Photochemical Studies of *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] (bpy = 2,2′-bipyridine): Ligand Exchange Reactions in Methanol

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The complex *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] (**1**) (bpy = 2,2′-bipyridine) complex was photoirradiated with visible light in methanol. Light-induced ligand substitution and alcohol coordination was observed under these conditions. The replacement of a carbonyl ligand with methanol is proposed to be the initial reaction step. The reaction product was characterized by NMR spectroscopy and cyclic voltammetry. The substitution of weakly bound alcohol occurred readily in acetonitrile, leading to the formation of more stable [Ru(bpy)(CO)(CH$_3$CN)Cl$_2$]. Extended (24 h) irradiation of *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] in methanol resulted in the formation of the dinuclear, mixed-valence complex [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl$_3$] (**2**). The structure of **2** consists of two Ru(bpy) moieties, which are linked by two methoxide bridges. These results showed that photoirradiation can be utilized in the synthesis of alkoxide-bridged ruthenium complexes.

Introduction

Alkoxides play an important role in organometallic chemistry owing to the increased need for the oxygenation of non-hydrocarbon ligands. The most straightforward way to synthesize metal alkoxides is the direct reaction of a main-group metal or metal complex with alcohols.[1,2] In the case of transition metals, the preparation of a metal−oxygen single bond is more complicated. The early transition metals tend to form more stable metal alkoxides than the late transition metals. The difference has been rationalized in terms of electronegativity: the more electropositive early transition metals form isolable alkoxo complexes.[2,3] Alkoxides are also hard, basic ligands while the late transition metals (groups 8−10) are seen as soft metals.[3]

In the course of the past ten years, the synthesis and reactions of (alkoxo)rhodium, -iridium, and -osmium complexes have been intensively studied.[4] However, much less attention has been paid to the ruthenium alkoxides, although complexes with the other related oxygen ligands such as aryloxo, or simple hydroxo, are well known.[4] Dinuclear, mixed-valence ruthenium complexes with bridging alkoxo ligands are even less common.[5−7] Mixed-valence complexes are of particular interest because they offer an opportunity to study electron transfer and electron delocalization in a dinuclear system.[8] Although alkoxy-bridged complexes are rare, there are several examples of other bridging ligand systems with mixed ruthenium valences. Probably the most familiar ones are the Creutz−Taube ion (Ru^{II}Ru^{III}) and dinuclear μ-oxo-ligated ruthenium complexes (Ru^{III}Ru^{IV}).[9]

Photoinduced reactions have been used as a synthetic route to the substituted (bipyridine)ruthenium(II) [Ru^{II}(bpy)] complexes. It is well known that in coordinating solvents such as CH$_3$CN, the photoirradiation of [Ru(bpy)(CO)$_2$Cl$_2$] leads to the replacement of monodentate ligands with a solvent molecule.[10−13] On the other hand, in weakly coordinating solvents such as CH$_2$Cl$_2$, the formation of the dimeric complex [Ru(bpy)(CO)Cl$_2$]$_2$ has been reported.[14] The solvent effects on Ru^{II}(bpy) complexes under UV/Vis irradiation have been studied and the coordination mode has been found to be associated with photoinduced oxidations and reductions.[15,16] It has also been shown that under steady-state irradiation the bipyridyl-based bridges in dinuclear Ru^{II} complexes are broken as a result of the photosolvation of acetonitrile or methanol.[17]

In the present paper we describe the photoirradiation of mono(bpy) complex *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] (**1**) in methanol. The stepwise reactions were monitored by means of cyclic voltammetry (CV) and spectroscopic methods.

Results and Discussion

Earlier studies[18,19] on the photochemical reactivity of the mono(bipyridine) complex [Ru(bpy)(CO)$_2$Cl$_2$] in a coordinating solvent (acetonitrile) showed that the initial photosubstitution takes place in two steps. In the first step, one

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CO ligand is photosubstituted with CH_3CN, leading to the formation of [Ru(bpy)(CO)(CH_3CN)Cl_2]. When photoirradiation continues, further substitution occurs and the complex [Ru(bpy)(CH_3CN)$_3$Cl]$^+$ is formed.[18,19] On the other hand, photoirradiation in a noncoordinating solvent, CH_2Cl_2, is reported to lead to the dichloro-bridged dimer [Ru(bpy)(CO)Cl_2]$_2$ through a five-coordinate intermediate.[14]

