Ruthenium(II) Bipyridine Complexes: Synthesis and Characterization of $Ru(bpy)(CO)_2(SCN)_2$, $Ru(dmbpy)(CO)_2Cl_2$, and $Ru(dmbpy)(CO)_2(NCS)H$ (bpy = 2,2′-Bipyridine; dmbpy = 6,6′-Dimethyl-2,2′-bipyridine)

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Summary: Ru(II) bipyridine complexes were synthesized and their spectroscopic properties studied. The replacement of 2,2′-bipyridine (bpy) by 6,6′-dimethyl-substituted 2,2′-bipyridine (dmbpy) is suggested to change the steric and electronic factors involved in these complexes, which in turn affect the coordination ability of Ru. In the case of thiocyanate ligand, the metal center is able to coordinate to either its S or N end, the bonding mode being dependent on both steric and electronic factors.

Introduction

$[Ru(CO)_3Cl_2]_2$ has been shown to be a useful source of new Ru(bpy) complexes.[1] $Ru(bpy)(CO)_2Cl_2$, which is one of the most versatile of these, has been further modified by ligand substitution reactions for the purpose of investigating the overall reactivity of Ru(II) complexes and improving their activity in various catalytic processes, such as the water-gas shift reaction and electrochemical or photochemical reduction of CO_2.[2] Although $Ru(bpy)(CO)_2Cl_2$ is relatively stable, the CO and Cl^- ligands can be replaced by NO and other halogen or pseudohalogen ligands, respectively.[3] Recent years have seen a growing interest in thiocyanato-substituted Ru complexes owing to their intriguing photoelectrochemical properties.[4] The general coordination chemistry of thiocyanate ligands is well-known, with IR spectroscopy being widely used to determine the type of thiocyanate bonding (three possibilities: N-bonded, S-bonded, or bridged). In contrast, only a few detailed studies on Ru thiocyanate complexes have been based on X-ray diffraction measurements.[5] To the best of our knowledge, only N-bonded and bridged thiocyanates have been characterized by single-crystal X-ray diffraction techniques.[5]

We have investigated the reaction of $Ru(bpy)(CO)_2Cl_2$ with KSCN in aqueous solution and analyzed the structure and spectroscopic properties of the new ruthenium(II) thiocyanates that resulted. Furthermore, we have examined the effect on the formation of Ru(II) complexes of replacing bipyridine by 6,6′-dimethyl-2,2′-bipyridine (dmbpy).

Experimental Section

Materials. The parent ruthenium compound $Ru(bpy)(CO)_2Cl_2$ was prepared by a literature method[1] and was shown by NMR spectroscopy to have a *trans*(Cl) structure.[1] The reagents and solvents were analytical grade and were used as received. $[Ru(CO)_3Cl_2]_2$ was purchased from Johnson & Matthey, and KSCN, from J. T. Baker. 6,6′-Dimethylbipyridine was synthesized as follows: 250 mL of water was warmed to 40 °C, and (6,6′-dimethyl-2,2′-bipyridine-*N*,*N*′)nickel dibromide[6] (15 g, 37.2 mmol) was added. The solution was kept at 40 °C for 90 min, during which time a green suspension formed. This was filtered and the precipitate washed with a small amount of chloroform. The crude product was extracted four times with 60 mL portions of chloroform, and the organic phase was dried with $MgSO_4$. After filtration the solvent was evaporated, and 6,6′-dimethyl-2,2′-bipyridine (6.0 g, 87%) was recrystallized from petroleum ether. Ligand substitution reactions were carried out in a Berghof 60 mL pressure vessel with PTFE liner. All manipulations were performed in air.

