Inorg. Chem. **2001,** *40,* 6139−6143

Oxidative Dehydrogenation on the α-Carbon of 4-Pyridylacetonitrile Complexes of Pentaammineruthenium(II)

Scot Liu,[†] Sheena Lee,[†] Sabina Wang,[†] Andrew Yeh,*,[†] Han-Mou Gau,[‡] and Ming-Yuan Shao[‡]

Departments of Chemistry, Tunghai Christian University, Taichung, Taiwan, ROC, and
National Chung Hsing University, Taichung, Taiwan, ROC

Received August 16, 2000

The oxidation of $Ru(NH_3)_5NCCH_2py^{2+}$ in 0.10 M HCl turns the solution from yellow to greenish blue with an absorption at $\lambda = 791$ nm. The absorbance reaches its maximum value when the complex undergoes a two-electron oxidation. The IR and ^1H NMR spectra of the product indicate that the metal center remains as Ru(II) and that the ligand is oxidized. The ^{13}C NMR spectral results suggest that the oxidation product is $[(NH_3)_5RuNCC(pyH)C(pyH)CNRu(NH_3)_5](ClO_4)_6$. Cyclic voltammetry of the product solution also indicates that the oxidation proceeds in two one-electron steps corresponding to $[Ru(III),Ru(II)] + e^- \rightleftharpoons [Ru(II),Ru(II)]$ and $[Ru(III),Ru(III)] + e^- \rightleftharpoons [Ru(III),Ru(II)]$. The structure of the product in deprotonated form $[(NH_3)_5RuNCC(py)C(py)CNRu(NH_3)_5](ClO_4)_4(H_2O)_2$ was determined crystallographically. $[(NH_3)_5RuNCC(py)C(py)CNRu(NH_3)_5](ClO_4)_4(H_2O)_2$ crystallizes in the orthorhombic *Pbca* space group with cell constants $a = 13.7138$ (16) Å, $b = 15.7553$ (18) Å, $c = 17.831(2)$ Å, and $Z = 4$. A mechanism for the oxidation has been proposed on the basis of the kinetic studies in the region of 0.01−0.20 M acid concentrations.

Introduction

The organonitrile complexes of pentaammineruthenium(II) have caught the attention of many inorganic chemists because of its catalytic effect on the hydrolysis of the nitriles upon oxidation.[1] The ability of Ru(II) for back-donation makes the coordination of nitriles highly favorable.[2] However, the oxidation of Ru(II) produces unstable Ru(III)−nitrile complexes which are activated toward the nucleophilic attack by water, forming ruthenium(III) amide complexes.[3,4] The amides can be liberated spontaneously from the metal center by further reduction of the complexes back to Ru(II).[4] Recently, we have prepared the $Ru(NH_3)_5NCCH_2py^{2+}$ complex for the purpose of investigating the substituent effect on the rate of ligand hydrolysis of the oxidized species. However, the solution turned blue upon oxidation and no trace of nitrile hydrolysis was observed. Moreover, the absorption of this blue colored species reached its maximum when equimolar amounts of oxidant were used. The metal remained as Ru(II) with $[(NH_3)_5Ru^{II}NCC(pyH){=}C(pyH)CNRu^{II}(NH_3)_5]^{6+}$ as the final product when the oxidation was performed in acidic medium. In this work we wish to report results based on the thermodynamic and kinetic studies and propose a possible mechanism which leads to this product.

Experimental Section

Materials. 4-Pyridylacetonitrile hydrochloride salt was purchased from Aldrich. $[Ru(NH_3)_5NCCH{=}CH_2](ClO_4)_2$ was prepared according to the literature method.[5] Ion exchange was performed on a glass column with purified Bio-Rad Ag 50WX2 200−400 mesh cation resin in the protonated form. All other chemicals were of reagent grade and were used without further purification.

Synthesis. Ligands. *N*-Methyl-4-pyridylacetonitrile iodide was prepared by adding 5.0 g of powdered 4-pyridylacetonitrile hydrochloride to a flask containing 60 mL of DMF. A 10 mL volume of triethylamine was added dropwise to the stirred solution to neutralize the hydrochloric acid. The Et_3NHCl thus formed was filtered out when the neutralization was complete. The filtrate was concentrated in a rotary evaporator to ∼50 mL. The solution was cooled in an ice bath, and 16 mL of methyl iodide was added dropwisely. The reaction was allowed to proceed for 4 h in an ice bath with constant stirring, and then the solution was stored in a refrigerator for 24 h. The desired solid precipitated out, and it was filtered off and washed with ethanol and ether. The product was recrystallized from hot water with the addition of a small amount of methanol to facilitate the dissolution. Yield: 5.62 g (67%). Anal. Calcd for $C_8H_9N_2I$: C, 37.0; H, 3.49; N, 10.8. Found: C, 37.2; H, 3.52; N, 10.2.