Photoirradiation of *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] (1)

When the photoirradiation of complex **1** was performed in a closed, water-cooled vessel, a photoinduced loss of a carbonyl ligand was observed. During irradiation, the carbonyl ligand was probably replaced with methanol, forming [Ru(bpy)(CO)(CH_3OH)Cl_2]. The IR spectrum of the methanol solution of the initial complex **1** contained two strong carbonyl stretching bands at 2065 cm^{-1} and 2005 cm^{-1}. After 2 min of irradiation, a new peak at 1965 cm^{-1} was observed in the IR spectrum. The original CO peak pair disappeared completely after 30 min. The color of the methanol solution of **1** changed from pale yellow to dark orange during irradiation. Simultaneously, the absorption maximum in the visible-region spectra shifted from 340 nm to 492 nm, respectively. The similarities between the previously reported IR and absorption spectra of the *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] irradiated in acetonitrile[19] and the current results in methanol, suggest the simple replacement of a carbonyl ligand by a neutral methanol ligand as the first reaction step.

The irradiation product was isolated as an orange-brown solid, which was dissolved in [D$_6$]DMSO and analyzed with ^{1}H NMR. The spectrum exhibited eight signals in the aromatic region, which are attributable to the two sets of aromatic protons. Such a pattern indicates that there are different ligands in *trans* positions to the bipyridine nitrogen atoms and that a structural rearrangement from *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] to a less symmetrical product has occurred. Furthermore, the ^{1}H NMR spectrum also showed the characteristic peaks of methanol (see Exp. Sect.), indicating coordinated methanol and supporting [Ru(bpy)(CO)(CH_3OH)Cl_2] as the first photoproduct.

The nature of the isolated photoproduct was further studied by dissolving it in strongly coordinating CH_3CN. The solution was then evaporated to dryness and the solid residue dried in a vacuum. The crystals obtained after this procedure were characterized by single-crystal X-ray crystallography. The X-ray analysis showed that the substitution of the MeOH ligand by CH_3CN had occurred, resulting in the formation of [Ru(bpy)(CO)(CH_3CN)Cl_2]. In this known structure,[19] the CH_3CN ligand is located in the *trans* position to the chloro ligand, which shows that a geometrical change takes place during the decarbonylation−acetonitrile coordination process.

The ligand replacement from CH_3OH to CH_3CN was also observed in CV studies. A clear, reversible-wave system ($E_{1/2}$ = 0.78 V, ΔE_p = 110 mV) was found with several weaker peak systems. It was found earlier that, after the irradiation of **1** in CH_3CN, a reversible-wave system appears at $E_{1/2}$ = 0.78 V, corresponding to the formation of [Ru(bpy)(CO)(CH_3CN)Cl_2].[19] The ligand electrochemical parameter E_L (Lever parameter)[20] for [Ru(bpy)(CO)(CH_3CN)Cl_2] was also calculated in order to find the most probable Ru^{II}/Ru^{III} potentials. The calculated value for [Ru(bpy)(CO)(CH_3CN)Cl_2] is 0.70 V, which is reasonably close to the observed value. According to the CV data, no change in the oxidation state of the ruthenium metal was observed during the replacement of CH_3OH to CH_3CN. The preservation of the original oxidation state +II further supports the assumption of simple CO replacement by a neutral ligand, i.e., methanol, as the initial reaction step.

Prolonged Photoirradiation (24 h) of 1 and the Formation of [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl$_3$] (2)

The infrared spectrum of the solution after long (24 h) irradiation in a closed, water-cooled reaction vessel showed the loss of the carbonyl peaks. The absorption spectrum of the final solution contained only one absorption maximum, in the visible-light region at 419 nm. The changes in the IR and UV/Vis spectra during the stepwise photoirradiation are shown in Figures 1 and 2.

