Selective Formation of *cis*(X)- and *trans*(X)-Ru(dmbpy)$(CO)_2X_2$ Complexes (X = Cl, Br, I, SCN) from Monomeric and Dimeric Ru−mono(dmbpy) Carbonyl Complexes (Dmbpy = 4,4′-Dimethyl-2,2′-bipyridine)

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Aqueous hydrogen halides HX (X = Cl, Br, I) are shown to be excellent halogen sources for the synthesis of a series of halogen-containing ruthenium mono(2,2′-bipyridine) carbonyl complexes Ru(dmbpy)$(CO)_2X_2$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine), as well as effective reagents for the attack of the Ru–Ru bond in the dimer [Ru(dmbpy)-$(CO)_2Cl]_2$. Selective syntheses were established for both *cis*- and *trans*-halogen complexes in the case of Cl- and of Br-containing derivatives, but the only stable isomer containing iodine was *trans*(I)-Ru(dmbpy)$(CO)_2I_2$. The failure to obtain the *cis* isomer was probably due to sterical effects. Furthermore, a novel *S*-bound *trans*(SCN) analogue was synthesized and structurally characterized. In all experiments, the reaction conditions selected led to complete halogen exchange; no mixed halogen or pseudohalogen complexes were detected.

Introduction

Mononuclear ruthenium 2,2′-bipyridine complexes exhibit excellent catalytic properties in the water-gas shift reaction[1−4] and the reduction of carbon dioxide.[5−9] These catalyst-precursor complexes have been chemically modified through the use of different halogen and pseudohalogen ligands and substituted bipyridine reagents.[9−15] Most recently, the various isomeric forms of these compounds[9][16] were studied as a means of clarifying the structure of the actual catalyst, which is believed to be polymeric. Electropolymerization experiments[16] have indicated that only *trans*-halogen complexes are able to form such polymeric species, which underlines the need for isomerically pure complexes.

This paper reports isomerically selective syntheses for chemically altered monomeric ruthenium−mono(2,2′-bipyridine) complexes. On the basis of results obtained earlier,[15] we chose to use only dimethyl-substituted bpy ligands, as this was believed likely to introduce some interesting new features to complexes with direct Ru−Ru bonds. A structural study of a dimeric complex containing the 4,4′-dimethyl-2,2′-bipyridine ligand has shown that methylated bpy ligands can be used to lock the rotation of both the carbonyl and the polypyridine ligands around the ruthenium backbone in corresponding structures, which may allow structural characterization of an ordered polymeric species. In addition, the methyl groups can be converted to carboxy or trichlorosilylethyl groups to achieve chemical anchoring of Ru−bpy complexes into oxide supports.[14,17−19]

The various halogen-containing derivatives of Ru−bpy carbonyl complexes form a useful series of compounds for investigating the Ru−Ru chain-forming properties of the oligomeric complexes, since the Ru−Ru chain-forming step will also be affected by the chemical nature of the *trans* leaving group (i.e. Cl, Br, I, SCN). Furthermore, the thiocyanate ligand, as well as various halogens, have been widely used for tuning the photo- and electrochemical properties of transition metal complexes,[20][21] most recently in modern solar-cell designs.[17][18] By far, the photochemical behavior of mono(2,2′-bipyridine) complexes has remained a relatively unexplored field of ruthenium bipyridine chemistry, and the chemically altered halogen and pseudohalogen derivatives presented in this paper thus also offer an intriguing series of compounds for future photochemical investigations.

Results and Discussion

The formation of monomeric ruthenium bipyridine carbonyl complexes, such as Ru(bpy)$(CO)_2Cl_2$,[10] is complicated by the various orientations of the carbonyl and halogen ligands, which allows the coexistence of both *cis*- and *trans*-halogen isomers (third isomer with axial carbonyl groups is energetically far less favored). The choices of solvent and ruthenium reagent have been shown to determine the reaction route: synthesis with $RuCl_3$/CO/bpy[24][31] may give pure *trans*(Cl)-Ru(bpy)$(CO)_2Cl_2$, whereas syntheses based on acid-controlled $[Ru(CO)_2Cl_2]_n$/MeOH/bpy and $[Ru(CO)_3Cl_2]_2$/THF/bpy[9][10] yield both isomers. In the latter case, use of ethylene glycol instead of THF as solvent gives either hydride Ru(bpy)$(CO)_2$ClH or dimeric complex $[Ru(bpy)(CO)_2Cl]_2$. As was learned in our earlier studies,[15] methylation of the 2,2′-bipyridine ligand tends to shift the balance between *cis*- and *trans*-halogen products toward the *cis*-halogen species.