2,2-Dimethylpyridylacetonitrile was prepared by a method similar to that for 2,2,3-triphenylpropionitrile[6] with modifications. A small piece of sodium metal was added under to a stirring three-necked flask containing 100 mL of liquid ammonia cooled in a dry ice−acetone bath. After the appearance of a blue color, a small amount of $FeCl_3\cdot 6H_2O$ was added, followed by a few small pieces of sodium. After all the sodium had been converted to amide, 3.0 g of 4-pyridylacetonitrile was added and the resulting solution was stirred for 5 min in the dry ice bath. To this was slowly added 20 mL of anhydrous ether solution containing 3.0 mL of methyl iodide. After being cooled in the dry ice bath with constant stirring for another 1 h, the solution was warmed to room temperature to allow the ammonia to evaporate. A 50 mL volume of anhydrous ether was then added, and the solution was transferred to a separation funnel. A 60 mL amount of water was added to the ether solution to remove the impurities whereupon the orange-yellow product

---

[†] Tunghai Christian University.

[‡] National Chung Hsing University.

(1) For a recent review, see the following: de Rocha, Z. N.; Chierecato, G., Jr.; Tfouni, E. *Adv. Chem. Ser.* **1997**, *253*, 297.

(2) Charke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227.

(3) Zanella, A. W.; Ford, P. C. *Inorg. Chem.* **1975**, *14*, 42.

(4) Diamond, S. E.; Grant, B.; Tom, G. M.; Taube, H. *Tetrahedron Lett.* **1974**, *46*, 4025.

(5) Ford, P. C.; Foust, R. D., Jr.; Charke, R. E. *Inorg. Chem.* **1970**, *9*, 1933.

(6) Hauser, C. R.; Dunnavant, W. R. *Org. Synth.* **1959**, *39*, 73.

10.1021/ic000944p CCC: $20.00

remained in the ether layer. The ether was then removed by rotary evaporation to dryness, and the orange product was collected. The crude product was purified on a silica gel column (Sephadex) prewashed with *n*-hexane. After impurities were eluted with 20% (EtOAc−hexane), the eluant collected with 30% EtOAc−hexane was concentrated by vacuum evaporation whereby a light yellow liquid was obtained. Yield: 2.21 g (60%). Anal. Calcd for $C_9H_{10}N_2$: C, 74.0; H, 6.90; N, 19.2. Found: C, 73.2; H, 6.63; N, 18.9.

Ruthenium(II) Complexes. We have tried a variety of counterions to precipitate the Ru complexes. However, perchlorate seems to be the only salt from which we can get acceptable elemental analysis results. Caution! Ruthenium perchlorate salts, especially those of Ru(II) complexes, may detonate upon scratching or heating.

$[Ru(NH_3)_5NCCH_2pyR](ClO_4)_3$ (R = H^+, CH_3). An 80 mg sample of silver oxide was suspended in 5 mL of hot water, and concentrated trifluoroacetic acid was added dropwise until all the solid was dissolved. A 100 mg amount of $[Ru(NH_3)_5Cl]Cl_2$[7] was then added with stirring to facilitate the dissolution. The silver chloride which formed was filtered off after cooling the solution in an ice bath, and the residue was washed with 3 mL of water. The filtrate, together with the washings, was reduced over zinc amalgam under an argon atmosphere for 20 min. At this point 0.60 g of the ligand was added and the pH of the solution was adjusted to ∼1 with 2 M NaOH. The reaction was allowed to proceed for 1 h, and the solution was then transferred anaerobically to 1 mL of predeaerated solution containing 2 g of $NaClO_4$. Upon cooling of the solution in an ice bath under argon atmosphere for 1 h, the solid formed was filtered off and washed with ethanol and ether. For R = CH_3, the product was further washed with methanol several times before drying with ether in order to remove the $[NCCH_2pyCH_3]ClO_4$ salt which might also precipitate along with the Ru(II) complex. The products were recrystallized from 0.1 M $HClO_4$ by using inert-atmosphere techniques. Yields: 0.16 g (76%) for R = H^+; 0.13 g (61%) for R = CH_3.

$[Ru(NH_3)_5NCR](ClO_4)_2$ (R = $PhCH_2$, PhCHOH, PhC=O) were prepared by using the procedure outlined for the pyridylacetonitrile complexes with the exception that, following the addition of the ligands to the reduced ruthenium solution, 5 mL of ethanol was added to the reaction mixtures to facilitate the dissolution of the ligands. The products were recrystallized from hot water.

