Coordination and Redox Chemistry of Substituted-Polypyridyl Complexes of Ruthenium

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The complexes [Ru(tpy)(acac)(Cl)], [Ru(tpy)(acac)(H_2O)](PF_6) (tpy = 2,2′,2″-terpyridine, acacH = 2,4 pentanedione) [Ru(tpy)(C_2O_4)(H_2O)] ($C_2O_4^{2-}$ = oxalato dianion), [Ru(tpy)(dppene)(Cl)](PF_6) (dppene = *cis*-1,2-bis(diphenylphosphino)ethylene), [Ru(tpy)(dppene)(H_2O)](PF_6)$_2$, [Ru(tpy)(C_2O_4)(py)], [Ru(tpy)(acac)(py)](ClO_4), [Ru(tpy)(acac)(NO_2)], [Ru(tpy)(acac)(NO)](PF_6)$_2$, and [Ru(tpy)(PSCS)Cl] (PSCS = 1-pyrrolidinedithiocarbamate anion) have been prepared and characterized by cyclic voltammetry and UV−visible and FTIR spectroscopy. [Ru(tpy)(acac)(NO_2)]$^+$ is stable with respect to oxidation of coordinated NO_2^- on the cyclic voltammetric time scale. The nitrosyl [Ru(tpy)(acac)(NO)]$^{2+}$ falls on an earlier correlation between ν(NO) (1914 cm^{-1} in KBr) and $E_{1/2}$ for the first nitrosyl-based reduction 0.02 V vs SSCE. Oxalate ligand is lost from [Ru^{II}(tpy)(C_2O_4)(H_2O)] to give [Ru(tpy)(H_2O)$_3$]$^{2+}$. The Ru(III/II) and Ru(IV/III) couples of the aqua complexes are pH dependent. At pH 7.0, $E_{1/2}$ values are 0.43 V vs NHE for [Ru^{III}(tpy)(acac)(OH)]$^+$/[Ru^{II}(tpy)(acac)(H_2O)]$^+$, 0.80 V for [Ru^{IV}(tpy)-(acac)(O)]$^+$/[Ru^{III}(tpy)(acac)(OH)]$^+$, 0.16 V for [Ru^{III}(tpy)(C_2O_4)(OH)]/[Ru^{II}(tpy)(C_2O_4)(H_2O)], and 0.45 V for [Ru^{IV}(tpy)(C_2O_4)(O)]/[Ru^{III}(tpy)(C_2O_4)(OH)]. Plots of $E_{1/2}$ vs pH define regions of stability for the various oxidation states and the pK_a values of aqua and hydroxo forms. These measurements reveal that $C_2O_4^{2-}$ and acac$^-$ are electron donating to Ru^{III} relative to bpy. Comparisons with redox potentials for 21 related polypyridyl couples reveal the influence of ligand changes on the potentials of the Ru(IV/III) and Ru(III/II) couples and the difference between them, $\Delta E_{1/2}$. The majority of the effect appears in the Ru(III/II) couple. A linear correlation exists between $\Delta E_{1/2}$ and the sum of a set of ligand parameters defined by Lever et al., $\Sigma E_i(L_i)$, for the series of complexes, but there is a dramatic change in slope at $\Delta E_{1/2} \approx -0.11$ V and $\Sigma E_i(L_i) = 1.06$ V. Extrapolation of the plot of $\Delta E_{1/2}$ vs $\Sigma E_i(L_i)$ suggests that there may be ligand environments in which Ru(III) is unstable with respect to disproportionation into Ru(IV) and Ru(II). This would make the two-electron $Ru^{IV}O/Ru^{II}OH_2$ couple more strongly oxidizing than the one-electron $Ru^{IV}O/Ru^{III}OH$ couple.

Introduction

A family of high-oxidation-state oxo complexes of Ru is known (*e.g.*, *cis*-[Ru^{IV}(bpy)$_2$(PPh_3)(O)]$^{2+}$, [Ru^{IV}(tpy)(bpy)-(O)]$^{2+}$; bpy = 2,2′-bipyridine; tpy = 2,2′,2″-terpyridine), in which there is an extensive redox chemistry toward organic and inorganic reductants.[1,2] In the same coordination environment, nitrosyl complexes have been shown to have an extensive reactivity at the nitrosyl, including six-electron reduction to ammine:[3]

$$[Ru^{II}(tpy)(bpy)(NO)]^{3+} \xrightarrow{+6e^-,\ +5H^+,\ -H_2O} [Ru^{II}(tpy)(bpy)(NH_3)]^{2+}$$

An important element in these reactivities is the ability to control redox potentials in a systematic way by varying the ancilliary ligands.[4,5] With this in mind, we report here on the influence of the O-donor ligands oxalate dianion ($C_2O_4^{2-}$) and acetylacetonate anion (acac$^-$) and of the phosphine chelate dppene ($Ph_2PCH{=}CHPPh_2$) on the ruthenium aqua/oxo chemistry and on the properties of the nitrosyl ligand.

Acetylacetonate-type ligands have played an important role in coordination chemistry.[6] Previous work has shown that acac$^-$ is potentially a σ donor, a π donor, or a π acceptor.[7] There is a somewhat limited coordination chemistry with Ru, examples including [$Ru^{III/II}$(bpy)$_2$(acac)]$^{2+/+}$ (acacH = 2,4-pentanedione),

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[Ru(η^5-Cp)(PPh_3)(acac)] (η^5-Cp = cyclopentadienyl anion), and Ru(bft)$(CO)_2$(acac) (bft = *N*,*N*-dimethyl-3-furancarbothioamide).[8,9] A limited number of mononuclear bis-acac complexes have also been reported.[10]

Ancillary ligands can play a role as σ donors (e.g. H_2O), π donors (e.g., Cl^-), or π acceptors, NO^+ or CO. Complexes of Ru^{II} provide a convenient basis for such studies because there is an extensive redox chemistry already in place based on well-characterized examples such as *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$, *cis*-[Ru(bpy)$_2$(py)(H_2O)]$^{2+}$, [Ru(tpy)(bpy)(NO_2)]$^+$, and [Ru(tpy)-(bpy)(NO)]$^{3+}$.

Experimental Section

Materials. The compounds and salts 2,4-pentanedione, 3-chloro-2,4-pentanedione, $Na_2C_2O_4$, 1-pyrrolidinecarbodithioic acid ammonium salt, sodium nitrite, hexafluorophosphoric acid, ammonium hexafluorophosphate, pyridine, and $RuCl_3 \cdot 3H_2O$ were purchased from Aldrich Chemical Co. and 2,2′:6,2″-terpyridine (tpy), $(NH_4)_2Ce(NO_3)_6$, and solutions of 0.5 N Ce(IV) in 6 N perchloric acid from G. F. Smith Chemicals. *cis*-1,2-Bis(diphenylphosphino)ethylene (dppene; Aldrich Chemical Co.) was recrystallized from argon-degassed absolute ethanol. Infrared analysis and ^{31}P NMR confirmed the absence of the corresponding arylphosphine oxides or dioxides. Spectrograde acetonitrile (Burdick & Jackson) was used as received. [N(*n*-Bu)$_4$](PF_6) was recrystallized once from 1:1 (v/v) ethanol−water and twice from absolute ethanol and dried under vacuum for 10 h at 80 °C. All other common reagents were ACS grade and were used without additional purification. High-purity, deionized water was obtained by passing distilled water through a Nanopure™ (Barnstead) water purification system.

Elemental Analysis. Microanalyses were conducted by Galbraith Laboratories, Knoxville, TN, and Oneida Research Services, Inc., Whitesboro, NY.