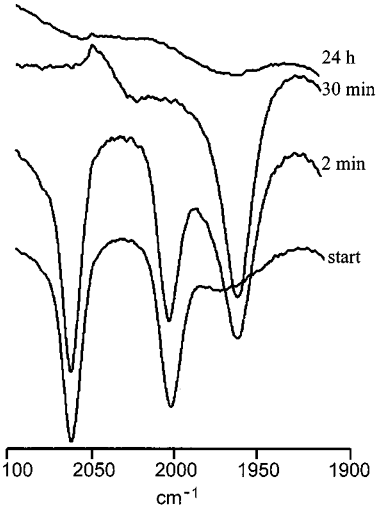

Figure 1. Changes in the ν(CO) region in methanol solution of *cis*(CO),*trans*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$ (**1**) as a function of the photoirradiation time

The evaporation of solvent from the reaction mixture after 24 h of photoirradiation in a closed reaction vessel resulted in the formation of a brownish solid photoproduct, which shows a single carbonyl band at 1941 cm^{-1} in KBr. The same product was obtained in crystalline form by slow evaporation of the methanol in a refrigerator. The structure of this mixed-valence Ru^{II}Ru^{III} dimer, [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl$_3$] (**2**), is shown in Figure 3. In **2** the coordination environment surrounding the ruthenium center is octahedral. The Ru−O bond lengths of 2.040(2) Å and 2.087(2) Å are quite similar to the reported distances in the alkoxy-bridged Ru^{II} or Ru^{II}/Ru^{III} complexes in general.[5−8,21] The O−Me bond is slightly bent from the plane determined by Ru−Ru−O. In the closely related compound

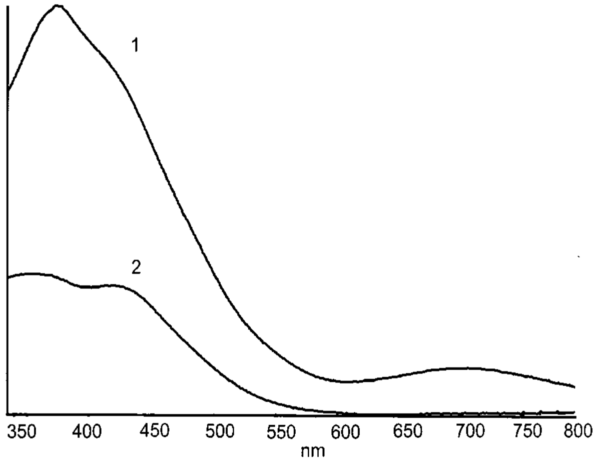

Figure 2. Absorption spectra of complex **1** after photoirradiation in open (1) and closed (2) reaction vessels measured directly from the methanol solutions

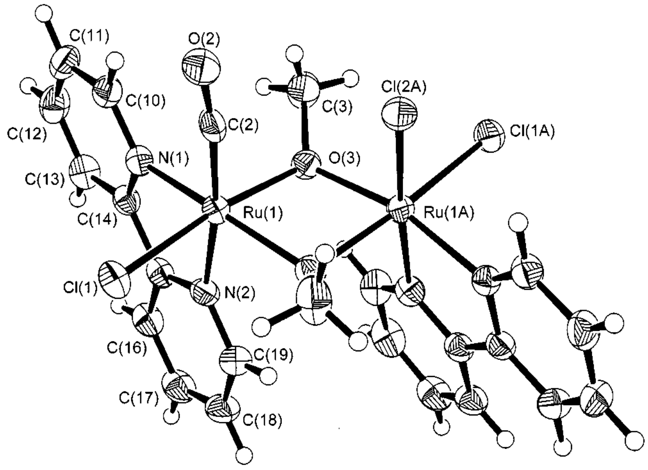

Figure 3. Structure of [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl$_3$]

[{Ru(bpy)$_2$}$_2$(OMe)$_2$](PF$_6$)$_2$ the corresponding Ru−Ru−O−C torsion angles are 167.0° and 169.0°.[21] However, the torsion angles of 137.7° and 138.8° found in complex **2** are comparable with the values found in the Ru^{II} complexes.[8,21]

The photoinduced chloride ligand exchange reactions of [(mono)bipyridine]ruthenium compounds in strongly coordinating solvents with extended irradiation have been reported earlier.[19] The photoinduced ejection of chloride is also required in the case of [Ru(bpy)(CO)(CH$_3$OH)Cl$_2$] to obtain the bimetallic complex [{Ru(bpy)}$_2$(μ-OMe)$_2$-(CO)Cl$_3$]. Figure 3 shows that isomerization has taken place at some point during the photoirradiation. The *trans*(Cl) geometry of the starting complex, [Ru(bpy)(CO)$_2$Cl$_2$], has been converted into the *cis*(Cl) isomer. This change occurs during the initial coordination of methanol, as was concluded in the case of 30 min of irradiation. Moreover, the deprotonation of methanol is needed to build up the methoxy bridges. The origin of this deprotonation process may lie in the photochemical basis, where the reaction intermediate abstracts protons from nucleophilic methanol molecules.