$[(Ru(NH_3)_5)_2NCC(pyR){=}C(pyR)CN](ClO_4)_6$ (R = H^+, CH_3). A 0.15 g amount of $[Ru(NH_3)_5NCCH_2pyR](ClO_4)_3$ was dissolved in 15 mL of predeaerated 0.1 M HCl, and an equimolar amount of $Na_2S_2O_8$ was added to the solution. After the reaction was allowed to proceed for 2 h, the solution was transferred to a Bio-Rad AG 50W-X2 cation-exchange columm. The greenish binuclear complexes were eluted with 2 M HCl, and the eluants were concentrated on a rotary evaporator to ∼20 mL. A 2 g amount of $NaClO_4$ was added, and the solution was cooled in an ice bath for 1 h. The precipitates thus formed were filtered off, washed with ethanol and ether, and dried in a vacuum desiccator for 2 h. Yields: 0.12 g (40%) for R = H^+; 0.10 g (33%) for R = CH_3.

Dark blue crystals of $[(NH_3)_5RuNCC(py)C(py)CNRu(NH_3)_5](ClO_4)_4(H_2O)_2$ used for crystallographic study were obtained by diffusing 10 mL of methanol into an equivolume of aqueous solution of the binuclear complex (by dissolving 5 mg of $[(NH_3)_5RuNCC(pyH)C(pyH)CNRu(NH_3)_5](ClO_4)_6$ in 15 mL of H_2O), which was cooled in the refrigerator for 2 weeks.

Instruments. UV−vis spectra were measured on a Hitachi U-2000 spectrophotometer. Near-IR spectra were measured on a Hitachi U3501 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1725X FT-IR spectrophotometer in KBr pellets. The ^1H and ^{13}C NMR spectra were obtained in D_2O or DMSO-d_6 on a Varian Unity 300 spectrophotometer. Electrochemistry was performed on a PAR model 273A potentiostat/galvanostat system as described before.[8]

Kinetic Measurements. The rates of the oxidation of $[Ru(NH_3)_5NCCH_2pyR]^{3+}$ complexes were carried out on the Hitachi U-2000 spectrophotometer. The measurements were performed at an ionic strength of 1.0 M (HCl−LiCl) and $T = 25$ °C with acid concentrations varied from 0.01 to 0.2 M. $[Ru(NH_3)_5NCCH_2pyR]^{3+}$ complexes were oxidized with an equimolar amount of peroxydisulfate ion, and reactions were monitored by following the formation of $[(Ru(NH_3)_5)_2NCC(pyR){=}C(pyR)CN]^{6+}$ complexes at their band maxima. The observed rate constants were obtained from the slopes of linear least-squares fits of $\ln(A_\infty - A_t)$ vs time plots.

Table 1. Crystallographic Data for $[(Ru(NH_3)_5)_2NCC(py){=}C(py)CN]^{4+}$

empirical formula	$C_{14}H_{38}Cl_4N_{14}O_{18}Ru_2$
unit cell dimens	$a = 15.755(2)$ Å $b = 13.714(2)$ Å $c = 17.831(2)$ Å
V	3852.6(9) Å^3
Z	4
fw	1034.5
space group	Pbca
temp (*T*)	20 °C
wavelength (λ)	0.710 73 Å
density (calcd)	1.784 Mg/m^3
abs coeff	1.146 mm^{-1}
F(000)	2080
R1 [1 > 2δ(1)]	0.0584
R1 (all data)	0.0904

Crystal Structure Determination. Crystals of $[(Ru(NH_3)_5)_2NCC(py){=}C(py)CN]^{4+}$ of size 0.50 × 0.70 × 0.80 mm in sealed capillaries were used for X-ray diffraction studies. The diffraction intensities were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The absorption correction was not performed on the samples. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a SGI Indigo computer. The positions of heavy atoms for the structure were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques. All non-hydrogen atoms were refined as individual anisotropic atoms. The hydrogen atoms were considered as the riding atom on the carbon atom with a C−H bond length of 0.96 Å, and the hydrogen atom temperature factor was fixed at 0.08. The hydrogen atoms were included for refinements in the final cycles. The crystallographic data are summarized in Table 1.