In this paper we describe the syntheses of halogen- and pseudohalogen-containing (Cl, Br, I, SCN) monomeric

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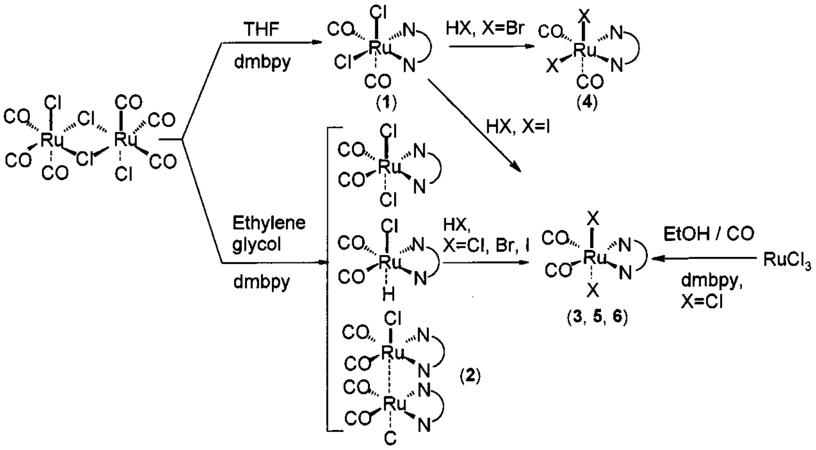

Scheme 1

Ru−dmbpy (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) complexes with controlled *cis*-*trans* isomerism. *trans*-Halogen complexes are achieved by treating the *trans*-chloro complex (synthesis based on "ruthenium red carbonyl solution" as starting material) or dimer **2** with the corresponding hydrogen halide. The syntheses are summarized in Scheme 1.

Ligand-Exchange Reactions Cl → Br, I based on *cis*(Cl)-Ru(dmbpy)(CO)$_2$Cl$_2$ (1)

Ligand-substitution reactions with aqueous hydrogen halides have previously been studied for the monomeric parent complex *trans*(Cl)-Ru(bpy)(CO)$_2$Cl$_2$.[12] As in the present study, the reactions were limited to halide exchange, even though decarbonylated complexes such as [Ru(bpy)Cl$_4$]$^-$, [Ru(bpy)Cl$_3$]$^-$, and [Ru(bpy)Cl$_2$]$^{2-}$[12] are known. The reaction conditions selected led to complete halogen exchange, i.e. no mixed-halogen complexes were detected.

Heating of complex **1** in aqueous HBr resulted in the formation of greenish yellow precipitate. The product was analyzed by spectroscopic and X-ray diffraction measurements and identified as *cis*(Br)-Ru(dmbpy)(CO)$_2$Br$_2$ (**4**, Figure 1). The NMR spectra of complex **4** (in CDCl$_3$) support an unchanged *cis*-halogen arrangement, the main proof being the double CO, Me, and aromatic carbon resonances detected in the ^{1}H- and ^{13}C-NMR spectra.

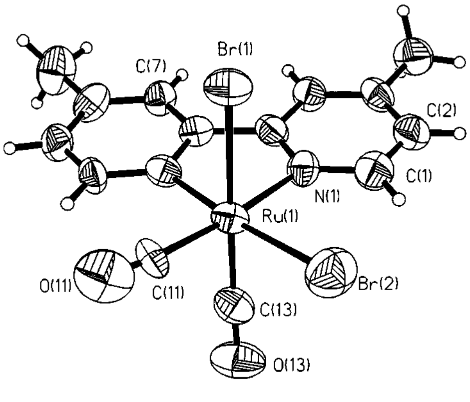

Figure 1. Structure of *cis*(Br)-Ru(dmbpy)(CO)$_2$Br$_2$ (**4**); the solvent molecule has been omitted for clarity

When aqueous HI was used as halogen source, the reaction changed markedly; despite several attempts, no traces of *cis*-halogen species were detected. Instead, the only product characterized (both spectroscopically and crystallographically) was *trans*(I)-Ru(dmbpy)(CO)$_2$I$_2$ (**6**, Figure 2). Usually, both *cis*- and *trans*-halogen forms of mono(bipyridine) complexes are highly stable, and rearrangements of coordination spheres invariably include ligand-substitution reactions. In this case, the larger size of the iodine ligand with respect to Cl and Br (ionic radii for Cl, Br, and I: 1.81, 1.95, and 2.16 Å, respectively) apparently prevents the *cis*-halogen arrangement, and strongly favors the *trans*(I) conformation.

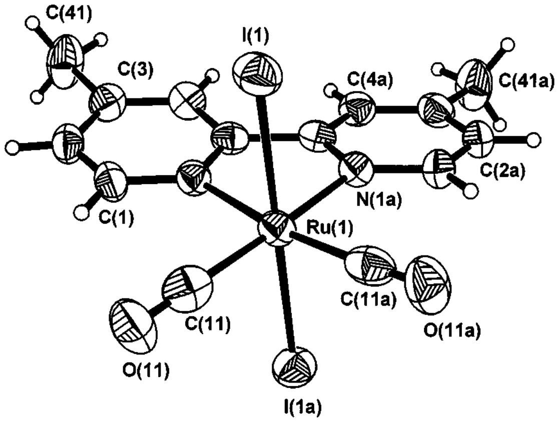

Figure 2. Structure of *trans*(I)-Ru(dmbpy)(CO)$_2$I$_2$ (**6**)