Preparation of the Complexes. $Ru(bpy)(CO)_2(SCN)_2$ (1). A mixture of $Ru(bpy)(CO)_2Cl_2$ (50 mg, 0.13 mmol), KSCN (30 mg, 0.31 mmol), and water (3 mL) was placed in a pressure vessel. The suspension was heated for 6 h at 100 °C and slowly cooled to room temperature (∼4.5 °C/h). The resulting orange-yellow solid was filtered out and carefully washed with water to remove the unreacted KSCN. Recrystallization of the precipitate (yield of the raw product about 40%) from dichloromethane yielded light yellow crystals suitable for X-ray diffraction measurement. The same product could also be obtained using an acetone−water mixture (1:1) as a solvent. Anal. Calcd for **1**: C, 39.16; N, 13.05; H, 1.88. Found: C, 39.21; N, 13.13; H, 1.81. IR (in CH_2Cl_2): ν_{CO}, 2071 (s) and 2020 (s) cm^{-1}, ν_{SC-N} 2116 (m) cm^{-1}. ^1H NMR for bpy (in DMSO): δ 9.2 (d), 8.2 (d), 8.1 (t), 7.7 (t) ppm. $^{13}C\{^1H\}$ NMR: for bpy (in DMSO), five singlets at 154−124 ppm; for CO, δ 194 (s) ppm; for thiocyanate, δ 118 (s) ppm.

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Ru(dmbpy)$(CO)_2Cl_2$ (2) (dmbpy = 6,6′-Dimethyl-2,2′-bipyridine). $[Ru(CO)_3Cl_2]_2$ (257 mg, 0.5 mmol) was added to 25 mL of THF, and the solution was refluxed for 45 min under nitrogen. Dmbpy (380 mg, 2.1 mmol) was separately dissolved in 15 mL of THF and added to the above solution with a syringe. The resulting yellowish-brown mixture was refluxed for 4.5 h and then allowed to cool to room temperature. Evaporation of the excess solvent to 15 mL resulted in the precipitation of a light yellow solid, which was filtered out, washed with small amounts of methanol, and air-dried (yield of the raw product about 66%). Well-formed single crystals were obtained by recrystallization from dichloromethane. Anal. Calcd for **2**: C, 40.79; N, 6.80; H, 2.93. Found: C, 40.94; N, 6.58; H, 2.88. IR (in CH_2Cl_2): ν_{CO}, 2063 (s) and 1999 (s) cm^{-1}. ^1H NMR for dmbpy (in $CDCl_3$): δ 8.2 (d), 7.7 (t), 7.1(d), and 2.6 (s) ppm. $^{13}C\{^1H\}$ NMR: for dmbpy (in $CDCl_3$), five singlets at 154−124 ppm and one singlet at 25.3 ppm; for CO, δ 191.4 (s) ppm.

Ru(dmbpy)$(CO)_2$(NCS)H (3). $[Ru(CO)_3Cl_2]_2$ (500 mg, 1.0 mmol) was introduced to 20 mL of ethylene glycol, and the mixture was gently heated under nitrogen. The resulting yellow solution was added with a syringe to a mixture of dmbpy (1.1 g, 6.0 mmol) and ethylene glycol (20 mL). The reaction mixture was then heated at 90 °C for 2 days, after which it was allowed to cool to room temperature (1-day period, continuously under nitrogen). During this time, a light yellow, needlelike precipitate was formed. The solid product was separated by filtration, washed with methanol, and dried in air. Structural characterization of the product was carried out by IR and NMR measurements. No single crystals suitable for X-ray analysis were obtained despite several attempts with various solvents and solvent mixtures. On the basis of spectroscopic studies, the compound was identified as Ru(dmbpy)$(CO)_2$(Cl)H (**4**). Anal. Calcd for **4**: C, 44.51; N, 7.42; H, 3.47. Found: C, 44.22; N, 7.33; H, 3.72.

A 100 mg (0.3 mmol) sample of compound **4**, KSCN (60mg, 0.6 mmol), and 4 mL of water were placed in a 60 mL pressure vessel. The mixture was heated at 100 °C for 5 h and cooled slowly to room temperature. The resulting brown powder was separated by filtration, washed with small amounts of water, and dried in air. The structure of the compound was verified by X-ray diffraction analysis (crystals obtained from CH_2Cl_2 solution). Anal. Calcd for Ru(dmbpy)$(CO)_2$(NCS)H: C, 44.99; N, 10.49; H, 3.27. Found: C, 44.52; N, 10.23; H, 3.23. IR (in CH_2Cl_2): ν_{CO}, 2040 (s) and 1969 (s) cm^{-1}; ν_{SC-N}, 2109 (m) cm^{-1}. ^1H NMR for hydride: δ −10.5 (s) ppm.