Result and Discussion

Characterization of the Oxidation Products. The electronic spectra of $Ru(NH_3)_5NCCH_2pyR^{3+}$ (R = H^+ and CH_3) complexes in 0.10 M HCl solution, as shown in Table 2, showed characteristic $d\pi \rightarrow \pi_{CN}{}^*$ charge-transfer absorptions. When the complexes were oxidized with peroxydisulfate ion, the solution turned greenish blue with absorptions at $\lambda_{max} = 791$ (R = H^+) and 808 nm (R = CH_3), respectively. These absorptions reached their maxima when equimolar amounts of the oxidant was added. When the oxidations were carried out in an unbuffered solution at pH = 6−7, the pH of the solutions at [Ru(II)] ≅ 1 × 10^{-3} M changed to ∼3 after oxidations. The ^1H NMR spectra of the product solutions showed chemical shifts of ammonia characteristic of the ruthenium(II) ammine complexes[9] and are similar to that of the $Ru(NH_3)_5NCCH_2pyR^{3+}$ complexes. The $\delta(NH_3)_{sym}$ in the IR spectra of the isolated products also favored the Ru(II) metal center.[10] Moreover, the IR spectra of the products also exhibited the ν_{CN} absorptions, indicating that the ligands did not undergo hydrolysis upon oxidation and the nitriles are actually still bound to the metal center.[2] The characteristic IR bands for the complexes under study are listed in Table 2. The absence of the ^1H NMR signals for the protons on the α-carbon of both the free and the coordinated $NCCH_2pyR$ ligands in DCl/D_2O solution suggests that the oxidation of

---

(7) Vogt, L. H.; Katz, J. L.; Wiberly, S. E. *Inorg. Chem.* **1965**, *4*, 1158.

(8) Chen, M. H.; Lee, S.; Liu, S.; Yeh, A. *Inorg. Chem.* **1996**, *35*, 2627.

(9) Malin, J. M.; Schmidt, C. F.; Toma, H. *Inorg. Chem.* **1975**, *14*, 2924.

(10) Huang, H. Y.; Chen, W. J.; Yang, C. C.; Yeh, A. *Inorg. Chem.* **1991**, *30*, 1862.

Table 2. Spectra and Reduction Potentials of Ruthenium(II) Complexes[a]

complex	λ_{max}, nm ($10^{-3}\varepsilon$, $M^{-1}cm^{-1}$)	υ_{CN} $cm^{-1,d}$	$\delta(NH_3)_{sym}$, $cm^{-1,d}$	$E_{1/2}$, V (vs NHE)[f]
$Ru^{II}(NH_3)_5NCCH_2PyH^{3+}$	232(18.9)	2222 (2250)[e]	1249	0.50
$Ru^{II}(NH_3)_5NCCH_2Py\text{-}CH_3{}^{3+}$	230(18.0)	2232 (2246)	1255	0.49
$Ru^{II}(NH_3)_5NC\overset{CH_3}{\underset{CH_3}{C}}PyH^{3+}$	235(10.1)	2218 (2242)	1282	0.51
$Ru^{II}(NH_3)_5NCCH_2Ph^{2+}$	223(13.9)	2232 (2252)	1282	0.45
$Ru^{II}(NH_3)_5NC\overset{OH}{C}HPh^{2+}$	252(10.2)	2195 (2250)	1262	0.51
$Ru^{II}(NH_3)_5NC\overset{O}{\overset{\|}{C}}Ph^{2+}$	499 (7.52)	2128 (2223)	1252	0.72
$[Ru^{II}(NH_3)_5NC\underset{H\text{-}Py}{C}=\overset{Py\text{-}H}{C}CNRu^{II}(NH_3)_5]^{6+}$	376 (6.64)[b] 791(20.6)[b]	2143	1297	0.70, 0.95
$[Ru^{II}(NH_3)_5NC\underset{py}{C}=\overset{py}{C}CNRu^{II}(NH_3)_5]^{4+}$	627(25.7)[b,c]			0.63, 0.83
$[Ru^{II}(NH_3)_5NC\underset{{}_3HC\text{-}Py}{C}=\overset{Py\text{-}CH_3}{C}CNRu^{II}(NH_3)_5]^{6+}$	380 (6.47)[b] 808(19.6)[b]	2137	1285	0.70, 0.96

[a] Only the dπ to π* charge-transfer bands are reported. Measured in 0.1 M HCl, unless otherwise specified. [b] The value reported is in units of per mole of dimer. [c] Measured at pH = 5 (acetate). [d] In KBr pellets. [e] Values of free ligands in parentheses. [f] μ = 0.10 M HCl, T = 25 °C. Scan rate = 100 mV/s.