Preparations. The compounds and salts [Ru(tpy)(acac)Cl], [Ru(tpy)-(3-Cl-acac)Cl], [Ru(tpy)(acac)(H_2O)](PF_6), and [Ru(tpy)(C_2O_4)(H_2O)] were prepared as described previously.[10]

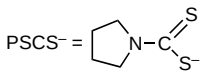
[Ru(tpy)(C_2O_4)(py)]·0.5H_2O. A 2.60 g (5.46 mmol) quantity of [Ru(tpy) (C_2O_4)(H_2O)]·2H_2O was suspended in 250 mL of dry methanol already deaerated with nitrogen gas. A 5 mL quantity of pyridine was added to the reaction vessel, and the reaction mixture was heated at reflux under nitrogen for 3 h to form the violet pyridine complex. The resulting solution was filtered hot to remove any unreacted solid. The volume was reduced on a rotary evaporator to ∼30 mL, and the remaining sample was left in the refrigerator overnight. The solid that formed was filtered, washed once with a minimum amount of cold methanol and twice with anhydrous diethyl ether, air-dried, and then dried in vacuo. Yield: 40%. Anal. Calcd for $C_{22}H_{17}N_4O_{4.5}Ru$: C, 51.76; H, 3.36; N, 10.98. Found: C, 51.67; H, 3.14; N, 11.08. UV−visible spectrum in CH_3OH (λ_{max}, nm (ϵ in M^{-1} cm^{-1})): 550 (6000), 505 (6050), 380 (11 850), 318 (41 450), 275 (27 400), 230 (28 350). Infrared in KBr pellets (ν_a(C═O) and ν_1(C═O) of oxalate (cm^{-1})): 1663, 1634. $E_{1/2}$(III/II) = 0.62 V (in CH_3OH, 0.1 M in [N(*n*-Bu)$_4$]-(PF_6) vs SSCE).

[Ru(tpy)(acac)(py)](ClO_4)·0.5H_2O. A 1.00 g quantity of [Ru(tpy)-(acac)Cl]·1.5H_2O was suspended in 100 mL of a methanol−water (4:1) mixture already deaerated with nitrogen. A 5.0 mL quantity of pyridine was added to the reaction vessel, and the reaction mixture was heated at reflux under nitrogen for 2 h. The resulting violet solution was filtered hot to remove any unreacted solid, and ∼15 mL of an aqueous solution saturated in sodium perchlorate was added to the filtrate. The volume was reduced on a rotary evaporator to ∼15 mL, and the remaining sample was left in the refrigerator overnight. The dark violet crystals that formed were collected on a glass frit, washed with a minimum amount of cold methanol and anhydrous diethyl ether, air-dried, and then dried in vacuo. Yield: 70%. Anal. Calcd for $C_{25}H_{24}N_4O_{6.5}ClRu$: C, 48.35; H, 3.90; N, 9.02; Cl, 5.71. Found: C, 48.23; H, 3.49; N, 8.95; Cl, 5.66. UV−visible spectrum in CH_3OH (λ_{max} in nm (ϵ in M^{-1} cm^{-1})): 543 (5800), 505 (5200), 369 (12 400), 317 (31 800), 275 (31 750), 237 (29 550). Infrared in KBr pellets (ν_s(C═C) and ν_1(C═O) of acetylacetonate (cm^{-1})): 1568, 1512; ν(NO), 1914. $E_{1/2}$(III/II) = 0.59 V (in CH_3OH, 0.1 M in [N(*n*-Bu)$_4$](PF_6) vs SSCE).

[Ru(tpy)(acac)(NO_2)]·1.5H_2O. A 0.25 g (0.42 mmol) quantity of [Ru(tpy) (acac)(H_2O)](PF_6) was suspended in 10 mL of water with stirring. A 0.145 g (2.1 mmol) quantity of sodium nitrite was added to the stirred solution and left to cool at 4 °C for ∼2 h. The red-brown solid that formed was filtered, washed twice with cold water, air-dried, and then dried in vacuo; yield 50%. Anal. Calcd for $C_{20}H_{21}N_4O_{5.5}Ru$: C, 47.43; H, 4.18; N, 11.06. Found: C, 47.38; H, 4.06; N, 11.52. UV−visible spectrum in neat H_2O (λ_{max} in nm (ϵ in M^{-1} cm^{-1})): 486 (8400), 360 (13 500), 312 (34 800), 272 (38 000), 230 sh, 212 (38 400). Infrared in KBr pellets (ν_s(C═C) and ν_1(C═O) of acetylacetonate (cm^{-1})): 1573, 1514.

[Ru(tpy)(acac)(NO)](PF_6)$_2$. A 0.25 g (0.5 mmol) quantity of [Ru-(tpy)(acac)(NO_2)]·H_2O was suspended and stirred in 10 mL of water, excess hexafluorophosphoric acid (1.05 mmol) was added slowly, and a yellow solution was formed. Ammonium hexafluorophosphate was added, and the yellow precipitate that formed was filtered, washed twice with a minimum amount of water, air-dried, and then dried in vacuo over P_2O_5; yield 50%. Anal. Calcd for $C_{20}H_{18}N_4O_3P_2F_{12}Ru$: C, 31.89; H, 2.41; N, 7.44. Found: C, 31.28; H, 2.28; N, 7.35. UV−visible spectrum in 0.1 M $HClO_4$ (λ_{max} in nm (ϵ in M^{-1} cm^{-1})): 342 sh (11 100), 284 sh (14 900), 230 (37 000), 200 (45 800). Infrared in KBr pellets (ν_s(C═C) and ν_1(C═O) of acetylacetonate (cm^{-1})): 1572, 1523.

[Ru(tpy)(PSCS)Cl] (PSCS$^-$ = 1-Pyrrolidinedithiocarbamate Anion):



A 0.50 g (1.13 mmol) quantity of [Ru(tpy)Cl_3] was suspended in 150 mL of methanol already deaerated with nitrogen gas. A 0.5 mL quantity of triethylamine was added to the reaction vessel, and to this mixture was added 0.204 g (1.24 mmol) of 1-pyrrolidine dithiocarbamate (10% excess). The resulting solution was heated at reflux for 2 h under N_2. The solution was filtered hot to remove any unreacted solid, and 0.1 g of LiCl was added to the filtrate. The volume was reduced to ∼20 mL on a rotary evaporator, and the remaining solution was left in the refrigerator overnight. The dark solid was filtered and washed twice with a minimum ammount of cold water. The crude [Ru(tpy)(PSCS)-Cl] product was purified by column chromatography. A slurry of alumina was made in pentane and packed into a glass column (15 cm × 2.5 cm). [Ru(tpy)(PSCS)Cl] (200 mg) was dissolved in a minimum amount of CH_2Cl_2 and filtered, and the filtrate was introduced into the alumina column. Pentane was used to equilibrate the column after the complex was adsorbed. The column was eluted by starting with 100% pentane followed by a gradual increase in the eluent polarity by addition of CH_2Cl_2. A red-purple band was obtained as the first eluate fraction. This solution was evaporated on a rotary evaporator to obtain dark fine crystals, which were washed twice with anhydrous diethyl ether, air-dried, and then dried in vacuo over P_2O_5: yield 45%. Anal. Calcd for $C_{20}H_{19}N_4ClS_2Ru$: C, 46.55; H, 3.71; N, 10.86; S, 12.43; Cl, 6.87. Found: C, 46.32; H, 3.96; N, 10.89; S, 12.40; Cl, 7.28. $E_{1/2}$(III/II) = 0.15 V (in CH_3CN, 0.1 M in [N(*n*-Bu)$_4$](PF_6) vs SSCE).