The structure of complex **4** does not exhibit any severe distortions compared with the chlorine-containing parent complex.[15] The bipyridine ring system is almost planar (angle between pyridine ring planes only 0.7°), although slightly bent away from the axial carbonyl group. The Ru−Br bond lengths of 2.565(1) (axial) and 2.502(2) Å (equatorial) are well within the range of bond lengths for related compounds reported earlier,[12] though, the axial halogen atom suffers slightly from the *trans* effect of the opposite carbonyl ligand. The bipyridine bite angle N(1)−Ru(1)−N(2) of 77.8(3)° is more or less typical for other Ru−bpy carbonyl complexes;[10−15] the slight distor-

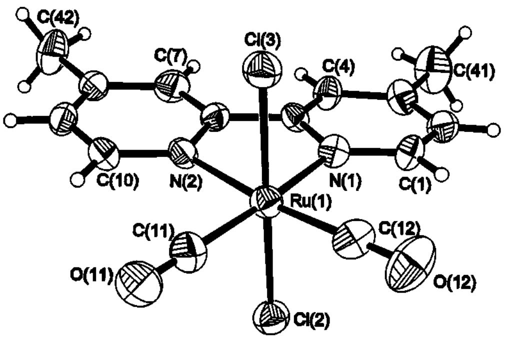

Figure 3. Structure of *trans*(Cl)-Ru(dmbpy)$(CO)_2Cl_2$ (**3**); the solvent molecule has been omitted for clarity

tion is due to the other carbonyl ligand positioned *trans* to N(1) [bond lengths Ru(1)−N(1) 2.126(8), Ru(1)−N(2) 2.076(8) Å].

Formation of Monomeric *trans*(X)-Ru(dmbpy)$(CO)_2X_2$ (X = Cl, Br, I, SCN) Complexes

Aqueous hydrogen halides proved to be excellent halogen sources in the above-described ligand-exchange reactions. In this study, we also investigated the attack of Cl^-, Br^-, and I^- on Ru−Ru bonds using dimeric [Ru(dmbpy)$(CO)_2Cl]_2$ (**2**) as starting material. In all experiments, reactions led to breaking of the metal−metal bond and complete halogen exchange. Not surprisingly, all monomeric Ru−dmbpy compounds formed (complexes **3**, **5**, **6**) adopted *trans*-halogen configuration. This was also the case for complex **3** (Figure 3), which was synthesized by treating monomeric co-products[15] from the synthesis of complex **2**, and possibly some dimeric residues, with HCl (see Scheme 1). This experiment indicates that ethylene glycol, which was originally used to direct the complexation reaction between $[Ru(CO)_3Cl_2]_2$ and dmbpy toward dimeric species, also favors the formation of monomeric *trans*-chloride or *trans*-chloride−hydride complexes.

Since the axial positions of octahedral mono(bipyridine) complexes are sterically not hindered, they allow the *trans* coordination of relatively large ligands, such as I or *S*-bound bent SCN. Changing the halogen or pseudohalogen groups in these positions has little structural effect on the overall Ru−bpy arrangements (see Tables 2 and 3). Nevertheless, all attempts to crystallize complex **5** failed, and the identification of this complex was carried out instead by elemental analysis and interpretation of spectroscopic data. Once again, the most valuable proof came from ^{13}C-NMR data; single resonances for CO, Me, and aromatic carbon atoms supporting the *trans*-halogen arrangement were detected for all three complexes **5**, **6**, and **7**. Probably the main reason for the difficulty in obtaining single crystals from complex **5** was the tendency to form solvated crystalline species. As in the case of complex **3**, the solvent molecules eventually escape from the solid structure, destroying the crystals. Consequently, a decent X-ray diffraction analysis requires very fast data collection.

Table 1. Crystallographic data for *trans*(Cl)-Ru(dmbpy)$(CO)_2Cl_2\cdot CH_2Cl_2$ (**3**), *cis*(Br)-Ru(dmbpy)$(CO)_2Br_2\cdot CDCl_3$ (**4**), *trans*(I)-Ru(dmbpy)$(CO)_2I_2$ (**6**), and *trans*(SCN)-Ru(dmbpy)$(CO)_2(SCN)_2$ (**7**); dmbpy = 4,4′-dimethyl-2,2′-bipyridine

complex	**3**·CH_2Cl_2	**4**·$CDCl_3$	**6**	**7**
formula	$C_{14}H_{12}Cl_2N_2O_2Ru$	$C_{14}H_{12}Br_2N_2O_2Ru$	$C_{14}H_{12}I_2N_2O_2Ru$	$C_{16}H_{12}N_4O_2S_2Ru$
formula weight	412.24	501.14	595.13	457.49
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a [Å]	6.516(1)	12.053(3)	6.835(1)	7.928(2)
b [Å]	22.034(4)	12.949(3)	19.009(4)	17.128(3)
c [Å]	13.263(3)	14.416(3)	13.650(3)	13.498(3)
β [°]	96.66(3)	113.14(2)	102.76(3)	93.87(3)
V [Å^3]	1891.4(6)	2069.0(8)	1729.7(6)	1828.7(7)
Z	4	4	4	4
$D_{calcd.}$ [g/cm^3]	1.746	1.992	2.285	1.662
crystal source	CH_2Cl_2	$CDCl_3/CH_2Cl_2$	CH_2Cl_2	H_2O
crystal size [mm]	0.05 × 0.1 × 0.1	0.2 × 0.3 × 0.4	0.1 × 0.2 × 0.4	0.05 × 0.1 × 0.2
color	yellow	yellow	reddish yellow	yellow
radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
μ [mm^{-1}]	1.404	5.02	4.48	1.10
θ limits [°]	4−26	3−25	2−30	4−26
h range	0−8	0−15	−9 to 0	0−9
k range	0−27	0−16	0−26	0−21
l range	−16 to 16	−18 to 17	−18 to 19	−16 to 16
no. of unique rflns	3455	3518	2526	3616
no. of obsd data[a]	1761	1948	1483	2047
no. of params	218	229	96	227
$R1(F_o)$	0.0680	0.0546	0.0341	0.0282
$wR2(F_o^2)$[b]	0.1784	0.1554	0.0860	0.0555
x	0.0872	0.0838	0.0468	0.0104
y	0.00	0.00	0.00	0.00
goodness of fit	0.947	0.897	0.828	0.749