the complexes maybe centered on this carbon. The DMSO solution of the complexes, where the proton exchange is slow, does not show color change upon oxidation. Moreover, both $Ru(NH_3)_5NCCH_2Ph^{2+}$ and $Ru(NH_3)_5NCC(CH_3)_2pyH^{3+}$ underwent one electron oxidation to Ru(III), followed by nitrile hydrolysis to form the amide complexes as final products. The $Ru(NH_3)_5NCCH_2ph^{2+}$ complex exhibited α-carbon proton signals as expected. To find out the identity of oxidation products, we carried out ^{13}C NMR measurements. All ^{13}C NMR spectra were measured in the DMSO-d_6 solvent because of the C−D coupling for both the free and the coordinated ligands in DCl/D_2O medium which made the α-carbon unobservable. The δ values of the α-carbon for the oxidation products are 115 and 112 ppm for R = H^+ and CH_3, respectively. Since the chemical shift are close to that expected for the C=C group (104−145 ppm),[11] the oxidation of the complexes therefore may result in the formation of the C=C bond. The ^{13}C NMR spectrum of $-CH{=}CH_2$ carbons (118 and 109 ppm) of the $Ru(NH_3)_5NCCH{=}CH_2{}^{2+}$ complex provided further evidence in favor of C=C formation. If this is the case, the only possibility would be that the ligands underwent coupling upon oxidation with $[Ru^{II}(NH_3)_5]_2NCC(pyR){=}C(pyR)CN^{6+}$ binuclear complexes as the final products. The exhibition of two reversible one-electron steps of oxidation in the cyclic voltammogram of the product also supported the formation of the binuclear complexes.

With the α-carbon being oxidized, other possible product, $Ru(NH_3)_5NCC(OH)HpyR^{2+}$ or $Ru(NH_3)_5NCC(O)pyR^{2+}$,[12] should also be considered. However, this possibility can be ruled out because the expected δ values[11] of the ^{13}C NMR spectra for >CHOH (45−85) ppm and >C=O (165−210 ppm) fall in ranges far from our observed values. The formation of binuclear complexes rather than the alcohol mononuclear complexes as oxidation products may arise from the back-bonding stabilization of the binuclear complexes as a result of the π-conjugation of the nitrile ligands. There is a bathochromic shift in absorption from 232 to 791 nm in going from $Ru(NH_3)_5NCCH_2pyH^{3+}$ to $[Ru(NH_3)_5]_2NCC(pyH){=}C(pyH)CN^{6+}$, while no significant difference in spectra is observed between $Ru(NH_3)_5NCCH_2Ph^{2+}$ and $Ru(NH_3)_5NCCH(OH)Ph^{2+}$. Morever, there will be a kinetic barrier in the formation of alcohol complexes because H_2O has to be deprotonated to OH^- in bringing it into alcohol product. This is not likely, especially in an acidic medium such as our case.

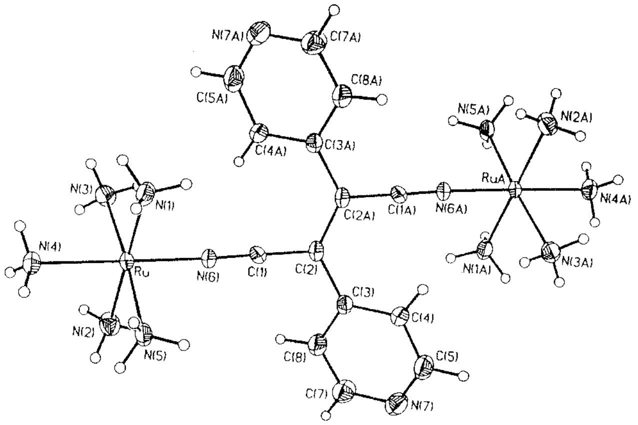

Figure 1. Molecular structure of the $[(NH_3)RuNCC(pyH){=}C(pyH)CNRu(NH_3)_5]^{6+}$ complex. The hydrogens on the ammine ligands, the ClO_4^-, and the H_2O molecules are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and the Bond Angles (deg) of the $[(NH_3)_5RuNC(py)C(py)CNRu(NH_3)_5]^{4+}$ Complex

Bond Lengths			
Ru−N(1)	2.128(7)	Ru−N(2)	2.136(7)
Ru−N(3)	2.141(7)	Ru−N(4)	2.137(7)
Ru−N(5)	2.134(7)	Ru−N(6)	1.933(7)
N(6)−C(1)	1.150(10)	C(1)−C(2)	1.416(11)
C(2)−C(3)	1.473(11)	C(2)−C(2A)	1.394(15)
Bond Angles			
N(1)−Ru−N(3)	90.8(3)	N(1)−Ru−N(4)	89.8(3)
N(1)−Ru−N(5)	90.4(3)	N(2)−Ru−N(3)	89.3(3)
N(2)−Ru−N(4)	90.4(3)	N(2)−Ru−N(5)	89.5(3)
N(3)−Ru−N(4)	88.4(3)	N(4)−Ru−N(5)	88.5(3)
N(4)−Ru−N(6)	178.1(3)	Ru−N(6)−C(1)	176.5(7)
N(6)−C(1)−C(2)	178.1(9)	C(1)−C(2)−C(3)	116.8(7)
C(1)−C(2)−C(2A)	119.0(9)	C(3)−C(2)−C(2A)	124.1(9)