Spectroscopic Studies. Infrared spectra were measured with a Nicolet Magna 750 FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer with DMSO-d_6 or $CDCl_3$ used as solvent.

X-ray Data Collection and Structure Solution for Ru(bpy)$(CO)_2(SCN)_2$ (1), Ru(dmbpy)$(CO)_2Cl_2$ (2) (dmbpy = 6,6′-Dimethyl-2,2′-bipyridine), and Ru(dmbpy)$(CO)_2$(NCS)H (3). X-ray diffraction data were collected with Nicolet R3m (compounds **1** and **2**) and Syntex $P2_1$ (compound **3**) diffractometers using graphite monochromatized Mo Kα radiation (λ = 0.710 73 Å). Crystals suitable for X-ray diffraction studies were carefully chosen by microscopic examination and mounted on glass fibers. All crystals studied were crystallized from CH_2Cl_2 solutions by slow evaporation of the solvent. Cell parameters were obtained from 25 automatically centered reflections. Intensities were corrected for background, polarization, and Lorentz factors. An experimental absorption correction was measured for all complexes but used only for **3**. Data collection, data reduction, and cell refinement were carried out with the SHELXTL PLUS program for **1** and **2** and with the P3/P4 diffractometer program V4.27 for **3**.[7] The structures were solved by direct methods. Structure solution was carried out with the SHELXS 86 program, and structure refinement, with the SHELXL 93 program.[7] The non-hydrogen atoms were refined anisotropically on F^2. Organic hydrogens in **1** and **3** were placed in idealized positions (aromatic C−H = 0.93 Å). All hydrogens in **2**, methyl group hydrogens, and the hydride in **3** were located from the difference Fourier maps and refined isotropically with fixed isotropic displacement parameters (U = 0.06 Å^2 for **2**, U = 0.08 Å^2 for **3**). The complexes studied in this work are stable in air, and no decompostion upon exposure to X-rays or air was observed during the data collection. The crystallographic data are summarized in Table 1.

Table 1. Crystallographic Data for Ru(bpy)$(CO)_2(SCN)_2$ (1), Ru(dmbpy)$(CO)_2(Cl)_2$ (2), and Ru(bpy)$(CO)_2$(NCS)H (3)

	1	**2**	**3**
fw	429.43	412.23	400.41
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	7.255(5)	8.767(3)	8.670(2)
b, Å	8.472(5)	7.566(2)	9.437(4)
c, Å	13.458(7)	23.828(7)	19.937(6)
α, deg	83.64(5)	90	90
β, deg	78.03(5)	95.74(3)	90.50(2)
γ, deg	75.27(5)	90	90
V, Å^3	781.1(8)	1572.61(8)	1631.2(9)
Z	2	4	4
D_{calc}, g/cm^3	1.826	1.741	1.631
cryst size, mm	0.1 × 0.1 × 0.2	0.2 × 0.3 × 0.4	0.1 × 0.5 × 0.6
color	yellow	yellow	yellow
μ, mm^{-1}	1.28	1.34	1.10
2θ limits, deg	5−45	5−55	5−55
h range	0−7	0−11	0−11
k range	−8 to 9	0−9	0−12
l range	−13 to 14	−30 to 30	−25 to 25
no. of unique rflns	2045	3612	3755
no. of obsd data[a]	1385	2430	1972
no. of params	209	226	220
$R1$	0.0507	0.0454	0.0419
w$R2$[b]	0.0787	0.0859	0.0921
x	0.0237	0.0402	0.0563
y	0.0000	0.0000	0.0000
goodness of fit	1.044	1.059	0.814