[Ru(tpy)(dppene)(Cl)](PF_6). A 0.68 g quantity of [Ru(tpy)$(Cl)_3$] (1.54 mmol) was suspended in 250 mL of ethylene glycol/water (60:40). A 0.86 g quantity of dppene (2.17 mmol) and 0.33 g of LiCl

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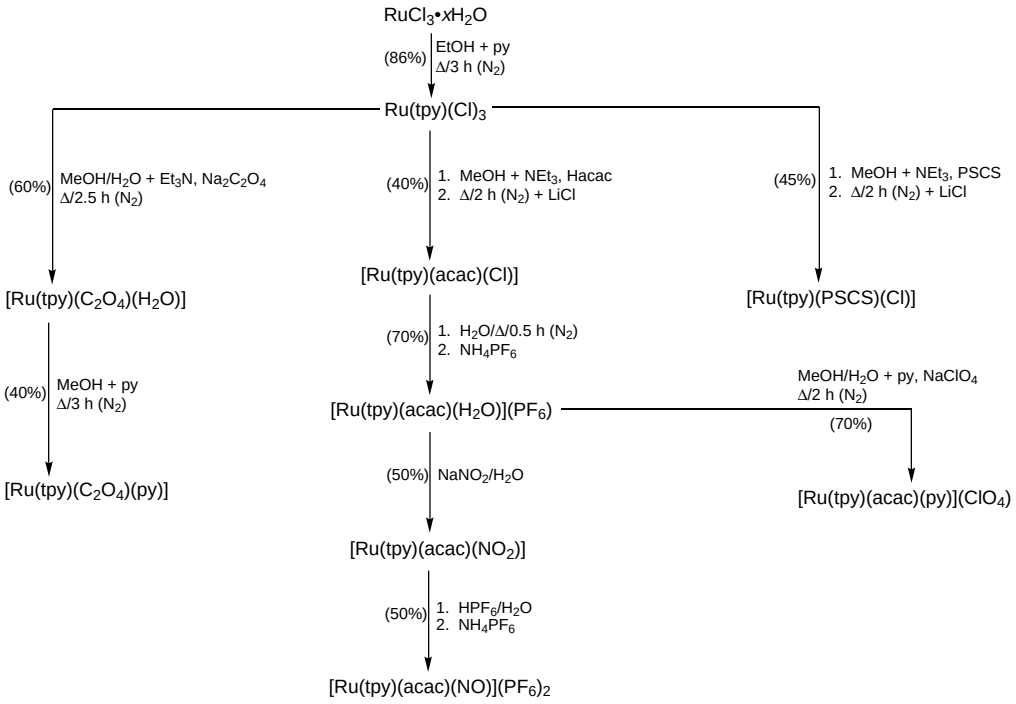
Scheme 1



were added to the reaction vessel. The mixture was heated at reflux for $2^1/_2$ h under N_2. The reaction solution was filtered hot, and 12 mL of concentrated NH_4PF_6 was added. The final solution was refrigerated overnight to obtain a cherry red solid. The solid was filtered and washed twice with a minimum volume of cold water. The crude product was purified by column chromatography. A slurry of alumina was made in acetone and packed onto a glass column (15 cm × 2.5 cm). $[Ru(tpy)(dppene)(Cl)]^+$ was dissolved in a minimum ammount of acetone, the solution was filtered, and the filtrate was introduced onto the alumina column. Acetone was used to equilibrate the column after the complex was adsorbed. The column was eluted with acetone. A cherry red band was obtained as the first eluate fraction. The byproduct $[Ru(tpy)_2]^{2+}$ remained adsorbed on the column. The eluate was evaporated on a rotary evaporator, and the residue was precipitated with anhydrous diethyl ether, filtered, air-dried, and dried in vacuo over P_2O_5; yield 58%. Anal. Calcd for $C_{41}H_{33}N_3P_3ClF_6Ru$: C, 54.05; H, 3.65; N, 4.61; Cl, 3.89; P, 10.20. Found: C, 54.46; H, 3.76; N, 4.52; Cl, 4.05; P, 10.35. $E_{1/2}$(III/II) = 1.23 V (in CH_2Cl_2, 0.1 M in $[N(n\text{-}Bu)_4](PF_6)$ vs SSCE).

$[Ru(tpy)(dppene)(H_2O)](PF_6)_2$. A 0.46 g (0.5 mmol) quantity of $[Ru(tpy)(dppene)(Cl)](PF_6)$ was suspended in 100 mL of H_2O/acetone/CH_2Cl_2 (50/30/20) already deaerated with nitrogen gas. A 0.60 mmol (0.15 g) quantity of $AgPF_6$ was added to the reaction vessel. The mixture was heated at reflux for 1 h under N_2 to form the aqua complex. The solution was filtered, and ~20 mL of an aqueous solution saturated in ammonium hexafluorophosphate was added. The volume was reduced to ~35 mL on a rotary evaporator. The dark brown precipitate that formed was filtered, washed twice with water, and air-dried; yield 70%.

Instrumentation and Measurements. UV−visible spectra were recorded by using a Hewlett-Packard Model 8452A diode array, and a Cary 14 spectrophotometer with 1 cm quartz cells. Infrared spectra were recorded on a Nicolet Model 20DX FTIR spectrophotometer in KBr pellets or in CH_3CN solution with NaCl plates. Electrochemical measurements were made with a Princeton Applied Research Model 173 potentiostat/galvanostat connected to a Princeton Applied Research Model 175 universal programmer as a sweep generator for voltammetric experiments. Spectroelectrochemical experiments were performed in a three-compartment electrochemical cell where the working electrode compartment was a 1-cm quartz cell. Controlled-potential electrolysis experiments were carried out by using a reticulated vitreous carbon electrode (ERG, Inc.). Cyclic voltammetric experiments were conducted in single one-compartment cells by using a Teflon-sheathed, 0.07 cm^2 glassy-carbon-disk working electrode, a platinum wire as the auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE). pH measurements were made on a Radiometer pHM62 pH meter and type C glass electrode vs SCE after calibration with standard buffers at 25 °C. Buffer solutions for the electrochemical measurements were prepared from aqueous perchloric acid ($HClO_4$) with $LiClO_4$ (pH 1 to pH 2), $HClO_4$ with $NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$, and $Na_3PO_4 \cdot 12H_2O$ (pH 2 to pH 9), and NaOH with Na_2SO_4 (pH 9 to pH 14) to maintain ionic strength at 0.1 M. The concentrations of the complexes in the cyclic voltammetric measurements were 1.0−1.5 mM. Electrochemical experiments in aqueous media for establishing $E_{1/2}$ vs pH profiles were performed on solutions containing $[Ru(tpy)(acac)(H_2O)]^+$. The $E_{1/2}$ values reported in this work were calculated from cyclic voltammetric waveforms as an average of the oxidative and reductive peak potentials, $(E_{pa} + E_{pc})/2$. For measurements in nonaqueous solutions the working electrode was a platinum disk and a $Ag/AgNO_3/CH_3CN$ reference electrode was used after it was calibrated against an SSCE by using an external standard. Working electrodes were polished by using 0.3 μm alumina.

Results

Syntheses. The synthetic chemistry that led to the compounds and salts prepared in this study are diagrammed in the flow chart in Scheme 1. $[Ru(tpy)Cl_3]$ proved to be a useful synthetic precursor in the scheme, which extends earlier synthetic routes.[11−13]

The reaction between [Ru(tpy)(acac)Cl] and excess py in $MeOH/H_2O$ at reflux proceeded through the aqua complex as an intermediate to give $[Ru(tpy)(py)(acac)]^+$:

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$$[Ru(tpy)(acac)Cl] + py \xrightarrow[N_2/\Delta]{CH_3OH/H_2O} [Ru(tpy)(acac)(py)]^+ + Cl^- \quad (1)$$

Similarly, substitution of py for H_2O in $[Ru(tpy)(C_2O_4)(H_2O)]$ gave $[Ru(tpy)(C_2O_4)(py)]$:

$$[Ru(tpy)(C_2O_4)(H_2O)] + py \xrightarrow[N_2/\Delta]{CH_3OH} [Ru(tpy)(C_2O_4)(py)] + H_2O \quad (2)$$

The complex $[Ru(tpy)(acac)(H_2O)]^+$ was prepared from [Ru(tpy)(acac)(Cl)] by aquation, and subsequent displacement by NO_2^- gave the corresponding nitro complex

$$[Ru(tpy)(acac)(H_2O)]^+ + NO_2^- \rightarrow [Ru(tpy)(acac)(NO_2)] + Cl^- \quad (3)$$

and addition of acid the nitrosyl

$$[Ru(tpy)(acac)(NO_2)] + 2H^+ \rightarrow [Ru(tpy)(acac)(NO)]^{2+} + H_2O \quad (4)$$

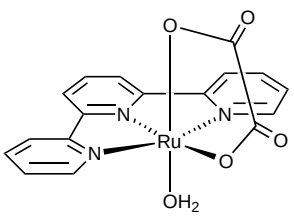
Addition of aqueous NaOH to $[Ru^{II}(tpy)(acac)(NO)]^{2+}$ gave $[Ru^{II}(tpy)(acac)(NO_2)]$, but we were unable to measure the equilibrium constant for

$$[Ru(tpy)(acac)(NO)]^{2+} + 2OH^- \rightleftharpoons [Ru(tpy)(acac)(NO_2)] + H_2O \quad (5)$$

because of precipitation of the nitro complex at high pH. Precipitation was not a problem below pH 9, from which we estimate that pK > 9.