Molecular Structure of $[(NH_3)_5RuNC(py)C(py)CNRu(NH_3)_5]^{4+}$. The molecular structure of the complex is shown in Figure 1, and the selected bond lengths and the bond angles are listed in Table 3. The binuclear complex contains a crystallographic inversion center. In addition to the ClO_4^- counterion, the crystal contains two water molecules of hydration per unit of the binuclear complex. One of the hydrogen atoms of the H_2O molecule was not located. The geometry around each Ru(II) metal center is nearly an ideal six-coordinate octahedral structure with the five Ru−N(ammine) bond lengths nearly identical ranging from 2.120(7) to 2.141(7) Å with an average of 2.135 Å. The *cis*-N−Ru−N angles are all near 90° ranging from 88.2(3) to 92.1(3)° with an average of 90.0°. It is interesting to know that the Ru−N(6) bond distance of the coordinating nitrile at 1.933(7) Å is considerably shorter than

---

(11) Leyden, D. E.; Cox, R. H. *Analytical Applications of NMR*; Wiley: New York, 1977; p 196.

(12) The formation of keto complex is not likely because the oxidation takes four electrons.

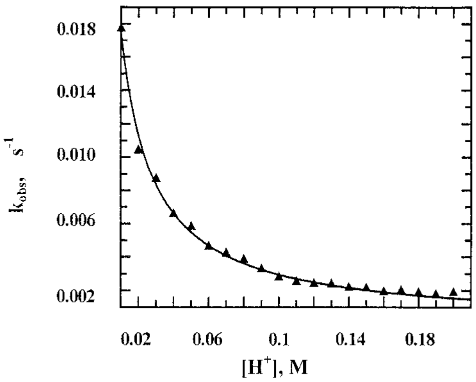

Figure 2. k_{obs} vs [H$^+$] plot for the oxidation of $Ru(NH_3)_5NCCH_2pyH^{3+}$ complex. Conditions: $\mu = 1.0$ LiCl/HCl; $T = 25$ °C; $[Ru(II)] = [S_2O_8^{2-}] = 2.0 \times 10^{-4}$ M.

the Ru−N(ammine) bond lengths by nearly 0.2 Å. The short bond may be attributed to the considerable π-back-bonding from the Ru(II) metal center to the π* orbital on the nitrile nitrogen. The N−C distance of the nitrile moiety at 1.150(10) Å is typical for the C−N triple bond. However, C(1)−C(2) bond length at 1.416(11) Å is short for an C(sp^2)−C(sp^2) single bond. The C(2)−C(2A) bond length at 1.394(15) Å and a C(1)−C(2)−C(2A) bond angle of 119° support a C═C double-bond character. For the RuNCC(C)═C(C)CNRu moiety, the 10 atoms form a nearly coplanar feature with the mean deviation of 0.0351 Å from the plane. The coplanar feature, the short Ru−N(nitrile), and the short C(sp^2)−C(sp^2) single bonds indicate substantial delocalization of π electrons among these atoms.

Kinetics of Oxidation. Good first-order fits for the rates of oxidations of $Ru(NH_3)_5NCCH_2pyR^{3+}$ (R = H$^+$ and CH$_3$) complexes at acid concentrations ranging from 0.01 to 0.20 M were observed at least over 3 half-lives for all measurements. The k_{obs} decreases with [H$^+$], as shown in Figure 2. When 1/k_{obs} is plotted against [H$^+$], a linear relationship is obtained. The kinetic behavior of the reaction corresponds to the mechanism as expressed by reactions 1−5.