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

Results and Discussion

Ru(bpy)$(CO)_2Cl_2$ reacts with KSCN in aqueous solution to yield Ru(bpy)$(CO)_2(SCN)_2$ (**1**). The coordination geometry of Ru in this complex is octahedral (Figure 1). Ru−C and Ru−N bond lengths as well as the bipyridine "bite angle" are typical of those for Ru bpy complexes reported earlier.[1,3a] CO ligands are coordinated *trans* to the bipyridine nitrogens confirming the chemical equivalence of the bpy rings suggested by the NMR study. Two pseudohalide ligands are in a *trans* position and coordinated to the metal via sulfur atoms. To the best of our knowledge, this is the first structurally characterized Ru thiocyanate complex with terminal S-bound thiocyanate groups. The Ru-S bond lengths are 2.419(3) and 2.434(3) Å, a result comparable to the Ru-S distances in Ru(II) thiourea complex (mean Ru-S

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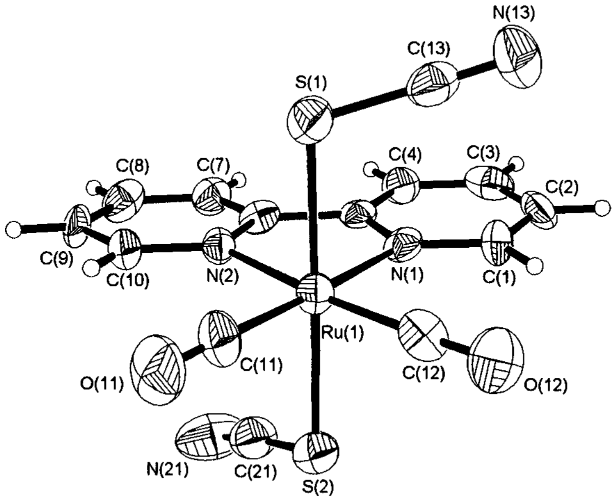

Figure 1. Structure of $Ru(bpy)(CO)_2(SCN)_2$ (**1**).

Table 2. Selected Bond Lengths (Å) for $Ru(bpy)(CO)_2(SCN)_2$ (1), $Ru(dmbpy)(CO)_2(Cl)_2$ (2), and $Ru(bpy)(CO)_2(NCS)H$ (3)

	1	**2**	**3**
Ru(1)−X(1)[a]	2.419(3)	2.390(2)	2.083(4)
Ru(1)−X(2)[b]	2.434(3)	2.397(2)	1.859(5)
Ru(1)−N(1)	2.107(7)	2.158(3)	2.225(4)
Ru(1)−N(2)	2.137(7)	2.155(4)	2.163(3)
Ru(1)−C(11)[c]	1.892(11)	1.873(6)	1.611(40)
Ru(1)−C(12)	1.898(11)	1.872(5)	1.875(5)
C(11)−O(11)	1.124(10)	1.131(7)	
C(12)−O(12)	1.140(10)	1.138(6)	1.123(6)
S(1)−C(13)	1.671(11)		1.637(5)
S(2)−C(21)	1.649(12)		
C(13)−N(13)	1.156(11)		1.112(5)
C(21)−N(21)	1.174(12)		
C(1)−C(61)		1.498(7)	1.497(7)
C(10)−C(62)		1.484(8)	1.481(8)

[a] X(1) = S(1) for **1**, Cl(1) for **2**, and N(13) for **3**. [b] X(2) = S(2) for **1**, Cl(2) for **2**, and C(33) for **3**. [c] C(11) = H(11) for **3**.

distance 2.421(3) Å).[8] Both bond lengths are long as compared to the range reported for Ru(II)−S bonds (2.262(1)−2.393(3) Å).[9] Even longer Ru-S distances have recently been observed for a thiocyanate-bridged Ru(IV) dimer (2.483(4) and 2.490(4) Å).[5c] Electronic factors have been reported to affect the stability of metal−thiocyanate bonds:[10] Effects decreasing the electron density in the metal center are suggested to change the bonding mode of thiocyanate ligand from M−SCN to M−NCS. It is possible therefore that the presence of strongly π-accepting ligands such as CO and the increasing oxidation state of the metal may lengthen the Ru−S bond distances.