During the formation of the mixed-valence complex **2**, one of the ruthenium centers is oxidized. However, the detailed reaction mechanism for this redox reaction is not clear. The first examples of alkoxy-bridged dinuclear ruthenium(II) complexes were reported by Ward et al. in the 1990s.[8,21] It should be noted that Ward et al. synthesized the [{Ru(bpy)$_2$}$_2$(μ-OMe)$_2$](PF$_6$)$_2$ complex in refluxing methanol using added KOH, while in our case the photoirradiation in MeOH resulted directly in [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl$_3$] without any added hydroxide. The simple photoirradiation in alcohol is thus a convenient way to synthesize dinuclear alkoxy-bridged ruthenium complexes.

It is worth mentioning that the ν(CO) of [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl$_3$] at 1941 cm^{-1} was observed only in the solid samples measured in KBr. In solution, no IR peaks were found after 24 h of irradiation. However, when, after a prolonged irradiation in a closed vessel, the solution was allowed to stand overnight in the dark, a partial recovery of the CO band at 1965 cm^{-1} was observed. This phenomenon must be due to the presence of a labile, completely decarbonylated reaction product in solution. In the dark, the liberated CO is then able to recoordinate and the formation of carbonyl-containing [Ru(bpy)(CO)(CH$_3$OH)Cl$_2$] occurs. Experiments in an open reaction vessel prevented the CO recovery completely, indicating the absence of a recoverable species in solution. When an open system was used during irradiation, the absorption spectrum also gave a different maximum at 711 nm, instead of the 419 nm found in the closed-vessel experiments (Figure 2). In this case, no recovery of CO bands was observed, even after the solution was extensively bubbled with CO for several hours.

Experimental Section

Materials: Methanol (Riedel−de Haën, p.a. grade) was used without further purification. Acetonitrile (J. T. Baker, analytical grade) and tetrabutylammonium perchlorate (TBAP) were used as received. Monomeric *trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] complex (**1**) (bpy = 2,2′-bipyridine) was prepared by a literature method.[22]

Spectroscopic Studies: The FTIR spectra were measured with a Nicolet Magna 750 spectrometer, ^{1}H NMR spectra with a Bruker AMX 400 (400 MHz) spectrometer in [D$_6$]DMSO, and UV/Vis spectra with a Perkin−Elmer Lambda 900 UV/Vis/NIR spectrometer. The elemental analyses were performed with an EA1110 CHNS-O (Carlo Erba Instruments) analyzer.

Photochemical Instrumentation and Procedure: In the photolysis experiments all of the samples were irradiated using a 450-W Xe discharge lamp (Oriel model 8540, UV light blocked out at 320 nm with a glass filter). The photolysis cell was water-cooled to prevent heating and the vessel was closed with a septum. When necessary, the CO was removed through a needle. The path length of the cell was 3 cm and the distance from the lamp was approximately 20 cm. Irradiation of the sample solutions (30 mg of [Ru(bpy)(CO)$_2$Cl$_2$] in 30 mL of solvent) was performed under air and monitored by the IR and UV/Vis spectra. The total period of irradiation was 24 h.

Electrochemical Instrumentation and Procedure: The CV was performed under argon at room temperature in a three-electrode cell using an Autolab PGSTAT20 potentiostat-galvanostat. The solutions for measurements were prepared by concentrating the photoproduct sample to dryness and dissolving this residue in 0.1 M TBAP/CH_3CN. The sample solutions were purged with argon prior to use. The working electrode was a platinum disk (Metrohm, area 1.28 cm^2), and the counter electrode a glassy carbon disk (Metrohm, area 0.28 cm^2). Potentials were referred to an Ag^+/Ag electrode (0.01 mol/dm^3 $AgNO_3$ in CH_3CN). Under the experimental conditions, the Fc^+/Fc couple potential was 0.01 V. In all of the experiments the potential scan rate was 100 $mV \cdot s^{-1}$. The cyclic voltammograms were mainly recorded in a positive region because in [mono(bpy)]ruthenium complexes the Ru^{II}/Ru^{III} redox reactions typically take place at the positive potentials versus the Ag/Ag^+ reference electrode. At the negative potentials all of the redox peaks were assigned to the bipyridine-based reactions.