$$2Ru^{II}(NH_3)_5NCCH_2pyR^{3+} + S_2O_8^{2-} \xrightarrow{\text{fast}} 2Ru^{III}(NH_3)_5NCCH_2pyR^{4+} + 2SO_4^{2-} \quad (1)$$

$$Ru^{III}(NH_3)_5NCCH_2pyR^{4+} \overset{K}{\rightleftharpoons} Ru^{III}(NH_3)_5NC\ddot{C}HpyR^{3+} + H^+ \quad (2)$$

$$Ru^{III}(NH_3)_5NC\ddot{C}HpyR^{3+} \underset{\text{rds}}{\overset{k}{\rightleftharpoons}} \underset{\text{A}}{Ru^{II}(NH_3)_5NC\dot{C}HpyR^{3+}} \quad (3)$$

$$2Ru^{II}(NH_3)_5NC\dot{C}HpyR^{3+} \xrightarrow{\text{fast}} \underset{\text{B}}{[Ru^{II}(NH_3)_5]_2NCCH(pyR)CH(pyR)CN^{6+}} \quad (4)$$

$$[(NH_3)_5Ru^{II}NCCH(pyR)-CH(pyR)CNRu^{II}(NH_3)_5]^{6+} + S_2O_8^{2-} \xrightarrow{\text{fast}} \underset{\text{C}}{[(NH_3)_5Ru^{II}NCC(pyR){=}C(pyR)CNRu^{II}(NH_3)_5]^{6+}} \quad (5)$$

The oxidation of Ru(II) complexes to Ru(III) in the first step (eq 1) is necessary because the reaction of $NCCH_2pyR^+$ with $S_2O_8^{2-}$ is very slow. The ^{13}C NMR spectra of the free ligands remained unchanged for at least 2 h upon oxidation. The specific rate constant of the oxidation of $Ru(NH_3)_5NCCH_2pyH^{3+}$ by $S_2O_8^{2-}$ is $(6.1 \pm 0.2) \times 10^3$ M^{-1} s^{-1} at 0.10 M HCl. With this rate of oxidation, eq 1 will not be involved in the rate law of the reactions and the Ru(III) concentration will be the same as the stoichiometric concentration of Ru(II). Therefore the rate law according to this mechanism will be

$$\frac{d[\text{product}]}{dt} = \frac{kK}{K + [H^+]}[Ru^{III}(NH_3)_5NCCH_2pyR^{4+}] \quad (6)$$

$$k_{obs} = \frac{kK}{K + [H^+]} \quad (7)$$

The nonlinear least-squares fits of k_{obs} vs [H$^+$] according to eq 7 give values of k and K as $(3.6 \pm 0.2) \times 10^{-2}$ s^{-1} and $(9.0 \pm 0.8) \times 10^{-3}$ M for R = H$^+$ and $(4.3 \pm 0.2) \times 10^{-2}$ s^{-1} and $(9.9 \pm 0.7) \times 10^{-3}$ M for R = CH$_3^+$, at $\mu = 1.0$ M (HCl/LiCl) and $T = 25$ °C. The reasonable agreement in results between R = H$^+$ and CH$_3$ implies that the pyridine nitrogen is protonated throughout the reactions under our experimental conditions.

Since eq 5 is not involved in the rate law as is evidenced by the first-order dependence of the rate law only on the Ru(III) concentrations, the oxidation of B to form C should be a rapid process, at least much faster than the rate-determining step (eq 3). This is expected because the strong electron withdrawing of CN and py will increase the acidity of the α-carbon which further facilitates the removal of hydrogen. Moreover, the stability of the product due to back-bonding may also be a driving force which favors the reaction to proceed.

Instead of forming the binuclear complex B in reaction 4 as an intermediate, an alternative possibility which involves the oxidation of A to form a carbonium ion $Ru(NH_3)_5NCCHpyR^{4+}$, D, following the coupling of D to form the final products has also been considered. However, the possibility can be excluded because the coupling between two carbonium ions is highly unlikely due to the electrostatic repulsion.

The oxidative dehydrogenations had been investigated previously also for other ruthenium complexes on the amine ligands.[13] However, the mechanism of the reactions are different from our system. In all these systems the effectiveness of the Ru center in the promotion of the oxidative dehydrogenation of the ligands was related to its ability to attain the Ru(IV) oxidation state, which was formed by the disproportionation of Ru(III) and stabilized by deprotonation. In our system the Ru(III) complexes do not disproportionate. Moreover, the free radical intermediate is involved in our reaction which results in the formation of the binuclear complex. In the other systems, free radical was not included in the mechanism and the complexes remained mononuclear with the amines being oxidized to imines.[14]

Electrochemistry. The reduction potentials for the complexes under study are listed in Table 2. The higher reduction potentials for the oxidation products reflected better MLCT stabilization of the binuclear complexes.