[a] $I \geq 2\,\sigma(I)$. − [b] $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; $P = (F_o^2 + 2\,F_c^2)/3$.

Table 2. Selected bond lengths [Å] for *trans*(Cl)-Ru(dmbpy)(CO)$_2$Cl$_2\cdot$CH$_2$Cl$_2$ (**3**), *cis*(Br)-Ru(dmbpy)(CO)$_2$Br$_2\cdot$CDCl$_3$ (**4**), *trans*(I)-Ru(dmbpy)(CO)$_2$I$_2$ (**6**), and *trans*(SCN)-[Ru(dmbpy)(CO)$_2$(SCN)$_2$]$_2$ (**7**); dmbpy = 4,4′-dimethyl-2,2′-bipyridine

	3	**4**	**6**	**7**
Ru(1)−X(1)[a]	2.405(2)	2.565(1)	2.705(1)	2.429(1)
Ru(1)−X(2)[b]	2.390(2)	2.502(2)		2.432(1)
Ru(1)−N(1)	2.118(7)	2.126(8)	2.131(4)	2.102(2)
Ru(1)−N(2)	2.129(7)	2.076(8)		2.118(2)
Ru(1)−C(11)	1.879(10)	1.967(11)	1.911(6)	1.891(3)
Ru(1)−C(12)[c]	1.866(12)	1.849(13)		1.874(4)
C(11)−O(11)	1.117(11)	1.000(11)	1.062(6)	1.134(3)
C(12)−O(12)[c]	1.129(11)	1.154(13)		1.127(4)
C(3)−C(41)	1.514(12)	1.488(13)	1.517(7)	1.510(4)
C(8)−C(42)	1.484(13)	1.523(15)		1.508(4)
S(13)−C(13)				1.666(4)
C(13)−N(13)				1.145(4)
S(14)−C(14)				1.657(4)
C(14)−N(14)				1.153(4)

[a] X(1) = Cl(3) for **3,** S(13) for **7**. − [b] X(2) = Cl(2) for **3**, S(14) for **7**. − [c] C(12) = C(13), O(12) = O(13) for **4**.

Table 3. Selected bond angles [°] for *trans*(Cl)-Ru(dmbpy)(CO)$_2$Cl$_2\cdot$CH$_2$Cl$_2$ (**3**), *cis*(Br)-Ru(dmbpy)(CO)$_2$Br$_2\cdot$CDCl$_3$ (**4**), *trans*(I)-Ru(dmbpy)(CO)$_2$I$_2$ (**6**), and *trans*(SCN)-[Ru(dmbpy)(CO)$_2$(SCN)$_2$]$_2$ (**7**); dmbpy = 4,4′-dimethyl-2,2′-bipyridine

	3	**4**	**6**	**7**
X(1)−Ru(1)−C(12)[a,c]	92.3(3)	177.4(3)		90.7(1)
X(1)−Ru(1)−N(1)[a]	86.2(2)	86.1(2)		92.5(1)
X(1)−Ru(1)−N(2)	90.6(2)	86.9(2)	88.3(1)	87.7(1)
X(1)−Ru(1)−C(11)	91.3(3)	88.9(3)	91.2(2)	91.0(1)
X(1)−Ru(1)−X(2)	175.3(1)	91.4(1)	179.3(0)	174.6(0)
N(1)−Ru(1)−N(2)	76.7(3)	77.8(3)	76.9(2)	77.3(1)
N(1)−Ru(1)−X(2)[b]	89.7(2)	86.1(2)	88.3(1)	82.4(1)
N(2)−Ru(1)−C(11)	96.9(4)	100.1(4)	172.4(2)	97.4(1)
C(11)−Ru(1)−X(2)	92.6(3)	85.4(3)	88.4(2)	94.0(1)
N(1)−Ru(1)−C(11)	173.0(4)	174.6(4)	96.5(2)	173.1(1)
N(2)−Ru(1)−X(2)	86.2(2)	174.2(2)	88.3(1)	89.6(1)
C(2)−C(3)−C(41)	119.8(9)	121.3(10)	121.6(5)	121.8(3)
C(7)−C(8)−C(42)	121.0(9)	119.9(10)		121.6(3)
S(13)−C(13)−N(13)				178.6(4)
Ru(1)−S(13)−C(13)				102.2(1)
Ru(1)−S(14)−C(14)				104.8(1)
S(14)−C(14)−N(14)				178.3(3)

[a] X(1) = Cl(3) for **3,** S(13) for **7**. − [b] X(2) = Cl(2) for **3**, S(14) for **7**. − [c] C(12) = C(13) for **4**.