Characterization of Complex [Ru(bpy)(CO)(CH_3OH)Cl_2]: FT-IR (CH_3OH): $\tilde{\nu}$ = 1965 cm^{-1} (vs, ν_{CO}). UV/Vis (CH_3OH): λ_{max} = 492 nm. ^1H NMR ([D_6]DMSO): δ = 9.53 (d, 1 6-H), 8.96 (d, 1 6′-H), 8.76 (d, 1 3-H), 8.67 (d, 1 3′-H), 8.38 (t, 1 4-H), 8.16 (t, 1 4′-H), 7.94 (t, 1 5-H), 7.61 (t, 1 5′-H), 4.12 (q, 1 H, CH_3OH), 3.17 (d, 3 H, CH_3OH). Note: satisfactory elemental analysis was not obtained for this complex owing to the small amounts of impurities, which could be seen in the NMR spectra.

Characterization of Complex [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3]: FT-IR (KBr): $\tilde{\nu}$ = 1941 cm^{-1} (vs, ν_{CO}). UV/Vis (CH_3OH): λ_{max} = 365 nm. [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3]·(CH_3OH) (742.98): calcd. C 38.80, N 7.54, H 3.53; found C 35.68, N 7.18, H 3.47. Note 1: ^1H NMR spectra measured in [D_6]DMSO revealed the different nature of the two aromatic bipyridine ligands and the non-equivalency of four pyridine rings. Note 2: The difference between the calculated and found values in the elemental analyses is due to the varying amounts of solvent or water present in the bulk material even though the sample was carefully dried in a vacuum. The crystal structure was solved with one CH_3OH molecule per [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3] unit.

Formation of [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3] Crystals, X-ray Data Collection, and Structure Solution for [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3]·(CH_3OH): Crystals of [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3] suitable for structural characterization were formed from the photolyzed methanol solution of **1** after slow concentration in a refrigerator. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å) and the Collect[23] data collection program. The Denzo-Scalepack[24] program package was used for cell refinements and data reduction. The structure was solved by direct methods using the SHELXS97[25] program and the WinGX[26] graphical user interface. The structural refinement was carried out by means of the SHELXL97[27] program. The structure was solved in the orthorhombic space group *Pbcn* and the asymmetric unit consisted of one half-molecule. The carbonyl ligand C(2)−O(2) and chloride Cl(2) were disordered and mixed in two positions with the equal population parameter 0.5. The solvent methanol was disordered around a special position with equal population parameter and was only refined isotropically. As a result of the disorder, the OH hydrogen atom of the solvent molecule was omitted. All of the other hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in Table 2. The molecular structure of the complex is presented in Figure 3. CCDC-168110 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3]·(CH_3OH)

	1
Empirical formula	$C_{24}H_{26}Cl_3N_4O_4Ru_2$
Formula mass	742.98
Crystal system	orthorhombic
Space group	*Pbcn*
λ [Å]	0.71073
a [Å]	8.43100(10)
b [Å]	16.5539(3)
c [Å]	19.0094(2)
V [$Å^3$]	2653.06(6)
T [K]	150(2)
Z	4
$D_{calcd.}$ [g/cm^3]	1.860
μ [mm^{-1}]	1.480
Number of refl. collected	5056
Number of refl. observed	2306
Number of unique refl.	2710
R_{int}	0.0126
*R*1 (*I* > 2)	0.0327
*wR*2 (*I* > 2)	0.0788

Table 2. Selected bond lengths and angles for [{Ru(bpy)}$_2$(μ-OMe)$_2$(CO)Cl_3]·(CH_3OH)

Bond	Å
Ru(1)−Cl(1)	2.3880(9)
Ru(1)−Cl(2)	2.322(4)
Ru(1)−N(1)	2.047(3)
Ru(1)−N(2)	2.091(3)
Ru(1)−C(2)	1.868(16)
Ru(1)−O(3)	2.040(2)
Ru(1)−O(3A)	2.087(2)
C(2)−O(2)	1.152(18)
O(3)−C(3)	1.406(5)
Angle	**°**
N(1)−Ru(1)−N(2)	78.64(11)
Ru(1)−C(2)−O(2)	171(2)
Cl(1)−Ru(1)−Cl(2)	92.06(16)
Ru(1)−O(3)−C(3)	120.4(2)
Ru(1A)−O(3)−C(3)	122.5(2)
Ru(1)−O(3)−Ru(1A)	101.33(10)

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