UV−Visible and Infrared Spectra. The dπ(Ru) → π*(tpy) metal-to-ligand charge transfer (MLCT) bands in the visible region for the complexes containing O-donor ligands are shifted to lower energy compared to bpy as a ligand. This is in agreement with stabilization of the $Ru^{III}(tpy^-)$ excited state by electron donation from $acac^-$ or oxalato(2−). The intense bands in the UV region arise from tpy-based $\pi \rightarrow \pi^*$ transitions,[11] for example at 312, 272, 230, and 212 nm for $[Ru(tpy)(acac)(NO_2)]$. Low-energy MLCT bands are lost for $[Ru(tpy)(acac)(NO)]^+$ because strong dπ(Ru) → π*(NO) back-bonding stabilizes the dπ levels and shifts the MLCT bands into the UV.

In the infrared, ν(NO) appears at 1914 cm^{-1} in $[Ru(tpy)(acac)(NO)](PF_6)_2$. In $[Ru(tpy)(acac)(NO_2)]$ $\nu_{as}(NO_2)$ appears at 1327 cm^{-1} and $\nu_{sym}(NO_2)$ at 1294 cm^{-1}. All the acetylacetonato complexes have bands between 1600 and 1500 cm^{-1} which are characteristic of the acetylacetonate ligand.[14] The infrared spectrum of $[Ru(tpy)(C_2O_4)(H_2O)]$ indicates that the oxalato(2−) dianion functions as a bidentate ligand with formation of a five-membered ring (ν_a(C═O) 1668 cm^{-1} and ν_1(C═O) 1636 cm^{-1}).[15]



Electrochemistry. In cyclic voltammograms of $[Ru(tpy)(acac)(H_2O)]^+$ at pH 6.0 and a scan rate of 20 mV s^{-1} distinct, reversible waves appear at 0.25 and 0.62 V (vs SSCE). They arise from the one-electron Ru(III/II) and Ru(IV/III) couples, as observed for related polypyridyl aqua complexes of ruthenium and osmium.[8] Controlled-potential electrolysis at $E_{app} = 0.30$ V (vs SSCE) at pH 6.0 occurred with $n = 1.0 \pm 0.1$ consistent with oxidation of Ru(II) to Ru(III). Electrolysis at $E_{app} = 0.65$ V occurred with $n = 1.0 \pm 0.2$ consistent with oxidation from Ru(III) to Ru(IV). The UV−visible spectral changes associated with the redox processes were monitored spectroelectrochemically in order to verify the one-electron nature of the couples.

The pH dependencies of the two couples are illustrated in Figure 1a from pH 0 to pH 14, and those for the analogous

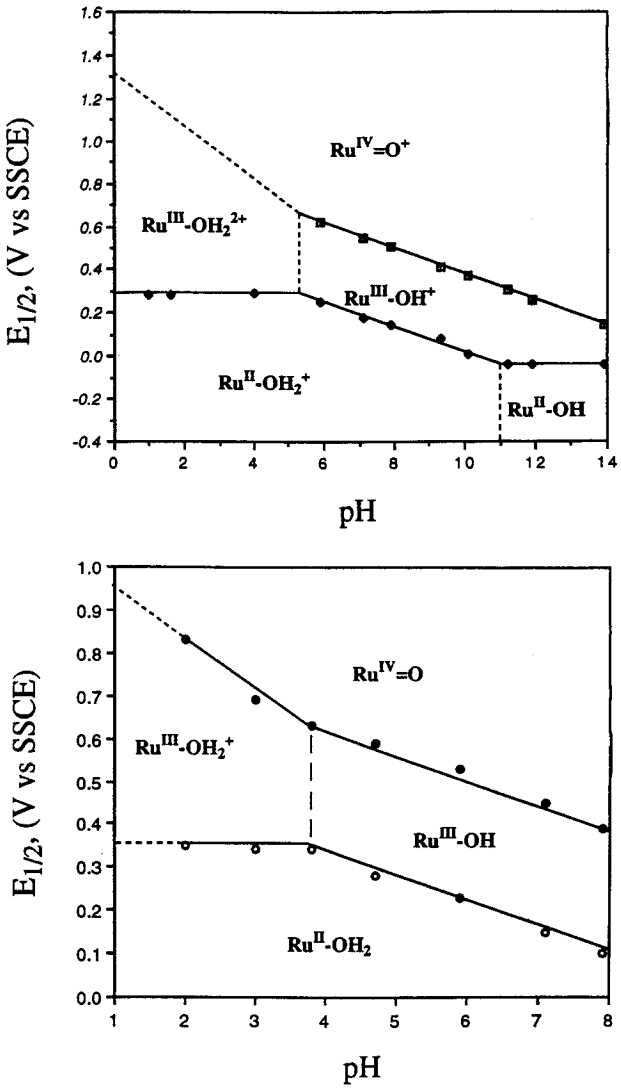


Figure 1. pH dependence of $E_{1/2}$ for the Ru(IV/III) and Ru(III/II) couples interrelating (a, top) $[Ru^{II}(tpy)(acac)(H_2O)]^+$, $[Ru^{III}(tpy)(acac)(OH)]^+$, and $[Ru^{IV}(tpy)(acac)(O)]^+$ and (b, bottom) $[Ru^{II}(tpy)(C_2O_4)(H_2O)]$, $[Ru^{III}(tpy)(C_2O_4)(OH)]$, and $[Ru^{IV}(tpy)(C_2O_4)(O)]$. The proton compositions of the various oxidation states are indicated. Vertical lines are drawn from the breaks in the $E_{1/2}$ lines and represent approximate pK_a values for the higher oxidation states. The potential−pH regions where the various oxidation states are the dominant forms and their proton compositions are shown. The dashed line-extension for the $Ru^{IV}=O^+/Ru^{III}-OH_2^{3+}$ couple was calculated by extrapolating the $Ru^{IV}=O^+/Ru^{III}-OH^{2+}$ couple to the pK_a for $Ru^{III}-OH_2^{2+}$ and adding 2×0.059pH to $E_{1/2}$.

(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
(15) Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, p 435.

oxalato complex from pH 0 to pH 8 are shown in Figure 1b. The lines drawn through the experimental points are of slopes of 0, −60, or −120 mV/pH unit as predicted by the Nernst equation in the form $E^{\circ\prime} = E_{1/2} - 0.05916m/n(\mathrm{pH})$, where m is the number of protons, n is the number of electrons, $E_{1/2}$ is the half-wave potential at pH 0, and $E^{\circ\prime}$ is the formal potential.[16] In the diagram, regions of stability for the various oxidation states and proton compositions are indicated. For example, the label $Ru-OH_2^{+}$ in the Ru(II) region represents the cation $[Ru(tpy)(acac)(H_2O)]^{+}$. The vertical dashed lines indicate the pK_a's of the corresponding oxidation state; for example, the pK_a for the first proton loss from $[Ru(tpy)(acac)(H_2O)]^{+}$ is 11.0.

$$[Ru^{II}(tpy)(acac)(H_2O)]^{+} \rightleftharpoons [Ru^{II}(tpy)(acac)(OH)]^{+} + H^{+}$$

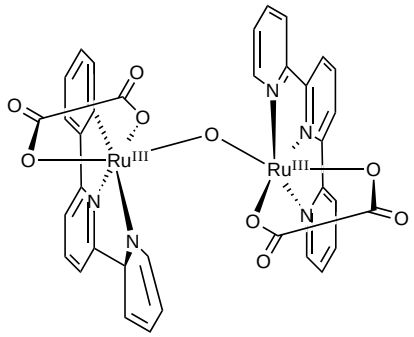
For the acac complex only the Ru(III/II) couple is observed below pH 5. The $E_{1/2}$−pH plot for the Ru(IV/III) complex shown by the extrapolation as the dotted line was inferred from the known proton composition and the pK_a of $[Ru^{III}(tpy)(acac)(H_2O)]^{2+}$. A similar behavior was observed for $[Ru^{II}(tpm)(bpy)(H_2O)]^{2+}$ (tpm is tris(pyrazolyl)methane), where no Ru(IV/III) wave was observed below pH 11, even though both the aqua ($[Ru^{II}(tpm)(bpy)(H_2O)]^{2+}$) and oxo ($[Ru^{IV}(tpm)(bpy)(O)]^{2+}$) forms are stable even in strongly acidic solutions.[17] Kinetic difficulties exist at the electrodes because of the mechanistic requirements imposed by combined electron−proton transfer. Summaries of thermodynamic acid−base and redox properties are shown in parts a and b of Scheme 2.

