, and after about 10 min at room temperature, a

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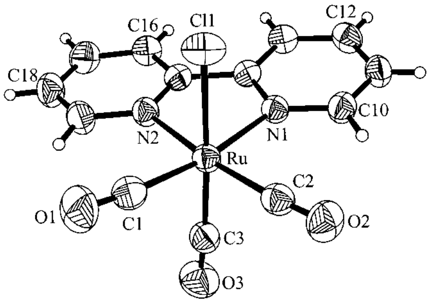

Figure 3. Crystal structure of $[Ru(bpy)(CO)_3Cl]^+$.

stable, colorless tricarbonyl species $[Ru(bpy)(CO)_3Cl]^+$ started to crystallize with a chloride counteranion (Figure 3).

Such results suggest that also the reaction S2 could proceed via the ionic tricarbonyl intermediate $[Ru(bpy)(CO)_3Cl]^+$. One of the carbonyls of $[Ru(bpy)(CO)_3Cl]^+$ is replaced by chloride, and $Ru(bpy)(CO)_2Cl_2$ and CO are produced in a final reaction step.

Conversion of $Ru(bpy)(CO)_2ClH$ to $Ru(bpy)(CO)_2Cl_2$ (S3). Similarly to $Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)$, also $Ru(bpy)(CO)_2ClH$ could be converted to $Ru(bpy)(CO)_2Cl_2$ with a suitable chlorine source. The conversion reaction was investigated by dissolving $Ru(bpy)(CO)_2ClH$ in ethylene glycol containing a small amount of HCl. When the solution was heated at 100 °C, almost pure *cis*(CO), *cis*(Cl) isomer of $Ru(bpy)(CO)_2Cl_2$ was precipitated. The simplest reaction route from $Ru(bpy)(CO)_2ClH$ to $Ru(bpy)(CO)_2Cl_2$ is independent of the organic solvent (S3 in Scheme 1). Gas phase analysis and GC/MS analysis of the reaction solution showed that only H_2 and the side product $HOCH_2CH_2OCH_2CH_2OH$ were formed in addition to ruthenium complex. Hydrogen formation is in agreement with the proposed reaction route S3. Since the reaction does not require the presence of ethylene glycol, it should also proceed easily in aqueous HCl solution. This was tested by dissolving $Ru(bpy)(CO)_2ClH$ in concentrated HCl. The ready occurrence of the reaction even at room temperature further supports reaction S3 as the principal reaction route.

Conversion of $[Ru(bpy)(CO)_2Cl]_2$ to $Ru(bpy)(CO)_2Cl_2$ (S4). When HCl was added to solid $[Ru(bpy)(CO)_2Cl]_2$, conversion occurred even at room temperature, although the reaction was very slow (it took several weeks to completion) due to stability of the dimer. At low temperature *cis*(CO),*trans*(Cl)-$Ru(bpy)(CO)_2Cl_2$ was favored as the main isomer. The reaction was repeated by heating $[Ru(bpy)(CO)_2Cl]_2$ in ethylene glycol/HCl solution at 80 °C for several days. In this case an approximately 1:1 isomer mixture of *cis*(CO),*trans*(Cl)- and *cis*(CO),*cis*(Cl)-$Ru(bpy)(CO)_2Cl_2$ was obtained. Gas phase analysis showed that H_2 was the only gas formed during the reaction. This suggests that the reaction follows a simple route which includes breakdown of the Ru−Ru bond, addition of chloride to the vacant coordination site, and formation of H_2 from HCl.