The coordination of thiocyanate ligands in complex **7** results in a strong $\nu_{\mathrm{SC-N}}$ single band at 2116 cm^{-1} (in CH$_2$Cl$_2$), a value close to that found for both the *S*- and the *N*-bound Ru$^{\mathrm{II}}$ mono(2,2′-bipyridine) thiocyanate complexes reported earlier[13] ($\nu_{\mathrm{SC-N}}$ values: 2116 for *S*-bound and 2109 cm^{-1} for *N*-bound, showing an unexpectedly weak tendency of the *N*-bound thiocyanate ligand to shift the SC−N stretching bands toward lower frequencies). A weak resonance at $\delta_{\mathrm{SCN}} = 120$ found in the ^{13}C-NMR spectrum of complex **7** matched that of the *S*-bound thiocyanate analogue [$\delta_{\mathrm{SCN}} = 118$ for *trans*(SCN)-Ru(bpy)(CO)$_2$(SCN)$_2$], and other *S*-bound Ru−SCN complexes[21] assigned spectroscopically. The coordination mode of the SCN ligands in complex **7** was verified by X-ray crystallography (Figure 4). Since there is no severe steric hindrance, both terminal thiocyanates are bent [angles Ru−S(13)−C(13) 102.2(1)°, Ru−S(14)−C(14) 104.8(1)°]; in crystalline form the rotation of the groups is locked roughly between the two carbonyl ligands and the opposite bipyridine ring halves. The bond lengths of 2.429(1) and 2.432(1) Å for Ru(1)−S(13) and Ru(1)−S(14) are almost identical with those of the above-mentioned Ru−bpy analogue, but long relative to the range reported for other Ru$^{\mathrm{II}}$−S bond lengths [2.262(1)−2.393(3) Å[32]]. The longer distances most probably are due to the competition of the carbonyl ligands for the π-electron density of the central metal atom.

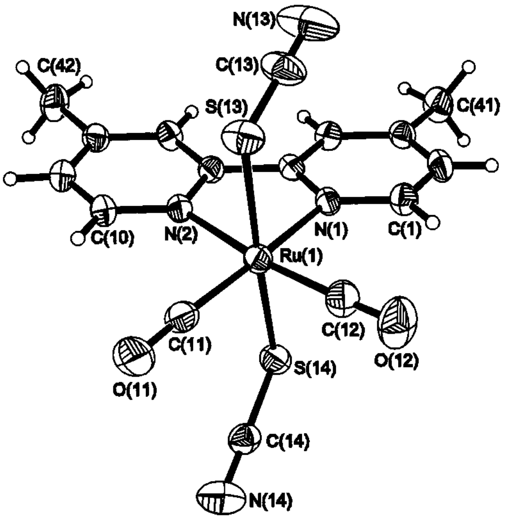

Figure 4. Structure of *trans*(SCN)-Ru(dmbpy)(CO)$_2$(SCN)$_2$ (**7**)

The ligand-exchange reaction Cl → SCN was also checked for complex **1** with reaction conditions similar to those used in the synthesis of complex **7**. Elemental analysis and heavily shifted ν_{CO} frequencies in the IR spectrum of the brownish-yellow product indicated the coordination of thiocyanate ligands in the complex (ν_{CO} in CH$_2$Cl$_2$: 2074 and 2020 cm^{-1}). The appearance of a strong $\nu_{\mathrm{SC-N}}$ band at 2103 cm^{-1} with shoulder at 2117 cm^{-1} suggested the restored *cis*(CO)-*cis*(X) arrangement in this compound, where, owing to steric hindrance, the equatorial coordination position most probably was occupied by a linear NCS ligand. The poor X-ray-crystallographic data collected for the brownish-yellow disordered crystal supported the *N*-bound (linear) coordination mode for the equatorial, and *S*-bound (bent) arrangement for the axial thiocyanate. Unfortunately, poor solubility of this complex prevented detailed NMR study.

The ν_{CO} bands in the IR spectrum of a transition metal complex may be taken as a measure of backdonation from the metal atom to the ligand, where the higher the electron density of the central metal, the lower the ν_{CO} frequency. The ν_{CO} values recorded for the complexes studied here showed a slightly increasing trend for σ-bonding ligands in the order Cl ≥ Br > I, while a considerably higher value was recorded for the π-accepting SCN group. Similarly, change in the monodentate ligand affected the CO resonances in the ^{13}C-NMR spectra. A slight upfield shift was detected in the order Cl > Br > I, which strictly follows the increasing electron affinities and decreasing ionic radii of these halogens. Interestingly, the thiocyanate ligands high-shifted the δ(CO) value of complex **7** relative to the halogen-containing derivatives, evidently due to effective shielding of the equatorial carbonyl groups by rotating SCN groups.