The oxalato complex $[Ru(tpy)(C_2O_4)(H_2O)]$ is stable at pH 6 for ∼2 h but at pH 1 undergoes rapid hydrolysis to give $[Ru^{II}(tpy)(H_2O)_3]^{2+}$ (eq 6).

$$[Ru^{II}(tpy)(C_2O_4)(H_2O)] + 2H_2O + 2H^{+} \rightarrow [Ru^{II}(tpy)(H_2O)_3]^{2+} + H_2C_2O_4 \quad (6)$$

Above pH 8, $[Ru^{II}(tpy)(C_2O_4)(H_2O)]$ is oxidized readily by O_2 to give $[Ru^{III}(tpy)(C_2O_4)(OH)]$, which undergoes further reaction to form the μ-oxo complex $[(tpy)(C_2O_4)Ru^{III}ORu^{III}(tpy)(C_2O_4)]$ (eq 7).[18]

$$2[Ru^{III}(tpy)(C_2O_4)(OH)] \rightarrow [(tpy)(C_2O_4)Ru^{III}ORu^{III}(tpy)(C_2O_4)] + H_2O \quad (7)$$



(tpy)(acac)Ru^{III}ORu^{III}(acac)(tpy)

For the nitrosyl $[Ru(tpy)(acac)(NO)]^{2+}$ in CH_2Cl_2 two ligand-based (NO) reductions are observed, the first chemically reversible one at $E_{1/2} = 0.02$ V. The second, at $E_{1/2} = -0.75$ V, is chemically irreversible. Reduction past the second wave resulted in the appearance of a wave for the Ru(III/II) couple ($E_{1/2} = 0.42$ V) for $[Ru(tpy)(acac)(NO_2)]$. Similar observations have been made for related nitrosyls.[3e] From the cyclic voltammetric measurements, oxidation of $[Ru^{II}(tpy)(acac)(NO_2)]$ to $[Ru^{III}(tpy)(acac)(NO_2)]^{+}$ is chemically reversible on the time scale of the scan rate used in the experiment (50 mV s^{-1}).

Discussion

The goal of this study was to advance the utilization of ligand effects to modulate the properties and reactivities of polypyridyl complexes of ruthenium. Our particular interest was the influence of the O-donor ligands $acac^{-}$ and $C_2O_4^{2-}$ relative to bpy in oxo/aqua redox chemistry and nitrosyl acid−base and redox chemistry. The linear correlation between ν(NO) and $E_{1/2}$ for the first (NO-based) reduction found in earlier work is extended in Figure 2 to include the value for $[Ru(tpy)(acac)(NO)]^{2+}$. In this sequence there is a nearly linear increase in $E_{1/2}$ for the first reduction with ν(NO) in cm^{-1}. The origin of the linear correlation is that reduction occurs at levels largely π^*(NO) in character.[19,20] As $d\pi \rightarrow \pi^*$(NO) back-bonding from Ru(II) decreases, the π^* level becomes a better electron acceptor and the bond order between N and O increases. Two ligand-based reductions occur for $[Ru(tpy)(acac)(NO)]^{2+}$. The potentials for these reductions are shifted negatively by 0.17 and 0.15 V compared to *cis*-$[Ru(bpy)_2(Cl)(NO)]^{2+}$ and by 0.51 and 0.38 V compared to *cis*-$[Ru(bpy)_2(py)(NO)]^{3+}$. The decreases for $[Ru(tpy)(acac)(NO)]^{2+}$ point to $acac^{-}$ as a σ and/or π donor relative to bpy. As a result there is greater $d\pi \rightarrow \pi^*$(NO) mixing in $[Ru^{II}(tpy)(acac)(NO)]^{2+}$ relative to the bpy complex. The acac complex also fits in the linear correlations found earlier between the redox potentials for $Ru^{III/II}-NO_2$ and $Ru^{III/II}-ONO_2$ couples and the potentials for the first and second nitrosyl-based reductions.

The influence of $acac^{-}$ compared to bpy also appears in the pK_a data in Table 1. These data show that there is a small increase in p$K_{a,1}$ from 10.8 for $[Ru(bpy)_2(py)(H_2O)]^{2+}$ to 11.0 for $[Ru(tpy)(acac)(H_2O)]^{+}$, and from the other examples in Table 1, p$K_{a,1}$, with the exception of that for $[Ru(NH_3)_5(H_2O)]^{2+}$, is relatively insensitive to the coordination environment at Ru(II). Taube and co-workers[8] have shown that pyrazine in *trans*-$[Ru^{II}(acac)_2(pyz)_2]$ is ∼100 times more basic than in *trans*-$[Ru^{II}(NH_3)_4(pyz)_2]^{2+}$. The contrast with the water-based example points toward $acac^{-}$ as a π-donating ligand enhancing the basicity of pyrazine by $\pi(acac^{-})-d\pi-\pi^*(p_3)$ mixing.

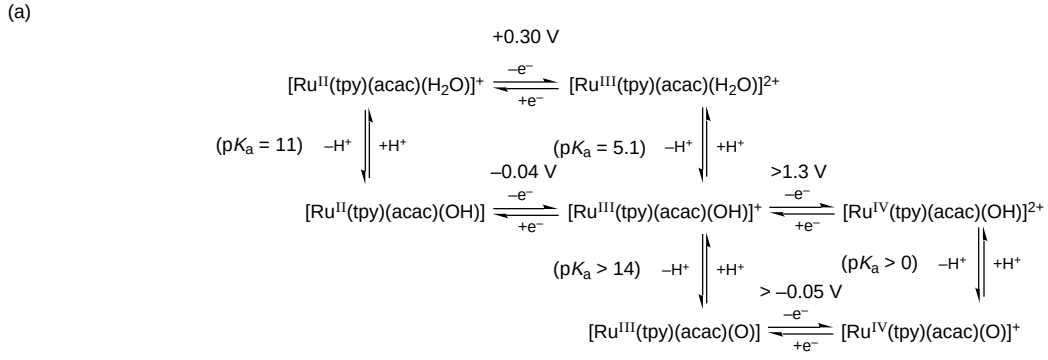
The effect on acidity at Ru(III) is more dramatic with p$K_{a,1} = 0.85$ for $[Ru^{III}(bpy)_2(py)(H_2O)]^{3+}$, p$K_{a,1} = 3.8$ for $[Ru^{III}(tpy)(C_2O_4)(H_2O)]^{+}$ and p$K_{a,1} = 5.2$ for $[Ru^{III}(tpy)(acac)(H_2O)]^{2+}$. In these cases $C_2O_4^{2-}$ and $acac^{-}$ are electron-donating ligands relative to bpy and increase electron content at Ru(III). In any detailed comparison involving relative pK_a values or redox potentials, differences in solvation energies as well as ligand electronic effects must be taken into account. Nonetheless, the decreased acidity of $[Ru^{III}(tpy)(acac)(H_2O)]^{2+}$ relative to the oxalato complex points to the importance of $\pi(acac^{-})$ to $d\pi(Ru^{III})$ electron donation.