Ruthenium Mono(bipyridines) in the Water-Gas Shift Reaction. Reactions of alcohol solvent with carbonyl ligands are especially interesting from the catalytic point of view. The behavior of the alkoxy group (−OR) closely resembles the proposed reactions of −OH in the water-gas shift reaction catalyzed by ruthenium bis(bipyridines). The reaction route for ruthenium bis(bipyridine) catalyzed WGS reaction has been well documented, including the isolation and characterization of the key intermediates.[6,27−31] Although ruthenium mono(bipyridines) such as $Ru(bpy)(CO)_2ClH$ and $[Ru(bpy)(CO)_2Cl]_2$ are highly active catalyst precursors for WGSR,[1] the reaction mechanisms have not been studied in detail. In the case of ruthenium bis(bipyridines), the WGS reaction is initiated by nucleophilic attack of −OH on the carbonyl group, leading to Ru−C(O)-OH. During the next step Ru−C(O)OH is decomposed to Ru−H and CO_2. Corresponding steps can also be found in Scheme 1 (steps A and B) with −OR as a nucleophile. The final step in the WGS reaction is formation of hydrogen gas from Ru−H and carbonylation of the ruthenium compound to Ru−CO under carbon monoxide. In Scheme 1 hydrogen is liberated in the corresponding step C, but of course no carbonylation occurs owing to lack of CO.

Table 3. Average Deviations in Calculated and Experimental Structures of Ruthenium Complexes

bond	av (Å)	no. of bonds[a]
Ru−Cl	0.026	19
Ru−C	0.034	30
Ru−N	0.046	22
C−O	0.022	35
Ru−Ru	0.042	2
angle	**av (deg)**	**no. of angles[a]**
N−Ru−N	0.89	9
Ru−C−O	1.67	27

[a] Number of bonds/angles compared.

Given the similarities between ethylene glycol reactions and WGS reactions, one could expect the WGS reaction route proposed for ruthenium bis(bipyridines) also to be valid for ruthenium mono(bipyridines). However, ruthenium mono(bipyridines) such as $Ru(bpy)(CO)_2ClH$ are not useful in WGSR without efficient activation. The poor activity may be explained by a look at the ethylene glycol reaction. Monomeric $Ru(bpy)(CO)_2ClH$ has a strong tendency to dimerize when heated, and formation of the relatively stable $[Ru(bpy)(CO)_2Cl]_2$ may hinder formation of the catalytically important Ru−CO compound from Ru−H.

Computational Results. A computational density functional approach was found to be successful in predicting geometries of the ruthenium mono(bipyridines). In calculated structures, Ru−N(bpy) bonds were typically slightly overestimated, especially when they were positioned trans to a carbonyl ligand. Similarly, calculated C−O bonds in the carbonyl groups tended to be slightly longer than the corresponding experimental values. Such results indicate that the back-bonding of the CO group was not accurately treated in calculations. Although there was a slight inaccuracy in the calculated C−O bond lengths, calculated Ru−C and Ru−X (X = Cl, Br) bond lengths were typically in good agreement with the experimental values. Both the bond angle of Ru−C−O in the carbonyl group and the bite angle of bipyridine N−Ru−N gave a good fit with the experimental values. A detailed comparison of experimental and calculated structures of selected complexes is shown in Table 3. Complete results are available as Supporting Information.

Although a comprehensive computational study on isomerism of ruthenium mono(bipyridines) and determination of the actual

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reaction mechanisms involved in Scheme 1 would require a detailed analysis of the transition states and consideration of the solvent effects, a simple total energy approach, taking into account only the reactants and products, can be used to estimate the role of thermodynamical factors in these processes.

Isomerism of Ru(bpy)(CO)$_2$Cl$_2$ and (Ru(bpy)(CO)$_2$Cl)$_2$. Two of the ruthenium mono(bipyridine) complexes, Ru(bpy)(CO)$_2$Cl$_2$ and (Ru(bpy)(CO)$_2$Cl)$_2$, have more than one isomer which has been structurally characterized by single-crystal X-ray crystallography. In principle, Ru(bpy)(CO)$_2$Cl$_2$ can appear as *cis*(CO),*trans*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$, *cis*(CO),*cis*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$, and *trans*(CO),*cis*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$. The last isomer has not been isolated experimentally, most probably because of the strong trans influence of the CO ligands. According to theoretical calculations the total energy difference between *cis*(CO),*trans*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$ and *cis*(CO),*cis*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$ is only +0.4 kJ/mol. It has been experimentally shown that both isomers are stable and they do not spontaneously isomerize. The fact that both isomers have been isolated in pure form[12] points to the existence of a higher energy transition state that prevents such isomerization. At the same time, the low total energy difference between the isomers explains why isomer mixtures are often obtained in the synthesis of Ru(bpy)(CO)$_2$Cl$_2$. The third possible isomer, *trans*(CO),*cis*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$, has the highest total energy. The total energy of *trans*(CO),*cis*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$ is +44.6 kJ/mol higher than the energy of *cis*(CO),*trans*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$. Computational results suggests that the last isomer is thermodynamically unfavorable and that the nonexistence of this isomer may not be solely due to kinetic factors.