Conclusions

In this paper we have described synthetic procedures for obtaining chemically altered Ru(dmbpy) species and presented the basic crystallographic and spectroscopic data for identification. The complexes were modified by fundamentally simple ligand-exchange reactions and with use of substituted polypyridine ligands. Aqueous hydrogen halides were shown to serve as effective halogen sources and as suitable reagents attacking Ru−Ru bonds in dimeric $[Ru(bpy)(CO)_2Cl]_2$, which consequently led to selective formation of monomeric *trans*-halogen species. The particular combination of ruthenium reagent and solvent used in the synthesis, as well as the sterical properties of the chromophore and non-chromophore ligands, were suggested to direct the complexation reaction toward mononuclear *cis*- or *trans*-halogen species.

Experimental Section

Materials: $[Ru(CO)_3Cl_2]_2$ was purchased from Johnson and Matthey and 4,4′-dimethyl 2,2′-bipyridine (dmbpy) from Aldrich Chemicals. All solvents were of analytical grade and used as received. The parent complexes *cis*(Cl)-Ru(dmbpy)$(CO)_2Cl_2$, and $[Ru(dmbpy)(CO)_2Cl]_2$[15] were synthesized under exclusion of air with use of traditional N_2/vacuum-line techniques. The ligand-exchange reactions with aqueous hydrogen halide solutions (HCl, 37%; HBr, 48%; HI, 67%, all from Merck) were carried out in a 60-mL Berghof digestive pressure vessel[22] with PTFE liner. All product manipulations were performed in air.

Spectroscopic Studies: Infrared spectra were measured in CH_2Cl_2 solutions with a Nicolet Magna 750 FTIR spectrometer. ^1H- and ^{13}C-NMR spectra were recorded with a Bruker AMX 400 spectrometer with $CDCl_3$ as solvent.

Syntheses: Parent complexes *cis*(Cl)-Ru(dmbpy)$(CO)_2Cl_2$ (**1**) and $[Ru(dmbpy)(CO)_2Cl]_2$ (**2**) were synthesized from $[Ru(CO)_3Cl_2]_2$ and 4,4′-dimethyl 2,2′-bipyridine with THF or ethylene glycol used as solvent in 72% and 68% yield[15], respectively.

***trans*(Cl)-Ru(dmbpy)$(CO)_2Cl_2$ (3):** Complex **3** was synthesized by using "ruthenium red" carbonyl solution[23][24] as starting material. $RuCl_3$·3 H_2O (1 g, 3.82 mmol) and 70 mL of dry ethanol were placed in a reaction vessel under nitrogen. The reaction mixture was refluxed for 8 h under CO flow, and cooled to room temperature, after which 4,4′-dimethyl-2,2′-bipyridine (0.63g, 3.82 mmol) was added. The solution was refluxed under nitrogen for an additional 2 h, and cooled to room temperature. The yellow precipitate was filtered, washed with small amounts of ethanol, and dried in vacuo (yield 83%). Additionally, a sample of complex **3** (300 mg, 0.73 mmol) was prepared as follows: A brownish-yellow mixture of monomeric by-products (ca. 500 mg) from the synthesis of complex **2**[15] was added to 15 mL of 37% hydrochloric acid and the mixture was allowed to stand at room temperature for several days. A yellow precipitate was formed during the concentration of the aqueous solution. This was washed with water and small amounts of methanol, dried in air, and analyzed by IR and NMR spectroscopy, X-ray diffraction [single crystals obtained from CH_2Cl_2 as solvated Ru(dmbpy)$(CO)_2Cl_2$ · CH_2Cl_2], and elemental analysis. − $C_{14}H_{12}Cl_2N_2O_2Ru$ (412.24): calcd. C 40.8, H 2.9, N 6.8; found C 40.9, H 2.9, N 6.6. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2063 (vs), 2001 cm^{-1} (vs) (both CO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 155.5−124.6 (five peaks, aromatic rings in dmbpy), 196.8 (CO), 22.0 (Me). − ^1H NMR ($CDCl_3$): δ = 8.99 (d, 6-H), 8.02 (s, 3-H), 7.44 (d, 5-H) (all aromatic H); 2.58 (s, Me).

Halogen-Ligand Exchange Reactions: The halogen-ligand exchange reactions were carried out in a Berghof pressure vessel using aqueous HBr (2 mL of 48% HBr/2 mL of H_2O) or HI (1.25 mL of 67% HI/3.25 mL of H_2O) and complexes **1** and **2** as starting materials.

***cis*(Br)-Ru(dmbpy)$(CO)_2Br_2$ (4):** Complex **4** was synthesized by weighing 80 mg (0.19 mmol) of complex **1** into the pressure vessel, adding 4 mL of aqueous HBr, and heating the mixture to 200°C. The temperature was maintained at 200°C for 6 h, after which the reaction vessel was cooled to room temperature. A light green precipitate was separated from the greenish solution, washed several times with water, and air-dried (yield ca. 70%). Complex **4** was analyzed by spectroscopic methods, elemental analysis, and X-ray diffraction analysis [single crystals obtained from CH_2Cl_2/$CDCl_3$ mixture as solvated Ru(dmbpy)$(CO)_2Br_2$·$CDCl_3$]. − $C_{14}H_{12}Br_2N_2O_2Ru$ (501.14): calcd. C 33.6, H 2.4, N 5.6; found C 33.9, H 2.4, N 5.6. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2063 (vs), 2000 cm^{-1} (vs) (both CO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 156.5−124.2 (ten peaks, aromatic rings in dmbpy); 197.4, 191.2 (both CO); 22.0 (Me). − ^1H NMR ($CDCl_3$): δ = 8.97 (d, 6-H), 8.68 (d, 6′-H), 8.01 (s, 3-H), 7.99 (s, 3′-H), 7.49 (d, 5-H), 7.43(d, 5′-H) (all aromatic H); 2.63 (s), 2.59 (s) (both Me).