Ligand effects also appear in Ru(IV/III) and Ru(III/II) redox potentials. Ligand effects on the Ru(III/II) couple are well-known. Ru(II) is stabilized by $d\pi-\pi^*$(L) back-bonding in the

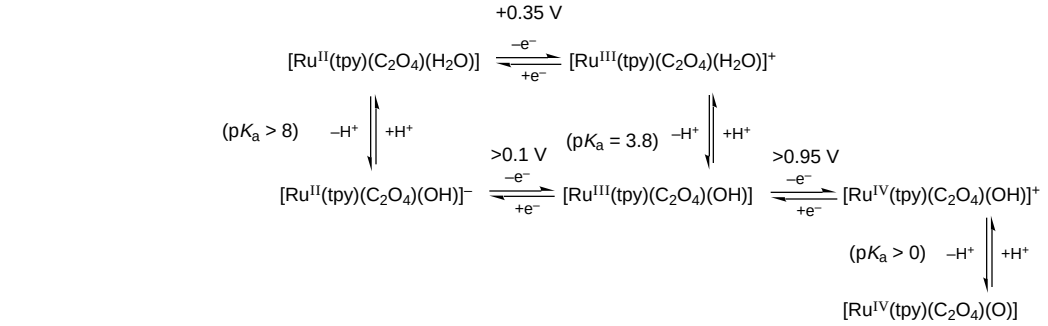
(16) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 213.
(17) Llobet, A.; Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 514.
(18) Adeyemi, S. A. Unpublished results.
(19) (a) Abruna, H. D.; Walsh, J. L.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1981**, *20*, 1481. (b) Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 574. (c) Nagao, H.; Nishimura, H.; Funato, H.; Ichikawa, Y.; Howell, F.; Mukaida, M.; Kakihana, H.; et al. *Inorg. Chem.* **1989**, *28*, 3955. (d) Godwin, J. B.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 2150.
(20) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2466.
(21) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruna, H. D.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1896.

Scheme 2[a]

(a)



(b)



[a] Conditions: 22 °C, $I = 0.1$ M, V vs SSCE.

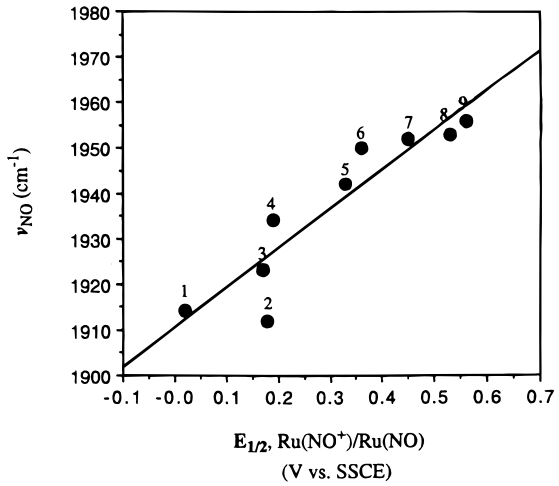


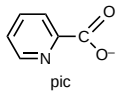
Figure 2. Plot of nitrosyl stretching frequency, ν_{NO} (cm^{-1}), vs the first nitrosyl-based reduction potential, $E_{1/2}(NO^+/NO)$, in CH_3CN vs SSCE for $[Ru(tpy)(acac)(NO)]^{2+}$ (**1**) in CH_2Cl_2, *trans*-$[Ru(bpy)_2(Cl)(NO)]^{2+}$ (**2**), *cis*-$[Ru(bpy)_2(N_3)(NO)]^{2+}$ (**3**), *cis*-$[Ru(bpy)_2(Cl)(NO)]^{2+}$ (**4**), *cis*-$[Ru(bpy)_2(NO_2)(NO)]^{2+}$ (**5**), *cis*-$[Ru(bpy)_2(NH_3)(NO)]^{3+}$ (**6**), $[Ru(tpy)(bpy)(NO)]^{3+}$ (**7**), *cis*-$[Ru(bpy)_2(py)(NO)]^{3+}$ (**8**), and *cis*-$[Ru(bpy)_2(CH_3CN)(NO)]^{3+}$ (**9**) (this work and refs 19 and 20; $T = 22 \pm 2$ °C, $I = 0.1$ M, PF_6^- salts). The infrared spectra for **1**, **2**, **4**, and **9** were recorded in KBr, for **5** in acetone, and for **3**, **6**, **7**, and **8** in CH_3CN.

presence of ligands such as PPh_3 and CH_3CN having low-lying acceptor levels. As evidenced by the data in Table 2, the resulting variation in potentials for polypyridyl complexes is impressive. Equally large variations are observed for other, non-aqua-containing Ru(III/II) couples. For example, Ru(III/II) potentials are 0.26 V (vs SSCE) for $[Ru^{III/II}(tpy)(acac)Cl]^{+/0}$, 0.31 V for $[Ru^{III/II}(tpy)(3\text{-Cl-acac})Cl]^{+/0}$, 0.77 V for $[Ru^{III/II}(tpy)(bpy)Cl]^{2+/+}$, 0.80 V for $[Ru^{III/II}(tpy)(phen)Cl]^{2+/+}$, and 1.23 V for $[Ru^{III/II}(tpy)(dppene)Cl]^{2+/+}$. The electron-donating characters of $C_2O_4^{2-}$ and $acac^-$ relative to bpy appear in the potentials of the $Ru^{III}-OH/Ru^{II}-OH_2$ couples for $[Ru^{II}(tpy)(acac)(H_2O)]^+$ at 0.19 V (pH 7, vs SSCE), for $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ at 0.49 V, and for $[Ru^{II}(tpy)(C_2O_4)(H_2O)]$ at 0.16 V. The stabilization of Ru^{II} by back-bonding is illustrated by the potential of 1.17 V for $[Ru^{II}(tpy)(dppene)(H_2O)]^{2+}$.

Table 1. pK_a Values for Aqua Complexes of Ru(II) and Ru(III)[a]

Ru(II)	$pK_{a,1}$	Ru(III)	$pK_{a,1}$
$[Ru(tpy)(bpy)(H_2O)]^{2+}$	9.7	$[Ru(bpy)_2(py)(H_2O)]^{3+}$	0.85
$[Ru(tpy)(phen)(H_2O)]^{2+}$	10.0	$[Ru(tpy)(bpy)(H_2O)]^{3+}$	1.7
trans-$[Ru(tpy)(pic)(H_2O)]^+$	10.0	$[Ru(tpy)(phen)(H_2O)]^{3+}$	1.7
cis-$[Ru(tpy)(pic)(H_2O)]^+$	10.0	$[Ru(tpm)(bpy)(H_2O)]^{3+}$	1.9
$[Ru(bpy)_2(py)(H_2O)]^{2+}$	10.8	*trans*-$[Ru(tpy)(pic)(H_2O)]^{2+}$	2.0
$[Ru(tpm)(bpy)(H_2O)]^{2+}$	10.8	*cis*-$[Ru(tpy)(pic)(H_2O)]^{2+}$	3.7
$[Ru(tpy)(acac)(H_2O)]^+$	11.0	$[Ru(tpy)(C_2O_4)(H_2O)]^+$	~3.8
$[Ru(tpy)(tmen)(H_2O)]^{2+}$	11.2	$[Ru(tpy)(acac)(H_2O)]^{2+}$	~5.2
$[Ru(NH_3)_5(H_2O)]^{2+}$	13.1	$[Ru(NH_3)_5(H_2O)]^{3+}$	4.1

[a] Determined by spectrophotometric titration and/or from $E_{1/2}$−pH diagrams; $I = 0.1$ M, $T = 22 \pm 2$ °C. Taken from refs 8 and 17 and: Ho, C.; Che, C. M.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **1990**, 967. tmen is *N*,*N*,*N*,*N*-tetramethylethylenediamine, and pic is picolinate anion:



pic

The electron-donating character of $acac^-$ also appears in the redox chemistry of $[Ru^{II}(tpy)(acac)(NO_2)]$. Typically, oxidation of $Ru^{II}-NO_2$ complexes to Ru(III) is followed by rapid disproportionation to give nitrosyl and nitrato products. Exceptions are *trans*-$[Ru(py)_4(NO_2)(Cl)]^+$ and *trans*-$[Ru(tpy)(NO_2)(PMe_3)_2]^{2+}$, reported by Mukaida and Takeuchi, respectively.[22] Because of electronic donation from $acac^-$ to Ru(III), $[Ru^{II}(tpy)(acac)(NO_2)]$ has the lowest Ru(III/II) potential yet reported for a nitro complex (0.42 V vs SSCE in CH_2Cl_2) and is stable as Ru(III), at least on the cyclic voltammetric time scale (50 mV s^{-1}).