The Ru−S−C angles (104.3(4) and 105.8(4)°) appear to be normal for S-bound thiocyanate complexes with other metals.[11−13] Selected bond lengths and angles for complexes **1**−**3** are summarized in Tables 2 and 3.

As described by several authors, the bonding mode of the thiocyanate group can be determined by IR spectroscopy.[14] The C−N stretching band (ν_{SC-N}), the S−C stretching band (ν_{S-CN}), and the NCS deformation mode (δ_{SCN}) as well as the integrated intensity of ν_{SC-N} have been used as indicators of the SCN bonding mode.[8] However, ν_{S-CN} and δ_{SCN} are often weak and are masked by other absorptions, such as those of solvent or other ligands. The C−N stretching is generally at lower frequency in N-bonded complexes (around 2050 cm^{-1}) than in S-bonded complexes (around 2100 cm^{-1}), but also this criterion must be applied with caution since the frequencies are sensitive to other factors such as spin state of the metal as described by Maroney et al. for Fe thiocyanates.[11] With some exceptions the *cis* and *trans* isomers can be distinguished by IR spectroscopy: thus ν_{SC-N} usually appears as a single band in the spectrum of the *trans* isomer.

Table 3. Selected Bond Angles (deg) for $Ru(bpy)(CO)_2(SCN)_2$ (1), $Ru(dmbpy)(CO)_2(Cl)_2$ (2), and $Ru(bpy)(CO)_2(NCS)H$ (3)

	1	**2**	**3**
X(1)−Ru(1)−X(2)[a,b]	177.7(1)	174.4(1)	175.3(2)
X(1)−Ru(1)−N(1)	89.0(2)	85.1(1)	87.9(2)
X(1)−Ru(1)−N(2)	87.0(2)	85.8(1)	87.5(1)
X(1)−Ru(1)−C(11)[c]	90.2(3)	90.7(2)	95.2(14)
X(1)−Ru(1)−C(12)	93.0(3)	91.3(2)	92.7(2)
N(1)−Ru(1)−N(2)	77.7(3)	77.3(1)	75.3(1)
N(1)−Ru(1)−C(12)	95.3(4)	99.2(2)	108.4(2)
N(2)−Ru(1)−C(11)[c]	99.0(4)	101.0(2)	98.2(14)
C(11)−Ru(1)−C(12)[c]	88.0(4)	82.3(2)	78.13(14)
N(1)−Ru(1)−C(11)[c]	176.6(4)	175.6(2)	172.7(14)
N(2)−Ru(1)−C(12)	173.0(4)	175.6(2)	176.3(2)
N(1)−C(1)−C(61)		120.4(4)	118.3(5)
N(2)−C(10)−C(62)		119.5(5)	119.9(5)
X(1)−C(13)−N(13)[a,d]	177.8(10)		178.8(4)
Ru(1)−X(1)−C(13)[a]	104.3(4)		177.7(4)
Ru(1)−S(2)−C(21)	105.8(4)		
S(2)−C(21)−N(21)	173.2(10)		

[a] X(1) = S(1) for **1**, Cl(1) for **2**, and N(13) for **3**. [b] X(2) = S(2) for **1**, Cl(2) for **2**, and C(33) for **3**. [c] C(11) = H(11) for **3**. [d] N(13) = S(1) for **3**.

The IR spectrum of **1** shows a strong single band at 2116 cm^{-1} assignable to ν_{SC-N} for the S bonded *trans* thiocyanate complex. The shift of the CO stretching bands (ν_{CO}) to higher frequency relative to the parent ruthenium complex $Ru(bpy)(CO)_2Cl_2$[1] (2071 and 2020 cm^{-1} vs 2066 and 2003 cm^{-1}, respectively) also indicates the coordination of thiocyanate group to the complex. The high frequency shift of (ν_{CO}) may be due to electronic effects. The C−O bonds are strengthened by π-bonding of the SCN groups withdrawing electron density from the d-orbitals of the metal thus reducing the π-back bonding of M−CO.