***trans*-Br−Ru(dmbpy)$(CO)_2Br_2$ (5):** Dimer **2** (60 mg, 0.08 mmol) was dissolved in 4 mL of aqueous HBr, and the mixture was heated at 200°C for 10 h. A greenish yellow precipitate was filtered off from the yellow solution, washed with water, and dried in air (yield 49%). Complex **5** was analyzed by spectroscopic methods and elemental analysis. − $C_{14}H_{12}Br_2N_2O_2Ru$ (501.14): calcd. C 33.6, H 2.4, N 5.6; found C 33.7, H 2.4, N 5.8. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2062 (vs), 2000 cm^{-1} (vs) (both CO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 155.4−124.6 (five peaks, aromatic rings in dmbpy); 197.4 (CO); 22.0 (Me). − ^1H NMR ($CDCl_3$): δ = 8.97 (d, 6-H), 8.01 (s, 3-H), 7.43 (d, 5-H) (all aromatic H); 2.60 (s, Me).

***trans*(I)-Ru(dmbpy)$(CO)_2I_2$ (6):** Complex **6** was synthesized similarly to the Br-containing derivatives of complexes **1** and **2**, except that 4.5 mL of an aqueous HI solution was used as halogen source in each synthesis and the reaction temperature was maintained at 200°C for 20 h. The bright yellow precipitate, yields ca. 65% (from complex **1**) and 72% (from complex **2**), was analyzed by spectroscopic methods and elemental analysis, and identified as pure complex **6** in both syntheses. Crystals suitable for X-ray diffraction analysis were obtained from CH_2Cl_2 solution. − $C_{14}H_{12}I_2N_2O_2Ru$ (595.13): calcd. C 28.3, H 2.0, N 4.7; found C 28.7, H 2.0, N 4.9. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2056 (vs), 1999 cm^{-1} (vs) (both CO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 155.3−124.6 (five peaks, aromatic rings in dmbpy); 198.7 (CO); 22.1 (Me). − ^1H NMR ($CDCl_3$): δ = 8.94 (d, 6-H), 8.00 (s, 3-H), 7.38 (d, 5-H) (all aromatic H); 2.60 (s, Me).

***trans*(SCN)-Ru(dmbpy)$(CO)_2(SCN)_2$ (7):** 70 mg (0.17 mmol) of complex **3**, 200 mg (2.0 mmol) of KSCN, and 3 mL of water were placed in an autoclave, and the mixture was heated at 140°C for 8

h. The reaction mixture was cooled slowly to room temperature, and the bright yellow precipitate was separated by filtration and washed thoroughly with water [yield 42 mg (0.09 mmol), 54%]. The product was dried under vacuum, and analyzed by spectroscopic measurements and X-ray diffraction analysis (single crystals obtained directly from the reaction vessel without recrystallization). − $C_{16}H_{12}N_4O_2S_2Ru$ (457.49): calcd. C 42.0, H 2.6, N 12.3; found C 41.7, H 2.7, N, 11.9. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2069 (vs), 2016 (vs) (both CO); 2116 cm^{-1} (SCN). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 155.5−125.4 (five peaks, aromatic rings in dmbpy); 195.0 (CO); 22.3 (Me); 119.6 (SCN). − ^1H NMR ($CDCl_3$): δ = 8.76 (d, 6-H), 8.11 (s, 3-H), 7.51 (d, 5-H) (all aromatic H); 2.63 (s, Me).