The comproportionation constant, K_C, according to eq 8, as

$$[Ru(II),Ru(II)] + [Ru(III),Ru(III)] \overset{K_C}{\rightleftharpoons} 2[Ru(II),Ru(III)] \quad (8)$$

calculated from the electrochemical data in Table 2, are 1.7×10^4 and 2.6×10^4 for R = H$^+$ and R = CH$_3$, respectively, in favor of the stability of the mixed-valence ions over isovalent species. The values are greater than those of the diruthenium complexes with 4,4′-dipyridylethylene (BPE, $K_C = 26$)[15] and

---

[13] Keene, F. R. *Coord. Chem. Rev.* **1999**, *187*, 121.
[14] Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733.
[15] Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

1,4-dicyanobenzene (DCB, $K_C = 23$)[16] bridge ligands by 3 orders of magnitudes. This indicates, at least for the most part, that the interaction between metal centers for mixed-valence binuclear complexes in our system is much greater than the other two. The difference may not simply arise from the difference in distance between metal centers, although the internuclear distance plays an important role in affecting the metal–metal interaction.[16,17] In the DCB-bridged binuclear complex, the benzene ring is free to rotate which will attenuate the electron exchange via the bridging ligand π_{MO}.[18] This in turn will weaken the communication between the metal centers. The pyridine rings in the BPE are not coplanar, and this will limit the overlap of the π systems for the two rings.[15] In our system, the influence of the noncoplanarity and the ability of free rotation of the bridge ligands are both absent. Consequencly, the delocalization of the π electrons will be favored,[19] and the coupling between metal centers in the mixed-valence state will be greatly enhanced.

The properties of the intervalence band of the mixed-valence species further support this argument. We have tried to measure the intervalence absorption of the mixed-valence binuclear complex $[(NH_3)_5RuNCC(pyH){=}C(pyH)CNRu(NH_3)_5]^{7+}$, obtained by the one-electron oxidation of the reduced species, both in 0.1 M acid solution and in dimethyl sulfoxide. Unfortunately, we were unable to get a stable dinitrile mixed-valence binuclear complex in the aqueous solution due to the interference of the ligand hydrolysis.[1] In the DMSO solution, the intervalence band was buried in the MLCT absorption and was observed only as a shoulder in the region of 1450 nm at high concentration of the binuclear complex (2.05×10^{-3} M). This absorption was absent for both the reduced and the fully oxidized forms at the same concentration. The analysis of the absorption between 800 and 2000 nm with Origin, a Gaussian fitting program,[20] yielded $\lambda_{max} = 1470$ nm ($\epsilon_{max} = 522$ M^{-1} cm^{-1}) and $\Delta\nu_{1/2} = 3.04 \times 10^3$ cm^{-1}. The bandwidth predicted by Hush's theory[21] gives $\Delta\nu_{1/2}(calcd) = 3.96 \times 10^3$ cm^{-1}, 30% greater than the observed value. Since the bandwidths of the intervalence bands for the weakly coupled symmetric mixed-valence binuclear complexes are expected to be somewhat broader than predicted by Hush's theory,[15,19] the narrower measured $\Delta\nu_{1/2}$ than the calculated value in our system apparently implies that there is a better electronic communication between the metal centers than the other systems.

Acknowledgment. The support of this work by the National Science Council of the Republic of China under Grant NSC-87-2113-M029-001 is gratefully acknowledged. We wish to thank Professor Henry Taube for helpful discussions.

Supporting Information Available: Tables S1–S3, listing elemental analyses of the Ru(II) complexes under study, ^1H and ^{13}C NMR chemical shifts of the Ru(II) complexes, and pseudo-first-order rate constants for the oxidation of $Ru(NH_3)_5NCCH_2pyR^{3+}$ ($R = H^+$, CH_3) complexes at various acid concentrations, Figures S1 and S2 showing the ^{13}C NMR spectrum of $[(NH_3)_5RuNCC(pyH){=}C(pyH)CNRu(NH_3)_5]^{6+}$ in DMSO-d_6 solvent and a cyclic voltammogram of $[(NH_3)_5RuNCC(pyH){=}C(pyH)CNRu(NH_3)_5]^{6+}$, and listings of crystal and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for all non-hydrogen atoms as well as hydrogen atom coordinates with isotropic displacement parameters and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000944P

---

(16) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.
(17) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
(18) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensimon, C.; Greedan. J. E.; Crutchley, R. J., *J. Am. Chem. Soc.* **1992**, *114*, 5130.
(19) Ribou, A. C.; Launay, J. P.; Takahashi, K.; Nihira, T.; Tarutani, S.; Spangler, C. W. *Inorg. Chem.* **1994**, *33*, 1325.
(20) Chen, Y. J.; Kao, C. H.; Lin, S. J.; Tai, C. C.; Kwan, K. S. *Inorg. Chem.* **2000**, *39*, 3189.
(21) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.