Conversion reactions of Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH), Ru(bpy)(CO)$_2$ClH, and [Ru(bpy)(CO)$_2$Cl]$_2$ in HCl provide good examples of the isomeric behavior of Ru(bpy)(CO)$_2$Cl$_2$. In all of these reactions the leaving group is located in an axial position trans to the Cl ligand and it could be expected that a simple replacement would produce mainly the *cis*(CO),*trans*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$ isomer. Such reactions would not require isomerization, but the leaving group would merely be changed to Cl. This was not the case, however, as usually there were at least traces of both isomers. The dependence of the isomerism of Ru(bpy)(CO)$_2$Cl$_2$ on the structure of the starting complex is thus less straightforward than assumed earlier.[12]

Rotamerism of [Ru(bpy)(CO)$_2$Cl]$_2$ has been studied earlier by X-ray crystallography.[12,32] It was found that the crystal structure of [Ru(bpy)(CO)$_2$Cl]$_2$ can be solved in two space groups, *C*2/*m* and *P*2/*c*.[32] The structure solution in space group *C*2/*m* gave a disordered mixture of the staggered and anti-eclipsed rotamers, whereas the structure solution in space group *P*2/*c* gave only the staggered rotamer without disorder.

Theoretical DF calculations showed that the staggered isomer is of lower total energy (the energy difference between the rotamers was +13.9 kJ/mol), suggesting that it is energetically the more stable rotamer. This is in agreement with the crystallographic results; both crystallographic solutions included the staggered rotamer. It should be remembered, however, that the total energies were calculated for the isolated gaseous molecules where there are no intermolecular interactions. In a true crystal these interactions might also stabilize the less favorable anti-eclipsed rotamer.

The Total Reaction Energies. Calculated reaction energies are shown in Scheme 1. All reaction energies were calculated using isomers with the lowest total energy (*trans*(Cl)-[Ru(CO)$_3$Cl$_2$]$_2$, *cis*(CO),*trans*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$, and staggered [Ru(bpy)(CO)$_2$Cl]$_2$). All primary reactions from A to C were found to be energetically favorable. Experimental observation that the reactions proceeds at mild conditions indicates low-energy transition states. However, both Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH) and Ru(bpy)(CO)$_2$ClH could be isolated, which suggests that at least a small activation energy barrier must exist. The kinetic factors are thus essential in formation of Ru(bpy)(CO)$_2$Cl(C(O)OCH$_2$CH$_2$OH) and Ru(bpy)(CO)$_2$ClH.

The side reactions S1 and S2 were endothermic, and it was expected that, if such reactions occur, they would be favored by elevated temperatures. The experimental observations supported the computational results. In the case of S2, the reaction was even stopped in the [Ru(bpy)(CO)$_3$Cl]$^+$ intermediate state at mild conditions, and additional heating was required in order to obtain Ru(bpy)(CO)$_2$Cl$_2$.

Reactions S3 and S4 were clearly exothermic. Energetically S3 was even more favorable than the corresponding primary reaction C. Similarly, the dimer should be easily converted to Ru(bpy)(CO)$_2$Cl$_2$ if HCl is present. Both of these reactions were found to occur even at room temperature. However, both reactions were facilitated by elevated temperatures. This was emphasized with (Ru(bpy)(CO)$_2$Cl)$_2$, which reacted very slowly at room temperature. In this reaction the kinetic factors are obviously in a key role. The reaction is limited by an energetically unfavorable transition state, which is most probably due to cleavage of the Ru−Ru bond.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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