$Ru(bpy)(CO)_2(SCN)_2$ crystallizes in a different space group with SCN$^-$ groups pointing in slightly different directions than in the above structure indicating virtu-

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[15] Crystal data for $Ru(bpy)(CO)_2(SCN)_2$ (rotamer of **1**): M_r 429.43, monoclinic, space group $P2_1/c$; $a = 7.091(4)$, $b = 20.853(7)$, $c = 11.290(5)$ Å; $\beta = 106.15(4)$°, $V = 1603.6(10)$ Å^3, $Z = 4$, $D_{calc} = 1.779$ g/cm^3, crystal source dichloromethane, crystal size = 0.2 × 0.2 × 0.3, brownish yellow, Mo Kα radiation ($\lambda = 0.709\ 34$ Å), 2θ limits = 5−50°, no. of unique reflections 3178, no. of observed data 2850, no. of parameters 208, $\mu = 1.779$ mm^{-1}, $R1 = 0.0782$, $wR2 = 0.1704$, GooF = 1.001. Complete structural data are available as Supporting Information.

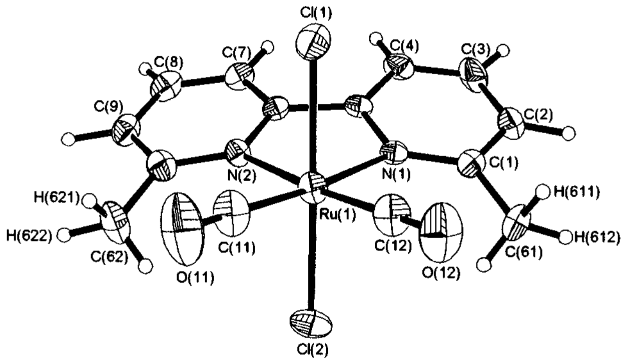

Figure 2. Structure of Ru(dmbpy)(CO)$_2$(Cl)$_2$ (**2**).

ally free rotation of the thiocyanate ligands.[15] Since no steric factors are present to prevent the rotation of the thiocyanate groups, the orientation of these ligands is most likely determined by packing effects.

6,6′-Dimethyl-2,2′-bipyridine is able to coordinate to Ru despite the bulky methyl substituents in the 6,6′-position in the bpy rings; Ru(dmbpy)(CO)$_2$(Cl)$_2$ (**2**) is formed in mild conditions, and the complex is relatively stable. The methyl groups nevertheless appear to contribute some strain to the bipyridine ring system, particularly here where two carbonyl ligands are coordinated *trans* to bpy nitrogens (Figure 2). The two pyridine subunits in bpy are slightly tilted, with the dihedral angle between the py planes about 16°. The whole ligand system is bent away from the plane formed by N(1), N(2), C(11), and C(12). In addition, the C(11)−Ru(1)−C(12) angle is considerably smaller than in the unsubstituted Ru bpy complex *cis*(CO),*trans*(Cl)-Ru(bpy)(CO)$_2$(Cl)$_2$ (82.3(2)° vs 88.0(8)°). Otherwise the coordination sphere around Ru is rather typical as compared with the Ru(II) complexes mentioned above.

The IR spectrum of **2** shows strong carbonyl stretching bands at 2063 and 1999 cm^{-1} (CH$_2$Cl$_2$ solutions). Compared with the spectrum of unsubstituted Ru bpy complex, the bands are slightly shifted to lower frequency. Again, this shift can be conveniently explained by changes in π-bonding between Ru and the CO groups. The two substituent methyl groups are electron donating, thus distributing excess negative charge to the π^* orbitals of the CO ligands via bpy rings and the metal center.