(22) (a) Nagao, H.; Mukaida, M.; Howell, F. S.; Kakihana, H. *Inorg. Chem.* **1986**, *25*, 4312. (b) Leising, R. A.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1988**, *110*, 4079. (c) Leising, R.; Kubow, S.; Churchill, M. R.; Buttrey, L. A.; Ziller, J. W.; Takeuchi, K. J. *Inorg. Chem.* **1990**, *29*, 1306.

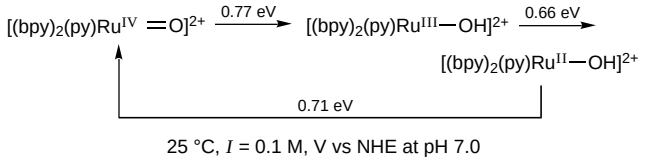
Table 2. Electrochemical Parameters for Aqua Complexes of Ru[a]

entry no.	complex	$E_{1/2}$ (V) $Ru^{III/II}$	$Ru^{IV/III}$	$Ru^{IV/II}$ [b]	$\Delta E_{1/2}$[c]	$\sum E_L$[d]
1	$[Ru(NH_3)(OH_2)]^{2+}$	−0.33	0.35	0.01	0.68	0.35
2	$[Ru(tpy)(acac)(H_2O)]^{+}$	0.19	0.56	0.38	0.37	0.59
3	$[Ru(tpy)(C_2O_4)(H_2O)]$	0.16	0.45	0.31	0.29	0.47
4	$[Ru(tpy)(H_2O)_3]^{2+}$ [c]	0.35	0.64	0.50	0.29	0.65
5	*trans*-$[Ru(tpy)(pic)(H_2O)]^{+}$	0.21	0.45	0.33	0.24	0.75
6	*cis*-$[Ru(tpy)(pic)(H_2O)]^{+}$	0.38	0.56	0.47	0.22	0.75
7	*cis*-$[Ru(6,6'\text{-}Me_2\text{-}bpy)_2(H_2O)_2]^{2+}$ [e]	0.57	0.73	0.65	0.16	0.83
8	$[Ru(tpy)(tmen)(H_2O)]^{2+}$	0.36	0.59	0.48	0.13	0.87
9	$[Ru(tpy)(phen)(H_2O)]^{2+}$	0.50	0.60	0.55	0.10	1.27
10	*cis*-$[Ru(bpy)_2(py)(H_2O)]^{2+}$	0.42	0.53	0.48	0.11	1.27
11	$[Ru(tpy)(bpy)(H_2O)]^{2+}$	0.49	0.62	0.56	0.13	1.27
12	$[Ru(tpy)(4,4'\text{-}((CO_2Et)_2bpy)(H_2O)]^{2+}$	0.66	0.80	0.73	0.13	1.30
13	$[Ru(tpy)(4,4'\text{-}Me_2\text{-}bpy)(H_2O)]^{2+}$	0.47	0.61	0.54	0.14	1.23
14	*cis*-$[Ru(bpy)_2(AsPh_3)(H_2O)]^{2+}$	0.50	0.67	0.59	0.17	1.33
15	*cis*-$[Ru(bpy)(biq)(PEt_3)(H_2O)]^{2+}$	0.45	0.63	0.54	0.18	1.30
16	$[Ru(tpm)(4,4'\text{-}(NO_2)_2\text{-}bpy)(H_2O)]^{2+}$	0.56	0.75	0.66	0.19	1.32
17	*cis*-$[Ru(bpy)_2(PEt_3)(H_2O)]^{2+}$	0.46	0.67	0.57	0.21	1.34
18	*cis*-$[Ru(bpy)(biq)(PPh_3)(H_2O)]^{2+}$	0.48	0.70	0.59	0.22	1.35
19	*cis*-$[Ru(bpy)_2(P(i\text{-}Pr)_3)(H_2O)]^{2+}$	0.45	0.68	0.57	0.23	1.35
20	*cis*-$[Ru(bpy)_2(PPh_3)(H_2O)]^{2+}$	0.50	0.76	0.63	0.26	1.39
21	*cis*-$[Ru(bpy)_2(SbPh_3)(H_2O)]^{2+}$	0.52	0.80	0.66	0.28	1.38
22	$[Ru(tpy)(dppene)(H_2O)]^{2+}$ [f]	1.17	1.53	1.35	0.36	1.45

[a] In H_2O at pH 7.0, $T = 22 \pm 2$ °C, $I = 0.1$ M vs SSCE taken from this work, refs 1 and 10, and: Diamantis, A. A.; Murphy, W. R., Jr.; Meyer, T. J. *Inorg. Chem.* **1984**, 23, 3230. Shiotani, M.; Lindgren, M.; Ichikawa, T. *J. Chem. Soc., Dalton Trans.* **1990**, 967. Abbreviations: biq = 2,2′-biquinoline; tmen = *N,N,N,N*-tetramethylethylenediamine; dppene = *cis*-1,2-bis(diphenylphosphino)ethylene; pic = picolinate anion. [b] $E_{1/2}$ values for the Ru^{III}—OH/Ru^{II}—OH_2 (Ru(III/II)), Ru^{IV}=O/Ru^{II}—OH_2 (Ru(IV/III)), and Ru^{IV}=O/Ru^{II}—OH_2 (Ru(IV/II)) couples. [c] $\Delta E_{1/2} = E_{1/2}$(Ru(IV/III)) − $E_{1/2}$(Ru(III/II)). [d] ΣE_L is a ligand electrochemical parameter calculated from the Lever parameters[23] for the five ligands that are not involved in the gain or loss of protons. [e] pH 4.0. [f] In CH_2Cl_2/H_2O (3:1).

The Ru(IV/III) couples are far less sensitive to ligand variations than are the Ru(III/II) couples. This is illustrated by the potentials of the Ru^{IV}=O/Ru^{III}—OH couples for $[Ru^{IV}(tpy)(acac)(O)]^{+}$/$[Ru^{III}(tpy)(acac)(OH)]^{+}$ at 0.56 V (pH 7, vs SSCE), for $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ at 0.62 V, for $[Ru^{IV}(tpy)(phen)(O)]^{2+}$ at 0.60 V, and for $[Ru^{IV}(tpy)(C_2O_4)(O)]$ at 0.45 V. π-Bonding effects in Ru(IV) are dominated by the oxo interaction arising from $d\pi(Ru)-p(O)$ mixing. Because of the different responses of the Ru(IV/III) and Ru(III/II) couples to ligand variations, the potential differences between the Ru(IV/III) and Ru(III/II) couples have a significant ligand dependence which mainly follows the ligand dependencies of the Ru(III/II) couples. $\Delta E_{1/2}$ values (where $\Delta E_{1/2} = E_{1/2}(Ru^{IV}O/Ru^{III}OH) - E_{1/2}(Ru^{III}OH/Ru^{II}OH_2)$) are 0.13 V for $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$, 0.29 V for $[Ru^{II}(tpy)(C_2O_4)(OH_2)]$, and 0.37 V for $[Ru^{II}(tpy)(acac)(OH_2)]^{+}$.