X-ray Data Collection and Structure Solutions: X-ray diffraction data were collected at 20°C with a Nicolet R3m (complexes **4** and **6**) or an Enraf−Nonius Kappa CCD (complexes **3** and **7**) diffractometers using graphite Mo-K_α radiation (λ = 0.71073 Å). Crystals suitable for X-ray diffraction studies were carefully chosen by microscopic examination and mounted on glass fibers. For **4** and **6**, cell parameters were obtained from 25 automatically centered reflections. Intensities were corrected for background, polarization, and Lorentz factors. Data collection, data reduction and cell refinement were carried out with the P3/P4 diffractometer program V 4.27.[25] The structures were solved by direct methods. The structure solution was carried out with the SHELXS 86 program[26] and structure refinement with the SHELXL 93 program.[27] For compounds **3** and **7**, data were collected using ϕ or combined ϕ-ω scan mode with a kcd program (Enraf−Nonius). Denzo and Scalepack programs[28] were used for cell refinements and data reductions. The structure solutions (direct methods) were carried out with the SHELXS 97 program,[29] and structure refinements with the SHELXL 97.[30] For complexes **3**, **4**, **6,** and **7**, all non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms and methyl group hydrogen atoms were placed in idealized positions (aromatic C−H = 0.93 Å, methyl C−H = 0.96 Å). Decomposition of the solvated crystalline complex **3** was relatively rapid, requiring fast data collection with the X-ray diffractometer. The crystallographic data are collected in Table 1, the selected bond lengths and angles in Tables 2−3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102482 (**3**), -102483 (**4**), -102484 (**6**), -102485 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] J. G. Haasnoot, W. Hinrichs, O. Weir, J. Voss, *Inorg. Chem.* **1986**, *25*, 4140.
[2] H. Ishida, K. Tanaka, M. Morimoto, T. Tanaka, *Organometallics* **1986**, *5*, 724.
[3] M. G. Richmond, *J. Organomet. Chem.* **1993**, *457*, 121.
[4] M. Haukka, T. Venäläinen, M. Kallinen, T. A. Pakkanen *J. Mol. Catal.*, in press.
[5] J.-M. Lehn, R. Ziesel, *J. Organomet. Chem.* **1990 382**, 157.
[6] M. Ishida, K. Fujiki, T. Omba, K. Ohkubo, K. Tanaka, T. Terarda, T. Tanaka, *J. Chem. Soc., Dalton Trans.* **1990**, 2155.
[7] M.-N. Collomb-Dunnand-Sauthier, A. Deronzier, R. Ziessel, *J. Chem. Soc., Chem. Commun.* **1994**, 189.
[8] M.-N. Collomb-Dunnand-Sauthier, A. Deronzier, R. Ziessel, *Inorg. Chem.* **1994**, *33*, 2961.
[9] S. Chardon-Noblat, A. Deronzier, R. Ziessel, D. Zsoldos, *Inorg. Chem.*, in press.
[10] M. Haukka, J. Kiviaho, M. Ahlgrén, T. A. Pakkanen, *Organometallics* **1995**, *14*, 825.
[11] M. Haukka, T. Venäläinen, M. Ahlgrén, T. A. Pakkanen, *Inorg. Chem.* **1995**, *34*, 2931.
[12] M. Haukka, M. Ahlgrén, T. A. Pakkanen, *J. Chem. Soc., Dalton Trans.* **1996**, 1927, and references therein.
[13] P. Homanen, M. Haukka, T. A. Pakkanen, J. Pursiainen, R. H. Laitinen, *Organometallics*, **1996**, *15*, 4081.
[14] P. Homanen, M. Haukka, M. Ahlgrén, T. A. Pakkanen, *Inorg. Chem.* **1997**, *36*, 3794.
[15] P. Homanen, M. Haukka, M. Ahlgrén, T. A. Pakkanen, P. N. W. Baxter, R. E. Benfield J. A. Connor, *J. Organomet. Chem.* 552, **1998**, 205.
[16] S. Chardon-Noblat, A. Deronzier, Zsoldos, D;R. Ziessel, M. Haukka, T. A. Pakkanen, T. Venäläinen, *J. Chem. Soc., Dalton Trans.* **1996**, 2581.
[17] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, *115*, 6382.
[18] K. Murakoshi, G. Kano, Y. Wada, S. Yanagida, H. Miyazaki, M. Matsumoto, S. Murasawa, *J. Electroanal. Chem.* **1995**, *396*, 27.
[19] P. K. Ghosh, T. G. Spiro, *J. Am. Chem. Soc.* **1980**, *102*, 5543.
[20] R. Ziessel, *Photosensitization and Photocatalysis Using Inorganic And Organometallic Compounds* (Eds.: K. Kalyanasundaram, M. Grätzel), Kluwer, Academic Publishers, Dordrecht, **1993**.
[21] O. Kohle, S. Ruile, M. Gräzel, *Inorg. Chem.* **1996**, *35*, 4779.
[22] http://www. berghofusa.com
[23] J. Chatt, B. L. Shaw, A. E. Field, *J. Chem. Soc.* **1964**, 3466.
[24] J. M. Kelly, C. M. O'Connell, J. G. Vos, *Inorg. Chim. Acta* **1982**, *64*, L75.
[25] *P3/P4 Diffractometer Program V4.27*, Siemens Analytical X-ray Instruments, **1989−1991**.
[26] G. M. Sheldrick, *SHELXS 86, Program for Crystal Structure Determination*, University of Göttingen, **1986**.
[27] G. M. Sheldrick, *SHELXL 93, Program for Crystal Structure Refinement*, University of Göttingen, **1993**.
[28] Z. Otwinowski, W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode" in *Methods in Enzymology*, vol. 276 ("Macromolecular Crystallography"), part A (Eds.: C. W. Carter Jr., R. M. Sweet), Academic Press, **1997**, p. 307−326.
[29] G. M. Sheldrick, *SHELXS 97*, Program for Crystal Structure Determination, University of Göttingen, **1997**.
[30] G. M. Sheldrick, *SHELXL 97*, Program for Crystal Structure Refinement, University of Göttingen, **1997**.
[31] M.-N. Collomb-Dunand-Sauthier, A. Deronzier, *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *319*, 347.
[32] S. C. Rawle, S. R. Cooper, *J. Chem. Soc., Chem. Commun.* **1987**, 308.

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