The coordination sphere of Ru is again octahedral in Ru(dmbpy)(CO)$_2$(NCS)H (**3**) (Figure 3). ^{1}H NMR measurement revealed the presence of hydride ligand in the complex (δ(Ru−H) −10.5 ppm). In this case, the hydride ligand could be located from the difference Fourier map. The chemical dissimilarity of the bpy rings indicated by the NMR study is due to the different ligands, H and CO, lying *trans* to the bpy nitrogens. The strong trans effect of the hydrogen ligand[16] tends to lengthen the Ru−N bond (2.225(4) Å) even relative to the carbonyl ligand at the same position (Ru−N bond length *trans* to CO is 2.163(3) Å).

The thiocyanate group in Ru(dmbpy)(CO)$_2$(NCS)H is N-bonded with a nearly linear Ru−NCS arrangement (Ru−N−C and N−C−S angles 177.7(4) and 178.8(4)°, respectively). The metal−NCS bond angles in metal complexes have been reported to vary from 130 to 180°, the linear bonds being expected when the metal can donate d$_\pi$ electron density to the π accepting thiocyanato group as in the case of Ru(II).[17] The Ru−NCS bond length in **3** (2.083(4) Å) is somewhat longer than the bond lengths observed for Ru(bpy)$_2$(NCS)$_2$ complexes (Ru−N distances from 2.025(5) to 2.059(6) Å),[5a] again indicating the trans effect of the carbonyl ligand.

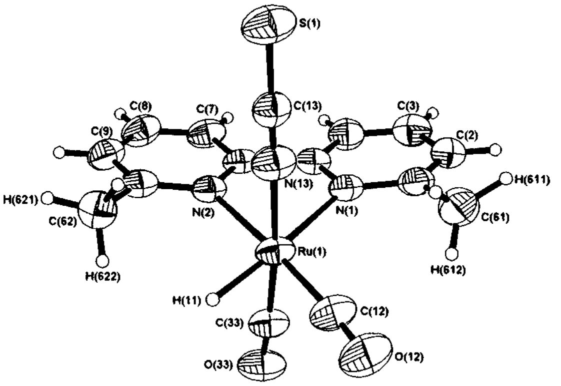

Figure 3. Structure of Ru(dmbpy)(CO)$_2$(NCS)H (**3**).

Although the two methyl groups in dmbpy do not seem to prevent the coordination of dmbpy to the metal in Ru(dmbpy)(CO)$_2$(NCS)H (or Ru(dmbpy)(CO)$_2$(Cl)$_2$), it may be that these bulky groups affect the bonding mode of the thiocyanate ligand. Sterically hindering ligands near the metal center are likely to stabilize the N-bonded linear structure of the pseudohalogen ligand.

The IR-spectrum of Ru(dmbpy)(CO)$_2$(NCS)H (**3**) consists of three distinctive peaks: two sharp CO stretching bands (2040 cm^{-1} and 1969 cm^{-1}, CH$_2$Cl$_2$ solution) and one adsorption at 2109 cm^{-1} (medium intensity, broad) assigned to $\nu_{\mathrm{SC-N}}$. As noted above, IR spectroscopy must be used with caution in determining the bonding mode of the thiocyanate group. In this case, the $\nu_{\mathrm{SC-N}}$ frequencies of complexes **1** and **3** are at the same spectral region, although the binding modes of the pseudohalide groups are different.

Conclusions

Ru(II) bipyridine complexes are easily modified by ligand exchange reactions or by adding various substituents to bpy ligands. These modifications may alter both the electronic and the steric factors involved in the complexes, which in turn may change the coordination ability of the metal center. In the case of thiocyanate ligand, ruthenium is able to coordinate either the S or N end; both electronic and steric effects determine the bonding mode of this ligand.

Supporting Information Available: Tables of atomic positional and *U* parameters, bond lengths and angles, anisotropic displacement coefficients, and H coordinates and *U* values for **1**−**3** and tables of crystallographic data, atomic coordinates and *U* values, bond lengths and angles, and anisotropic displacement coefficients and a figure showing the structure for Ru(bpy)(CO)$_2$(SCN)$_2$ (rotamer of **1**) (13 pages). Ordering information is given on any current masthead page.

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