In Table 2 are listed reduction potentials for the Ru(IV/III), Ru(III/II), and Ru(IV/II) couples for a series of polypyridyl complexes. The corresponding half-wave reactions for *cis*-$[Ru^{II}(bpy)_2(py)(H_2O)]^{2+}$ are



25 °C, I = 0.1 M, V vs NHE at pH 7.0

$\Delta E_{1/2}$ is a quantitative measure of the driving force for comproportionation

$$[Ru^{IV}(bpy)_2(py)(O)]^{2+} + [Ru^{II}(bpy)_2(py)(H_2O)]^{2+} \underset{K_{com}}{\rightleftharpoons} 2[Ru^{III}(bpy)_2(py)(OH)]^{2+}$$

with

$$\Delta G^{\circ}_{com} = -nF\Delta E_{1/2} \quad (8a)$$

$$K_{com} = \exp[-(\Delta G^{\circ}_{com}/RT)] \quad (8b)$$

As can been seen from the data in Table 2, the magnitude of $\Delta E_{1/2}$ for the polypyridyl complexes varies from 0.11 to 0.36−0.37 V. $\Delta E_{1/2}$ reaches a minimum in the middle part of Table 2. The increase in $\Delta E_{1/2}$ occurs when bpy in $[Ru^{II}(tpy)(bpy)(H_2O)]^{2+}$ is replaced by $acac^{-}$ in $[Ru^{II}(tpy)(acac)(H_2O)]^{+}$ and is the result of stabilization of Ru(III) by $acac^{-}$ with a much smaller effect on Ru(IV). In the other direction, if py in *cis*-$[Ru^{II}(bpy)_2(py)(H_2O)]^{2+}$ is replaced by PPh_3, the Ru(III/II) potential is increased by stabilization of Ru(II) by back-bonding to the phosphine. A number of factors determine the magnitude of $\Delta E_{1/2}$. However, as ligand variations are made, their effect on $\Delta E_{1/2}$ can be accounted for qualitatively by assuming (1) that the Ru(III/II) couple is most strongly affected and (2) that the net effect represents a balance between stabilization of Ru(II) by back-bonding and of Ru(III) by electron donation.

The difference in potentials for the Ru(IV/III) and Ru(III/II) couples may have relevance to mechanism. Because of the accessibility of both Ru^{III} and Ru^{II}, Ru^{IV} can function as a one- or two-electron oxidant. In the middle part of Table 2, the driving force for the two-electron process is nearly the same as for the one-electron process. For *cis*-$[Ru^{II}(bpy)_2(py)(O)]^{2+}$, the driving force for Ru(IV) as a two-electron oxidant is only 55 mV lower than the driving force as a one-electron oxidant. From the viewpoint of the oxidant there is no significant thermodynamic advantage to mechanisms involving initial one-electron transfer and radical formation by organic or inorganic reductants compared to more complex pathways involving two-electron transfer and O atom or hydride transfer.

In all cases in Table 2 the reaction between Ru(IV) and Ru(II) to give Ru(III) is spontaneous; Ru(III) is stable with respect to disproportionation. The free energy changes for comproportionation vary from $\Delta G^{\circ}_{com} = -8.7$ kcal mol^{-1} ($K_{com} = 2.5 \times 10^6$) for $[Ru^{III}(tpy)(acac)(OH)]^{+}$ to $\Delta G^{\circ}_{com} = -2.5$ kcal mol^{-1} ($K_{com} = 72$) for $[Ru^{III}(bpy)_2(py)(OH)]^{2+}$. An interesting question is whether or not it is possible by ligand changes to stabilize Ru(IV) and Ru(II) relative to Ru(III) to such a degree that Ru(III) would become unstable with respect to dispropor-

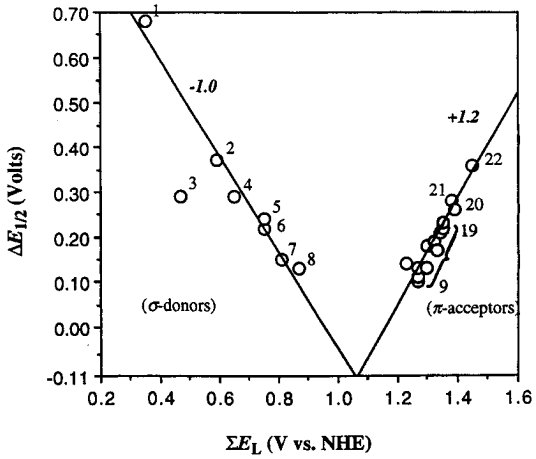


Figure 3. Plot of observed $\Delta E_{1/2}$ ($=E_{1/2}$(Ru(IV/III)) − $E_{1/2}$(Ru(III/II))} vs ΣE_L (see text). The numbering scheme for the individual couples is defined in Table 2.

tionation ($K_{com} < 1$). In such a case or cases, the Ru(III/II) couple would be more strongly oxidizing than the Ru(IV/III) couple.

An interesting way to visualize this possibility is shown in Figure 3, which is a plot of $\Delta E_{1/2}$ vs ΣE_L. The individual E_L values are ligand parameters defined by Lever and co-workers based on reduction potential measurements on Ru(III/II) couples.[23] The ligand parameters (E_L) are derived by assuming that electrochemical potentials are additive with substitution of one ligand for another.

On the basis of over 200 ligands, reasonable linear correlations are found between $E_{1/2}$(Ru(III/II)) and these parameters according to

$$E_{1/2}(\mathrm{Ru(III/II)}) = S_M[\sum a_i E_L(L_i)] + I_M$$

In this equation $E_L(L_i)$ is the characteristic parameter for ligand L_i and a_i the number of such ligands. The quantities S_M and I_M are constants which depend on coordination number, stereochemistry, and spin state. For Ru(III/II) couples in H_2O, $E_{1/2}(\mathrm{Ru(III/II)}) = 1.14[\Sigma_i E_L(L_i)] - 0.35$.

In Figure 3, ΣE_L is the sum of the Lever electrochemical parameters for the five ancillary ligands in the Ru^{IV}═O/Ru^{III}—OH and Ru^{III}—OH/Ru^{II}—OH_2 couples. The remaining ligands are oxo/hydroxo for the Ru(IV/III) couple and hydroxo/aqua for the Ru(III/II) couple in all cases.

The Lever parameters are derived for Ru(III/II) couples. Their successful application to the correlation in Figure 3 and the redox potential data in Table 2 is consistent with the effect of ligand variations on the comproportionation equilibria arising largely from the Ru(III/II) couple. Variations in the Ru(IV/III) couple are smaller and parallel the variations in Ru(III/II), since ligand effects in the couple are exerted mainly at Ru(III).

The change in slope in Figure 3 between $\Sigma E_L \approx 0.8$ and 1.2 is striking. The effect of ligand variations on $\Delta E_{1/2}$ appears to fall into two distinct classes. As suggested by the labels in Figure 3, increasingly effective back-bonding ligands increase $\Delta E_{1/2}$, mainly by stabilizing Ru(II) by back-bonding. Increasingly effective electron-donor ligands increase $\Delta E_{1/2}$ mainly by stabilizing Ru(III) by electron donation.

The lines drawn through the data points are best-fit lines of slopes −1.0 and +1.2. By extrapolation, the separate parts of the correlation intersect at $\Sigma E_L = 1.06$ V, at which point $\Delta E_{1/2} = -0.11$ V. This leads to the interesting suggestion that in complexes in which ΣE_L is near 1.06 for the five ancillary ligands, Ru(III) should be unstable with respect to disproportionation. In such a case, $E_{1/2}$(IV/II) > $E_{1/2}$(IV/III), and Ru(IV), as noted above, would become a more powerful two-electron oxidant than a one-electron oxidant.

Conversely, the tendency to act as a one-electron oxidant at Ru^{IV}═O is increased for both those cases where Ru(III) is stabilized by donor ligands, $[Ru^{IV}(NH_3)_5(O)]^{2+}$, and Ru(II) by back-bonding, $[Ru^{IV}(tpy)(dppene)(O)]^{2+}$.

The fact that the potentials for the two couples are as close as they are is a consequence of the coupled proton−electron nature of the couples. For example, the potential difference between the Ru(IV/III) and Ru(III/II) couples of $[Ru^{II}(bpy)_2Cl_2]$ is ~1.7 V. $\Delta E_{1/2}$ values for the oxo/hydroxo/aqua couples are much less. This is because proton loss occurs in the higher oxidation states, which leads to a stabilization by pπ(O) to dπ electron donation. The holes produced in the dπ levels of dπ^5 Ru(III) or dπ^4 Ru(IV) by oxidation are stabilized by π electron donation and bonding from the oxo or hydroxo ligands.

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